

Course Notes for

CHEM 120

# General Chemistry 1

Winter 2023

These course notes belong to: \_\_\_\_\_

Contact info for the CHEM 120 Course Coordinator

Prof. German Sciaiani  
[gsciaiani@uwaterloo.ca](mailto:gsciaiani@uwaterloo.ca)



The content and figures in this document were prepared by/for the course instructors unless otherwise noted.

All copyrighted material is used with permission from the copyright holder.

**Reproduction and/or sharing of the CHEM 120 course notes is strictly prohibited.**

## 1.1 Elements: The “building blocks” of all materials

At the present time, there are 118 known elements. Over time, and with contributions from many scientists, these elements have been arranged into a single document (the periodic table), one of the most recognizable icons in science.

For chemists, the periodic table is a tool that serves to organize their discipline. It helps them rationalize and unify what has already been discovered about the known substances and their reactions. It also guides their thinking about substances and reactions that are still to be discovered.

**Did you know?** Elements 1 through 92, except for elements 43 (Tc) and 61 (Pm), occur naturally on Earth. On the other hand, elements 93 through 118 must be synthesized in particle accelerators. Elements with the highest atomic numbers are typically produced in very small quantities, only a few atoms at a time.

Notes:

1. The periodic table shown below is based on the latest release (December 1<sup>st</sup>, 2018) from the International Union of Pure and Applied Chemistry (IUPAC). The highlighted elements are associated with very recent changes to the periodic table, which are discussed in the following sections.
2. For H, Li, B, C, N, O, Mg, Si, S, Cl, Br, and Tl, the *conventional atomic mass*, a representative value from the *atomic mass interval*, is provided.
3. For certain radioactive elements, the mass number of the most stable isotope is provided in (parentheses).

1 1 <b>H</b> 1.008	2 3 <b>Li</b> 6.94	4 <b>Be</b> 9.0122															18 2 <b>He</b> 4.0026											
11 <b>Na</b> 22.990	12 <b>Mg</b> 24.305	3	4	5	6	7	8	9	10	11	12	13 <b>Ca</b> 40.078	14 <b>Sc</b> 44.956	15 <b>Ti</b> 47.867	16 <b>V</b> 50.942	17 <b>Cr</b> 51.996	18 <b>Mn</b> 54.938	19 <b>Fe</b> 55.845	20 <b>Co</b> 58.933	21 <b>Ni</b> 58.693	22 <b>Cu</b> 63.546	23 <b>Zn</b> 65.38	24 <b>Ga</b> 69.723	25 <b>Ge</b> 72.630	26 <b>As</b> 74.922	27 <b>Se</b> 78.96	28 <b>Br</b> 79.904	29 <b>Kr</b> 83.798
37 <b>Rb</b> 85.468	38 <b>Sr</b> 87.62	39 <b>Y</b> 88.906	40 <b>Zr</b> 91.224	41 <b>Nb</b> 92.906	42 <b>Mo</b> 95.96	43 <b>Tc</b> (98)	44 <b>Ru</b> 101.07	45 <b>Rh</b> 102.91	46 <b>Pd</b> 106.42	47 <b>Ag</b> 107.87	48 <b>Cd</b> 112.41	49 <b>In</b> 114.82	50 <b>Sn</b> 118.71	51 <b>Sb</b> 121.76	52 <b>Te</b> 127.60	53 <b>I</b> 126.90	54 <b>Xe</b> 131.29											
55 <b>Cs</b> 132.91	56 <b>Ba</b> 137.33	57-71 <b>La-Lu</b> 178.49	72 <b>Hf</b> 180.95	73 <b>Ta</b> 183.84	74 <b>W</b> 186.21	75 <b>Re</b> 190.23	76 <b>Os</b> 192.22	77 <b>Ir</b> 195.08	78 <b>Pt</b> 196.97	79 <b>Au</b> 200.59	80 <b>Hg</b> 204.38	81 <b>Tl</b> 207.2	82 <b>Pb</b> 208.98	83 <b>Bi</b> (209)	84 <b>Po</b> (210)	85 <b>At</b> (210)	86 <b>Rn</b> (222)											
87 <b>Fr</b> (223)	88 <b>Ra</b> (226)	89-103 <b>Ac-Lr</b> (261)	104 <b>Rf</b> (262)	105 <b>Db</b> (266)	106 <b>Sg</b> (264)	107 <b>Bh</b> (277)	108 <b>Hs</b> (277)	109 <b>Mt</b> (268)	110 <b>Ds</b> (271)	111 <b>Rg</b> (272)	112 <b>Cn</b> (271)	113 <b>Nh</b> (272)	114 <b>Fl</b> (272)	115 <b>Mc</b> (272)	116 <b>Lv</b> (272)	117 <b>Ts</b> (272)	118 <b>Og</b> (272)											

Lanthanoids	57 <b>La</b> 138.91	58 <b>Ce</b> 140.12	59 <b>Pr</b> 140.91	60 <b>Nd</b> 144.24	61 <b>Pm</b> (145)	62 <b>Sm</b> 150.36	63 <b>Eu</b> 151.96	64 <b>Gd</b> 157.25	65 <b>Tb</b> 158.93	66 <b>Dy</b> 162.50	67 <b>Ho</b> 164.93	68 <b>Er</b> 173.05	69 <b>Tm</b> 168.93	70 <b>Yb</b> 173.05	71 <b>Lu</b> 174.97
Actinoids	89 <b>Ac</b> (227)	90 <b>Th</b> 232.04	91 <b>Pa</b> 231.04	92 <b>U</b> 238.03	93 <b>Np</b> (237)	94 <b>Pu</b> (244)	95 <b>Am</b> (243)	96 <b>Cm</b> (247)	97 <b>Bk</b> (247)	98 <b>Cf</b> (251)	99 <b>Es</b> (252)	100 <b>Fm</b> (257)	101 <b>Md</b> (258)	102 <b>No</b> (259)	103 <b>Lr</b> (262)

**Did you know?** To incorporate the lanthanoids and actinoids into their proper spots in the 6<sup>th</sup> and 7<sup>th</sup> periods, we would have to expand the periodic table to 32 columns. A periodic table with 32 columns is inconveniently wide, so the lanthanoids and actinoids are usually listed at the bottom of the table.

The Chemical Abstract Services (CAS) registry is arguably the best database for all known compounds. Currently, it contains information on **over 143 million unique chemical substances**.

Astonishingly, these substances are made up of only 90 naturally occurring elements.

**FYI:** Chemical Abstract Services (CAS) is a division of the American Chemical Society (ACS). CAS provides databases (for example, the CAS Registry) and search tools (for example, SciFinder) for finding chemical information.

## The Newest Elements

Elements 112 through 118 were recently added to the periodic table to complete the 7<sup>th</sup> period.

Element	Symbol	Name	Added	
112	Cn	copernicium	2010	Did you know? These elements have been made only a few atoms at a time, but that does not stop scientists from speculating on their properties.
113	Nh	nihonium	2016	For example, some scientists have predicted that Cn will be a liquid metal like mercury but more volatile. Others have suggested it will be very unreactive and more like a noble gas than a metal.
114	Fl	flerovium	2012	
115	Mc	moscovium	2016	
116	Lv	livermorium	2012	
117	Ts	tennessine	2016	
118	Og	oganesson	2016	There is also an interesting debate about the properties of Og. Some scientists have predicted that, unlike the noble gases above it, Og will be a liquid or solid at room temperature and quite reactive.

**Did you know?** When claims are made that a new element has been discovered, IUPAC reviews the evidence, sorts out who gets credit for the discovery (when competing claims are made) and ultimately, decides who gets to name the new element. According to IUPAC rules, an element can be named after a mythological concept, a mineral, a place or country, a property, or a scientist.

The table below highlights some (hopefully, interesting) facts about a few other elements.

<b>The first element to be discovered?</b>	Although metallic elements such as gold, silver, tin, copper, lead and mercury were known and used for many centuries, phosphorus (P) is considered the first element to be discovered scientifically. It was isolated in 1669 by Hennig Brandt, a German chemist, from samples of his own urine.
<b>Most abundant elements, by mass, in the Earth's crust?</b>	oxygen (O) > silicon (Si) > aluminum (Al) > iron (Fe)
<b>Most abundant elements, by mass, in the human body?</b>	oxygen (O) > carbon (C) > hydrogen (H) > nitrogen (N)
<b>Most abundant elements, by mass, in the universe?</b>	hydrogen (H) > helium (He) > oxygen (O) > carbon (C)
<b>Densest elements?</b>	osmium (Os) > iridium (Ir) > platinum (Pt) 22.6 g cm <sup>-3</sup> 22.5 g cm <sup>-3</sup> 21.5 g cm <sup>-3</sup>
<b>Which elements have the most isotopes?</b>	Cesium (Cs) and xenon (Xe) each have 36 known isotopes.
<b>Which elements have the most allotropes?</b>	According to the Samara Carbon Allotrope Database (SACADA), <a href="http://sacada.sctms.ru/">http://sacada.sctms.ru/</a> , carbon (C) has more than 500 different allotropic forms. Sulfur (S) has a few dozen allotropic forms.
<b>The only elements to be named after a living person at the time of naming?</b>	Seaborgium (Sg) and Oganesson (Og) were named after Glenn T. Seaborg (b. 1912, d. 1999) and Yuri Oganessian (b. 1933) to honour their contributions to the discovery of many heavy elements.

**Isotopes** refer to atoms that have the same number of protons but a different number of neutrons in their nuclei. **Allotropes** refer to different molecular forms of the same element. For example, graphite, diamond, and buckminsterfullerene ( $C_{60}$ ) are allotropes of carbon.  $S_2$ ,  $S_8$ , and  $S_{20}$  are allotropes of sulfur.

## 1.2 The Measurement and Evolution of Atomic Masses

The measurement of atomic mass was central to the emergence of chemistry as a scientific discipline, and the development of the periodic table. Prior to 1858, several sets of atomic weights were in use, each assigning different relative masses to the known elements. The uncertainty over atomic masses persisted until scientists recognized that some elements consisted of molecules, not individual atoms.

The first set of reliable atomic masses, reported in 1858 by the Italian chemist Stanislao Cannizzaro, were obtained from measurements of gas volumes and application of **Avogadro's law**: Equal volumes of different gases, compared at the same temperature and pressure, contain equal numbers of molecules.

With estimates of atomic masses in hand, Dmitri Mendeleev, a Russian chemist, showed that when the elements that were known at the time were arranged in order of increasing atomic mass, their properties seemed to repeat in a regular way. In 1869, he presented a tabular arrangement of elements that placed elements with similar properties in the same vertical column (group), leaving gaps in certain places for elements he believed had not yet been discovered. The validity of Mendeleev's arrangement was reinforced by the fact that seven of the 10 elements he predicted were eventually discovered. (See page 378 in Petrucci, 11<sup>th</sup> edition, for a reproduction of Mendeleev's periodic table.)

In Mendeleev's table, the elements were arranged essentially in order of increasing atomic mass. However, to place elements with similar properties in the same group, Mendeleev had to place some elements "out of order" with respect to their atomic masses. We now know that the correct ordering principle is **atomic number**, not atomic mass. In the modern version of the periodic table, the elements are in order of increasing atomic number. (The atomic number of an element is equal to the number of protons in the nucleus of any of its atoms.)

**Did you know?** Although Mendeleev is widely considered the "father" of the periodic table, that honour should be shared with Lothar Meyer, a German chemist. Meyer developed a similar but abbreviated version of the periodic table several years before Mendeleev. However, Mendeleev's version was the first to be published and therefore, the first to be widely disseminated to the scientific community.

**Want to know more?**  
See [this link](#) to learn about Cannizzaro's method for determination of atomic mass.

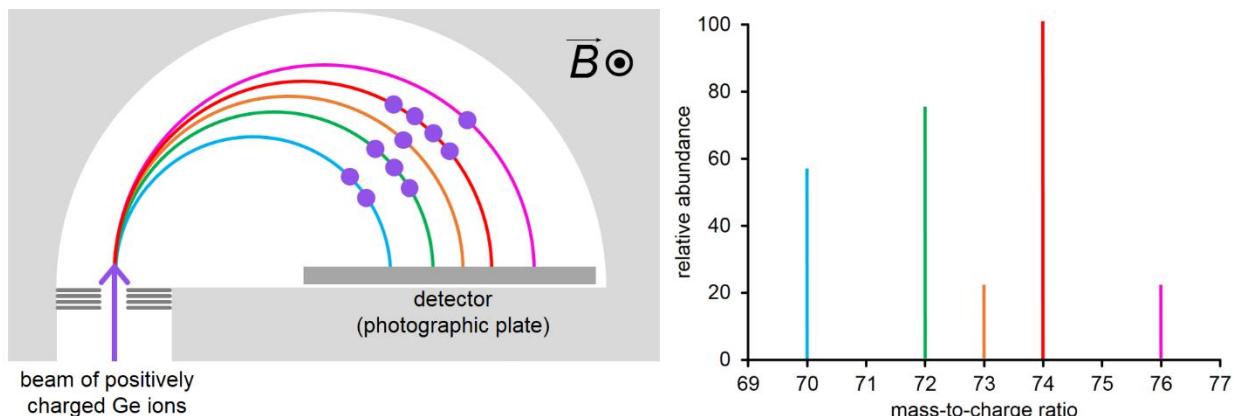
### Digging Deeper: Mass Spectrometry

(If you're interested, see <http://www.chemguide.co.uk/analysis/masspec/howitworks.html> for additional information.)

These days, atomic masses can be measured with a very high degree of accuracy using a **mass spectrometer**. A mass spectrometer operates on the principle that an atom or molecule, once ionized, can be deflected by a magnetic field. The extent to which the particle is deflected from its original path depends on the speed of the particle, the strength of the magnetic field, and the mass-to-charge ratio,  $m/z$ , of the ionized atom or molecule.

A particle goes through the following stages as it passes through a mass spectrometer.

- 1. Ionization:** A gas sample is ionized, with formation of +1 ions being highly favoured. The first mass spectrometers used bombardment with high energy electrons to knock off one or more electrons from each atom or molecule. Modern instruments use other methods of ionization.
- 2. Acceleration:** The positive ions are accelerated into a finely focused beam by electrically charged velocity selector plates. Only ions with a specific velocity make it through to the magnetic field.
- 3. Deflection:** The positive ions that reach the magnetic field all have the same velocity. However, their paths will be deflected to varying extents depending on the mass and charge of the ion. Lighter (less massive) ions are deflected to a greater extent than heavier ions. Ions with higher charges are deflected to a greater extent than ions with smaller charges. Consequently, the finely focused beam that entered the magnetic field is split into components of different mass-to-charge ratios. Since the conditions typically favour the formation of +1 ions, the incoming beam is split essentially into beams of ions with different masses.
- 4. Detection:** The different beams of ions strike different regions of the detector. The greater the number of ions of a given type, the greater the intensity of the response from the detector. Thus, the detector provides a measure of the number of ions of each type, which is represented graphically as a **mass spectrum**. A mass spectrum is a graph of intensity versus the mass-to-charge ratio.



▲ The image on the left is a schematic diagram of a mass spectrometer. A finely focused beam of Ge ions is split into different components by a magnetic field that is perpendicular to the plane of the page. The image on the right is a mass spectrum. It provides information about the relative amounts and masses of the ions.

### 1.3 Atomic Mass Intervals and Conventional Atomic Masses

Technological improvements in mass spectrometry have provided highly accurate measurements of atomic masses. For example, the mass of  $^{13}\text{C}$  has been measured accurate to 12 figures. (See the table below.) These highly accurate measurements have led to the discovery that, for certain elements, the isotopic abundances vary from one sample to another. For example, the isotopic abundance of  $^{13}\text{C}$  ranges from 0.9629% (in samples obtained from the ocean bottom in the Northern Pacific) to 1.1466% (in samples of deep sea pore water). *This discovery contrasts the previously held view that the isotopic abundances (and therefore, the average atomic mass) of an element were constants of nature!!*

	$^{12}\text{C}$	$^{13}\text{C}$
Isotopic masses	12 u (defined)	13.0033548378 u (from mass spectrometry)
Fractional abundances for samples from the ocean bottom in the Northern Pacific	0.988534	0.011466
Fractional abundances for samples from deep sea pore water	0.990371	0.009629

To understand the implications of this discovery, we must first discuss the concept of average atomic mass. For elements that have two or more isotopes, the (average) atomic mass,  $m_{\text{av}}$ , is the weighted average of the masses,  $m_i$ , of its isotopes. The weights,  $w_i$ , are the fractional isotopic abundances (i.e., the isotopic abundances expressed as decimal numbers with values between 0 and 1).

$$m_{\text{av}} = \sum_{i=1}^{\# \text{ of isotopes}} w_i m_i$$

For this reason, IUPAC recommends that the average atomic mass of carbon, and that of several other elements, be reported as an **atomic mass interval**, not as a single specific value. (See the table on the next page.) For carbon, in any material normally encountered, the calculated average atomic mass is greater than or equal to 12.0096 u and less than or equal to 12.0116 u. Thus, the atomic mass interval for carbon is given as [12.0096, 12.0116].

The data for an **atomic mass interval** is calculated and reported as,

$$\text{lower bound} = m_{\text{av}}(\text{lower}) - U$$

$$\text{upper bound} = m_{\text{av}}(\text{upper}) + U$$

where  $U$  is a combined uncertainty value specific to each element. The uncertainty correction ensures that neither the lower or upper bounds have any uncertainty associated with them. (**Want to know more?** See *Pure Appl. Chem.*, Vol 85, No. 5, pp 1047-1078, 2013).

**For you to try:** If the uncertainty correction for measurements of the atomic masses for Carbon is calculated as 0.000 027, can you use the data in the table above to show how the atomic mass interval for carbon is determined?

For elements with atomic masses given as intervals, IUPAC also provides **conventional atomic mass** values. These values can be used when a specific, representative value of the atomic mass is required. These conventional values have been selected so that, for materials normally encountered, the atomic mass should be within in an interval of plus or minus one in the last digit.

### Atomic Mass Intervals and Conventional Atomic Masses for Selected Elements

Atomic Number	Atomic Symbol	Atomic Mass, u	
		Interval	Conventional
1	H	[1.00784, 1.00811]	1.008
3	Li	[6.938, 6.997]	6.94
5	B	[10.806, 10.821]	10.81
6	C	[12.0096, 12.0116]	12.011
7	N	[14.00643, 14.00728]	14.007
8	O	[15.99903, 15.99977]	15.999
12	Mg	[24.304, 24.307]	24.305
14	Si	[28.084, 28.086]	28.085
16	S	[32.059, 32.076]	32.06
17	Cl	[35.446, 35.457]	35.45
35	Br	[79.901, 79.907]	79.904
81	Tl	[204.382, 204.385]	204.38

**Note carefully:** The interval designation  $[a, b]$  does **not** imply any statistical distribution of values between the lower and upper bounds nor does it represent a measure of the statistical uncertainty. For example, the average of  $a$  and  $b$  is neither the most likely value nor the most representative value. The difference  $b - a$  does **not** represent the uncertainty.

**Summary of key ideas:** What is the difference between the atomic mass interval and the conventional atomic mass?

The **atomic mass interval** is used for certain elements to indicate the range of values expected for the atomic mass because of observed variations in the isotopic abundances of these elements. The interval is expressed in the form  $[a,b]$ , which indicates that the atomic mass will be greater than or equal to  $a$  atomic mass units and less than or equal to  $b$  atomic mass units.

The **conventional atomic mass** is provided for elements having their atomic masses defined in terms of an atomic mass interval and may be used in situations when a representative value of the atomic mass is required.

**Example 1-1:** Bromine has two naturally occurring isotopes, bromine-79 and bromine-81, with masses of 78.918338 u and 80.916291 u, respectively, and an atomic mass interval of [79.901, 79.907]. Estimate the variation in the percent isotopic abundance of  $^{79}\text{Br}$  using (a) the lower bound; and (b) the upper bound of the atomic mass interval. (Note: the atomic weight uncertainty for bromine is very small, thus the atomic mass interval can be represented as [ $m_{\text{av}}(\text{lower})$ ,  $m_{\text{av}}(\text{upper})$ ]).

## 1.4 Essential Review – Chemical Reactions

Now that we have reviewed the periodic table, elements, atoms, and atomic masses, let's review the different chemical reactions you may have learned about. Throughout your first-year chemistry courses, you will need to be able to identify reactions, predict products, and balance the equation for any type of the reactions described below.

**Keep in mind:** The summary below is a general summary of things you may have seen in your previous courses. There are many kinds of chemical reactions that you will learn about as you further your education in science!

Reaction type	Description and Example
Synthesis	$\text{C}_7\text{H}_6\text{O}_3 + \text{C}_4\text{H}_6\text{O}_3 \rightarrow \text{C}_9\text{H}_8\text{O}_4 + \text{C}_2\text{H}_4\text{O}_2$ Two or more species react to produce a new reagent (or reagents).
Decomposition	$\text{H}_2\text{O}_2(\text{l}) \rightarrow \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})$ A single reactant breaks down into two or more simple reagents.
Single Displacement	$2 \text{ HCl}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2(\text{g})$ One element is replaced by another more reactive element (Example: Redox Reactions).
Double Displacement	$\text{AgNO}_3(\text{aq}) + \text{NaCl}(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})$ The positive or negative ions of two ionic compounds replace each other. (Example: Precipitation Reactions)
Combustion	$2 \text{ C}_8\text{H}_{18}(\text{l}) + 25 \text{ O}_2(\text{g}) \rightarrow 16 \text{ CO}_2(\text{g}) + 18 \text{ H}_2\text{O}(\text{g})$ A compound reacts with an oxidant (usually oxygen) in a highly exothermic reaction. For hydrocarbons, the products are carbon dioxide and water.
Acid-Base	$\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ A proton is transferred from a proton donor (acid) to a proton acceptor (base).

**Example 1-2:** At room temperature, elemental potassium reacts with liquid bromine to produce potassium bromide. What is the balanced chemical equation for the reaction?

**Example 1-3:** Acetylene,  $C_2H_2$ , is a colourless gas that is traditionally used in the welding industry. What is the balanced chemical equation for the combustion of acetylene?

## Review: Reactions in Aqueous Solution

### Definitions and terminology

**Solution** homogeneous mixture of one or more solutes in a solvent

**Homogeneous** uniform composition, right down to the molecular level; the molecules of one substance are mixed uniformly amongst the molecules of the others

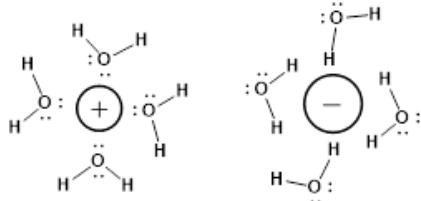
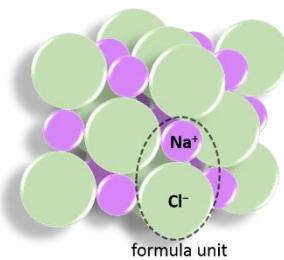
**Solvent** determines the phase of the solution (i.e., solid, liquid, or gas); usually the most abundant component

**Solutes** all other components of the solution

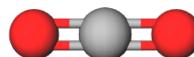
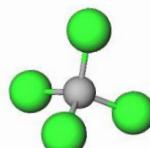
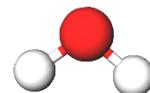
Aqueous solutions have water as solvent. To emphasize that a substance has been dissolved in water, we use the notation "(aq)" after its chemical formula, e.g.  $CH_3COOH(aq)$ ,  $HCl(aq)$ ,  $NaCl(aq)$ , etc. Water is an inexpensive and versatile solvent. Most **ionic compounds** and some **molecular compounds** dissolve in water, to some extent at least.

**Ionic compounds**

- comprised of positive and negative ions arranged in regular, repeating patterns
- the ions are held in their positions by strong ionic bonding forces
- solids at room temperature
- when an ionic solid dissolves in water, positive and negative ions break away from the solid surface and become "hydrated" (i.e., surrounded by water molecules)
- when an ionic compound dissolves, we get ions in solution

**vs.****Molecular Compounds**

- comprised of stable, neutral molecules
- the compound may be solid, liquid or gas at room temperature depending on the strength of the intermolecular attractions
- examples are CO<sub>2</sub>(g), CCl<sub>4</sub>(l), and C<sub>10</sub>H<sub>8</sub>(s)
- when a molecular compound dissolves in water, 1 molecules become hydrated
- when a molecular compound dissolves, we may or may not get ions in solution; it depends on whether the molecules react with water to produce ions.



Images generated using [molview.org](http://molview.org). Not to scale.

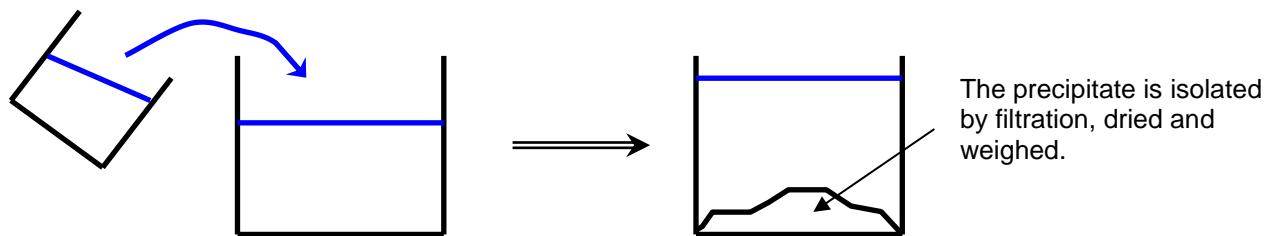
**Review: Common Polyatomic Ions**

H <sub>3</sub> O <sup>+</sup>	hydronium ion	HSO <sub>4</sub> <sup>-</sup>	hydrogen sulfate ion	O <sub>2</sub> <sup>2-</sup>	peroxide ion
OH <sup>-</sup>	hydroxide ion	SO <sub>4</sub> <sup>2-</sup>	sulfate ion	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	acetate ion
NH <sub>4</sub> <sup>+</sup>	ammonium ion	PO <sub>4</sub> <sup>3-</sup>	phosphate ion	ClO <sub>4</sub> <sup>-</sup>	perchlorate ion
NO <sub>3</sub> <sup>-</sup>	nitrate ion	HPO <sub>4</sub> <sup>2-</sup>	hydrogen phosphate	ClO <sub>3</sub> <sup>-</sup>	chlorate ion
NO <sub>2</sub> <sup>-</sup>	nitrite ion	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	dihydrogen phosphate	ClO <sub>2</sub> <sup>-</sup>	chlorite ion
CN <sup>-</sup>	cyanide ion	PO <sub>3</sub> <sup>3-</sup>	phosphite ion	ClO <sup>-</sup>	hypochlorite ion
CNO <sup>-</sup>	cyanate ion	CO <sub>3</sub> <sup>2-</sup>	carbonate ion	CrO <sub>4</sub> <sup>2-</sup>	chromate ion
SCN <sup>-</sup>	thiocyanate ion	HCO <sub>3</sub> <sup>-</sup>	hydrogen carbonate	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	dichromate ion
				MnO <sub>4</sub> <sup>-</sup>	permanganate ion

### Precipitation reactions

In a precipitation reaction, ions in solution combine to form an insoluble solid that precipitates from the solution. The precipitate can be filtered off, dried and weighed.

Precipitation reactions are very important for chemical analysis because chemists have learned how to exploit differences in solubilities to separate the components of a mixture. Precipitation reactions are used to carry out gravimetric analysis. In a gravimetric analysis, the amount of substance in a sample is deduced from the mass of precipitate that is produced.



To understand precipitation reactions, you must learn the solubility rules for common substances. These rules allow us to predict when (or if) a precipitation reaction will occur.

#### Solubility Rules for Ionic Compounds (See Table 5.1 in Petrucci, 11<sup>th</sup> edition.)

- 1. Salts of the alkali metals are soluble.** (Note: The alkali metals are in group 1.)  
e.g. If M = Li, Na or K, then MX, M<sub>2</sub>X, M<sub>3</sub>X, etc. are soluble regardless of what X is.
  - 2. Ammonium (NH<sub>4</sub><sup>+</sup>) salts are soluble.**  
e.g. (NH<sub>4</sub>)X, (NH<sub>4</sub>)<sub>2</sub>X, (NH<sub>4</sub>)<sub>3</sub>X, etc. are soluble regardless of what X is.
  - 3. Nitrates (NO<sub>3</sub><sup>-</sup>) are soluble.**  
e.g. MNO<sub>3</sub>, M(NO<sub>3</sub>)<sub>2</sub>, M(NO<sub>3</sub>)<sub>3</sub>, etc. are soluble regardless of what M is.
  - 4. Chlorides (Cl<sup>-</sup>), bromides (Br<sup>-</sup>) and iodides (I<sup>-</sup>) are soluble except for the chlorides, bromides and iodides of lead (Pb<sup>2+</sup>), mercury (Hg<sup>+</sup> and Hg<sup>2+</sup>) and silver (Ag<sup>+</sup>).**  
e.g. If X = Cl, Br or I, then MX, MX<sub>2</sub>, MX<sub>3</sub>, etc. are soluble unless M = Pb, Hg or Ag.
  - 5. Sulfates (SO<sub>4</sub><sup>2-</sup>) are soluble except for the sulfates of calcium, strontium, barium, silver mercury and lead.**  
e.g. M<sub>2</sub>SO<sub>4</sub>, MSO<sub>4</sub>, M<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, etc. are soluble unless M is from Ca, Sr or Ba (from group 2) or M = Pb, Hg or Ag.
  - 6. Carbonates (CO<sub>3</sub><sup>2-</sup>), phosphates (PO<sub>4</sub><sup>3-</sup>) and sulfides (S<sup>2-</sup>) are insoluble except for**  
(i) the carbonates/phosphates/sulfides of the alkalis (because of Rule 1), and  
(ii) ammonium carbonate/phosphate/sulfide (because of Rule 2).
  - 7. Hydroxides (OH<sup>-</sup>) are insoluble or slightly soluble except for the hydroxides of the alkalis (because of Rule 1).**
- Note: The hydroxides of group 2 (the alkaline earth metals) are slightly soluble. Virtually all other hydroxides are insoluble

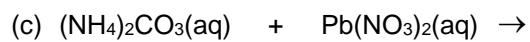
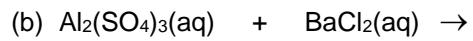
**Pre-Class Example:** Can you explain why a precipitate forms when 1.0 M aqueous solutions of calcium chloride ( $\text{CaCl}_2$ ) and sodium phosphate ( $\text{Na}_3\text{PO}_4$ ) are mixed?

**Example 1-4:** Aqueous solutions of  $\text{Bi}(\text{NO}_3)_3$  and  $\text{Na}_2\text{S}$  are mixed. Does a reaction occur? If so, what are the molecular and net ionic equations for the reaction?



See problems 5-19 to 5-22 from Petrucci (11<sup>th</sup> edition).

**Example 1-5 (On your Own):** In each of the following cases, write the net ionic equation for the reaction, if a reaction occurs.



## Acid-base reactions

There are a variety of definitions for the terms acid and base. We will focus on the Bronsted-Lowry definitions:

acid = proton ( $H^+$ ) donor

base = proton ( $H^+$ ) acceptor

According to these definitions, an acid-base reaction is a proton transfer reaction, where the proton is transferred **from the acid to the base**.

When an acid is dissolved in water, water molecules are protonated. (i.e., an acid produces  $H_3O^+$  ions in when dissolved in water). When a base is dissolved in water, water molecules are de-protonated (i.e., a base produces  $OH^-$  ions when dissolved in water).

An acid is classified as a “strong” acid if every acid molecule reacts with water. Similarly, a base is classified as a “strong” base if every molecule of the base reacts with water. It is important that you **know the names and formulas of the common strong acids and strong bases**.

### Common strong acids

HCl	hydrochloric acid	}	These are “binary acids”. They contain H and one other element (X). The general formula of a binary acid is $H_nX$ . In a binary acid, H is bonded directly to X. Note carefully: HF is not a strong acid, even though HCl, HBr and HI are.
HBr	hydrobromic acid		
HI	hydroiodic acid		
$HClO_4$	perchloric acid	}	These are “oxo acids”. In an oxo acid, H is bonded directly to oxygen. Sulfuric acid is a “diprotic acid” with two acidic hydrogen atoms. Sulfuric acid ionizes in two distinct steps:
$HBrO_4$	perbromic acid		
$HIO_4$	periodic acid		
$H_2SO_4$	sulfuric acid		$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$
$HNO_3$	nitric acid		$HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$
			The first ionization reaction goes to completion, but the second ionization reaction does not. (i.e. $H_2SO_4$ is a strong acid, but $HSO_4^-$ is not.)

### Common strong bases

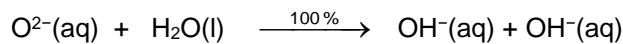
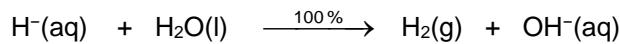
group 1 hydroxides: LiOH, NaOH, KOH, RbOH, ...

The group 1 hydroxides are very soluble, but the group 2 hydroxides are only slightly soluble or sparingly soluble.

group 2 hydroxides:  $Mg(OH)_2$ ,  $Ca(OH)_2$ ,  $Sr(OH)_2$ ,  $Ba(OH)_2$

Hydroxide salts are ionic compounds containing  $OH^-$  ions. These salts produce  $OH^-$  ions directly upon dissolving.

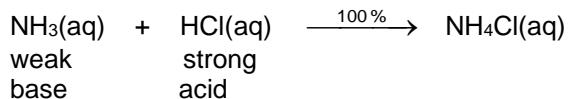
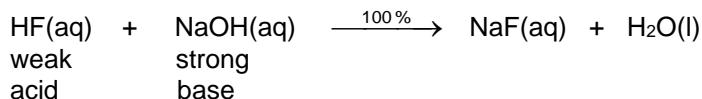
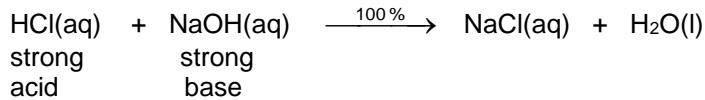
You should also be aware that the hydride ( $H^-$ ) and oxide ( $O^{2-}$ ) ions are also strong bases.



These reactions occur when compounds such as NaH or Na<sub>2</sub>O are dissolved in water.

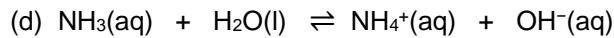
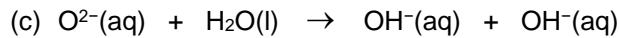
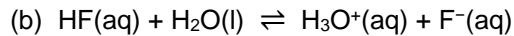
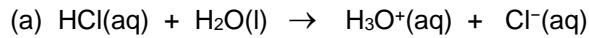
**Acid-base neutralization reactions**

In a neutralization reaction, an acid and base react to form a salt. Often, but not always, water is also produced. If either the acid or the base is “strong”, then the neutralization reaction goes essentially to completion. Here are some examples of neutralization reactions that go 100% to completion.



**Did you know?** A neutralization reaction that goes 100% to completion can be used in the laboratory to carry out an acid-base titration. A titration is an important method of analysis.

**Example 1-6:** Identify the acids and bases in the following reactions.



### Oxidation-reduction reactions

We can think of an oxidation-reduction reaction as an electron transfer reaction, provided we can agree on a method or a set of rules for assigning electrons to the atoms of the various species involved in a reaction. Unfortunately, the electrons are “hidden” in the balanced chemical equation for a reaction. Therefore, it is not always easy to recognize an oxidation-reduction reaction.

Chemists have devised a way of keeping track of electrons: they use an accepted set of rules to assign oxidation states to all the atoms involved in the reaction. You need to be able to assign oxidation states using these rules.

#### Rules for assigning oxidation states (See also Table 3.2 of Petrucci, 11<sup>th</sup> edition)

1. **The oxidation state is zero for an atom in elemental form.**  
e.g., In H<sub>2</sub>(g), the oxidation state of H is zero. In Na(s), the oxidation state of Na is zero.
2. **The sum of oxidation states must equal the total charge.**  
e.g., In C<sub>2</sub><sup>2-</sup>, the oxidation state of C is -1.
3. **In their compounds, the group 1 metals always have an oxidation state of +1 and the group 2 metals always have an oxidation state of +2.**  
e.g., In NaCl, the oxidation state of Na is +1. The oxidation state of Cl must be -1 (by rule 2).
4. **In its compounds, F always has an oxidation state of -1.**  
But note that in F<sub>2</sub>, the elemental form of F<sub>2</sub>, the oxidation state of F is zero.
5. **In its compounds, H normally has an oxidation state of +1, except when H combines with a group 1 or group 2 metal.**  
e.g., In H<sub>2</sub>O, the oxidation state of H is +1. In CaH<sub>2</sub> and NaH, the oxidation state of H is -1.
6. **In its compounds, O normally has an oxidation state of -2, except when oxygen is bonded to itself (e.g., in peroxides) or when oxygen is bonded to fluorine.**  
e.g., In H<sub>2</sub>O, the oxidation state of oxygen is -2. In H<sub>2</sub>O<sub>2</sub>, the oxidation state of O is -1 and in F<sub>2</sub>O, the oxidation state of O is +2.
7. **In their compounds, Cl, Br and I normally have an oxidation state of -1, unless the preceding rules dictate otherwise.**

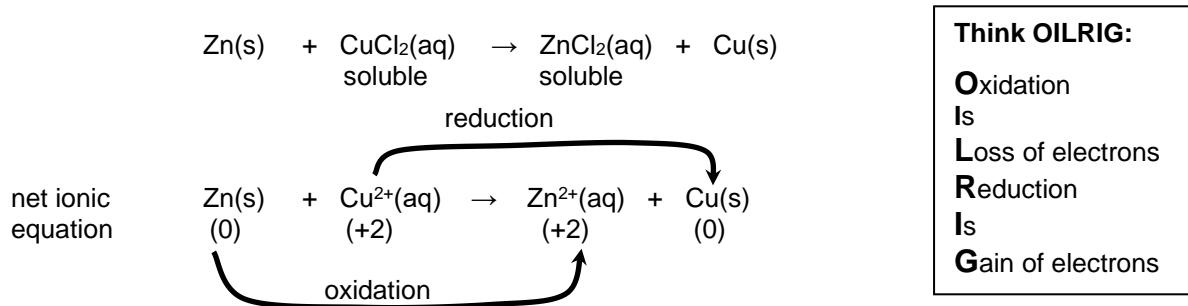
increasing priority

**Pre-Class Example:** For each species below, identify the oxidation state of the underlined element.



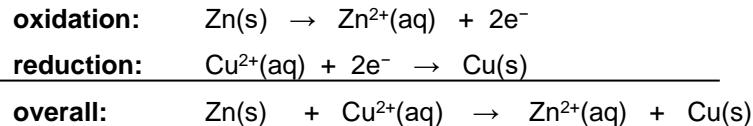
The **oxidation state** of an atom in a compound is equal to the hypothetical charge the atom would acquire if the bonding electrons between each pair of atoms were given to the atom having the greatest electronegativity. Sometimes, we need to resort to this “formal” definition when assigning oxidation states because the rules given above don’t cover all possible cases. (e.g.,  $\text{CN}^-$ ).

In an oxidation-reduction reaction, the oxidation states of one or more atoms (or ions) changes. For example, consider the reaction between Zn(s) and CuCl<sub>2</sub>(aq) to give ZnCl<sub>2</sub>(aq) and Cu(s):



In the reaction above, the oxidation state of Zn increases and the oxidation state of Cu decreases. We say that Zn has been oxidized (from  $Zn^0$  to  $Zn^{2+}$ ) and Cu has been reduced (from  $Cu^{2+}$  to  $Cu^0$ ). In general, oxidation is associated with the loss of electrons and reduction is associated with the gain of electrons.

Every electron transfer reaction can be written as the sum of an oxidation process and a reduction process, each of which is referred to as a “half-reaction”. For the oxidation of Zn by Cu<sup>2+</sup>, the half-reactions and overall reaction are:



The stoichiometry of the overall reaction is determined by the number of electrons involved in the half-reactions. The number of electrons produced in the oxidation step must equal the number of electrons consumed in the reduction step.

Not all oxidation-reduction reactions are as simple as the one just considered. This is especially true for oxidation-reduction reactions that occur in acidic or basic solutions. Such reactions are difficult to balance by inspection and we must use a systematic approach to balance them. The following approach is recommended. (Our method is different from the method described in the text. We want you to learn and use our method because our method emphasizes oxidation states. The method in the text ignores oxidation states!)

**Completing and balancing redox reactions that occur in aqueous solution**

1. Assign oxidation states to each element in the reaction and identify the species being oxidized and reduced.
2. Write separate half-reactions for the oxidation and reduction processes.
3. Balance the half-reactions separately:
  - a) first with respect to the element being oxidized or reduced, and
  - b) then by adding electrons to one side or the other to account for the number of electrons produced (oxidation) or consumed (reduction).
4. Combine the half-reactions algebraically so that the total number of electrons cancels out.
5. Balance the net charge by either adding  $\text{OH}^-$  to one side of the equation (for basic solutions) or  $\text{H}^+$  to the other (for acidic solutions).
6. Balance the O and H atoms by adding  $\text{H}_2\text{O}$ . Check that the final equation is balanced with respect to each type of atom and with respect to charge.



See problems 5-37 through 5-42  
from Petrucci (11<sup>th</sup> edition)

**Example 1-7:** Complete and balance the equations below.

- (a)  $\text{C}_2\text{H}_5\text{OH}(\text{aq}) + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) \rightarrow \text{C}_2\text{H}_4\text{O}_2(\text{aq}) + \text{Cr}^{3+}(\text{aq})$  in acidic solution.  
(b) (on your own)  $\text{Ag}(\text{s}) + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Ag}_2\text{O}(\text{aq}) + \text{Zn}(\text{s})$  in basic solution

## 1.5 Essential Review – Solving Stoichiometry Problems

Most stoichiometric problems provide a known quantity of one substance, and you are required to calculate the quantity of another substance that is used or produced in a reaction involving those substances. Chemists solve stoichiometry problems routinely in planning their experiments, and when developing systems or devices that rely on chemical reactions to function properly. In the lab, we are (usually) restricted to using samples of matter that are large enough to see and manipulate using laboratory equipment. Such samples typically contain uncountable numbers of atoms or molecules. Consequently, counting atoms and molecules directly is simply out of the question. We are forced to deduce the number of atoms or molecules indirectly from macroscopic quantities such as mass, volume, or pressure.

### Review: The mole, molar mass, and mass.

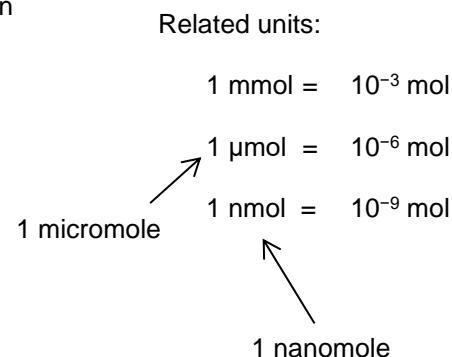
The SI unit for the amount of substance is the **mole**. The abbreviation for the mole is **mol**.

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

Why is the mole defined as such a funny number?

The formal definition of the mole is that it is the number of atoms in exactly 12 grams of  $^{12}\text{C}$ . (Note:  $^{12}\text{C}$  is the most abundant isotope of carbon.) Scientists have measured the mass of one  $^{12}\text{C}$  atom, using a mass spectrometer, and its mass is  $1.9927 \times 10^{-23} \text{ g}$ . Therefore:

$$12 \text{ g } ^{12}\text{C} \times \frac{\text{one } ^{12}\text{C atom}}{1.9927 \times 10^{-23} \text{ g } ^{12}\text{C}} = 6.022 \times 10^{23} \text{ } ^{12}\text{C atoms}$$



See “The Mole Concept”  
[open.science.uwaterloo.ca](http://open.science.uwaterloo.ca)

**Avogadro's number ( $N_A$ ):**  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$  (Avogadro's number has units of  $\text{mol}^{-1}$ )

**The molar mass of a substance allows us to calculate the number of moles,  $n$ , in a weighed sample.**

If 1 mol of X has mass  $m$ , then “ $n$ ” moles of X has mass  $m = nM$ . Therefore:  $n = \frac{m}{M}$ .

You may also recall that the **density** of a material ( $\rho$ ) can be calculated as mass per unit volume:  $\rho = \frac{m}{V}$ , and the **concentration** of a solution is calculated as amount in moles per unit volume,  $C = \frac{n}{V}$ .

**Review: The Mole Method**

The mole method for solving stoichiometry problems involves three basic steps.

**Convert to moles**

*Convert the known macroscopic quantities into amounts in moles*

**Convert between moles**

*Use coefficients from the balanced equation to convert from moles of one substance to moles of another.*

**Convert from moles**

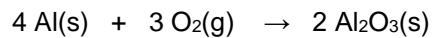
*Convert the calculated amount in moles to the required macroscopic quantity*

**General example:** For the reaction below, how do you determine the quantity of **C** that can be produced from a given quantity of **A** and an excess quantity of **B**?



See "Solving Stoichiometry Problems" at [open.science.uwaterloo.ca](http://open.science.uwaterloo.ca)

**Pre-Class Example:** What is the maximum mass of Al<sub>2</sub>O<sub>3</sub> that can be obtained from 5.0 g Al and excess O<sub>2</sub>, given that Al and O<sub>2</sub> react according to the chemical equation below?



**Example 1-8:** Lithium metal reacts with nitrogen gas forming Li<sub>3</sub>N(s). Assuming the reaction goes to completion, what mass of lithium metal would be required to react with excess nitrogen gas to produce 3.35 g of Li<sub>3</sub>N?

**Example 1-9:** A compound contains only C, H, and O. A 0.875-g sample of the compound is burned in excess O<sub>2</sub> yielding 2.21 g CO<sub>2</sub> and 0.387 g H<sub>2</sub>O.

- (a) What is the % composition of the compound?
- (b) What is the empirical formula?
- (c) In a separate experiment, the molar mass of the compound is found to be 245 g mol<sup>-1</sup>. What is the molecular formula of the compound?



See problems 3-44 through 3-46 from Petrucci (11<sup>th</sup> edition).

**Example 1-10:** Small amounts of N<sub>2</sub>, for lab use, can be made via the reaction below.



See problems 4-69, 4-70, and 4-74  
from Petrucci (11<sup>th</sup> edition).

A reaction mixture contains 18.1 g NH<sub>3</sub> and 90.4 g CuO. If 6.63 g N<sub>2</sub> is obtained, then what is the percentage yield for this experiment?

Recall: % **yield** =  $\frac{\text{actual yield}}{\text{theoretical yield}} \times 100$

### Consecutive and Simultaneous Reactions

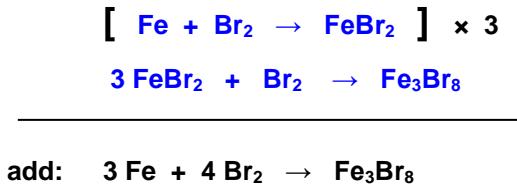
When faced with two or more reactions (as in the next example), we may be tempted to add together the chemical equations to obtain a single chemical equation for the overall reaction. When considering adding chemical equations together, we must first establish whether we are dealing with **simultaneous reactions** or **consecutive reactions**.

consecutive reactions = a series of reactions that occur sequentially; the products from one reaction are consumed as reactants in a subsequent reaction.

simultaneous reactions = reactions that are independent and occur at the same time

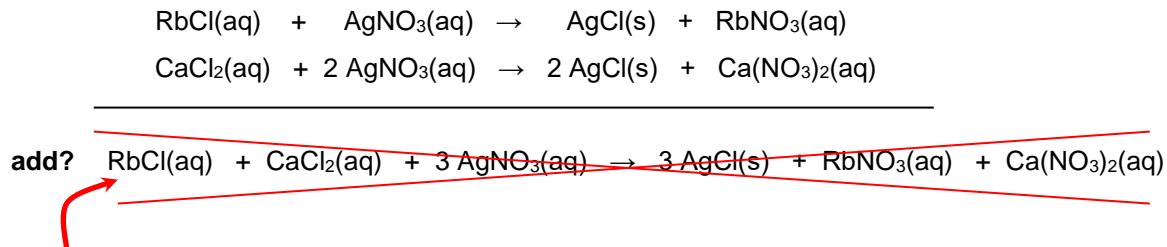
#### Important

For consecutive reactions, you can add the chemical equations together.



In this example, we must multiply the first reaction by 3 before adding it to the second equation because we need 3 moles of  $\text{FeBr}_2$  for the second reaction. Notice that  $\text{FeBr}_2$  is an "intermediate" that does not appear in the overall chemical equation.

For independent reactions, never add the chemical equations together!



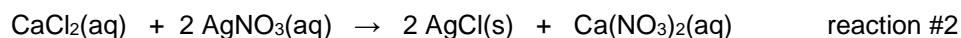
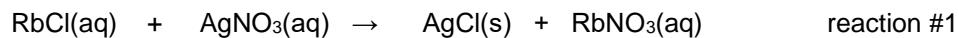
Wrong! The last chemical equation might be balanced but it is wrong. It implies that  $\text{AgCl}$  will be produced only if both  $\text{RbCl}$  and  $\text{CaCl}_2$  are present and that they must be present in a 1-to-1 mole ratio!! From the reactions given, we can see that  $\text{RbCl}$  will react with  $\text{AgNO}_3$  to produce  $\text{AgCl}$  whether or not  $\text{CaCl}_2$  is present. (Similarly,  $\text{CaCl}_2$  will react with  $\text{AgNO}_3$  whether or not there is any  $\text{RbCl}$  present.)

**Example 1-11:** A 2.00 g sample of a mixture of  $\text{CaCl}_2$  and  $\text{RbCl}$  is treated with excess  $\text{AgNO}_3(\text{aq})$ , causing  $\text{AgCl}(\text{s})$  to precipitate from the solution. If 3.45 g of  $\text{AgCl}$  is obtained, then what is the percentage by mass of  $\text{RbCl}$  in the original mixture?



You should also try problem 4-91  
from Petrucci (11<sup>th</sup> edition.)

Two **simultaneous reactions** contribute to the formation of  $\text{AgCl}(\text{s})$ .

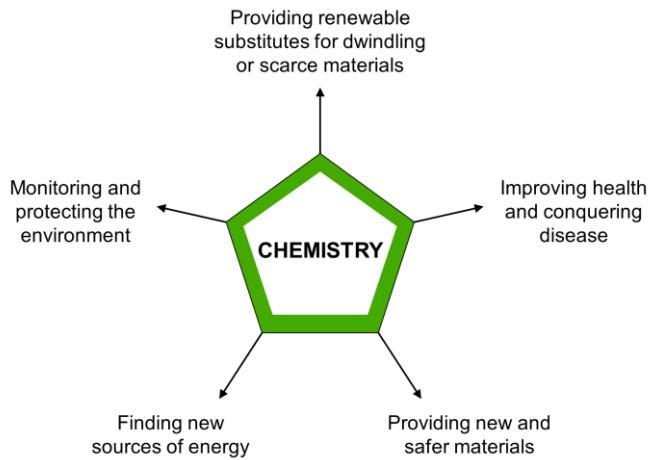


**Hint:** Although it is very tempting to add the two chemical equations together, don't add them!

Simultaneous reactions occur independently of each other, so the equations representing them should never be combined.

## 1.6 Using Atoms Wisely: Green Chemistry Metrics

Ultimately, chemistry is about transformation: re-arranging the atoms in a given set of substances to form another set of substances. The reasons for doing so are uncountable, but in part, to address the many challenges society faces today.



Everything we have now, and for the foreseeable future, comes from the atoms that exist in limited quantities here on Earth. Atoms are the “currency” of chemistry and, to a chemist, a valuable commodity. Chemists have always been concerned with keeping track of the atoms they use. They strive to maximize the yield of their reactions, by designing synthetic methods and processes that are efficient in their use of atoms and which minimize waste.

The efficient use of atoms and the minimization of waste are central principles in **green chemistry**, a term coined in the 1990s by the United States Environmental Protection Agency. Green chemistry is an approach to chemistry that is intentionally focused on not only the efficient use of atoms (and energy) but also chemical methods that reduce or eliminate reagents, products, solvents, by-products, wastes, etc. that are hazardous to human health or the environment. Two of the principles of green chemistry are as follows. (The Digging Deeper section on page 29 provides a full listing.)

- (1) It is better to prevent waste than to treat or clean it up afterwards.
- (2) Methods should be designed to maximize the incorporation of all materials used in the process into the final product.

**Atom economy** and the **E-factor** are quantities that can be calculated by a chemist to help assess the “green-ness” of a chemical reaction or process. Atom economy (expressed as a percentage) is defined in terms of the theoretical amounts of reactants and products involved in a reaction or process.

$$\% \text{ atom economy} = \frac{\text{stoichiometric mass of the desired product}}{\text{mass of a stoichiometric mixture of reactants}} \times 100\%$$

The **stoichiometric mass** of the desired product is the maximum mass that can be expected from a stoichiometric mixture of reactants. (In a **stoichiometric mixture** of reactants, the mole ratio of reactants is equal to the ratio of the stoichiometric coefficients. None of the reactants is present in excess.) By comparing atom economy values for different synthetic routes, a chemist can determine which provides the “best” use of atoms in the reactants. Therefore, the concept of atom economy is helpful for choosing the least wasteful synthetic route.

The E-factor is defined in terms of quantities that are easily measured and therefore, the E-factor is easily calculated, no matter how many substances, reactions, or processes are involved.

$$\text{E - factor} = \frac{\text{mass of waste produced}^*}{\text{mass of product obtained}}$$

**fyi:** “E-factor” is an abbreviation for “environmental factor”.

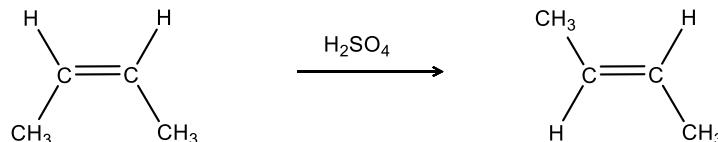
\* If the reaction or process produces waste water, the mass of the water is not included. However, the masses of substances dissolved in the water are included.

A large value for the E-factor indicates that many kilograms of waste are generated for every kilogram of product obtained. A small value for the E-factor is desirable.

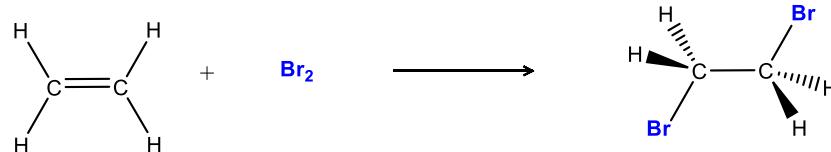
The E-factor is particularly useful for real-time monitoring of the impact of making many changes in a synthesis, process, or company. A company could easily calculate its E-factor, before and after making changes, using “kilograms of raw materials purchased” and “kilograms of product sold”.

**Example 1-12:** Consider the following reactions. Which, if any, have 100% atom economy? Which, if any, have an E-factor of zero?

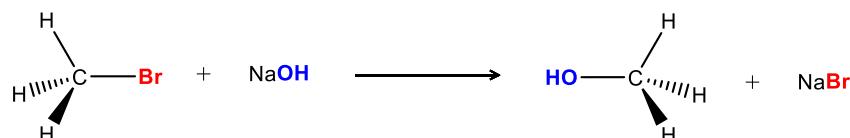
(i) Re-arrangement:  
(Isomerization)



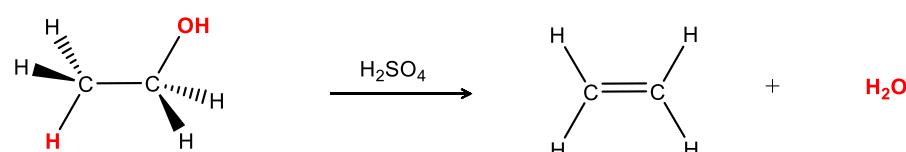
(ii) Addition:



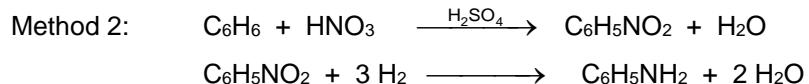
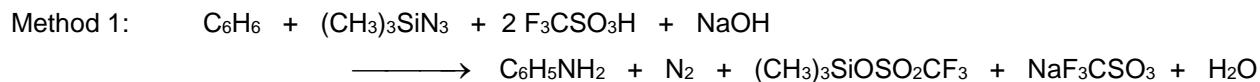
(iii) Substitution:



(iv) Elimination:



**Example 1-13:** Calculate the % atom economy for each of the following synthetic routes for converting benzene, C<sub>6</sub>H<sub>6</sub>, to aniline, C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>.



**Keep in mind:** When comparing different synthetic routes, a chemist must also consider other practical matters including the ease of isolation or purification of the desired product, the potential for side reactions, and the toxicity or hazards of the substances used.

**Solution:**

The molar masses, in g/mol, are as follows.

C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, 93.126    C<sub>6</sub>H<sub>6</sub>, 78.108    (CH<sub>3</sub>)<sub>3</sub>SiN<sub>3</sub>, 115.222    F<sub>3</sub>CSO<sub>3</sub>H, 150.088    NaOH, 39.998  
HNO<sub>3</sub>, 63.018,    H<sub>2</sub>, 2.016

## [ Digging Deeper ... Green Chemistry

**Before you ask:** You are not responsible for knowing these principles. They are included to provide context for the use of atom economy or the E-factor as a measure of the “green-ness” of a reaction or process. Want a “pocket guide” from the American Chemical Society? Go to <https://www.acs.org/content/acs/en/greenchemistry/what-is-green-chemistry/principles/12-principles-of-green-chemistry.html>

### The Twelve Principles of Green Chemistry

(Ref: P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998.)

- 1. Prevent waste:** It is better to prevent waste than to treat or clean up waste after it has been created.
- 2. Atom economy:** Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
- 3. Design less hazardous chemical syntheses:** Synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
- 4. Design benign chemicals:** Chemical products should be designed to provide their desired function while minimizing their toxicity.
- 5. Use benign solvents and auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
- 6. Design for energy efficiency:** Energy requirements of chemical processes should be evaluated for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
- 7. Use renewable feedstocks:** A raw material or feedstock should be renewable rather than non-renewable whenever technically and economically feasible.
- 8. Reduce derivatives:** Unnecessary derivatization (e.g., the use of blocking or protecting groups) should be minimized or avoided, because such steps require additional reagents and can generate waste.
- 9. Catalysis:** Catalytic reagents are superior to consumable reagents. A catalyst is not consumed and can be re-used to carry out additional transformations.
- 10. Design for degradation:** Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
- 11. Real-time analysis for pollution prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.
- 12. Inherently benign chemistry for accident prevention:** Substances and the forms in which they are used should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

**Evaluating the “true” green-ness of a reaction or process?** Atom economy and the E-factor are useful for evaluating how wasteful a reaction or process is, but they ignore the environmental impacts of the substances involved. A complete assessment of the “green-ness” of a reaction or process also requires consideration of the substances’ human toxicity, aquatic ecotoxicity, persistence in the environment, acidification potential, ozone depletion potential, smog formation potential, and global warming potential.

**Has green chemistry made a difference?** Figures published by the U.S. Environmental Protection Agency indicate that, every year in the U.S., green chemistry eliminates more than 6 million kilograms (60,000 metric tonnes) of hazardous substances, saves more than 200 million litres of water, and prevents 25 million kilograms (26,000 metric tonnes) of CO<sub>2</sub> emissions.

**A specific example?** The industrial synthesis of ibuprofen (a medication for treating pain, fever, and inflammation) was originally a 6-step process with an atom economy of about 40%. It is now made using a 3-step process that has an atom economy of 77%. The new process eliminates millions of kilograms of waste each year. ]

## 2.1 Overview of Quantum Theory

In this module, we focus on the theory and principles required to understand the behaviour and distribution of electrons in atoms and molecules. The laws of “classical physics”, as formulated by Newton and others, including Hamilton and Lagrange, are not appropriate for describing the behaviour of particles at the atomic and molecular level. Electrons in atoms and molecules are governed by the laws of quantum theory. A remarkable consequence of quantum theory is captured by the following statement.

***When an electron is “confined” to a finite region of space by the forces exerted on it, its total energy is restricted to certain special values!***

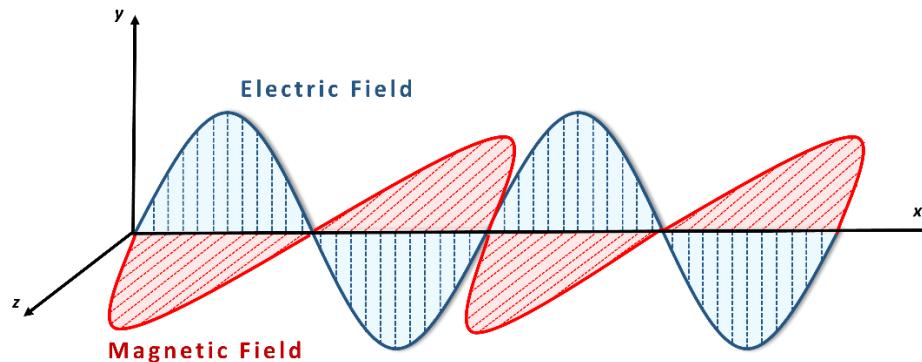
This is called quantization! This is a key concept for Module

The idea that the energy of an object, in this case an electron, is restricted to certain special values contradicted the laws of classical physics. At the time, the laws of classical mechanics were based on observations of macroscopic systems. (e.g. the trajectory of a ball in the earth’s gravitational field). As it turns out, Newton’s Laws of motion don’t hold at the atomic and molecular levels.

The development of quantum theory was driven by key experiments, each of which involved the interaction of light and matter. The results of these experiments forced physicists to re-think the physical laws that govern the behaviour of electrons in atoms and molecules, leading to, arguably, the biggest scientific revolution in the past 100 years! Before we delve into a discussion of these experiments, we’ll review some fundamental concepts about light itself.

## 2.2 Nature of Light

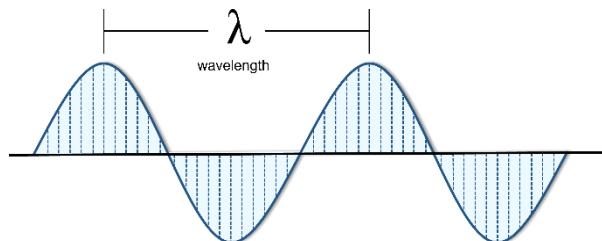
Light is electromagnetic (EM) radiation that transmits energy through space or some other medium. Light has an electric field that oscillates at a certain frequency, and a magnetic field that oscillates at the same frequency, perpendicular to the plane of the electric field.



Electromagnetic radiation is produced when electrical charges (e.g. electrons) undergo some sort of acceleration. For example, light from a white light bulb is produced from the oscillations of the tungsten atoms in the wire filament. As the wire heats up, the atoms in the filament vibrate back and forth.

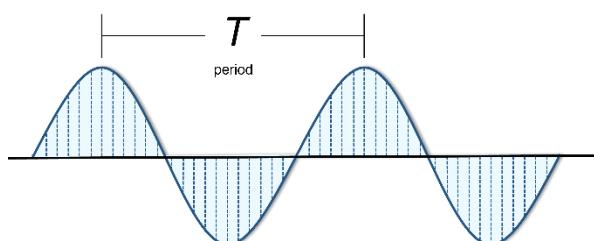
The back-and-forth oscillations of the atoms produce electric and magnetic fields that propagate away from the light bulb. To an observer, these electric and magnetic fields exhibit both spatial and temporal oscillations. Let's focus on the electric field:

**At a particular instant in time:**



The wavelength,  $\lambda$ , is the distance between adjacent maxima.

**At a particular point in space:**



The period,  $T$ , is the time it takes for the electric field to return to its maximum strength

### The Wavelength-Frequency relationship

Wavelength,  $\lambda$  (in metres) = distance between successive maxima

Period,  $T$  (in seconds) = time it takes for the electric field to return to its maximum strength

Frequency,  $v = \frac{1}{T}$  (in  $s^{-1}$ ) = # of times per second the electric field reaches its maximum value

The wavelength and frequency obey the following relationship:

$$\lambda v = c$$

$c = 2.998 \times 10^8 \text{ m s}^{-1}$  is the speed of light.

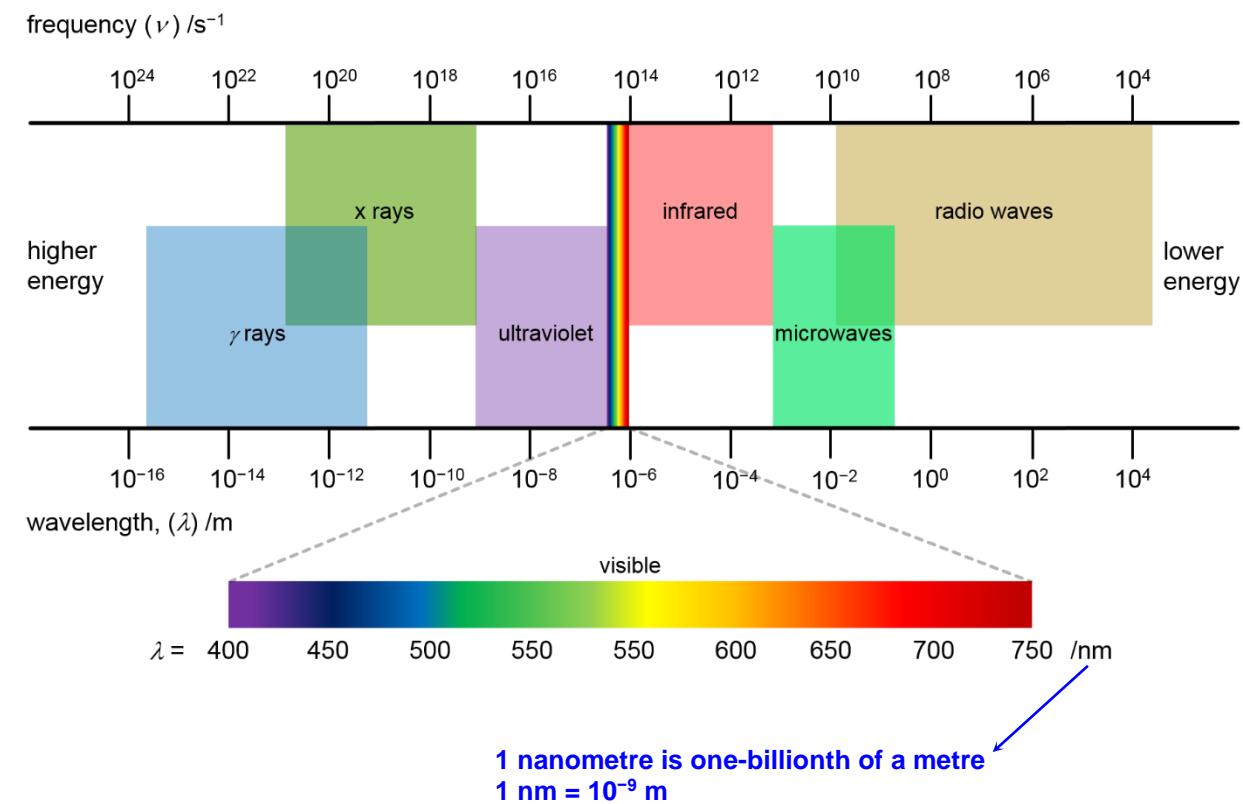
### Did you know?

- $\lambda$  and  $v$  are the Greek letters lambda and nu.
- 1 Hertz (Hz) equals  $1 \text{ s}^{-1}$ .

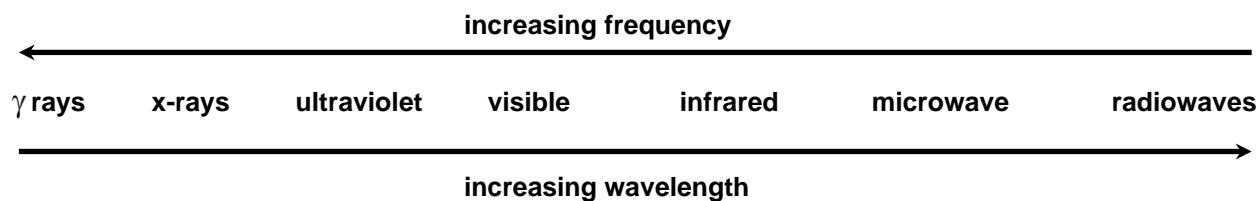
**Example 2-1:** What is the wavelength (in nm) of light having a frequency of  $5.45 \times 10^{14} \text{ Hz}$ ? What colour is this light?

## The Electromagnetic Spectrum

Light is classified according to its wavelength. For example, visible light corresponds to the wavelength range  $\lambda \approx 400 - 750 \text{ nm}$ .



Make sure you know the names and order (from longest  $\lambda$  to shortest  $\lambda$ ) of the various regions of the electromagnetic spectrum.



Also remember that **the visible region extends from  $\lambda \approx 400 \text{ nm}$  to  $\lambda \approx 750 \text{ nm}$** . As we shall soon see, the energy content of electromagnetic radiation is inversely proportional to its wave length (i.e. the shorter the wave length, the higher the energy.) Therefore, gamma rays and x-rays are much more energetic and (potentially) dangerous than are radiowaves.

## 2.3 A Historical Perspective – The Key Experiments

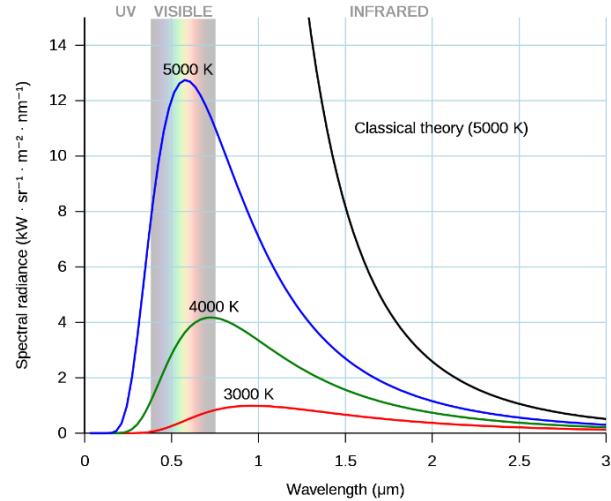
As indicated in section 2.1, the development of quantum theory was driven by key experiments, each of which involved the interaction of light and matter. There are three key experiments that support the concept of energy being quantized at the molecular level, each covered in the next few pages: (i) Blackbody Radiation, (ii) The Photoelectric Effect, and the (iii) Line Spectra of Atoms.

### (i) Blackbody Radiation

What is blackbody radiation? Regardless of composition, an object at 300 K will emit light in the mid-IR region. This is called Black Body Radiation.

**The experiment (1850's):** A heated solid produces electromagnetic radiation that consists of many  $\lambda$ 's. The emitted radiation is passed through a prism to split the light into its component wavelengths. We can generate an intensity profile by measuring the intensity ( $I$ ) of light for each of the wavelengths emitted.

**The results:** The intensity distributions obtained from this experiment (image to the right) *could not be explained at the time!* Classical Theory (Rayleigh-Jeans Law) did not predict or explain the fact that a maximum wavelength was observed in the intensity profile. The study of blackbody radiation began in the 1850's but most of the theoretical investigations of the intensity profile occurred in the 1890's with only moderate success.



In 1900, [Max Planck](#) finally resolved the discrepancy between theory and experiment by suggesting that **quanta of energy are absorbed by and emitted from matter**. (Keep in mind, these were strange assumptions at the time...)

His assumptions that can be re-phrased as follows:

- (1) The emitted radiation of frequency  $\nu = c/\lambda$  was produced by a group of atoms in the solid that oscillate with that same frequency.
- (2) The energy of oscillation for a particular group of atoms was restricted to certain special values given by  $E_{\text{osc}} = nh\nu$ , where  $n$  is an integer ( $n = 0, 1, 2, \dots$ ) and  $h$  is a constant to be determined.

**Assumption (2) introduces a radical new way of thinking:** the energy of oscillation does not vary continuously but rather, it is restricted to one of the following special values:

$$E_{\text{osc}} = 0 \quad \text{or} \quad E_{\text{osc}} = h\nu \quad \text{or} \quad E_{\text{osc}} = 2h\nu \quad \text{or} \dots$$

**This is the first suggestion of the quantization of energy!** Planck used his quantum hypothesis to calculate the intensity of light produced by each group of atoms, and then summed over all groups of atoms to obtain the intensity profile. He discovered that he could reproduce the experimental intensity profile if  $h$  was set equal to  $6.626 \times 10^{-34} \text{ J s}$ .

According to Planck's quantum hypothesis, the energy of oscillation could change by an amount equal to  $h\nu$ . An energy change of  $10^{-20} \text{ J}$  or  $10^{-25} \text{ J}$  seems inconceivably small to us, but on the atomic scale, it is appreciable.

On the atomic scale, particle masses are about  $10^{-27} \text{ kg}$ , and their energies are of the order of  $10^{-20} \text{ J}$ , and distances are measured in picometres ( $10^{-12} \text{ m}$ ).

### What is the significance of Planck's analysis?

- It suggests that there is some validity to the notion that energy is quantized at the molecular level.
- $h = 6.626 \times 10^{-34} \text{ J s}$  is a new and important physical constant.  
The constant  $h$  is known today as "Planck's constant".

**For you to try:** Using Plank's suggestion that the energy of a single quantum of energy is  $E = h\nu$ , and the wavelength-frequency relationship, can you derive the relationship between energy and wavelength?

**Are you wondering...** How did Plank reproduce the intensity profile from the blackbody radiation experiment?

The equation derived by Planck can be written in the form given below. ( $T$  is the Kelvin temperature.)

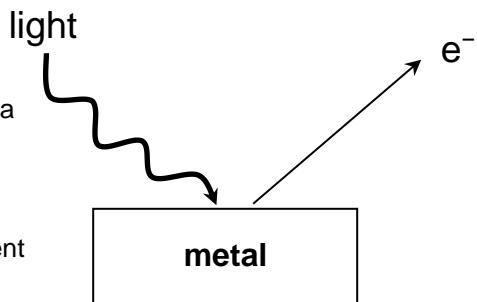
$$I = \frac{8\pi hc}{\lambda^5} \left( \frac{e^{-\frac{hc}{\lambda kT}}}{1 - e^{-\frac{hc}{\lambda kT}}} \right)$$

$$h = 6.626 \times 10^{-34} \text{ J s} \quad k = R / N_A = 1.3806 \times 10^{-23} \text{ J K}^{-1}$$

The constant  $k$  is known as Boltzmann's constant. Its value can be obtained from the gas constant  $R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}$  and Avogadro's number,  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ . You are not responsible for, nor will you have to use, this equation in this course.

### (ii) The Photoelectric Effect

**The experiment** (initially 1887, [Heinrich Rudolf Hertz](#)): In the photoelectric effect, light is used to dislodge electrons from the surface of a metal. A schematic diagram of the effect is shown on the right. In the experiment, the maximum kinetic energy of the ejected electrons was monitored as a function of the frequency ( $\nu$ ) and intensity ( $I$ ) of the incident light.



**Observations:** The following observations were noted when studying the photoelectric effect.

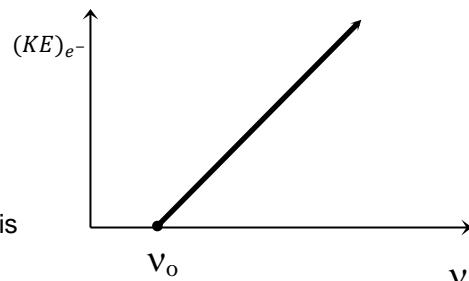
- (1) electrons were ejected only if the frequency of light was greater than some “threshold” frequency,  $\nu_0$ .
- (2) For  $\nu \geq \nu_0$ , the kinetic energy (KE) of an ejected electron increased proportionally with  $\nu$ .
- (3) Provided  $\nu \geq \nu_0$ , electrons were ejected instantaneously (i.e. *with no observable time delay*) regardless of the intensity of the incoming light.

A typical plot of  $(KE)_{e^-}$  versus  $\nu$  is shown to the right.

**The slope of the line was found to be equal to  $6.626 \times 10^{-34} \text{ J s}!!$**

(i.e. the slope of the line was equal to Planck's constant,  $h$ )

The first two observations indicate clearly that the energy of the light is proportional to its frequency and moreover that the proportionality constant is equal to  $h$  !!



**The third observation indicates that the energy of the light must be highly localized in space.** If the energy of the light was spread out over the entire light wave, then for “dim” (i.e. less intense) light, it would take longer for an electron to acquire enough energy to break free from the surface. No time lag was observed for dim light.

#### Einstein's explanation of the photoelectric effect (1905, Nobel Prize in 1921):

Albert Einstein offered a theoretical explanation of the photoelectric effect. Einstein proposed that the energy of light cannot be spread out over the entire wave. It must be concentrated into small, particle-like bundles. (i.e. photons). The energy of a photon must be proportional to the frequency of the light:

$$E_{\text{photon}} = h\nu$$

The energy of an incoming photon is transferred instantly to an  $e^-$  at the surface. The energy of the photon is used to dislodge the  $e^-$  from the surface and the excess energy is converted into kinetic energy of the ejected  $e^-$ . The collision of a photon and an electron at the surface obeys conservation of energy:

$$E_{\text{photon}} = w + (KE)_{e^-}$$

In the equation above,  $w$  is called the **work function** and it is the minimum energy required to dislodge an electron from the metal's surface. Einstein was showed that a plot of  $(KE)_{e^-}$  versus frequency should be linear and the value of  $h$  is obtained from the slope of the line! The value of  $h$  was expected to be (and found to be) equal to  $6.626 \times 10^{-34} \text{ J s}!!$  The “appearance” of  $h$  in another physical situation suggested that Planck's quantum hypothesis was not that crazy after all.

The work function is related to the threshold frequency (and threshold wavelength) as follows:

$$w = h\nu_0 = \frac{hc}{\lambda_0}$$

**Example 2-2:** A domestic microwave employs radiation of wavelength 12.2 cm. What is the energy in, in joules, of one photon of this radiation? What is the energy content of one mole of these photons?



See problems 8-11 and 8-12  
from Petrucci (11<sup>th</sup> edition).

**Example 2-3:** The work function for calcium metal is  $4.60 \times 10^{-19}$  J. What is the speed of an ejected electron if the surface is irradiated with light having  $\lambda = 400.0$  nm? The mass of an electron is  $m_e = 9.109 \times 10^{-31}$  kg.



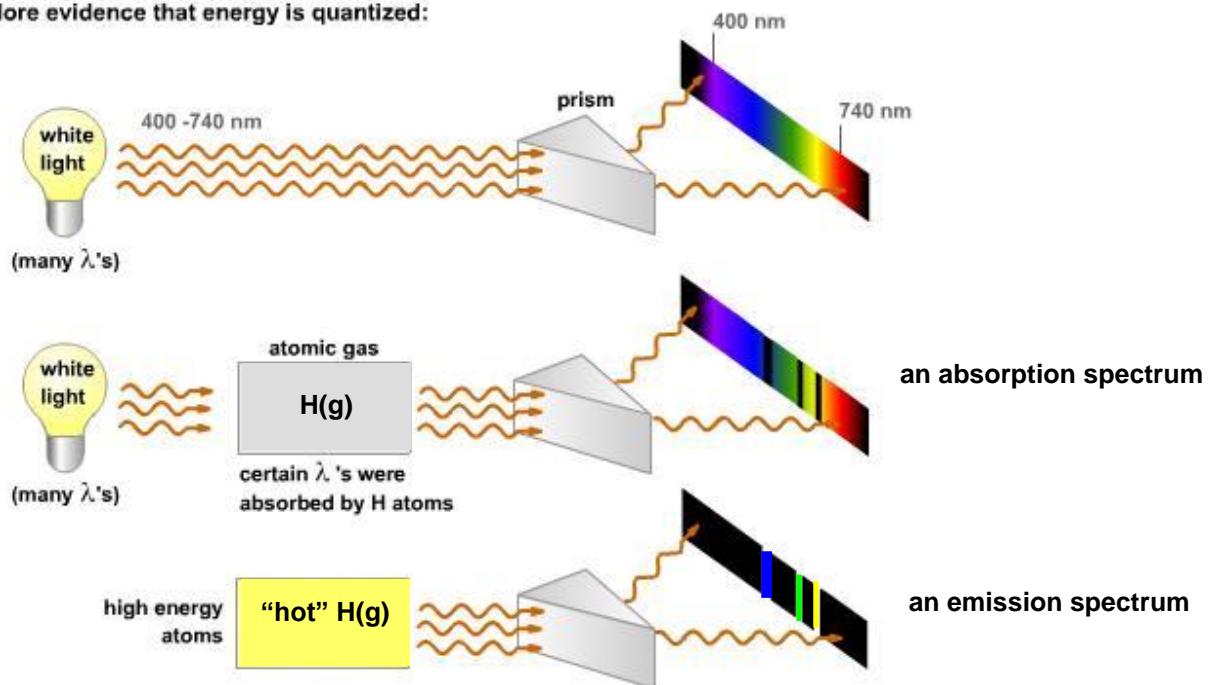
See problem 8-17 from  
Petrucci (11<sup>th</sup> edition).

### (iii) Line spectra of atoms

The emission spectrum of any substance can be obtained by energizing the sample of material (for example, supplying thermal energy or electrical energy).

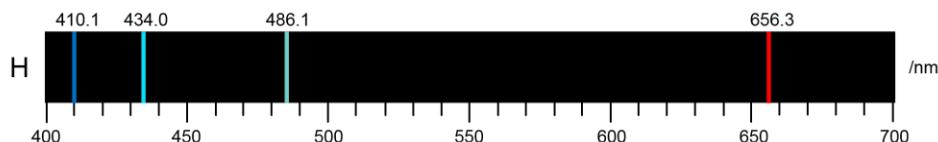
**The experiment:** White light can be dispersed into a rainbow of colours using a prism (*a continuous spectrum*). If you place a sample of atomic gas (e.g. H) between the light source and the prism, dark lines appear, suggesting certain **quanta of energy** were absorbed by the atomic gas. Alternatively, if the light emitted from a sample of high energy atoms is dispersed into its component wavelengths, only certain colours of lines appear.

More evidence that energy is quantized:



**The results:** The photoelectric effect established that the energy of a photon was determined by the colour of the light. If only certain colours were absorbed or emitted, then it must be true that atoms absorb or emit photons with certain specific energies (i.e. “quanta of energy”) Experiments continued to show that each atom has a unique set of absorption (or emission) lines. **The line spectra of atoms provided proof that the energy of an atom is “quantized”.**

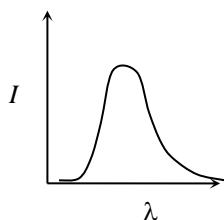
A portion of the emission spectrum for the hydrogen atom is shown below. With enough experimental evidence pointing to the idea of quantization of energy at the atomic level, an atomic model to explain the observed phenomena was needed.



### Summary of Key Experiments

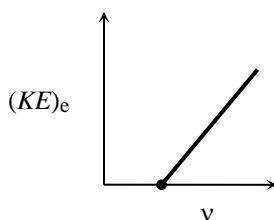
Experiment	Observation(s)	Key Idea(s)
------------	----------------	-------------

Blackbody radiation  
(Planck, 1900)



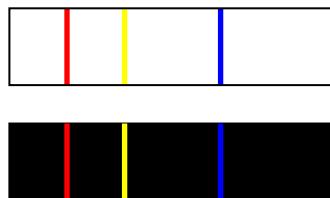
Atoms in a heated solid oscillate with certain energies only. ( $E_{\text{osc}} = nh\nu$ )

Photoelectric effect  
(Einstein, 1905)



The energy of light is highly localized and is proportional to its frequency. ( $E_{\text{photon}} = h\nu$ )

Line spectra of atoms



The energy of an electron in an atom is not arbitrary, but rather, it is restricted to have certain "special" values.

## 2.4 Bohr's Model of The H Atom

Neils Bohr postulated that the  $e^-$  moved around the nucleus with speed  $v$  in a circular orbit of radius  $r$ . He suggested further that the stable orbits were those for which the stated condition holds:

$$\underbrace{mvr}_{\text{angular momentum } (\ell)} = n \left( \frac{\hbar}{2\pi} \right)$$

In other words, Bohr assumed that the angular momentum of the electron was "quantized" (i.e.  $\ell$  was restricted to the quantities  $(\hbar/2\pi)$ ,  $\hbar/\pi$ ,  $3\hbar/2\pi$ ,  $2\hbar/\pi$ , etc.)

The integer  $n$  was used to label the orbits.

$n = 1$  was the innermost orbit

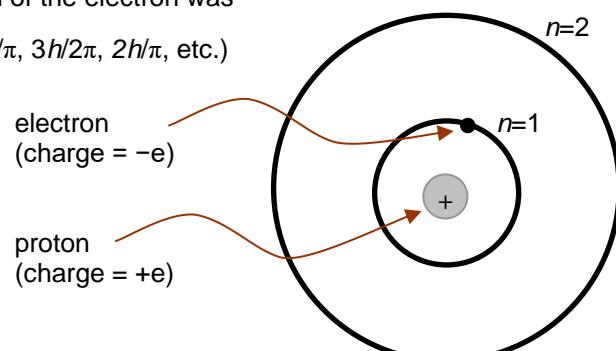
$n = 2$  was the next innermost orbit

etc. etc.

For an electron in the  $n^{\text{th}}$  orbit, we must have:

$$(1) \quad 2\pi mvr = nh$$

(2) the magnitude of the centrifugal force ( $m_e v^2 / r$ ) equals the magnitude of the attractive force between proton and electron ( $e^2 / 4\pi \epsilon_0 r^2$ )



With these two conditions, Bohr derived the following formula for the energy of the electron:

$$E_n = - \left( \frac{R_H}{n^2} \right) \quad \text{with} \quad R_H \approx \frac{m_e e^4}{8 \varepsilon_0^2 h^2} = 2.179 \times 10^{-18} \text{ J}$$

$R_H$  is called the Rydberg constant. Bohr also showed that the radius of the innermost orbit was 52.9 pm. Nowadays, this radius is known as the Bohr radius ( $a_0 = 52.9$  pm).

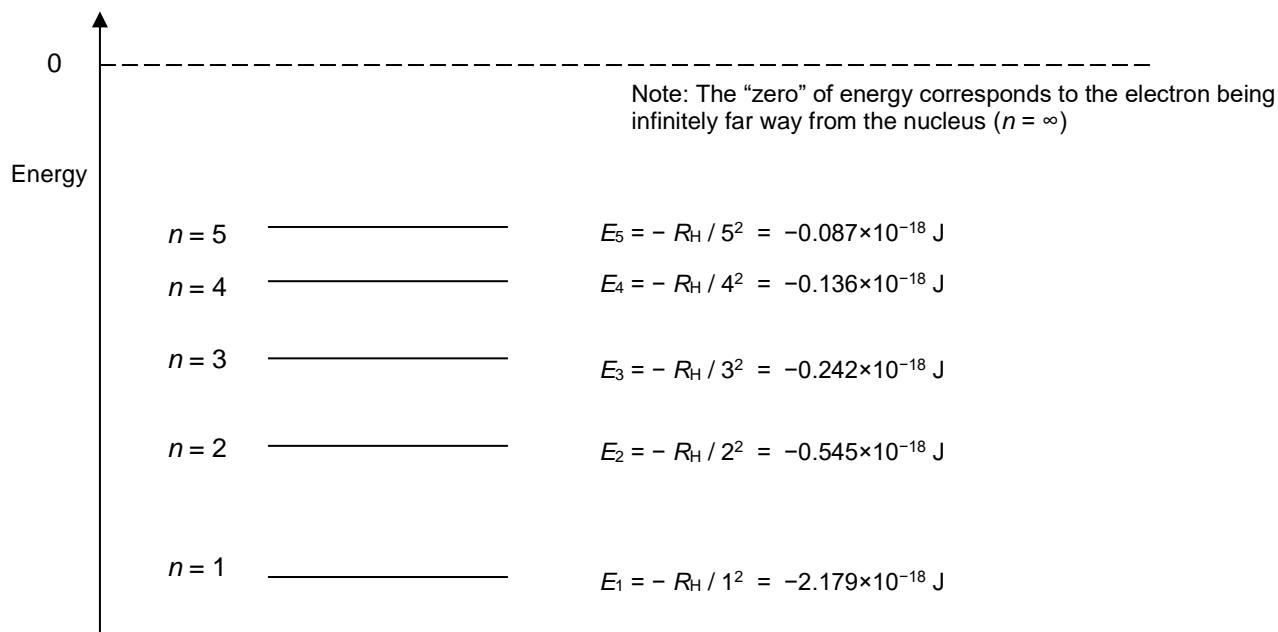
$$\begin{aligned} m_e &= \text{mass of the electron} \\ &= 9.109 \times 10^{-31} \text{ kg} \end{aligned}$$

$$\begin{aligned} e &= \text{charge on proton} \\ &= 1.602 \times 10^{-19} \text{ C} \end{aligned}$$

$$\begin{aligned} \varepsilon_0 &= \text{permittivity of vacuum} \\ &= 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1} \end{aligned}$$

$$\begin{aligned} h &= \text{Planck's constant} \\ &= 6.626 \times 10^{-34} \text{ J s} \end{aligned}$$

Bohr's formula gives rise to the following energy level diagram for the H atom:



### Remarks:

- The energies are negative because  $E = 0$  corresponds to the situation in which the electron is infinitely far away from the nucleus. As the distance between the electron and the nucleus decreases, so too does the energy of the electron. So, if the energy is zero when the electron is infinitely far away, then the energy must be negative for all other distances.
- When  $n$  is very large, the energy levels are very closely spaced.
- When the electron “drops” from a higher energy level ( $E_{\text{upper}}$ ) to a lower energy level ( $E_{\text{lower}}$ ), the atom emits a photon with energy equal to  $E_{\text{upper}} - E_{\text{lower}}$ .
- In order for the electron to “jump” from a lower energy level to a higher energy level, the atom must absorb a photon with energy equal to  $E_{\text{upper}} - E_{\text{lower}}$ .
- For electronic transitions of the hydrogen atom, we can write:  $\Delta E = h\nu = -R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$

**Are You Wondering** ... why we provide an approximation for the Rydberg constant rather than the accurate expression?

To be completely correct, we need to account for the mass of the nucleus, too. Because the hydrogen atom is a two-body system (one proton and one electron), we can use a mathematical trick to calculate a reduced mass,  $\mu_H = (m_e \times m_p) / (m_e + m_p)$ , where  $m_e$  is the mass of the electron and  $m_p = 1.6726219 \times 10^{-27}$  kg is the mass of the proton. For the  ${}^1H$  atom,  $\mu_H = 9.104 \times 10^{-31}$  kg, which is close to (but not quite) the mass of the electron.

**Are You Wondering** ... How did Bohr derive his expression for the energy levels of the H atom?

The total energy of the electron is  $E = KE + PE$ , with the kinetic energy given by  $KE = \frac{1}{2} m_e v^2$  and the potential energy given by  $PE = -e^2/(4\pi\epsilon_0 r)$ . Using the two conditions (1) and (2), given above, Bohr was able to eliminate both  $v$  and  $r$  from the expression for  $E$ . The derivation involves a lot of tedious algebra. Before you ask: **You are not responsible for the derivation!**

Please keep in mind: **The Bohr model is wrong!!** The electron does not move around the nucleus in a fixed orbit. Bohr was able to derive the correct result for the wrong reasons. However, Bohr's work was important because it provided more evidence that, on the atomic level, certain physical quantities – such as energy or angular momentum – are quantized.

**Example 2-4:** Is light absorbed or emitted when the electron in a hydrogen atom makes a transition from the  $n = 5$  level to the  $n = 2$  level? What is the wavelength of light associated with this transition?



See problems 8-21 to 8-23 from Petrucci (11<sup>th</sup> edition).

**For you to try:** Can you identify the transitions involved with each of the lines in the emission spectrum for the hydrogen atom, shown on page 8?

### Problems with the Bohr model

Bohr's model for the H atom accounts for the experimental observations but ...

- (1) it doesn't explain why the angular momentum and energy of the electron is quantized; the quantization conditions were imposed
- (2) the model could not be extended to other atoms
- (3) why doesn't the H atom emit radiation continuously?

}  $\Rightarrow$  There is something fundamentally wrong with the model.

We need a new set of physical laws to describe the behaviour of electrons in atoms!! There were two very important ideas that provided the breakthrough that physicists were waiting for:

- de Broglie's hypothesis
  - particles exhibit a wave-particle duality.
- the Heisenberg uncertainty principle
  - we can never know the "true" behaviour of a system

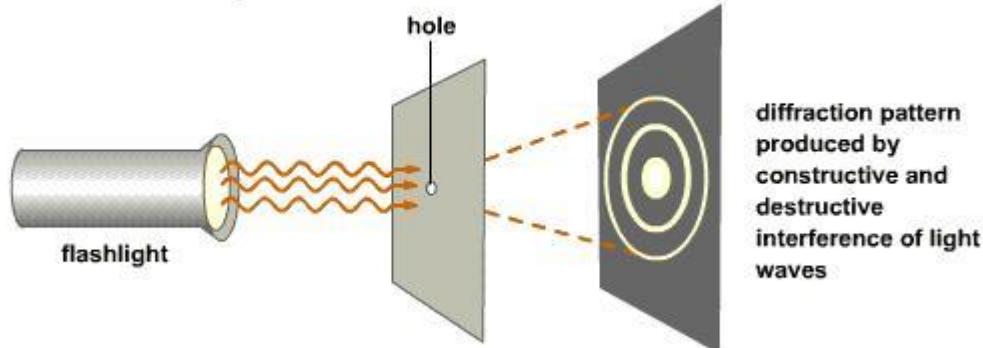
## 2.5 de Broglie's hypothesis

Einstein showed that light exhibited a wave-particle duality. (i.e. in some experiments, light behaved as a wave and in other experiments, it behaved as a stream of photons.)

- Diffraction suggests light behaves as a wave
- The photoelectric effect suggests light behaves as particles

Diffraction is observed when light passes through a hole or slit whose size is comparable to the wavelength of the light.

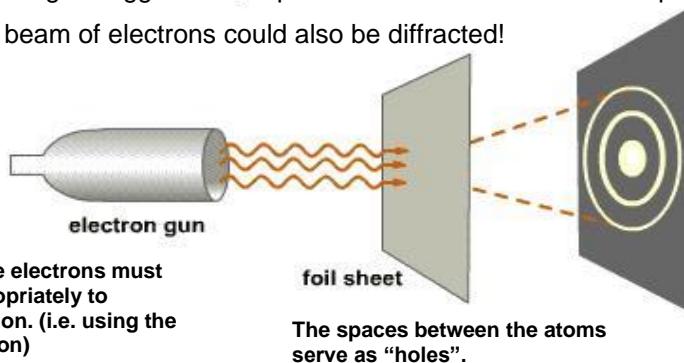
### Evidence for Wave Properties



In 1924, [Louis de Broglie](#) reasoned that if light could exhibit a wave-particle duality, then particles should also exhibit a wave-particle duality. According to classical physics, a particle of mass  $m$  traveling with speed  $v$  possesses momentum  $p = mv$ . Using Einstein's theory of special relativity, de Broglie argued that such a particle will behave as a wave with a wavelength given by:

$$\lambda_{dB} = \frac{h}{p} = \frac{h}{mv}; \quad \text{where } \lambda_{dB} \text{ is called the "de Broglie wavelength".}$$

A few years after de Broglie suggested that particles could exhibit wave-like properties, in 1927, scientists demonstrated that a beam of electrons could also be diffracted!



This was experimental verification that de Broglie's hypothesis was correct. (i.e. Electrons are not simply particles or waves but some strange combination of both!) This wave-particle duality is more than an intellectual curiosities: the electron microscope is a practical application of the wave properties of electrons.

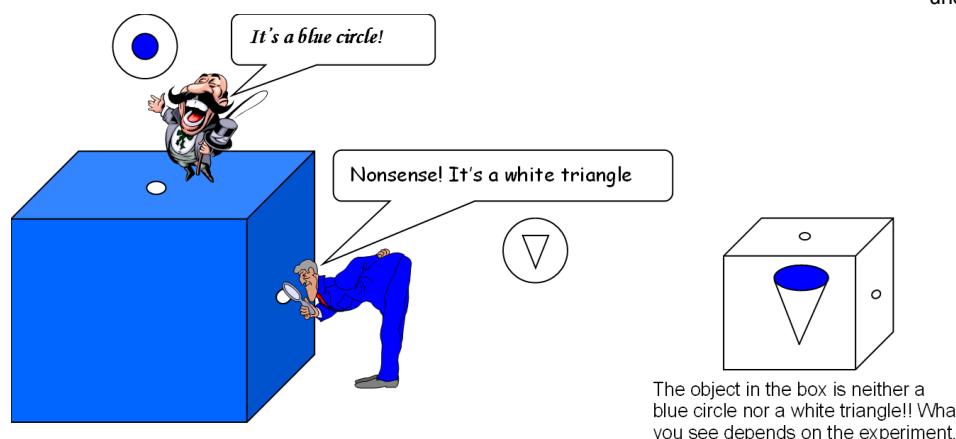
The significance of de Broglie's hypothesis is this:

***A complete description of the behaviour of an electron in an atom must incorporate wave-particle duality.***

**Seem confusing? You're not alone!**

In some respects, electrons behave like particles and in other respects like waves. How can an electron be both a particle, which is a localized entity, and a wave, which is nonlocalized? The answer is that an electron is neither a wave nor a particle but something else.

Evolution has shaped the human brain to allow it to understand and deal with macroscopic phenomena (e.g. particles and waves). Our nervous system was not developed to deal with phenomena at the atomic and molecular level, so it is not surprising that we cannot fully understand the true nature of an electron.



**Example 2-5:** What is the de Broglie wavelength for an electron ( $m_e = 9.109 \times 10^{-31} \text{ kg}$ ) moving with speed  $v = 10 \text{ m s}^{-1}$ ? What is the de Broglie wavelength for a car ( $m = 2000 \text{ kg}$ ) moving with the same speed? Comment on the results.

How fast is  $10 \text{ m s}^{-1}$ ?  
This speed is equal to  
 $36 \text{ km/h}$  or  $22 \text{ mph}$ .



See problems 8-40 and 8-41 from Petrucci (11<sup>th</sup> edition).

### Solution:

Make sure you use SI units!!

For the electron we have:

$$\lambda_{\text{dB}} = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ J s})}{(9.109 \times 10^{-31} \text{ kg})(10 \text{ m s}^{-1})} = 7.27 \times 10^{-5} \text{ m} = 73 \mu\text{m}$$

For the car we have:

$$\lambda_{\text{dB}} = \frac{h}{mv} = \frac{(6.626 \times 10^{-34} \text{ J s})}{(2000 \text{ kg})(10 \text{ m s}^{-1})} = 3.31 \times 10^{-38} \text{ m}$$

Significance?

In order to observe diffraction of electrons moving with a speed of  $10 \text{ m s}^{-1}$ , we would have to pass them through a hole with an approximate diameter of  $73 \mu\text{m}$ . A hole of this size is quite significant (and realistic) on the atomic scale. To observe diffraction of a car, we would have to pass it through a hole of diameter  $3.31 \times 10^{-38} \text{ m}$ . Of course, this is not possible. Stated another way, the de Broglie wavelength of a car is insignificantly small on the macroscopic scale of our world and (thankfully) we don't observe diffraction of cars.

## 2.6 Heisenberg Uncertainty Principle (H.U.P.)

Werner Heisenberg recognized that it is impossible to isolate an observer from the system he/she is studying. When an observer makes an observation or measurement, he/she becomes connected to the system and there is no way to ascertain how, or by how much, this connection affects the system under study. Consequently, we must live with the fact that we can never know what the exact or true behaviour of a system is.

With regard to the behaviour of electrons, Heisenberg reasoned that if we tried to measure the position ( $x$ ) of an electron, we will change its momentum ( $p$ ) in an indeterminable way (and vice versa). Heisenberg derived the following relationship that applies when we make simultaneous measurements of position and momentum:

$$\Delta x \Delta p \geq \frac{h}{4\pi} \quad \Rightarrow \quad \Delta p \geq \frac{h}{4\pi \Delta x}$$

$\Delta x$  = uncertainty in the position of the particle

$\Delta p$  =  $m\Delta v$  = uncertainty in the momentum of the particle

The H.U.P. tells us that it is impossible to know simultaneously both the position and the momentum of a particle with absolute certainty. (The result above shows that the smaller the uncertainty in the particle's position, the greater the uncertainty in its momentum. So, the more certain we are about a particle's position, the less certain we are about where it's going.) Because of the H.U.P., we cannot determine an "exact" trajectory" for the particle and, consequently, Newton's laws become useless for describing atomic and molecular systems.

As a result of Heisenberg's work, physicists realized that we should not think in terms of the "exact" behaviour of a particle. Instead, **we should focus on "What is the most probable behaviour?"**

It has been argued by Max Jammer,<sup>1</sup> that "certain philosophical ideas of the late 19<sup>th</sup> century not only prepared the intellectual climate for, but contributed decisively, to the formation of the new conceptions of the modern quantum theory." In constructing his argument, Jammer points out, for example, that Niels Bohr was strongly influenced by philosophical ideas. Bohr's interest and knowledge of philosophy was partly the result of circumstance. His father, a professor of philosophy, was a colleague and close friend of Harald Hoffding, a brilliant philosopher at the University of Copenhagen. Bohr attended Hoffding's lectures, read his writings and was certainly influenced by his work. Hoffding was a strong proponent of the idea that the originator of a system is a part of what he is trying to explain, and so, he cannot conceive of himself as an impartial spectator or impersonal observer. Bohr's impact on physics was felt through his influence on others. For example, Heisenberg admitted repeatedly that he had been strongly influenced by Bohr and particularly by the "philosophical presumptions underlying Bohr's conception of physics."

1. *The Conceptual Development of Quantum Mechanics*, M. Jammer, McGraw-Hill, New York, 1966.

## 2.7 The “new” quantum theory for describing electrons in atoms

de Broglie  $\Rightarrow$  the  $e^-$  exhibits a wave particle duality

Heisenberg  $\Rightarrow$  the exact behaviour of an  $e^-$  cannot be known

**Erwin Schrodinger** (and others) realized that the equation they needed for describing the behaviour of the electron in the H atom must

- incorporate the wave nature of the  $e^-$
- yield results that are interpreted in terms of “probability”

### The Schrodinger Equation

Schrodinger proposed that the following equation was appropriate for describing the behaviour of a single electron moving about the nucleus.

$$-\frac{\hbar^2}{8\pi m_e} \left[ \frac{d^2\Psi}{dx^2} + \frac{d^2\Psi}{dy^2} + \frac{d^2\Psi}{dz^2} \right] + V(x, y, z)\Psi = E\Psi$$

$\Psi$  is a mathematical function that depends on three coordinates ( $x, y, z$ ).

$d^2\Psi/dx^2$  is the second-derivative of  $\Psi$  with respect to  $x$ . (You will understand what this means only if you have taken calculus. If you have not taken calculus, don't worry because we don't have to use or solve the Schrodinger equation. The solutions have been worked out by others already!!)

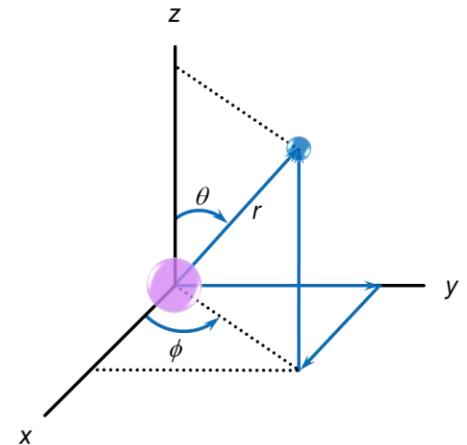
**Before you ask!** You do not need to memorize, use or solve the Schrodinger equation in this course. It's included only to give you an idea of what it looks like!

In the equation above,  $V$  is the potential energy associated with the electron-proton interaction.

$$V(x, y, z) = \frac{(+e)(-e)}{4\pi\epsilon_0 r}$$

The “unknowns” in the Schrodinger equation are  $E$  and  $\Psi$ . The goal is to find the values of  $E$  for which the Schrodinger equation can be solved. Solving the Schrodinger equation to find these  $E$ 's (and the corresponding  $\Psi$ 's) is complicated business. We will focus only on the results.

**But first ...what is the meaning of  $\Psi$  ?**



$$x^2 + y^2 + z^2 = r^2$$

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

The position of an electron can be given in terms of the coordinates ( $x, y, z$ ) or in terms of the coordinates ( $r, \theta, \phi$ )

$\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$  is a physical constant called the “permittivity of vacuum”.

$e = 1.602 \times 10^{-19} \text{ C}$  is the charge on a proton. The SI unit for charge is the coulomb (C).

### The meaning of $\Psi$ ?

$\Psi$  is simply a mathematical function. It exhibits “wave-like” variations when plotted and for this reason it is usually referred to as a “wave function”.  $\Psi$  itself has no physical interpretation. However,  $|\Psi|^2$  does have physical meaning.

$$|\Psi(x_o, y_o, z_o)|^2 dV = \begin{cases} \text{the probability of finding the } e^- \text{ within a small region of volume } dV \\ \text{near the point } (x_o, y_o, z_o) \\ \text{or} \\ \text{the density of the electron "cloud" contained within a small region} \\ \text{of volume } dV \text{ near the point } (x_o, y_o, z_o) \end{cases}$$

The first interpretation is the so-called **Born interpretation**; it emphasizes the particle-nature of the electron. The second interpretation, offered by Schrodinger himself, suggests that that the electron is “smeared out” into a charge cloud. There are some problems with Schrodinger’s interpretation. For example, experimentally, one never detects a fraction of an electron. Thus, we must consider electrons to behave as indivisible entities.

The Born and Schrodinger interpretations can be reconciled to a certain extent by imagining a “cloud” centred on the nucleus. The density of the cloud at a particular point represents the probability of finding the electron there. Thus, denser regions of the cloud represent locations where the electron is more likely to be found. The cloud picture offers some conceptual advantages (for example, when we come to talk about molecules, it is perfectly acceptable to refer to electron density, a “charge cloud”, or a “charge distribution”); however, for describing the electron in a hydrogen atom, the charge cloud interpretation should not be taken too literally.

Think of it this way – if we were to measure the position of the electron in the hydrogen atom, we’d observe it to be at a certain point in space. If we made another measurement of its position, we’d observe it to be somewhere else. If we made many, many measurements, we’d be able to construct a scatter point plot that shows us where the electron is most likely to be found. The scatter point plot shows us how the electron would be “distributed” in space, when a very large number of measurements of position have been made and in this regard, the electron is distributed over a region of space “like a cloud”.

There is a “problem” with Schrodinger’s interpretation. If the charge of a single electron was really “smeared out”, then there would be repulsions between the various parts of the cloud. Such repulsions are not accounted for in the expression for the potential energy that appears in the Schrodinger equation. Nevertheless, this “electron-cloud” model has significant use, partly because it offers computational simplicities when dealing with multi-electron systems. Just don’t take the electron-cloud model too literally when talking about the H atom.

**Did you know?** We cannot derive the Schrodinger equation from more fundamental principles. However, every application of it has given the correct result. We know the equation is valid, but we can’t prove why.

**For your info:** It is not known how Schrodinger arrived at “his” equation. However, it is interesting to point out that the Schrodinger equation bears some resemblance to the one used to describe the stable wave-like vibrations of a circular drumskin. Perhaps that equation provided the original inspiration for Schrodinger.

### Results obtained for the H atom

When you solve the Schrodinger equation for the H atom (as is done in CHEM 356 or PHYS 234), you get many solutions, each of which is characterized by a unique mathematical function ( $\Psi$ ) and a specific energy ( $E$ ). So ...

- 1) Each stable state of the H atom has a unique mathematical function  $\Psi$ , the square of which gives the probability of finding the electron at a particular point. The functions are solutions to the one-electron Schrodinger equation and they are called **orbitals**. Each orbital is a function of three coordinates (e.g.  $x$ ,  $y$  and  $z$ ). Rather than focusing on the mathematical equations themselves, we normally represent the orbitals using diagrams. (We'll encounter such diagrams shortly and will see that the orbitals differ in their size, shape and orientation.)

An **orbital** is a mathematical function,  $\Psi$ , whose square  $|\Psi|^2$  gives the probability of finding the electron at a particular point.

- 2) Each stable state of the H atom has a unique set of integers (called "quantum numbers") that identifies the orbital and characterizes the size, shape and orientation of the orbital.

$n \leftrightarrow$  **principal quantum number** (determines the "size" of an orbital)

$\ell \leftrightarrow$  **orbital angular momentum quantum number** (determines the "shape" of an orbital)

$m_\ell \leftrightarrow$  **magnetic quantum number** (the number of  $m_\ell$  values tells us about the number of distinct orientations that are allowed for a particular orbital)

These quantum numbers are not imposed or assumed (e.g. as they were by Planck and Bohr). They arise naturally from the mathematics involved with solving the Schrodinger equation!

There are relationships that inter-relate the values of  $n$ ,  $\ell$ ,  $m_\ell$ :

$$n = 1, 2, 3, \dots \infty$$

$$\ell = 0, 1, 2, \dots n-1$$

$$m_\ell = 0, \pm 1, \pm 2, \dots \pm \ell$$

- 3) Each stable state of the H atom has a well-defined energy

$$E_n = -\left(\frac{R_H}{n^2}\right)$$

$$\text{with } R_H = \frac{m_e e^4}{8 \varepsilon_0^2 h^2} = 2.179 \times 10^{-18} \text{ J}$$

You will notice that this is exactly the same energy formula that Bohr derived! Keep in mind that Bohr obtained the "right result" for the "wrong reasons".

**Example 2-6: (Important!)**

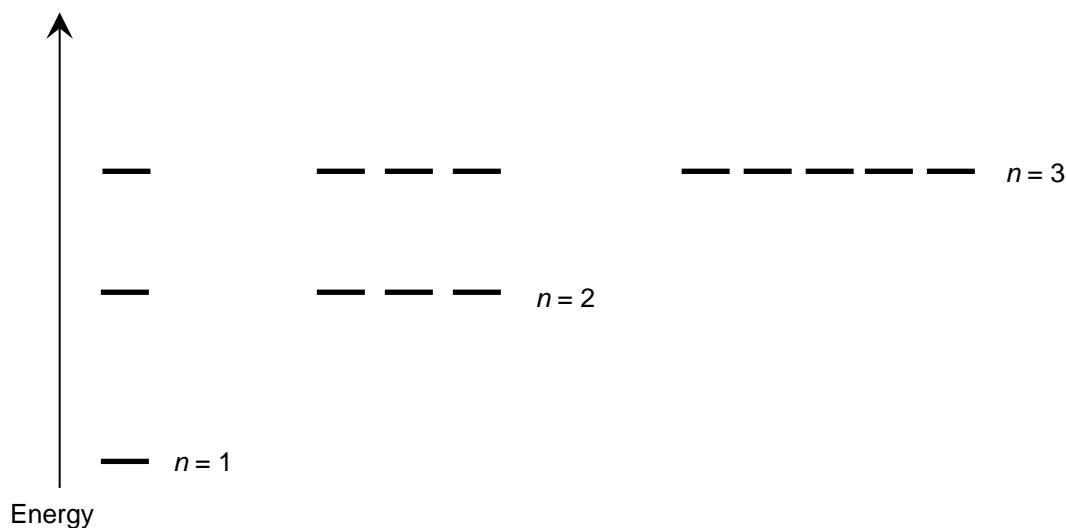
Use the energy level formula and the relationships among  $n$ ,  $\ell$  and  $m_\ell$  to construct an energy diagram for the H atom. Show all states that have  $n \leq 3$ .



See problems 8-58 to 8-62 from Petrucci (11<sup>th</sup> edition).

**Example 2-6 (continued) ...**

The energy level diagram for the H atom is shown below. Note the similarities and differences between this diagram below and the one given previously for Bohr's model of the H atom. (In particular, Bohr's energy level diagram had the correct energy-level spacings but it was incomplete; it had only one energy level for each value of  $n$ .)



To simplify the labeling of the energy levels, chemists use the following letter designations for the possible values of  $\ell$ :

$\ell = 0$	$\ell = 1$	$\ell = 2$	$\ell = 3$	$\ell = 4$	$\ell = 5$
"s"	"p"	"d"	"f"	"g"	"h"

The diagram given above is for the H atom, which is a one-electron system. (The corresponding diagram for a multi-electron atom is different!) The electron in the H atom can exist in any one of an infinite number of these levels. The lowest energy level is the 1s state. For a given value of  $n$ , the "s", "p" and "d" states in the H atom have exactly the same energy!

## Digging Deeper: Hydrogen Atom Wavefunctions

Orbital	Radial Factor, $R(r)^*$	Angular Factor, $Y(\theta,\phi)**$
1s	$2e^{-r}$	
2s	$\frac{1}{2\sqrt{2}} (r - 2) e^{-r/2}$	$\frac{1}{2\sqrt{\pi}}$
2p <sub>x</sub>		$\frac{\sqrt{3}}{2\sqrt{\pi}} \frac{x}{r}$
2p <sub>y</sub>		$\frac{\sqrt{3}}{2\sqrt{\pi}} \frac{y}{r}$
2p <sub>z</sub>	$\frac{1}{2\sqrt{6}} r e^{-r/2}$	$\frac{\sqrt{3}}{2\sqrt{\pi}} \frac{z}{r}$
3s	$\frac{2}{81\sqrt{3}} (27 - 18r + 2r^2) e^{-r/3}$	$\frac{1}{2\sqrt{\pi}}$
3p <sub>x</sub>		$\frac{\sqrt{3}}{2\sqrt{\pi}} \frac{x}{r}$
3p <sub>y</sub>	$-\frac{4}{81\sqrt{6}} r(r - 6) e^{-r/3}$	$\frac{\sqrt{3}}{2\sqrt{\pi}} \frac{y}{r}$
3p <sub>z</sub>		$\frac{\sqrt{3}}{2\sqrt{\pi}} \frac{z}{r}$
3d <sub>x<sup>2</sup>-y<sup>2</sup></sub>		$\frac{\sqrt{15}}{4\sqrt{\pi}} \frac{x^2 - y^2}{r^2}$
3d <sub>z<sup>2</sup></sub>	$\frac{4}{81\sqrt{30}} r^2 e^{-r/3}$	$\frac{\sqrt{5}}{4\sqrt{\pi}} \frac{3z^2 - r^2}{r^2}$
3d <sub>xz</sub>		$\frac{\sqrt{15}}{2\sqrt{\pi}} \frac{xz}{r^2}$
3d <sub>xy</sub>		$\frac{\sqrt{15}}{2\sqrt{\pi}} \frac{xy}{r^2}$
3d <sub>yz</sub>		$\frac{\sqrt{15}}{2\sqrt{\pi}} \frac{yz}{r^2}$

**Before you ask  
(or start to panic)!!**

You do not need to know, use or memorize these wave functions. They are here only to convince you that each orbital is based on a unique mathematical function.

Notice that there is a relationship between the name of the orbital and the mathematical function associated with it.

\* In the radial factor,  $r$  is actually  $r / a_0$  where  $a_0 = 5.29 \times 10^{-11} \text{ m}$  is the Bohr radius

\*\* In the angular factors, one must use the following transformations:

$$x = r \sin\theta \cos\phi \quad y = r \sin\theta \sin\phi \quad z = r \cos\theta$$

## 2.8 Graphical representations of H atom wave functions

A quick glance at the table of wave functions for the H atom (on the previous page) should convince you that they are complicated, three-variable functions. Each function has the following general form, where  $R(r)$  is called the **radial factor** and  $Y(\theta, \phi)$  is called the **angular factor**.

$$\Psi = R(r) Y(\theta, \phi)$$

It is impossible to use a single graph to describe the probability density associated with each state. We are forced to look at a variety of plots. In this section, we will examine various ways to visualize the results of the Schrodinger Equation (Hydrogen Atom Wavefunctions):

- (i) Probability Density Plots (“scatter point plots”)
- (ii) Boundary Surface Plots (“balloon pictures”)
- (iii) Radial Factors
- (iv) Radial Electron Densities
- (v) Radial Distribution Plots



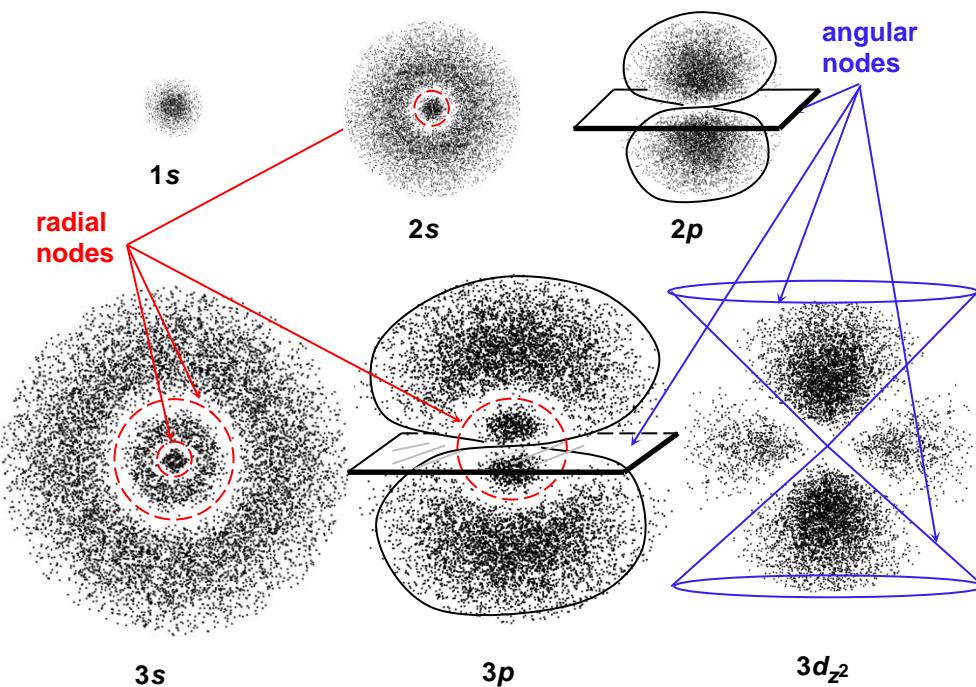
Visit the website below.

<http://winter.group.shef.ac.uk/orbitron/>

This is an amazing site devoted to atomic orbitals. It was developed by Dr. Mark Winter of the University of Sheffield. The graphics and animations are of exceptionally high quality.

### (i) Probability density plots (“scatter point” plots)

A density plot is like the “scatter plot” one might use to illustrate how the population of a geographic region (e.g Waterloo Region) is distributed across the area.



These diagrams show that:

- (1) **s** orbitals are spherical  
**p** orbitals are “dumbbell” shaped.
- (2) Orbitals can have **radial nodes** or **angular nodes**.

A **radial node** corresponds to a value of  $r$  where  $R = 0$  (strictly speaking, where  $R$  changes from positive to negative, or vice versa).

An **angular node** corresponds to points where  $Y$  changes sign, i.e. where  $Y = 0$ .

#### General rules:

$$\# \text{ radial nodes} = n - \ell - 1$$

$$\# \text{ angular nodes} = \ell$$

$$\text{total } \# \text{ nodes} = n - 1$$

**Angular nodes appear as surfaces** (e.g. planes or cones). For a given orbital, the number of angular nodes is equal to  $\ell$ . The greater the value of  $\ell$ , the greater the number of angular nodes and the greater the number of “lobes” the orbital has.

A radial node corresponds to a given value of  $r$ . **A radial node is represented by a circle (in a two dimensional diagram) or a sphere (in a three dimensional diagram)**. The number of radial nodes equals  $n - \ell - 1$ .

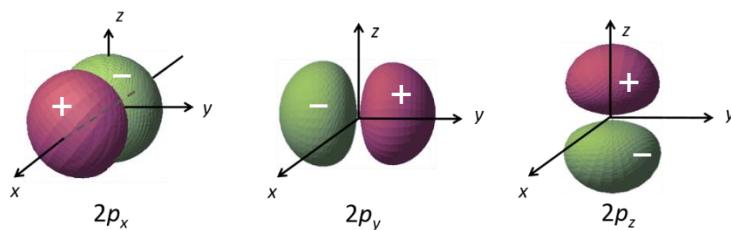
## (ii) Boundary Surface Plots (“balloon” pictures)

A boundary surface defines a region of space within which the probability of finding the electron is high (e.g. 90% or 95% or 99%). Alternatively, it tells us about the “shape” and “orientation” of the electron cloud. These pictures are useful because, for many applications, we are interested only in the overall shape and directionality of the orbital. In most cases, such a plot does not convey information about how the probability (or density) varies within that region of space.

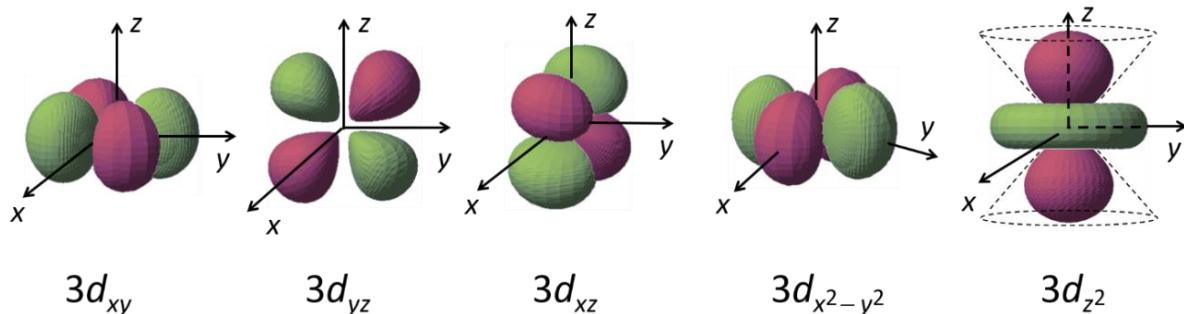
The size of an orbital increases as  $n$  increases, as illustrated below for  $s$  orbitals. Similarly, a  $3p$  orbital is larger than a  $2p$  orbital and a  $4d$  orbital is larger than a  $3d$  orbital.



An  $s$  orbital has no angular nodes and  $n - \ell - 1$  radial nodes.



A  $p$  orbital has one angular node (i.e. one nodal plane) and  $n - \ell - 1$  radial nodes



A  $d$  orbital has two angular nodes. The angular nodes are either planes or cones. A  $d$  orbital also has  $n - \ell - 1$  radial nodes

The colours (shades) on the lobes of the orbitals are used to indicate the phase (i.e. sign) of  $\Psi$  in various regions of space. Additionally, the “+” and “-” signs are used to identify the phase; the “+” and “-” signs do NOT represent charges. The net charge of an electron “cloud” is always negative.

You need to be able to recognize and sketch each “ $s$ ”, “ $p$ ”, and “ $d$ ” orbital with the proper orientation and phase indicated on the lobes.

### (iii) Radial factors, $R(r)$

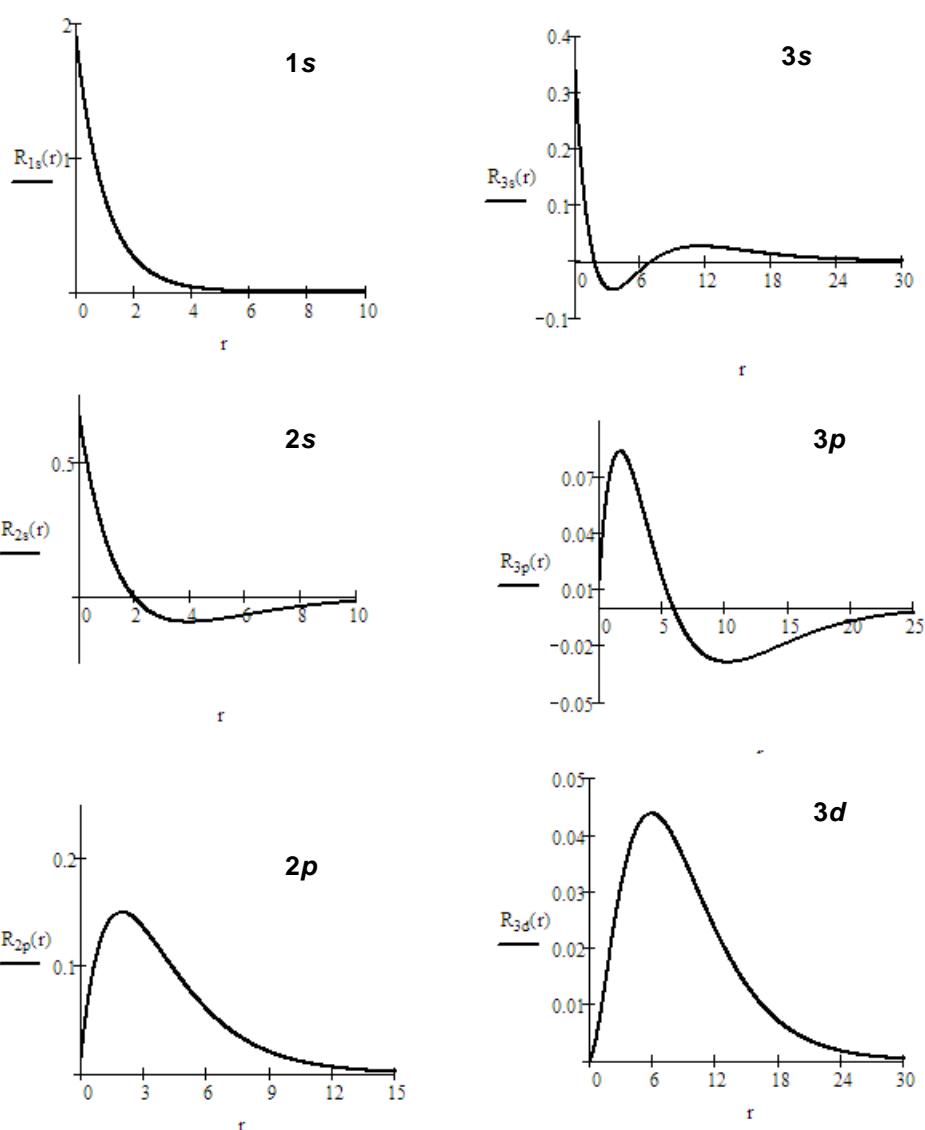
The radial factor depends on the values of  $n$  and  $\ell$  for the state in question. For example, the radial factor for a  $3p$  orbital is  $R(r) = -\frac{4}{81\sqrt{6}} r(r-6)e^{-r/3}$ , where  $r$  is actually  $\frac{r}{a_0}$  with  $a_0 = 52.9177\dots$  pm (the Bohr radius). Therefore, a value of  $r = 3$  corresponds to an actual  $r$  value of  $3a_0$  or 158.7531,, pm. The general form of the radial factor is:

$$R(r) = A f(r) r^\ell e^{-\frac{r}{na_0}}$$

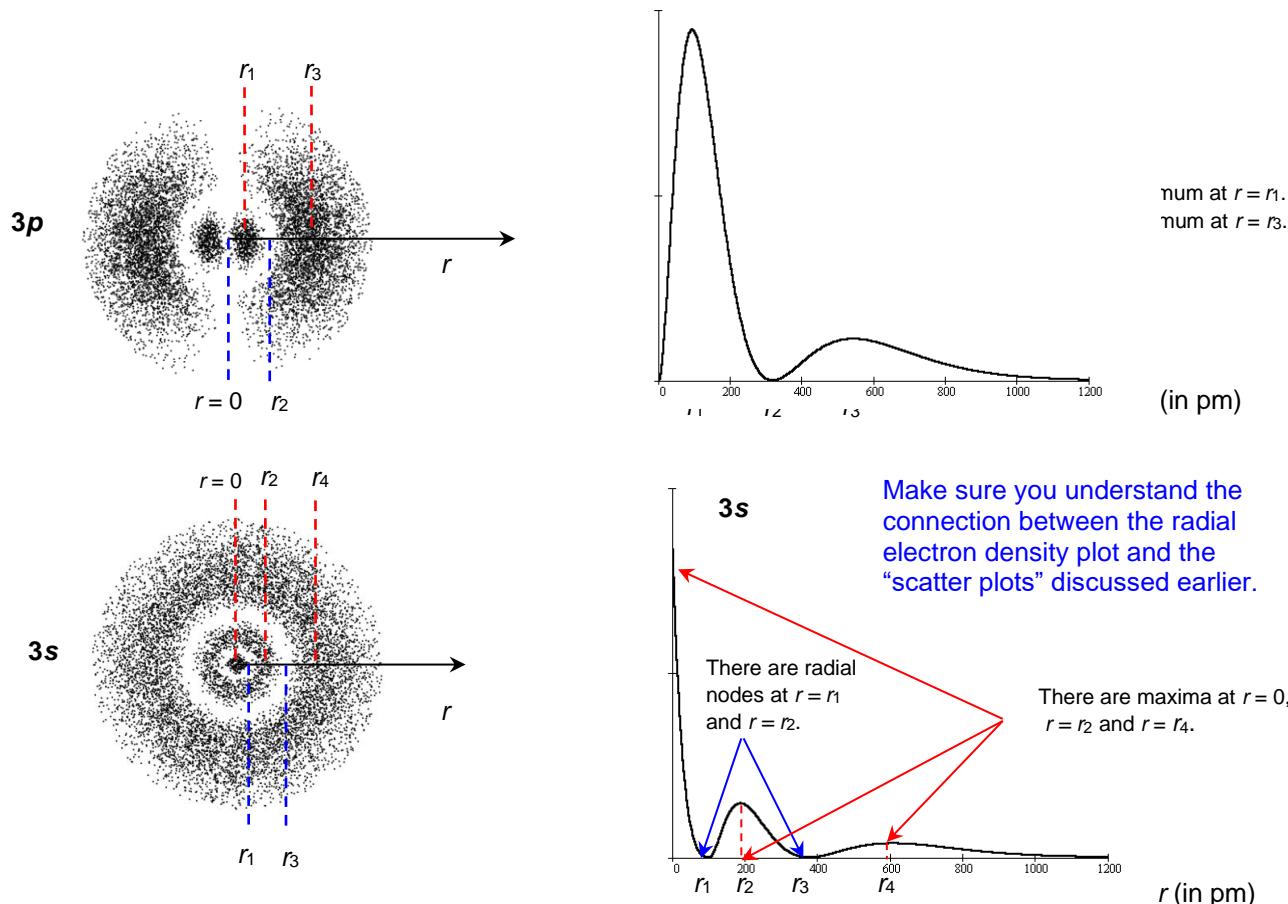
where  $A$  is a constant and  $f(r)$  is a polynomial of order  $(n - \ell - 1)$ . Plots of  $R(r)$  versus  $r$  for the  $n \leq 3$  are shown below.

Careful examination of these plots show that the radial factors,  $R(r)$ , have the following general characteristics.

- $R(r)$  decreases exponentially as  $r$  increases
- $R(r)$  crosses the  $r$  axis  $n - \ell - 1$  times. We say that  $R(r)$  has  $n - \ell - 1$  **radial nodes**.
- For  $s$  states (i.e.  $\ell = 0$ ),  $R(r)$  has its maximum value at  $r = 0$ .
- For  $p, d, f$ , states, etc. (i.e.  $\ell > 0$ ),  $R(r)$  has a value of zero at  $r = 0$ .



**Exercise for you!** Sketch plots of  $R$  versus  $r$  for (a) a  $4s$  orbital; (b) a  $4p$  orbital; (c) a  $4d$  orbital.

(iv) Radial Electron Densities - plots of  $R(r)^2$  versus  $r$ .

There are two interpretations for these plots. Such a plot tells us:

- (i) how the probability of finding the electron changes as we move away from the nucleus in a certain direction.
- (ii) how the density of the electron "cloud" changes as we move away from the nucleus in a certain direction

#### General features of radial electron density plots:

- a series of maxima that get progressively smaller as  $r$  increases

Notice that the number of radial nodes for a particular orbital and the number of maxima in a plot of  $R(r)^2$  versus  $r$  can be deduced from the  $n$  and  $\ell$  quantum numbers.

$$\boxed{\# \text{ radial nodes} = n - \ell - 1}$$

$$\boxed{\# \text{ maxima} = n - \ell}$$

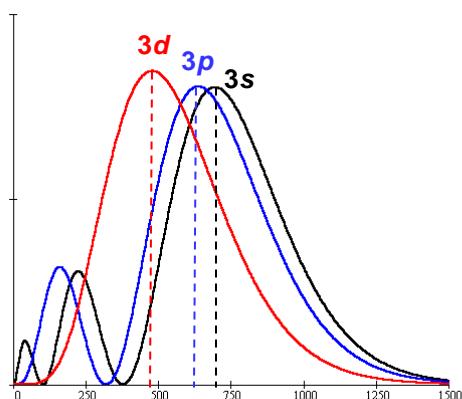
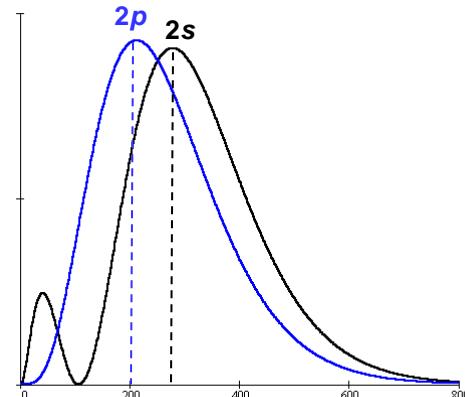
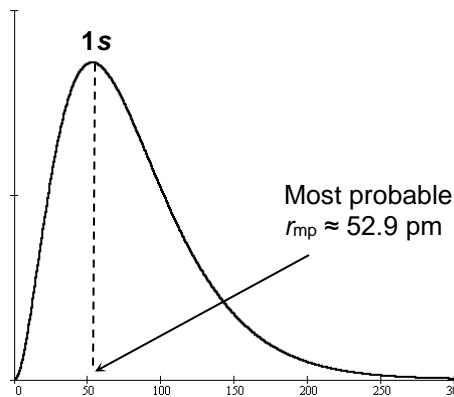
For example,  $n = 3$  and  $\ell = 1$  for a  $3p$  orbital, so a  $3p$  orbital has  $3 - 1 - 1 = 1$  radial nodes and a plot of  $R_{3s}(r)^2$  versus  $r$  should have  $3 - 1 = 2$  maxima

- for "s" states, the density is greatest at the nucleus
- for "p", "d", "f", etc. states, the density is zero at the nucleus

When the  $e^-$  is in an s orbital, there is a high probability of finding it at the nucleus. i.e. It "penetrates" all the way to the nucleus. When the  $e^-$  occupies a p, d, f, etc. orbital, there is zero probability of finding it at the nucleus. i.e. It does not penetrate all the way to the nucleus.

(v) Radial Distribution Plots – plots of  $r^2 R(r)^2$  versus  $r$ 

The quantity  $r^2 R(r)^2$  is called the radial distribution function (RDF).



***The value of  $r$  for which the RDF attains its maximum value corresponds to the most probable distance between the electron and the nucleus.***

The RDF for the 1s state has its maximum value at  $r \approx 52.9$  pm. The most probable distance between the electron and the nucleus is 52.9 pm.

#### General features & observations of radial distribution plots:

- all plots consist of a series of maxima that get progressively larger as  $r$  increases

Again, the number of maxima is predictable: # maxima =  $n - \ell$ .

- all plots start out at zero (i.e. RDF = 0 for  $r = 0$ )

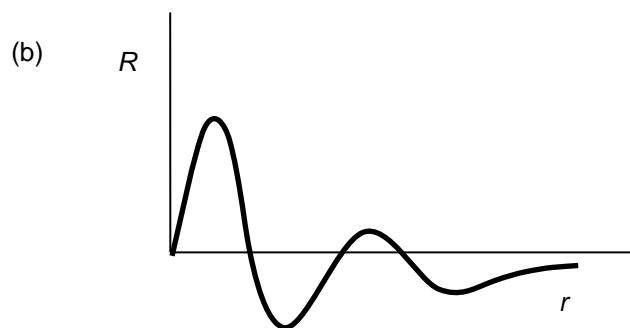
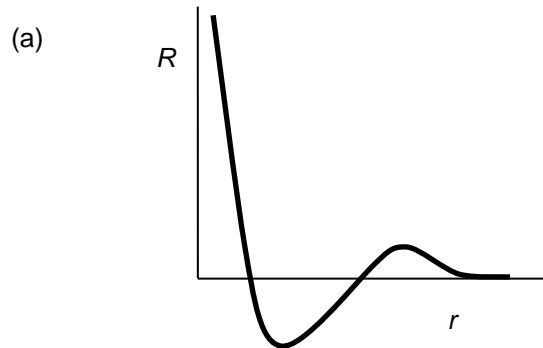
- $r_{mp}$  increases as  $n$  increases

orbital	1s	2s	3s
$r_{mp}$	53 pm	$\approx 300$ pm	$\approx 750$ pm

- for fixed a fixed  $n$  value,  $r_{mp}$  decreases as  $\ell$  increases

orbital	2s	2p
$r_{mp}$	$\approx 300$ pm	$\approx 200$ pm

**Example 2-7:** Plots of  $R$  versus  $r$  are given below. Which orbitals might they be? Explain your reasoning.



**Example 2-8:** For each of the following orbitals, specify the number of radial nodes and the number of angular nodes. Also, sketch plots of  $R$  versus  $r$ ,  $R^2$  versus  $r$  and  $r^2 R^2$  versus  $r$ .

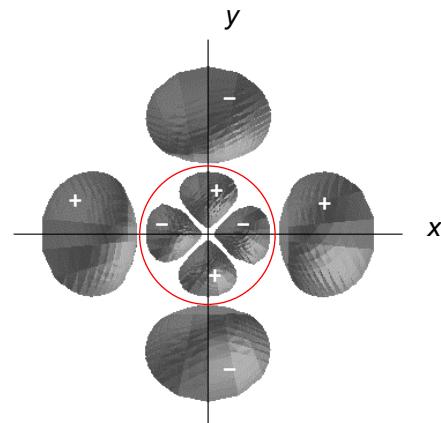
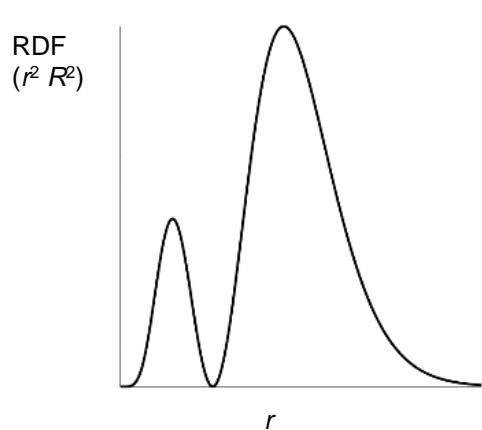
(a) a  $4s$  orbital

(b) a  $5d$  orbital



See problems 8-71 and 8-72 from Petrucci (11<sup>th</sup> edition).

**Example 2-9:** What is the correct orbital designation for the hydrogen atom orbital depicted in the diagrams below?



| Digging Deeper .... **Why is the RDF defined as  $r^2 R^2$ ?**

A rigorous mathematical proof is complicated. However, the result can be justified by considering the special case of an electron in the 1s orbital. We start from the Born interpretation:

$|\Psi|^2 dV$  = the probability of finding the  $e^-$  within a small region of space of volume  $dV$

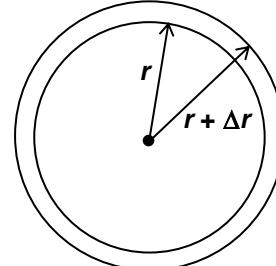
Therefore:

$|\Psi|^2 dx dy dz$  represents the probability of finding the electron in a small cubical box of volume  $dV = dx dy dz$  near a single point ( $x, y, z$ ).

$|\Psi|^2 dV_{\text{shell}}$  represents the total probability of finding the electron at any point within a thin spherical shell of thickness  $\Delta r$  and inner radius  $r$ .

But ...

$$\begin{aligned} dV_{\text{shell}} &= \frac{4}{3}\pi(r + \Delta r)^3 - \frac{4}{3}\pi r^3 \\ &= \frac{4}{3}\pi[r^3 + 3r^2\Delta r + 3r(\Delta r)^2 + (\Delta r)^3] - \frac{4}{3}\pi r^3 \\ &= 4\pi r^2 \Delta r + 4r(\Delta r)^2 + \frac{4}{3}\pi(\Delta r)^3 \\ &\approx 4\pi r^2 \Delta r \end{aligned}$$



When  $\Delta r$  is small (e.g.  $10^{-2}$  pm), then  $(\Delta r)^2$  and  $(\Delta r)^3$  are very small (e.g.  $10^{-4}$  and  $10^{-6}$ ). To a good approximation, we can neglect the terms that involve  $(\Delta r)^2$  and  $(\Delta r)^3$ .

When we substitute the result above for  $dV_{\text{shell}}$  into the expression  $|\Psi|^2 dV_{\text{shell}}$ , we obtain the following result.

Probability of finding the electron in a thin spherical shell of inner radius $r$ and thickness $\Delta r$	$\approx$	$ \Psi ^2 4\pi r^2 \Delta r$
--	-----------	------------------------------

For the 1s orbital,  $\Psi_{1s} = (1/4\pi)^{1/2} R_{1s}(r)$ , so the expression above becomes  $r^2 [R_{1s}(r)]^2$ . So, we see that the probability of finding the electron between  $r$  and  $r + \Delta r$  is proportional to  $r^2 R^2$ . Although we proved the result by considering an electron in a 1s orbital, the result turns out to be completely general. ]

## 2.9 Electron Spin Quantum Number

The Schrodinger description of the H atom is incomplete!

Schrodinger's equation

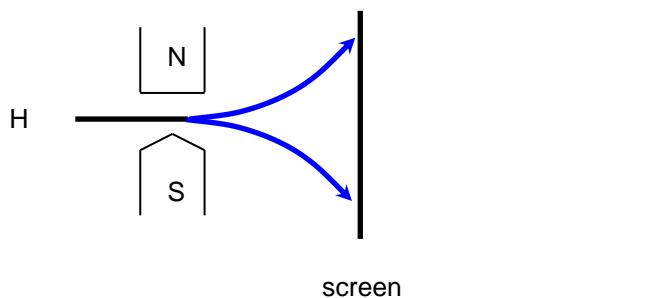


The state of an electron is characterized by three quantum numbers:  $n$ ,  $\ell$ ,  $m_\ell$ .

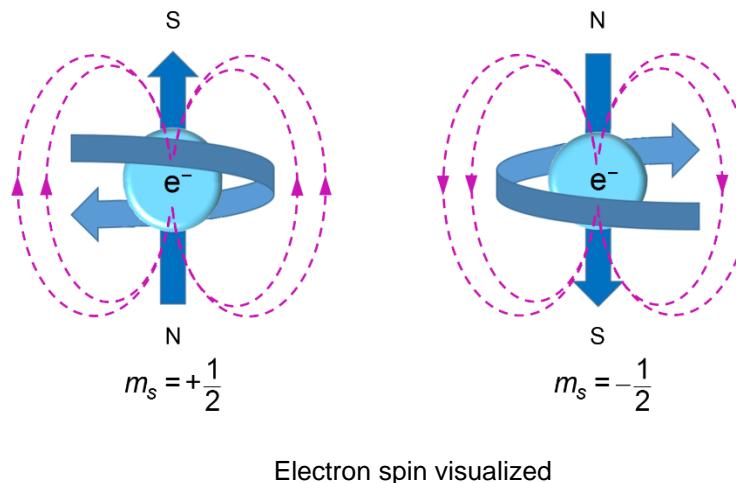
As complicated as it may be, Schrodinger's picture is incomplete! There are other quantum numbers to worry about. These additional quantum numbers were discovered experimentally and then explained theoretically using a more "complete" version of quantum mechanics.

In 1928, Paul Dirac, an English physicist and mathematician, developed a relativistic version of quantum mechanics. In Dirac's version, the spin quantum numbers appear together with the other quantum numbers. Dirac shared the 1933 Nobel Prize in Physics with Schrodinger.

Here is a schematic diagram of a simple experiment that proves the Schrodinger picture is incomplete.



The beam of H atoms is split into two separate beams! The results of this experiment tell us that the H atoms are behaving like tiny magnets that are either attracted to, or repelled by, the north pole of the magnet. How can we rationalize this observation? The electron in the H atom seems to behave as if it is "spinning" about an axis passing through its centre.



The "spin" characteristics (i.e., the "spin state") of an electron is characterized using two quantum numbers,  $s$  and  $m_s$ . There are only two spin states possible for an electron.

$s = \frac{1}{2}$  with  $m_s = +\frac{1}{2}$  "spin up"

$s = \frac{1}{2}$  with  $m_s = -\frac{1}{2}$  "spin down"

**Electrons are "spin-1/2" particles.** Other atomic particles have different amounts of spin.

photon = spin-1

$^{12}\text{C}$  nucleus = spin-0

$^{13}\text{C}$  nucleus = spin-1/2 particle

$^{127}\text{I}$  nucleus = spin-5/2 particle

## 2.10 Overview of Quantum Theory: Putting it all together

The orbital concept is everywhere in chemistry. Chemists use them to describe, electron by electron, the electronic structures of atoms and molecules. That is why we feel it is important to take the time to develop the orbital concept properly and to “tell it like it is”. Much of what we need to know about orbitals comes from studying the orbitals of the hydrogen atom. Thus, we’ve spent considerable time on the H atom.

### Summary: The Quantum Model of the Hydrogen Atom

1. The electron moves around the nucleus in an **orbital** which has a particular size, shape, and orientation.
2. The lowest energy atomic orbital is the 1s orbital. It is a spherical orbital. When the electron occupies this orbital, the most probable distance between the electron and the proton (nucleus) is  $a_0 = 52.9 \text{ pm}$ .
3. The stable (quantum) state of the electron is described by a unique set of quantum numbers,  $n$ ,  $l$ ,  $m_l$ , and  $m_s$ .
4. The energy of a state is given by  $E_n = -\left(\frac{R_H}{n^2}\right)$

Don’t be too alarmed if the material in this module seems daunting and confusing the first time through. However, before moving on, make sure you are able to answer the following questions.

- What does “quantized” mean in terms of energy of the electron in a Hydrogen atom?
- What are the three key experiments that lead to the development of modern quantum theory?
- What is the significance of the Schrodinger Equation?
- What is an orbital?
- What quantum numbers are used to identify and characterize an orbital?
- What are the possible values for these quantum numbers and what are the relationships among them?
- What is a node? What is a radial node? What is an angular node? For a given orbital, how many radial and angular nodes are there?
- How does “size” of an orbital change with  $n$ ?
- How does the energy of an orbital change with “ $n$ ”?
- What is the significance of a plot of  $R^2$  versus  $r$  for a given orbital? (i.e. what information does it provide?)

- What is the significance of a plot of  $r^2 R^2$  versus  $r$  for a given orbital? (i.e. what information does it provide?)
- Given the traditional symbol for an orbital (e.g.  $2p$ ,  $3s$ ,  $4d$ ,  $5f$ , etc), can you
  - Identify the corresponding values of  $n$  and  $\ell$ ?
  - Sketch a plot of  $R$  versus  $r$
  - Sketch a plot of  $R^2$  versus  $r$
  - Sketch a plot of  $r^2 R^2$  versus  $r$
- Can you sketch diagrams showing the shape and orientations of all three types of  $p$  orbitals and all five types of  $d$  orbitals, including axes that are properly labeled and with correct signs (+ or -) on the various lobes? And, given a sketch of a specific  $p$  or  $d$  orbital, can you identify which one it is? (e.g. Is it a  $p_x$ ,  $p_y$ ,  $p_z$ ,  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $d_{z2}$  or  $d_{x2-y2}$  orbital?)
- When we draw a sketch of a  $p$  or  $d$  orbital, we include “+” or “-“ signs on the various lobes, or use different colours or shading for the various lobes. What is the significance of the signs/colours on the lobes?

In the “new” quantum theory, the electron is described in terms of quantum numbers and orbitals. Notice that the energy of H atom increases with the number of nodes in the wave function,  $\Psi$ , as summarized below.

State/Orbital	Energy	# radial nodes (= $n - \ell - 1$ )	# angular nodes (= $\ell$ )	total # nodes (= $n - 1$ )
$1s (n = 1, \ell = 0)$	$E_1$	0	0	0
$2s (n = 2, \ell = 0)$	$E_2$	1	0	1
$2p (n = 2, \ell = 1)$	$E_2$	0	1	1
$3s (n = 3, \ell = 0)$	$E_3$	2	0	2
$3p (n = 3, \ell = 1)$	$E_3$	1	1	2
$3d (n = 3, \ell = 2)$	$E_3$	0	2	2

**If all of this is confusing you are not alone!**

*Those who are not shocked when they first come across quantum theory cannot possibly have understood it.* Niels Bohr

*It is safe to say that nobody understands quantum mechanics.* Richard Feynman

*If [quantum theory] is correct, it signifies the end of physics as a science.* Albert Einstein

*I do not like [quantum mechanics], and I am sorry I ever had anything to do with it.* Erwin Schrödinger

*Quantum mechanics makes absolutely no sense.* Roger Penrose

**More tidbits ...**

On October 12 1925, Werner Heisenberg wrote to Wolfgang Pauli:

*With respect to both of your last letters I must preach you a sermon, and beg your pardon for proceeding in Bavarian: It is really a pigsty that you cannot stop indulging in a slanging match. Your eternal reviling of Copenhagen and Göttingen is a shrieking scandal. You will have to allow that, in any case, we are not seeking to ruin physics out of malicious intent. When you reproach us that we are such big donkeys that we have never produced anything new in physics, it may well be true. But then, you are also an equally big jackass because you have not accomplished it either . . . . (The dots denote a curse of about two-minute duration!) Do not think badly of me and many greetings.*

(Source: <http://www.oberlin.edu/physics/dstyer/StrangeQM/history.html>)

And then, on June 8 1926, Heisenberg wrote again to Pauli:

*The more I think of the physical part of the Schrödinger theory, the more detestable I find it. What Schrödinger writes about visualization makes scarcely any sense, in other words I think it is shit ...*

(Source: <http://www.oberlin.edu/physics/dstyer/StrangeQM/history.html>)

### 3.1 Multielectron Atoms

The results obtained for the H atom help us understand how one  $e^-$  behaves when it interacts with a single nucleus. We will extend these ideas to understand and explain the properties of multielectron atoms. Recall:

- the state of the  $e^-$  is characterized using the quantum numbers ( $n, \ell, m_\ell, m_s$ )
- the  $e^-$  occupies a certain region of space (i.e. it occupies a particular “orbital”)

In principle, it is an “easy” matter to extend the approach of the last module from the hydrogen atom (with only one electron) to the helium atom (with two electrons). The nuclear charge increases by one, from  $Z=+1$  to  $Z=+2$ , and the number of electrons increases by one. There are only three interactions to worry about: electron 1 interacting with the nucleus; electron 2 interacting with the nucleus; and electron 1 interacting with electron 2. The Schrodinger equation for the system can be written down immediately, as it is a simple generalization of the Schrodinger equation given previously for the hydrogen atom. (There are more coordinates because there are more particles, but that’s about it.) All we need to do is solve the Schrodinger equation and analyze the results. Writing down the Schrodinger equation for the helium atom (or any multi-electron atom) is not that hard. The hard part is solving it, and the difficulty arises from the electron-electron interactions. **Fortunately, we do not have to solve the Schrodinger equation for every atom to understand how the electrons in a multielectron atom “pack around” the nucleus.**

#### A conceptual model for multi-electron atoms

A many-electron atom has a full set of hydrogen-like orbitals at its disposal (i.e. 1s, 2s, 2p, 3s, ...) governed by the same quantum numbers as before, ( $n, \ell, m_\ell, m_s$ ). Into these orbitals will go the electrons of the atom, each electron occupying a certain region of space and experiencing an average “attraction” towards the nucleus and an average “repulsion” from the other electrons.

Some fundamental questions that we must answer include:

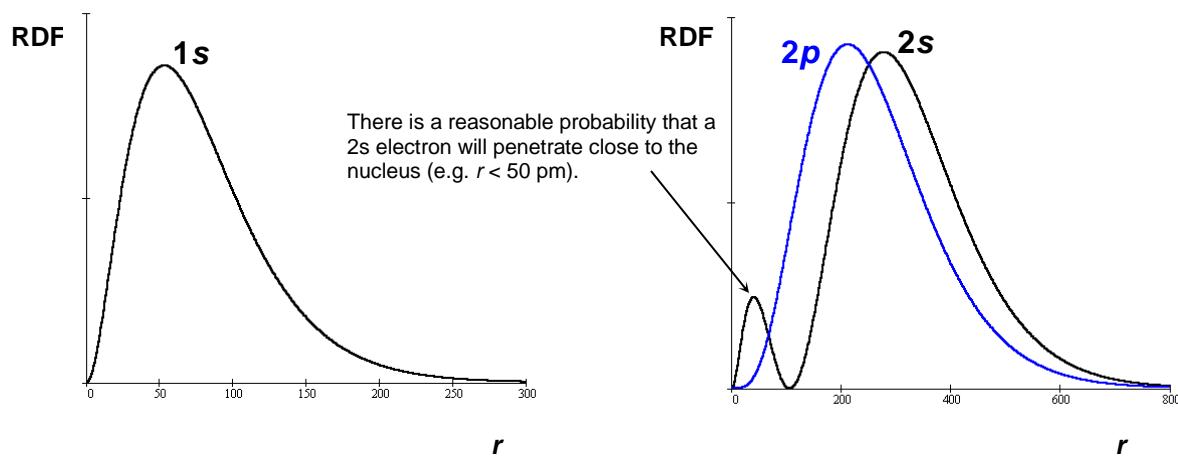
- How many electrons can occupy the same orbital?
- What arrangement of electrons gives the atom the lowest possible energy?

We know intuitively that each electron would like to be close to the nucleus but at the same time, electrons would like to avoid each other. Before we consider how the electrons in an atom “distribute” themselves amongst the various possible orbitals, it is instructive to consider how the electrons in a multielectron atom influence each other.

### Penetration and shielding

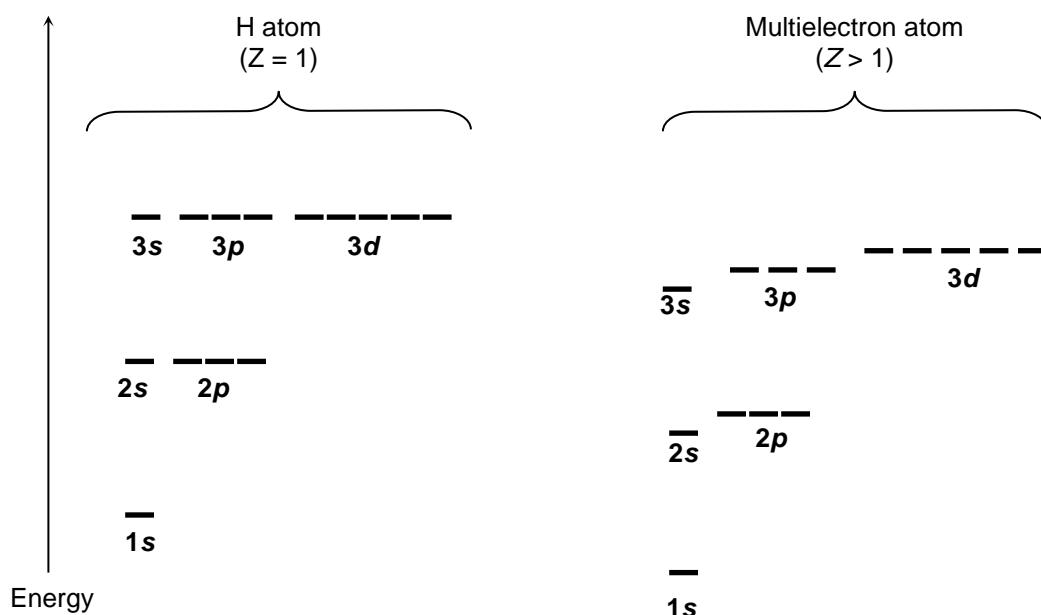
Penetration is a measure of how close a particular electron gets to the nucleus. Shielding indicates how thoroughly a particular electron is blocked (or shielded) from the nucleus. In a multielectron atom, the electrons shield each other from feeling the full nuclear charge. Careful examination of the RDF's below shows that:

- a  $1s e^-$  is more likely to be found close to the nucleus than is a  $2s$  or  $2p e^-$ . Consequently, a  $1s e^-$  “shields” the  $2s$  and  $2p$  electrons from feeling the full nuclear charge.
- a  $2p$  electron partially shields a  $2s$  electron from the feeling the full nuclear charge. (For the H atoms, we see that  $r_{mp} \approx 200$  pm for  $2p$  and  $r_{mp} \approx 300$  pm for  $2s$ )
- a  $2s e^-$  “penetrates” towards the nucleus more effectively than does a  $2p e^-$ . Therefore, a  $2s$  electron partially shields a  $2p$  electron. Since a  $2s$  electron penetrates more effectively than does a  $2p$  electron, a  $2s$  electron will actually feel more of the nuclear charge than will a  $2p$  electron.



The position of the maximum in a plot of the RDF versus  $r$  tells us the most probable radial distance between the electron and the nucleus. The area under the curve between two distances, say  $r_1$  and  $r_2$ , provides a measure of the amount of time the electron spends between  $r_1$  and  $r_2$ . For example, a  $1s$  electron in the H atom spends most of its time between 0 and 150 pm and very little time at distances greater than 150 pm. A  $2s$  electron spends most of its time between 100 pm and 600 pm but it does spend some of its time between 0 and 100 pm.

### Orbital energy diagram for multielectron atoms



### Some terminology: Shells and subshells

$n$  defines a “shell” and so we have an “ $n = 1$  shell”, an “ $n = 2$  shell”, etc. etc.

$\ell$  defines a subshell. For each shell, we have  $n$  different subshells because for a given value of  $n$ , the quantum number  $\ell$  can have one of  $n$  different values: 0, 1, ...  $n - 1$ . For example, for the  $n = 3$  shell, we have three subshells: a “3s subshell”, a “3p subshell” and a “3d subshell”.

### A few important points:

- the energy and size of a given orbital (e.g. 1s) both decrease as  $Z$  increases

**As  $Z$  increases, the attraction between the nucleus and any given electron increases. The increased attraction lowers the energy of the orbital and causes the orbital to contract.**

- For a multielectron atom, the orbitals in the same “shell” are not of the same energy ( $s < p < d < f$ , etc.)

**Because of electron-electron repulsions, the subshells are not of the same energy in a multi-electron atom. In a given shell, the “s” subshell is lowest in energy, then “p”, then “d”, etc.**

### 3.2 Ground state electron configurations for neutral atoms

**How do electrons distribute themselves to obtain the lowest possible energy for the atom?**

There are three basic rules that help us predict how the electrons in an atom distribute themselves among the possible states to achieve the lowest possible energy for the atom.

#### (1) The Pauli Exclusion Principle

**No two electrons can have the same set of quantum numbers  $n$ ,  $\ell$ ,  $m_\ell$  and  $m_s$ .**

Note: If two electrons occupy the same orbital, then  $n_1 = n_2$ ,  $\ell_1 = \ell_2$  and  $m_{\ell 1} = m_{\ell 2}$ . Therefore, we must have  $m_{s1} \neq m_{s2}$ . i.e., If two electrons occupy the same orbital, they must have different spins.

subshell	# orbitals? ( $= 2\ell + 1$ )	max # electrons?
$ns$	1	2
$np$	3	6
$nd$	5	10

#### (2) The Aufbau Procedure

**For neutral atoms**, orbitals are filled according to the  $n + \ell$  rule:

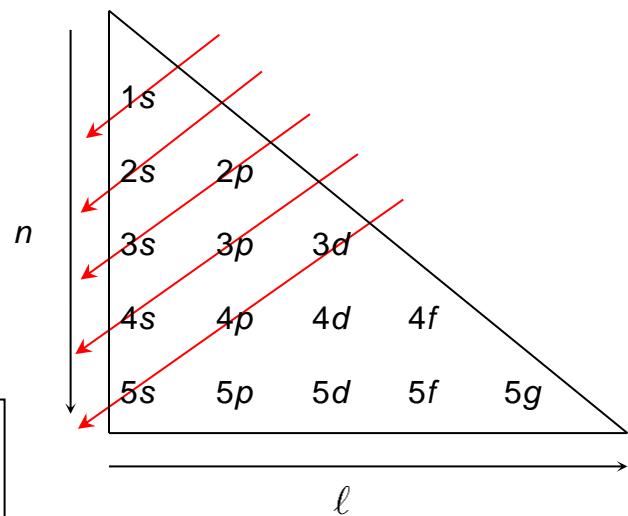
filling order →										
	1s	2s	2p	3s	3p	4s	3d	4p	5s	4d
$(n + \ell) =$	1	2	3	3	4	4	5	5	5	6
max. # e <sup>-</sup> 's?	2	2	6	2	6	2	10	6	2	10

The triangle shown below can be used to help you remember the orbital filling order.

**There are only two exceptions to the  $(n+\ell)$  rule for  $Z \leq 36$ . The exceptions are Cr and Cu. You should know these two exceptions.**

For  $Z > 36$ , there are many exceptions! (You don't need to know, nor could you possibly know, all of the exceptions for  $Z > 36$ .)

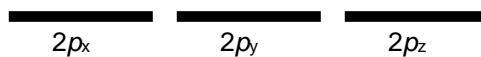
**Did you know?** The orbital energies themselves do not follow the  $n + \ell$  rule. The rule corresponds simply to the order in which orbitals must be filled to give the lowest possible energy for the atom. The orbital filling rule has been established by experiment.



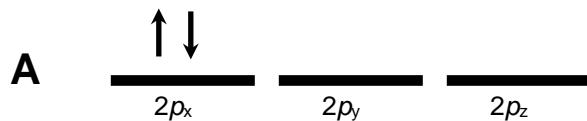
**(3) Hund's Rule**

**If there are not enough electrons to fill completely a set of energetically degenerate orbitals, the lowest energy arrangement is the one which has the maximum number of parallel spins.**

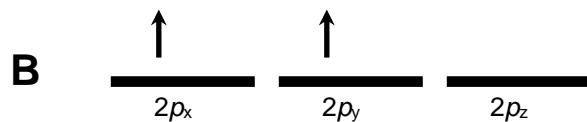
For example, we have learned that a set of  $2p$  orbitals can accommodate a total of 6 electrons. (There are three  $2p$  orbitals and each one can accommodate two electrons.) The three  $2p$  orbitals are of equal energy. We say that the three  $2p$  orbitals are **energetically degenerate**.



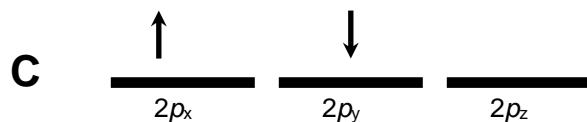
What are the possible arrangements for two electrons in these three orbitals? There are several possibilities. Here are a few possible arrangements.



We can generate two more arrangements like this one by putting the two electrons in  $2p_y$  or  $2p_z$  instead.



We can generate four more arrangements like this one by putting the two electrons in  $2p_x$  and  $2p_z$  or in  $2p_x$  and  $2p_z$  instead.



We can generate other arrangements that are equivalent to this one (e.g. put one electron in  $2p_y$  with its spin up and one electron in  $2p_x$  with its spin down; or, put one electron in  $2p_z$  with its spin down and one electron in  $2p_y$  with its spin up; etc. etc.)

Q. Which one of the arrangements above is the lowest in energy?

Q. In arrangement "B", does it matter whether both spins are up or both spins are down?

When electrons have parallel spins, they avoid each other to a greater extent. Thus, they shield each other less and this increases the attraction each electron feels towards the nucleus. The increased electron-nucleus attraction results in a lower total energy for the atom.

**Example 3-1:** What is the ground-state electron configuration for an Ar atom? What is the ground-state electron configuration for a Ni atom?

Determine the number of unpaired electrons. (The ground-state configuration is the configuration of lowest energy.)



See problems 8-77 and 8-79  
from Petrucci (11<sup>th</sup> edition).

### 3.3 The Periodic Table

#### s block

$ns^G$

G = 1	
1 H $1s^1$	G = 2
3 Li $2s^1$	4 Be $2s^2$
11 Na $3s^1$	12 Mg $3s^2$
19 K $4s^1$	20 Ca $4s^2$ $4s^2 3d^1$
37 Rb $5s^1$	38 Sr $5s^2$ $5s^2 4d^1$
55 Cs $6s^1$	56 Ba $6s^2$ $57-71$ La-Lu
87 Fr $7s^1$	88 Ra $7s^2$ 89-103 Ac-Lr

#### d block

$(n-1)d^{G-2} ns^2$

G = 3

4

5

6

7

8

9

10

11

12

18

1 H $1s^1$	4 Be $2s^2$	5	6	7	8	9	10	11	12	13 B $2s^2 2p^1$	14 C $2s^2 2p^2$	15 N $2s^2 2p^3$	16 O $2s^2 2p^4$	17 F $2s^2 2p^5$	18 He $1s^2$			
3 Li $2s^1$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr* $4s^2 3d^5$	25 Mn $4s^2 3d^6$	26 Fe $4s^2 3d^7$	27 Co $4s^2 3d^8$	28 Ni $4s^2 3d^10$	29 Cu* $4s^2 3d^10$	30 Zn $4s^2 3d^10$	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr		
11 Na $3s^1$	12 Mg $3s^2$	40 Zr $5s^2 4d^2$	41 Nb* $5s^2 4d^5$	42 Mo* $5s^2 4d^6$	43 Tc $5s^2 4d^7$	44 Ru* $5s^2 4d^8$	45 Rh* $5s^2 4d^9$	46 Pd* $5s^2 4d^10$	47 Ag* $5s^2 4d^10$	48 Cd $5s^2 4d^10$	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe		
19 K $4s^1$	20 Ca $4s^2$ $4s^2 3d^1$	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt*	79 Au*	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn		
37 Rb $5s^1$	38 Sr $5s^2$ $5s^2 4d^1$	56 Cs $6s^1$	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt*	79 Au*	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr $7s^1$	88 Ra $7s^2$	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og	

#### f block

57 La*	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd*	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
89 Ac*	90 Th*	91 Pa*	92 U*	93 Np*	94 Pu	95 Am	96 Cm*	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The rows of the periodic table are called **periods**. There are seven periods.  
Each period starts a new shell.

The columns are called **groups**. The groups are numbered 1-18.

#### Remarks

- The group number provides info about the number of **valence electrons** in the atom.

**Valence electrons** are electrons in the outermost shell of an atom. They are the electrons that participate in bond formation.

$$\# \text{ valence } e^- = \begin{cases} \text{group #, if group # < 12} \\ \text{group # - 10, if group # \geq 12} \end{cases}$$

- Atoms in the same group have similar *spdf* configurations.

e.g. **F** has ground state config. [He]  $2s^2 2p^5$   
**Cl** has ground state config. [Ne]  $3s^2 3p^5$

- The periodic table can be divided into s-, p-, d- and f-blocks

e.g. **Ca** is in the **s-block** because the last  $e^-$  added goes into an **s orbital**  
**V** is in the **d-block** because the last  $e^-$  added goes into a **d orbital**

In the table above, \* is used to identify elements that have a ground state configuration that is different from that expected from its position in the periodic table. For example, the configuration expected for Cr, based on its position, is [Ar]  $4s^2 3d^4$ . The actual configuration is [Ar]  $4s^1 3d^5$ .

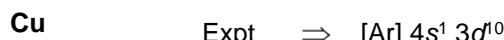
**Learn to use the periodic table to write abbreviated e<sup>-</sup> configurations quickly!**

**Example 3-2:** Use the periodic table to write the abbreviated ground state electron configurations for As and Fe. How many unpaired electrons does each atom have?



See problems 8-75, 8-85 and 8-86 from Petrucci (11<sup>th</sup> edition).

**Example:** Based on their positions in the periodic table, what do you expect for the ground-state configurations of Cr and Cu?



This example illustrates that the Aufbau procedure does not always give the correct result.

We expect you to know these two exceptions (Cr and Cu) but not any other exceptions to the building up principle. By their very nature, exceptions are difficult to predict with certainty. However, please be aware that exceptions do exist. The exceptions are numerous for  $Z > 36$ , and the majority of exceptions involve atoms from the f-block.

**What conclusions can we draw from this example?** Not many – except for the points already made above. A number of textbooks refer to a supposed “special stability” of half-filled subshells. This is a “cop-out” because it begs the question “What is the origin of this special stability?” The mythical concept of a special stability of half-filled subshells and filled shells has been demolished but it still lingers in some books. (Note: The ground-state electron configuration of W is [Xe] 6s<sup>2</sup> 4f<sup>14</sup> 5d<sup>4</sup> not [Xe] 6s<sup>1</sup> 4f<sup>14</sup> 5d<sup>5</sup>. The special stability of half-filled subshells is obviously a myth!)

### 3.4 Ground-state electron configurations for monatomic ions

When dealing with monatomic ions (e.g. O<sup>-</sup>, Cl<sup>-</sup>, S<sup>+</sup>, Ni<sup>2+</sup>, etc.), the following rules are used to predict the correct ground-state electron configuration.

**(i) negative monatomic ions (monatomic anions)**

**Write the e<sup>-</sup> configuration for the neutral atom first.** Then use the ( $n + \ell$ ) rule to add e<sup>-</sup>'s to the appropriate orbitals.

**(ii) positive monatomic ions (monatomic cations)**

**Write the e<sup>-</sup> configuration for the neutral atom first.** Then remove electrons from orbitals with the highest value of  $n$  first. If we must choose between removing two e<sup>-</sup>'s that have the same value of  $n$ , then remove the e<sup>-</sup> with the highest value of  $\ell$  first.

Rule (ii), has particular significance for cations derived from atoms of the *d*-block elements.

For atoms in the *d* block, the valence shell electron configuration is usually  $ns^2 (n-1)d^{G-2}$ , where  $G$  is the group number. **Experiment shows that when electrons are removed from atoms of the *d* block, the *ns* electrons are removed first.**

**Example 3-3:** What is the ground-state electron configuration for each of the following ions?

(a) S<sup>-</sup>      The ground state e<sup>-</sup> configuration of S is [Ne] 3s<sup>2</sup> 3p<sup>4</sup>

So, for S<sup>-</sup> the ground state e<sup>-</sup> configuration is ...

(b) Br<sup>+</sup>      The ground state e<sup>-</sup> configuration of Br is [Ar] 4s<sup>2</sup> 3d<sup>10</sup> 4p<sup>5</sup>

So, for Br<sup>+</sup>, the ground state e<sup>-</sup> configuration is ...

(c) Mn<sup>2+</sup>      The ground state e<sup>-</sup> configuration of Mn is [Ar] 4s<sup>2</sup> 3d<sup>5</sup>.

So, for Mn<sup>2+</sup>, the ground state e<sup>-</sup> configuration is ...

Notice that Mn<sup>2+</sup> has 23 electrons. If you had "blindly" applied the ( $n + \ell$ )-rule to Mn<sup>2+</sup>, then you would predict the ground-state configuration [Ar] 4s<sup>2</sup> 3d<sup>3</sup>, which is wrong!! That is, when you use the ( $n + \ell$ )-rule with 23 electrons, you get the ground electronic state for the neutral atom that has 23 electrons (i.e. vanadium, V) and not the electron configuration for Mn<sup>2+</sup>!!

### 3.5 Atomic Properties & Periodic Trends

The electron configurations of atoms change in a predictable way as we move across a period and down a group. It should not be too surprising that there are systematic and predictable variations in atomic properties. We shall consider the magnetic properties of atoms as well as trends in atomic radii, ionization energies and electron affinities.

#### A. Paramagnetic and Diamagnetic Atoms

As a result of electron spin, each electron produces a magnetic field.

If all of the electrons in an atom are paired up, then the magnetic fields cancel so that there is no net magnetic field for the atom.

If there are unpaired electrons, then the magnetic fields do not cancel.

We say the atom possesses a magnetic moment.

diamagnetic atoms  $\leftrightarrow$  all electrons are paired; the atom does not possess a magnetic moment; the atom interacts only weakly with an external magnetic field

paramagnetic atoms  $\leftrightarrow$  one or more unpaired electrons; the atom possesses a magnetic moment; the atom interacts strongly with an external magnetic field

**Example 3-4:** Which groups of atoms are diamagnetic in their ground electronic states?



See problem 9-35 from Petrucci (11<sup>th</sup> edition).

## B. Atomic Radii

The radius of an atom is a little more difficult to define than you might think. There is no precise outer boundary to an atom and even if there was, we couldn't really measure the size of a single atom anyway. **The size of an atom is determined by measuring the distance between nuclei in a certain environment.**

**covalent radius** =  $\frac{1}{2}$  of the diatomic bond length for the  $X_2$  molecule (of X)

**The covalent radius is especially useful for elements that form diatomic molecules.**

**metallic radius** =  $\frac{1}{2}$  of the distance between “nearest neighbours” in a metallic solid

**The metallic radius is especially useful for elements that are metals. Most elements in the periodic table are metals at room temperature and atmospheric pressure.**

### Remarks:

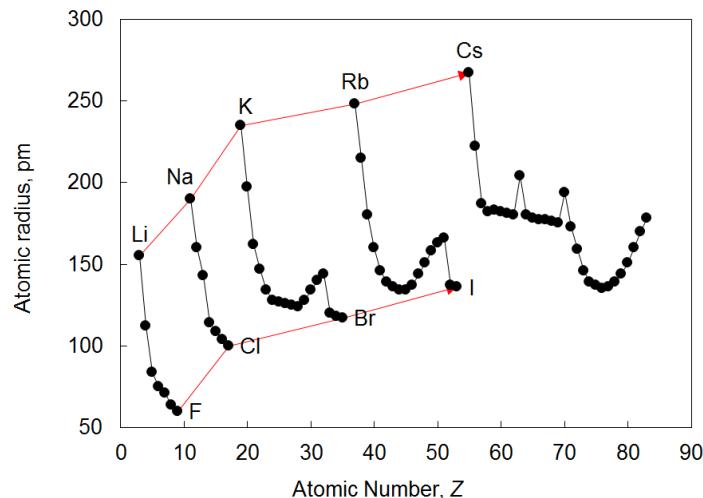
- atomic radii decrease across a period

**As we move from left to right across a period, we are adding electrons into vacancies in an existing shell. The nuclear charge increases from left to right, and because electrons in the same shell do not shield each other effectively (only partially), the increased nuclear charge brings all the electrons closer to the nucleus.**

- atomic radii increase down a group

**As we move from top to bottom within a group, we begin a new shell and each new shell has its maximum electron density a greater distance from the nucleus.**

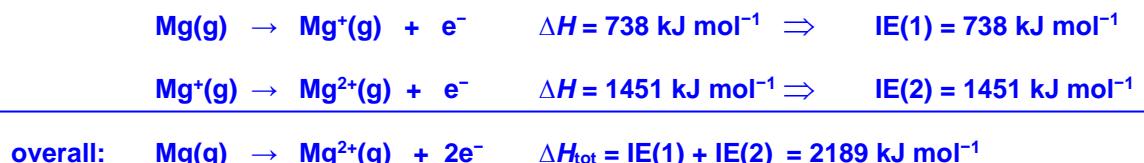
**For you to think about ...**  
In order to answer the question “How big is an atom?”, one must first answer the questions “How are we going to measure the size of the atom?” and “How hard are we going to push on the atom when we measure its size?” If we are going to measure the size of an overripe peach using a pair of calipers, for example, then the value we get depends on how hard we squeeze. The size we measure depends on the environment of the atom and how we plan to make the measurement!!



### C. Ionization Energy

ionization energy  $\longleftrightarrow$  **energy required to remove an electron from a gas-phase atom (often reported as an enthalpy change,  $\Delta H$ )**

e.g. Consider the ionization energies of the magnesium atom, Mg.



#### Remarks:

- It becomes increasingly difficult to remove electrons if one or more electrons have already been removed.

**It always takes energy to remove an electron from an atom. Therefore, ionization is always an endothermic process and ionization energies are always positive.**

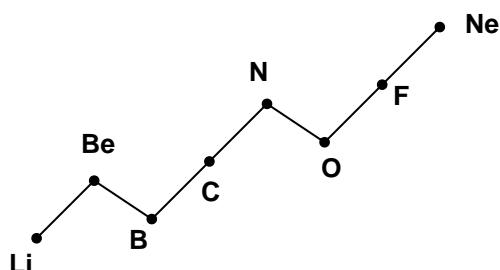
**So,  $\text{IE(1)} < \text{IE(2)} < \text{IE(3)} < \dots$**

- Ionization energies decrease down a group

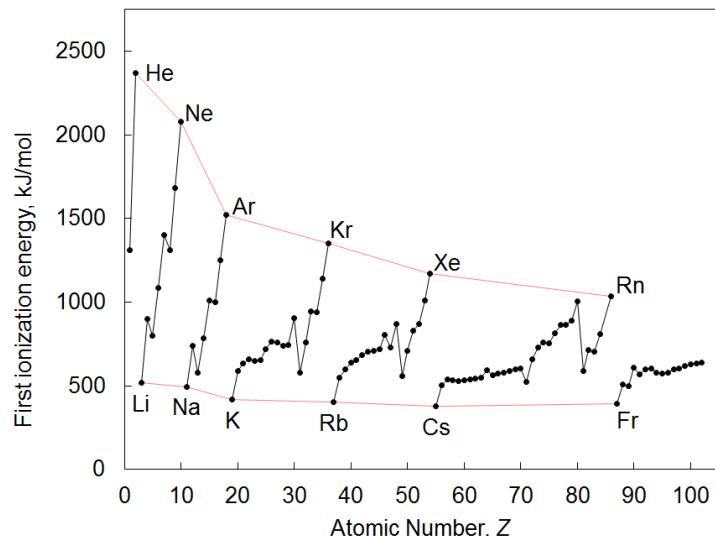
**The valence electrons of larger atoms occupy orbitals with higher  $n$  values and these electrons have higher energies. The valence electrons of larger atoms are more easily removed.**

- Ionization energies generally increase across a period (but there are easily explained exceptions!)

**The atomic radius decreases as we move left to right across a period. The outer electrons are closer to the nucleus and held more strongly, so more energy is required to remove them from the atom.**



**IE decreases as we go from group 2 to group 13 and from group 15 to group 16.**



**Why does IE decrease as we move from Be to B?**Be has configuration [He] 2s<sup>2</sup>B has configuration [He] 2s<sup>2</sup> 2p<sup>1</sup>

The 2p electron in B is in a higher energy orbital and is easier to remove than the 2s electron in Be.

**Why does IE decrease as we move from N to O?**

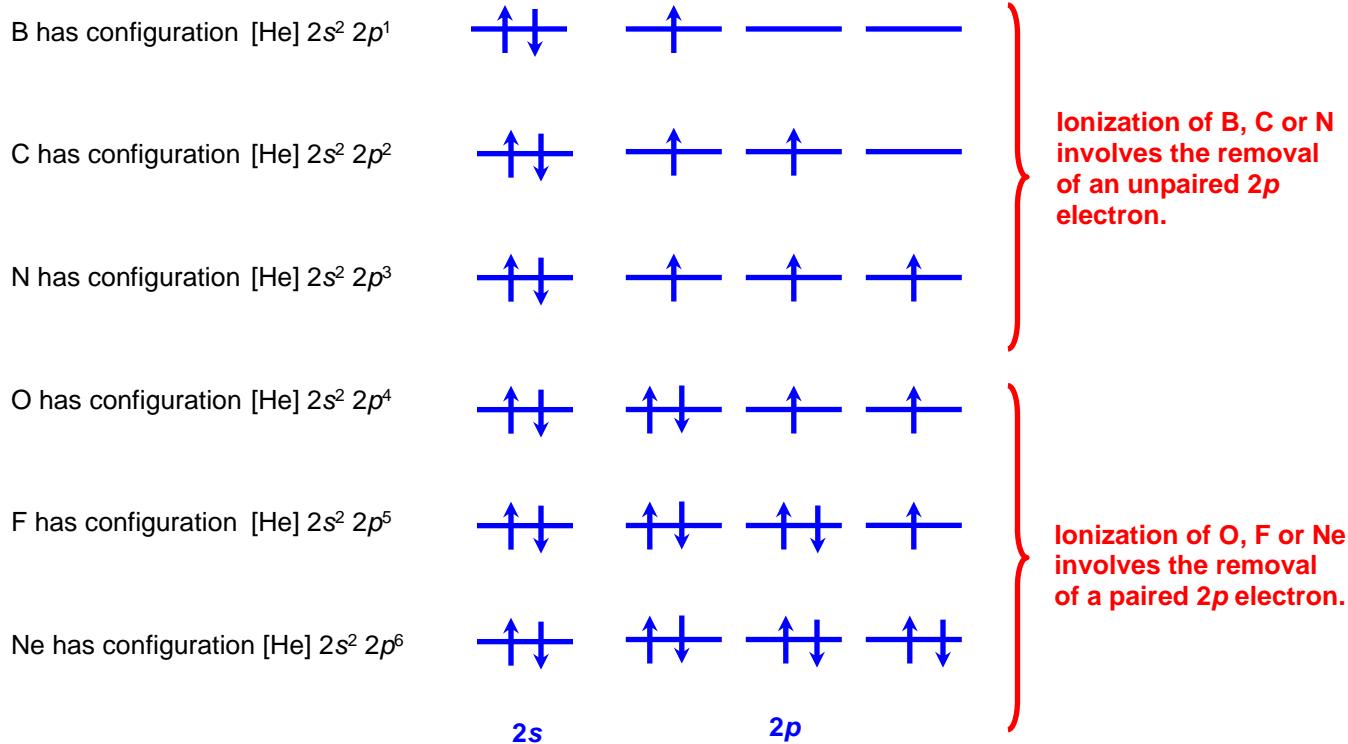
This may not be the appropriate question to ask. As suggested by the diagram on the preceding page, not only is the first ionization of O lower than that of N, but the first ionization energies of O, F and Ne are all lower than expected. That is, the first ionization energies of O, F and Ne are considerably lower than the values predicted by extrapolating the first ionization energies of B, C and N. Thus, it may be more appropriate to ask: **Why are the first ionization energies of O, F and Ne lower than expected?** We shall consider two explanations, both of which focus on the fact that the ionization of O, F and Ne involves the removal of a paired 2p electron whereas the ionization of B, C or N involves the removal of an unpaired 2p electron.

According to one explanation, electron-electron repulsions are the key consideration. Paired electrons occupy the same orbital and are, on average, closer together than electrons in separate orbitals. Thus, they experience "extra" repulsion and are more easily removed. Although the electron-electron repulsions increase with the number of electrons in the 2p orbitals, there is a significant increase in the electronic repulsions, and a corresponding decrease in ionization energy, once orbital sharing begins, that is, as we proceed from N([He] 2s<sup>2</sup> 2p<sup>3</sup>) to O([He] 2s<sup>2</sup> 2p<sup>4</sup>).

Another explanation focuses instead on the extent of shielding and the strength of the electron-nucleus attractions. Unpaired electrons with parallel spins tend to avoid each other, screen each other less, experience a higher effective nuclear charge, interact more strongly with the nucleus, and are harder to remove. According to this line of reasoning, the "extra" electron-nuclear attraction causes the ionization energy for N([He] 2s<sup>2</sup> 2p<sup>3</sup>) to be greater than expected by the backward-extrapolation of the first ionization energies of O, F, and Ne. Conversely, because paired electrons do not avoid each other to the same extent, they shield each other to a greater extent, interact less strongly with the nucleus and are more easily removed.

Is the observed "dip" in ionization energy that occurs as we move from group 15 to 16 caused by increased electron-electron repulsions or by decreased electron-nucleus attractions? It is difficult to answer this question with complete certainty, but it is clear that the dip occurs once orbital sharing begins. The difficulty of providing an unambiguous explanation for the observed dip in IE(1) is not totally unexpected. As we have already pointed out, the energy of an atom is a delicate balance of electron-electron repulsions and electron-nucleus attractions. The rationalization of ionization energies is further complicated by the fact that, for example, the ionization energy of N depends on the energies of both

$\text{N}([\text{He}] 2s^2 2p^3)$  and  $\text{N}^+([\text{He}] 2s^2 2p^2)$ . Similarly, the ionization energy for the O atom depends on the energies of both  $\text{O}([\text{He}] 2s^2 2p^4)$  and  $\text{O}^+([\text{He}] 2s^2 2p^3)$ . Thus, the drop in ionization energy that occurs as we move from N to O depends upon a delicate balance of electron-electron repulsions and electron-nucleus attractions in four different species.

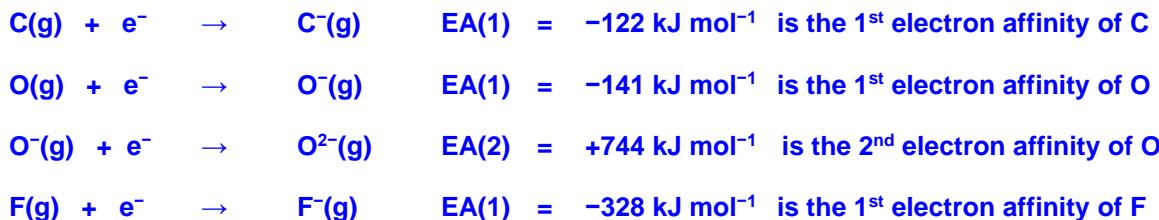


Although we have not provided a definitive answer to the question “Why does the ionization energy decrease as we move from N to O?”, it is important to remember that the decrease in ionization energy occurs once the sharing of 2p orbitals begins.

### D. Electron Affinities

electron affinity (EA)  $\longleftrightarrow$  energy change that accompanies the addition of an electron to a gas-phase atom

e.g. Consider the electron affinities of C, O, and F.



**Remarks:** (focusing on the “main group” elements, i.e. the “s” and “p” blocks)

- Most atoms (except for N and those in groups 2 and 18) release energy when they acquire an electron.

group 2:  $ns^2$  filled subshell  
 group 18:  $ns^2 np^6$  filled shell } These atoms do not “want” more  $e^-$ s.

- For atoms near the right-hand end of a period (except for the noble gases in group 18), a large quantity of energy is released when an electron is added.

**For O and F, the EA's are quite large.**

- For atoms near the left-hand end of a period, only a small quantity of energy is released. (For group 2, energy is required to add an electron to the atom!)

**For Li, Na, K, etc. the EA's are quite small.**

EA values for the main group elements

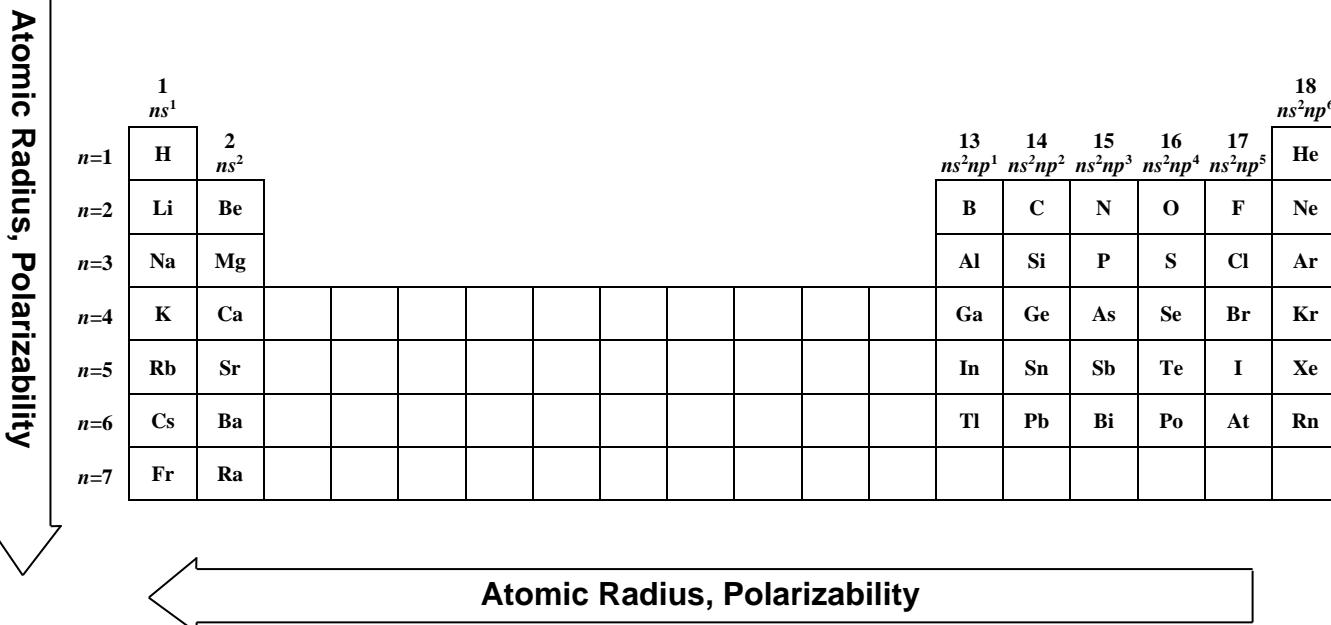
1								18
H -73	2	13	14	15	16	17	He > 0	
Li -60	Be > 0	B -27	C -122	N +7	O -141	F -328	Ne > 0	
Na -53	Mg > 0	Al -43	Si -134	P -72	S -200	Cl -349	Ar > 0	
K -48	Ca -2	Ga -29	Ge -119	As -78	Se -195	Br -325	Kr > 0	
Rb -47	Sr -5	In -29	Sn -107	Sb -103	Te -190	I -295	Xe > 0	
Cs -46	Ba -14	Tl -19	Pb -35	Bi -91	Po -186	At -270	Rn > 0	

## Summary of Periodic Trends



See problem 9-42 from  
Petrucci (11<sup>th</sup> edition).

### Ionization Energy (IE), Electron Affinity (EA), Electronegativity (EN)



**A summary of trends in atomic radius, first ionization energy, electron affinity, electronegativity and atomic polarizability.** Atomic radius<sup>a</sup> and polarizability<sup>b</sup> decrease from left to right in a given a period and increase from top to bottom in a given group. Ionization energy, electron affinity, and electronegativity increase from left to right in a given period and decrease from top to bottom in a given group.

<sup>a</sup>Atomic radius refers to metallic radius for metals and covalent radius for nonmetals.

<sup>b</sup>Polarizability will be discussed in Module 6. It provides a measure of the extent to which the electron cloud of an atom can be distorted.

<sup>c</sup>Ionization energy refers to the first ionization energy. It is the energy change for the process  $X(g) \rightarrow X^+(g) + e^-$ .

<sup>d</sup>Electron affinity refers to the first electron affinity. It is the energy change for the process  $X(g) + e^- \rightarrow X^-(g)$ . An atom has a large electron affinity if the addition of an electron leads to the release of a large quantity of energy (and the formation of an anion that is much lower in energy than the atom from which it was formed). An atom has a small electron affinity if the addition of an electron leads to the release of a small quantity of energy or requires the input of energy.

<sup>e</sup>Electronegativity will be discussed in more detail in Module 4. It provides a measure of the “power” of an atom to attract electrons to itself.

## 4.1 Introduction to chemical bonding: The octet rule

The electron configurations of atoms can help us understand how atoms combine to form compounds. We shall focus only on compounds formed from “main group” elements. (The main group elements are those from the s and p blocks.)

Our first concern is: What type of bond will two atoms form? Is it ionic or covalent? Ionic bonding involves electron transfer and covalent bonding involves sharing of electron pairs.

When electrons are transferred from one atom to another, monatomic ions are formed. The ions are attracted to each other and form an ionic bond. For example, if an electron is transferred from atom X to atom Y, the ions  $X^+$  and  $Y^-$  are formed. The  $X^+$  and  $Y^-$  ions are attracted to each other and form an ionic bond.

When electron pairs are shared between a pair of atoms, the nuclei of the two atoms are simultaneously attracted to the electron pair and drawn towards each other, forming a covalent bond.

Recall:

- metals from groups 1, 2: have low IE's and low EA's
- atoms from groups 14, 15: have large IE's and large EA's
- atoms from groups 16, 17: very large IE's and very large EA's

**Keep in Mind**  
IE = ionization energy  
EA = electron affinity

We anticipate that metals generally prefer to lose electrons while atoms from groups 14-17 prefer to gain electrons. The following guidelines are useful.

- (1) When metals from the s block combine with atoms from the p block to form a binary compound, we usually get an **ionic compound** with ionic bonds holding the ions together.
- (2) When atoms from the p block combine with each other to form a compound, we usually get a **molecular compound** with covalent bonds holding the atoms together.

Here are some other questions we'll consider.

- What are the stable ions an atom will form?
- How many bonds will an atom form?
- How strong will the bond between two ions or atoms be? What factors affect the strength of the bond?
- How will the bonds in a molecule be oriented in space?
- What are resonance structures?

## The Octet Rule

A simple, yet very useful, rule of thumb is the **octet rule**:

**An atom exhibits the tendency to attain a noble gas configuration either by sharing or transferring electrons.**

The octet rule is based on the observation that the noble gases are very unreactive, i.e. there must be a special stability associated with the noble gas configurations. The noble gases are so unreactive that they were once known as the “inert gases”. However, chemists have now successfully synthesized a plethora of compounds involving the noble gases.

He:  $1s^2$

Ne:  $[He] 2s^2 2p^6$

Ar:  $[Ne] 3s^2 3p^6$

Kr:  $[Ar] 4s^2 3d^{10} 4p^6$

Xe:  $[Kr] 5s^2 4d^{10} 5p^6$

Rn:  $[Xe] 6s^2 4f^{14} 5d^{10} 6p^6$

Notice that all of the noble gases, except for He, have  $ns^2 np^6$  as part of their valence configuration. These eight electrons are an “octet” of electrons.

**Example:** The ground-state electron configurations of H, O, Na and Cl are shown in the box below. Use this information, together with the octet rule to answer the following questions.

H,  $1s^1$

O,  $[He] 2s^2 2p^4$

Na,  $[Ne] 3s^1$

Cl,  $[Ne] 3s^2 3p^5$

(i) What are the ions most commonly formed by Na, O, and Cl in their compounds?

To attain a noble gas configuration, Na must lose  $1e^-$  or gain  $7e^-$ . It is energetically much more favourable to lose one electron than it is to gain  $7e^-$ . We expect Na to form  $Na^+$  ions when it forms an ionic compound.

To attain a noble gas configuration, O must gain  $2e^-$  or lose  $6e^-$ . Both processes require energy but it requires much less energy to add  $2e^-$  to O than it does to remove  $6e^-$ . We expect that, in ionic compounds, oxygen will exist as  $O^{2-}$ .

To attain a noble gas configuration, Cl must gain  $1e^-$  or lose  $7e^-$ . Following the same line of reasoning that we used above, we predict that chlorine will exist as  $Cl^-$  when it forms ionic compounds.

(ii) What is type of bond (ionic or covalent) is formed between Na and O? What is the formula of the binary compound formed?

Na is an s-block metal and oxygen is a p-block element, so we expect these elements will combine to form an ionic compound comprised of  $Na^+$  and  $O^{2-}$  ions. The formula of the compound is  $Na_2O$ . Although energy is required to create these ions, we get this energy back (plus a lot more!) when the positive and negative ions pack together to form an ionic compound.

FYI: Nothing is as simple as it first seems! Sodium and oxygen form a variety of compounds, including  $Na_2O$ ,  $Na_2O_2$ ,  $NaO_2$ ,  $NaO_3$ , etc.

- (iii) What type of bond (ionic or covalent) is formed between Na and Cl? What is the formula of the binary compound formed?

**Na is an s-block metal and chlorine is a p-block element, so we expect these elements will combine to form an ionic compound comprised of  $\text{Na}^+$  and  $\text{Cl}^-$  ions. The formula of the compound is  $\text{NaCl}$ . Energy is required to create these ions, but we get this energy back (plus a lot more!) when the positive and negative ions pack together to form an ionic compound.**

- (iv) What type of bond (ionic or covalent) is formed between H and Cl? What is the formula of the binary compound formed?

**Generally speaking, it is energetically more favourable for hydrogen and chlorine to gain electrons than it is to remove them. We expect hydrogen and chlorine to form a covalent compound by sharing electrons. An H atom has one unpaired electron and requires one additional electron to attain a noble gas configuration. Similarly, a Cl atom has one unpaired electron and requires one additional electron to attain a noble gas configuration. The H atom shares its unpaired electron with Cl and Cl shares its unpaired electron with H. They combine 1:1 to form a compound with formula  $\text{HCl}$ .**

The simple approach used in this example is useful (and helps us rationalize some observations) but we can't push it too far. For example, what if we used this approach to consider the nature of the bond formed by carbon and hydrogen and tried to predict the formula of the resulting compound?

**Because an H atom requires one electron to attain a noble gas configuration and a carbon atom requires four electrons to attain a noble gas configuration, we might expect C and H to combine in a 1:4 ratio to form a compound with the formula  $\text{CH}_4$ . Carbon and hydrogen do indeed form such a compound. However, they also form many other compounds (e.g.  $\text{C}_n\text{H}_{2n+2}$ ,  $\text{C}_n\text{H}_{2n}$ ,  $\text{C}_n\text{H}_n$ , ...)**

## 4.2 Review: Lewis Symbols and Lewis Structures

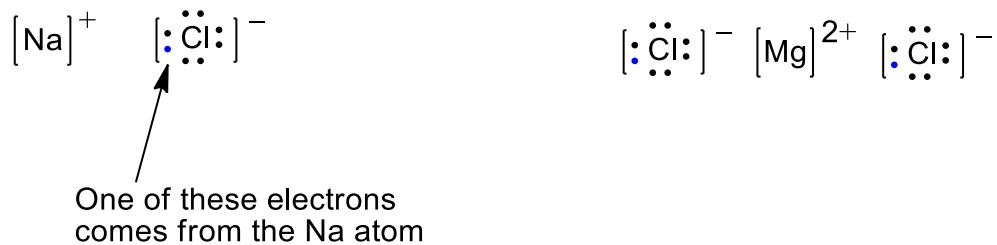
The Lewis symbol for an atom is the atomic symbol surrounded by the correct number of valence electrons. Lewis symbols for the atoms of the second period are:

Li	• Be	• B	• C	• N	• O	• F	• Ne
group #	1	2	13	14	15	16	17
# valence e <sup>-</sup>	1	2	3	4	5	6	8

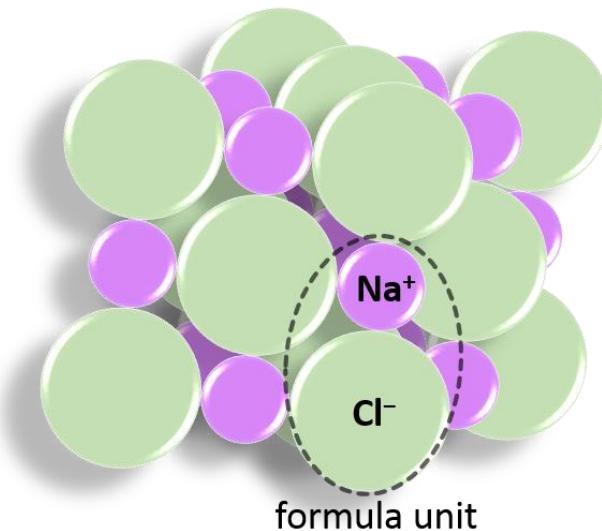
A Lewis structure is comprised of Lewis symbols and it shows how the ions or atoms are bonded together.

### Lewis structures for Ionic Compounds

Here are the Lewis structures for NaCl and MgCl<sub>2</sub>.



We almost never write Lewis structures for ionic compounds, except when we want to emphasize the ions involved and the ratio in which the ions combine. The structure of an ionic compound is much more complicated than what is suggested by these simple Lewis structures. An ionic compound is an extended, three dimensional array of ions in which the ions are arranged in regular, repeating patterns. The “true” structure of NaCl is shown on the right.



### Lewis structures for Molecular Compounds

- Use group #'s to determine the # of valence e<sup>-</sup>'s
- Put a pair of e<sup>-</sup>'s between each pair of bonded atoms
- Distribute the remaining valence e<sup>-</sup>'s around atoms but keep in mind the following:
  - (i) An H atom **never** has more than 2 valence e<sup>-</sup>'s  
Therefore, the H atom never forms more than one bond and is always a "terminal" atom.
  - (ii) 2<sup>nd</sup> row atoms **never** have more than 8 valence e<sup>-</sup>'s  
Also: C, N, O and F atoms almost never have less than 8 valence e<sup>-</sup>'s around them.
  - (iii) Atoms from the 3<sup>rd</sup> period (and beyond) might have an "expanded" octet (more than 8 valence e<sup>-</sup>'s).
- Assign a **formal charge** to each of the atoms in your structure.

$$\text{formal charge} \quad = \quad \left[ \begin{array}{l} \text{the number of valence} \\ \text{electrons that atom X} \\ \text{brings to the molecule} \end{array} \right] - \left[ \begin{array}{l} \text{the number of valence} \\ \text{electrons "owned" by} \\ \text{atom X in the structure} \\ \text{under consideration} \end{array} \right]$$

For the purposes of assigning formal charges, an atom "owns" all of its unshared electrons (i.e. lone pairs) but only half of its bonding electrons.

Note carefully: The assignment of formal charges is based on a set of rules for counting electrons. Since we cannot create or destroy electrons, **the sum of the formal charges must always equal the total charge on the molecule or ion!!**

The formal charge concept is important in chemistry because it helps us assess whether or not a particular Lewis structure is important or reasonable. As we will soon see, it is sometimes possible to draw more than one acceptable Lewis structure for a molecule. For such cases,

- The "true" structure is a hybrid (weighted average) of the resonance structures. **Resonance structures** have the same spatial arrangement of atoms, but a different distribution of electrons around the atoms.
- All else being equal, the most important structure is (usually) the one with the smallest formal charges. Almost always, formal charges do not exceed ±1. Structures having atoms with high formal charges (e.g. +2, -2, +3, -3, etc.) are usually not important.



See problems 10-3, 10-4, 10-11, 10-12, 10-17 to 10-19 and 10-25 from Petrucci (11<sup>th</sup> edition).

**Learning Tip:** Chemists rationalize the physical and chemical properties of matter in terms of the structures of the molecules involved. In order to think like a chemist, **you must become proficient in drawing Lewis structures for molecules.**

#### Use these conventions when drawing Lewis structures:

- (1) A bonding pair of electrons is represented by a line (—).
- (2) A nonbonding pair of electrons is represented by a pair of dots (••).
- (3) Always show any nonzero formal charges.

the number of valence electrons "owned" by atom X in the structure under consideration

**Learning Tip:** A "quick" way to determine the number of valence electrons owned by an atom is to count the number of lines and the number of dots.

$$\# \text{ e}^- \text{ owned} = \# \text{ lines} + \# \text{ dots}$$

This quick way works because an atom "owns" only half of its bonding electrons and

$$\# \text{ lines} = \frac{1}{2} \times \# \text{ bonding electrons}$$

#### Other considerations:

- Avoid placing like formal charges (e.g., +1 and +1 or -1 and -1) on adjacent atoms.
- Place formal charges according to electronegativity, if possible (e.g. in the NCO<sup>-</sup> ion, it is better to place the -1 formal charge on O rather than N because the O atom is more electronegative than the N atom).

**Example 4-1:** Draw Lewis structures for the following molecules.

(If an atom is underlined, the underlined atom is the central atom.)

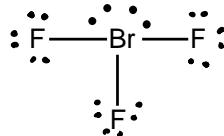
Show any nonzero formal charges.



See problems 10-29,  
10-30 and 10-51 from  
Petrucci (11<sup>th</sup> edition).

- (a) CCl<sub>4</sub>      (b) C<sub>2</sub>H<sub>4</sub>      (c) BF<sub>3</sub>      (d) BrF<sub>3</sub>      (e) XeF<sub>4</sub>

In the previous example, we saw that in the  $\text{BrF}_3$  molecule, Br had an expanded octet.



The ground state electron configurations of Br and F are:

**Br**

[Ar]  $4s^2 3d^{10} 4p^5$

**F**

[He]  $2s^2 2p^5$

Based on the ground state electron configurations, we'd expect that Br and F would share only one pair of electrons to form  $\text{BrF}$ . Why do we get  $\text{BrF}_3$  and how can the Br atom accommodate more than 8 e<sup>-</sup>'s in its valence shell?

**fyi:** The  $\text{BrF}$  molecule is stable and does exist. By varying the conditions, including the relative amounts of  $\text{Br}_2$  and  $\text{F}_2$ , a variety of  $\text{BrF}_n$  compounds can be synthesized.

For a time, the explanation for expanded octets in some molecules was based on the availability of "empty" d orbitals in the valence shell of the central atom.

According to this line of reasoning, the Br atom in  $\text{BrF}_3$  makes use of "empty" 4d orbitals that are only slightly higher in energy than the 4s and 4p orbitals. The ground-state electron configuration of Br can be written as follows:

[Ar]  $4s^2 3d^{10} 4p^5 4d^0$

If some of the 4s or 4p electrons in the Br atom are "promoted" into the empty 4d orbitals as single, unpaired electrons, then more Br-F bonds can be formed. According to the argument, the promotion of the 4s or 4p electrons requires the input of only a small amount of energy. Because bond formation is very exothermic, the amount of energy required to promote electrons to 4d orbitals is small compared to the energy released by forming additional Br-F bonds. That is, the promotion of electrons to empty valence orbitals is a small price to pay for return of energy obtained by forming a greater number of bonds. **However, theoretical studies of molecules with expanded octets have shown rather conclusively that such an explanation is wrong!!** It is beyond the scope of this course to explain in detail why atoms from the third period and beyond can have expanded octets. The simplest (and perhaps surprisingly more correct) explanation is that, as the central atom gets larger, it is possible to pack an increasing number of atoms around the central atom. Because atoms from the second row are rather small, they can accommodate only a small number of atoms around them and thus, **atoms from the second row never have expanded octets!!**

[Reference: Chemical Bonding and Molecular Geometry: From Lewis to Electron Densities, by R. J. Gillespie and P. L. A. Popelier, Oxford University Press, New York, 2001.]

### Oxidation states versus formal charges: What's up with that?

[Source: G. Parkin, J. Chem. Ed. 83, 791 (2006)]

In this course, we have used two very different concepts (i.e. oxidation state and formal charge) when referring to the “charge” on an atom in a molecule. In most cases, the oxidation state and the formal charge have very different values, and neither one is equal to the “true” charge on an atom in a molecule. It is important to keep in mind that the oxidation state and formal charge are determined by two fundamentally different formalisms.

oxidation states = the charge an atom would have if the bonding electrons in each bond were transferred to the more electronegative atom

formal charge = the charge an atom would have if the bonding electrons in each bond were divided equally between the two atoms involved

Both concepts are important in chemistry but neither one is representative of the “true” charge on an atom in a molecule. Oxidation states are useful for electron bookkeeping and for predicting the chemical properties. Consequently, some chemists focus more on the oxidation state. Formal charges are most useful for predicting which resonance structure may be the most representative of the true structure. Some useful guidelines concerning formal charges are as follows:

- (i) structures with negative formal charges on electronegative elements are favoured
- (ii) structures that minimize the number of formal charges, and with formal charges between  $-1$  and  $+1$  are favoured
- (iii) structures with the same formal charges on adjacent atoms are highly unfavoured

◀ The “true” charge on an atom in a molecule can be calculated using quantum mechanics by comparing the electron densities around the “free” atom and around the atom when it is bonded to other atoms.

The “true” charge on an atom is usually between  $-1$  and  $+1$ . A large charge separation between atoms within a molecule is unnatural: The atoms that surround a given atom act as sources or sinks of electrons and greatly reduce the likelihood that a particular atom will carry a very positive or very negative net charge.

It should be no surprise, however, that neither the oxidation state nor the formal charge is representative of the “true” charge on an atom in a molecule. The oxidation state concept exaggerates the ionic character of the bonding and the formal charge concept exaggerates the covalent character of the bonding. In most cases, the “true” charge on an atom in a molecule is numerically closer to the formal charge and that’s why we tend to focus more on formal charges when assessing the importance of different resonance structures, and why we prefer structures with small formal charges. But keep the following in mind: the notion that the structure that minimizes the number and magnitude of the formal charges is the “best” structure is still being questioned and debated.

**Oxidation States and Formal Charges compared: A Summary**

<b>Oxidation state</b>	The oxidation state is the hypothetical charge an atom would have if the bonding electrons in each bond were <i>transferred</i> to the more electronegative atom.  The oxidation state concept tends to exaggerate the ionic character of the bonding between atoms.  Oxidation states are used to predict and rationalize chemical properties of compounds.
<b>Formal charge</b>	The formal charge is the hypothetical charge an atom would have if the bonding electrons in each bond were <i>divided equally</i> between the two atoms involved.  The formal charge concept tends to exaggerate the covalent character of the bonding between two atoms.

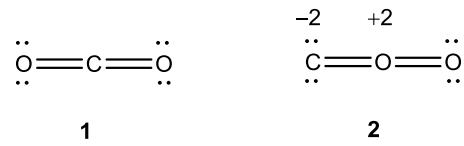
**See the Are You Wondering feature on page 431 of Petrucci (11<sup>th</sup> edition) for more information about formal charges and oxidation states.**

**Example 4-2:** Determine the oxidation state and formal charge for the underlined atom in each of the following molecules: (a) HBr    (b) OF<sub>2</sub>    (c) H<sub>2</sub>CO    (d) CO<sub>2</sub>

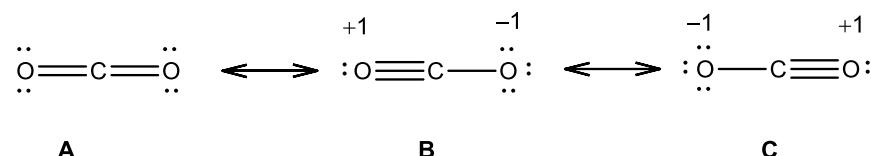
### 4.3 Resonance Structures

The structures to the right are isomeric structures for  $\text{CO}_2$ . Isomer 1 is the structure we associate with the compound called carbon dioxide.

**Isomers** are compounds having the same molecular formula but a different spatial arrangement of atoms. Isomers are different compounds with different physical properties. To convert one isomer into another, chemical bonds must be broken.

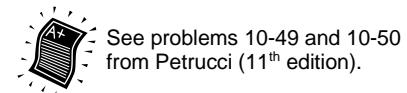


**Resonance structures** have the same spatial arrangement of atoms but **a different distribution of electrons around the atoms**. A double-headed arrow ( $\longleftrightarrow$ ) is placed between each pair of resonance structures to indicate that for the given arrangement of atoms, there are different possible arrangements for the electrons around them. The true structure is a hybrid (weighted average) of the various resonance structures. The following structures are resonance structures for isomer 1 of  $\text{CO}_2$ .



**Note carefully:** The  $\text{CO}_2$  molecule does **NOT** oscillate rapidly from one structure to another. All of these structures contribute to the true structure, but not necessarily equally.

**Example 4-3:** For resonance structures A, B and C shown above, which one(s) is(are) the most important? Explain your reasoning. Note: The “most important” structure is commonly called the *major resonance contributor*.



### Drawing Resonance Structures

For some molecules or ions, the bonding cannot be represented by a single Lewis structure. When we draw Lewis structures, the accepted convention is that electrons are drawn as “dots” with physical locations. *Keep in mind, as we learned in Module 2, its best to think of electrons as “clouds of electron density”.* Remember that electron density can be distributed around different regions of a molecule. We use Lewis structures to represent the location of electron density because we do not have a convention to draw electron clouds to represent electron density.

One of the main limitations of drawing Lewis structures is that for some molecules and ions, no single drawing can adequately describe the nature of the electron density spread. To solve this problem, we need to draw several **resonance structures**.

**When more than one equivalent resonance structure can be drawn, the actual structure is the average of the equivalent resonance structures.**

### Review of Arrows in Chemistry.

It is very important to use the proper arrow when writing out reactions and mechanism. Master this early and continue the use of proper arrows throughout your career. **Draw an example of each below.**

**Reaction Arrow.** A straight arrow that points from reactants to products indicating a non-reversible reaction.

**Dynamic Equilibrium Arrows.** Harpoon arrows of equal length that signify a steady state in the concentrations of reactants and products.

**Resonance Arrows.** Straight double-headed arrows between two equivalent resonance structures.

**“Curved” or “Curly” Arrows.** Represent the movement of a mobile pair of electrons. The tail of the arrow is the origin of the electron pair and the head of the arrow points to the destination.

**Fishhook Arrow.** Indicates the movement of a single electron, widely used in radical chemistry.

**Did you know?** There are many other types of arrows used for chemical notation. There are specific arrows that represent gas production, precipitation, retrosynthesis, stereocentres, reflux conditions,  $\gamma$ -radiation, rearrangements and dipole moments.

Key points to remember when drawing resonance structures:

- The skeletal structure remains unchanged. **Never** break a single (sigma) bond.
- Each resonance structure follows the rules for writing proper Lewis Structures.
- **Delocalized** electrons are those that are not associated with a single atom but can be distributed between 3 or more atoms. Electrons forming single (sigma) bonds are never delocalized. Electrons in lone pairs, or double- or triple-bonds (pi bonds) may be delocalized.

Questions to consider when drawing resonance structures:

- Can we convert a lone pair into a pi bond?
- Can we convert a pi bond into a lone pair?
- Can we convert a pi bond into a pi bond?

Structural arrangements to look for when drawing resonance structures:

- A lone pair of electrons next to a pi bond.
- A lone pair of electrons next to a positive charge.
- A pi bond next to a positive charge.
- A pi bond between two atoms, where one of those atoms is electronegative.
- Pi bonds alternating all the way around a ring.

**Example 4-4:** Consider the structure of acetic acid ( $\text{CH}_3\text{COOH}$ ) and the acetate anion ( $\text{CH}_3\text{COO}^-$ ). For each molecule, draw possible resonance structures. Where possible, identify the **major** and **minor** contributors.

**Example 4-5:** Explain why the two O–O bond lengths in ozone ( $\text{O}_3$ ) are equal. Use the bond length table on page 15 to predict a possible range for the O–O bond lengths for the ozone molecule.

**Example 4-6:** Draw the possible resonance structures for the each of the molecules and ions below and indicate any major and minor resonance contributors.



## 4.4 The strength of a covalent bond

The strength of a covalent bond depends upon

- the sizes of the atoms
- the bond-order
- whether the bond is polar or non-polar

Tabulated bond energies show how the bond strength is affected by the sizes of the atoms, the bond-order, and the polarity of the bond.

See the tables given on the next page.

**Bond Dissociation Energy** = energy required to break a particular covalent bond

General observations:

- (1) small atoms tend to form strong, compact bonds

H–H	vs	Cl–Cl
74 pm		199 pm
436 kJ mol <sup>-1</sup>		243 kJ mol <sup>-1</sup>

- (2) bond length decreases and bond strength increases as the bond order increases. (Note that a double bond, e.g. C=C, is not twice as strong as a single bond, e.g. C–C. i.e., the second bond is not as strong as the first! We'll soon see why.)

C–C	vs	C=C	vs	C≡C
154 pm		134 pm		120 pm
347 kJ mol <sup>-1</sup>		611 kJ mol <sup>-1</sup>		837 kJ mol <sup>-1</sup>

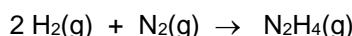
Bond	Bond Length / pm	Bond	Bond Length / pm	Bond	Bond Length / pm	A covalent bond is typically 100 to 200 pm in length.
H-H	74	C-C	154	N-N	145	
H-C	110	C=C	134	N=N	123	
H-N	100	C≡C	120	N≡N	110	
H-O	97	C-N	147	N-O	136	
H-F	92	C=N	128	N=O	120	
H-S	132	C≡N	116	O-O	145	
H-Cl	127	C=O	120	O=O	121	
H-Br	141			F-F	143	
H-I	161	C-Cl	178	Cl-Cl	199	
				Br-Br	228	
				I-I	266	

Bond	Bond Energy / kJ mol <sup>-1</sup>	Bond	Bond Energy / kJ mol <sup>-1</sup>	Bond	Bond Energy / kJ mol <sup>-1</sup>	The bond dissociation energy for a covalent bond is typically a few hundred kJ mol <sup>-1</sup> .
H-H	436	C-C	347	N-N	163	
H-C	414	C=C	611	N=N	418	
H-N	389	C≡C	837	N≡N	946	
H-O	464	C-N	305	N-O	222	
H-F	565	C=N	615	N=O	590	
H-S	368	C≡N	891	O-O	142	
H-Cl	431	C-O	360	O=O	498	
H-Br	364	C=O	736	F-F	159	
H-I	297	C-Cl	339	Cl-Cl	243	
				Br-Br	193	
				I-I	151	

Bond energies are approximate (because they are “average” values obtained by considering a variety of different compounds) but they are useful because they can be used to estimate  $\Delta_f H$  for a **gas-phase reaction**.

◀ The enthalpy of reaction,  $\Delta_f H$ , is the amount of heat absorbed or released by a reaction when it is carried out at constant pressure.

**Example 4-7:** Use bond energies to estimate  $\Delta_f H$  for the reaction below.

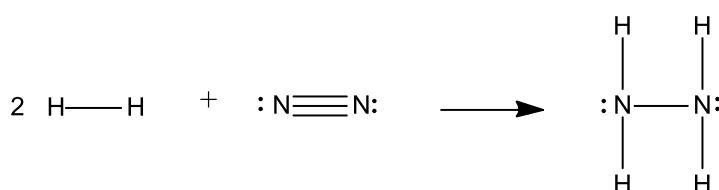


$\Delta_f H > 0 \Rightarrow$  heat is absorbed; the reaction is said to be **endothermic**

$\Delta_f H < 0 \Rightarrow$  heat is released; the reaction is said to be **exothermic**

### Solution:

Re-write the equation for the reaction using the Lewis structures for all reactants and products.  
Then, we identify how many bonds of each type must be broken and formed to convert the reactant molecules into product molecules.



Breaking the H-H bonds	$\Rightarrow +2(436 \text{ kJ mol}^{-1})$	These are positive because energy is required to break bonds.
Breaking the N≡N bonds	$\Rightarrow +1(946 \text{ kJ mol}^{-1})$	
Forming the N-H bonds	$\Rightarrow -4(389 \text{ kJ mol}^{-1})$	These are negative because energy is released when bonds are formed.
Forming the N-N bonds	$\Rightarrow -1(163 \text{ kJ mol}^{-1})$	

Add:  $\Delta_f H = +99 \text{ kJ mol}^{-1}$

Here, “mol<sup>-1</sup>” refers to “per mole of reaction” for the reaction as written. For example:

- For 1 mole of reaction, 2 moles of H<sub>2</sub> and 1 mole of N<sub>2</sub> react to form 1 mole of N<sub>2</sub>H<sub>4</sub>. 99 kJ of heat is absorbed.
- For 10 moles of reaction, 20 moles of H<sub>2</sub> and 10 moles of N<sub>2</sub> react to form 10 moles of N<sub>2</sub>H<sub>4</sub>. 990 kJ of heat is absorbed.

Note carefully:  $\Delta_f H \neq \sum_{\text{products}} \text{BDE's} - \sum_{\text{reactants}} \text{BDE's}$ . In fact, it is the other way around!!

$$\Delta_f H = \sum_{\text{reactants}} \text{BDE's} - \sum_{\text{products}} \text{BDE's}$$

Think carefully about what you are doing when using bond dissociation energies (BDE's) to calculate  $\Delta_f H$  for a gas-phase reaction.

## 4.5 Electronegativity and Polar Covalent Bonds

Electronegativity values can help us determine whether two atoms will share a pair of electrons equally.

**Electronegativity**  $\leftrightarrow$  provides a quantitative measure of the “pull” an atom has on the electrons in its bonds

Bond polarities are important because they affect

- acid strength of hydrogen-containing molecules
- how a molecule interacts with light

Some electronegativity values, based on the Pauling scale, are shown in the table below.

1																18	
H 2.1		2														He	
Li 1.0	Be 1.5																
Na 0.9	Mg 1.2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	
K 0.8	Ca 1.0	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne
Rb 0.8	Sr 1.0	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Al 1.5	Si	P 2.1	S 2.5	Cl 3.0	Ar
Cs 0.8	Ba (57-71) La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	In 1.6	Sn	Sb 2.0	Te 2.1	I 2.5	Xe
Fr 0.7	Ra (89-103) Ac-Lr	104 Rf	Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	Pb	Bi 2.0	Po 2.2	At 2.2	Rn		

Note:

- F, O, Cl and N are the most electronegative elements
- s block metals (not H!) have EN  $\approx$  1
- d block metals have EN  $\approx$  1-2 (values not shown)
- p block: EN > 1 and increase left to right

Electronegativity values can help us decide whether the bond formed between two atoms is primarily ionic or primarily covalent.

General rule of thumb:

$$\Delta\text{EN} > 1.7 \Rightarrow \text{bond is primarily ionic}$$

$$0 < \Delta\text{EN} < 1.7 \Rightarrow \text{bond is polar but primarily covalent}$$

**Digging Deeper:** The most commonly used electronegativity scale is the “Pauling scale”. The Pauling scale is based on bond dissociation energies. If the EN of atom X is known, then the EN of atom Y is obtained using the equation

$$\text{EN}(X) - \text{EN}(Y) = a \sqrt{D_{XY} - \bar{D}}$$

where  $a$  is a constant,  $D_{XY}$  is the bond dissociation energy of XY and

$$\bar{D} = \sqrt{D_{X_2} D_{Y_2}}$$

is the “geometric mean” of the bond dissociation energies for  $X_2$  and  $Y_2$ .

Fluorine is assigned an EN value of 4.0. The EN for H could then be obtained from EN(F) together with the bond dissociation energies of  $H_2$ ,  $F_2$  and HF.

There are many exceptions to this rule, so the rule is actually not that useful.

For example, for H-F,  $\Delta\text{EN} = 4.0 - 2.1 = 1.9$ , yet the bond is only 40% ionic.

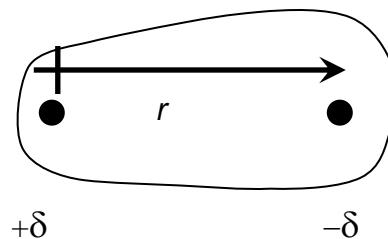
It is better that you remember the guidelines given on page 1 of this module:

When an s block metal combines with a p block element, we get an ionic compound. When atoms from the p block combine, we get a molecular compound with covalent bonds holding the atoms together.

### Polar Covalent Bonds and Dipole Moments

When electron pairs are not shared equally, the bond will have a dipole moment ( $\mu$ ) because one end of the bond will be slightly positive ( $+δ$ ) and the other will be slightly negative ( $-δ$ ). Often,  $δ$  is less than the magnitude of the charge on a single electron. The magnitude of the dipole moment depends on both the magnitude of the charges and on the distance between them.

$$\mu = |\delta| r$$

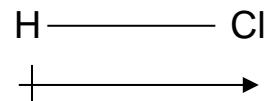


Polar covalent bonds have “covalent character” plus some “ionic character” plus. As a result, polar covalent bonds are often much stronger than pure covalent bonds!

N–N	vs	O–O	vs	N–O
145 pm		145 pm		136 pm
163 $\frac{\text{kJ}}{\text{mol}}$		142 $\frac{\text{kJ}}{\text{mol}}$		222 $\frac{\text{kJ}}{\text{mol}}$

**Example 4-8:** Experimental measurements indicate that the HCl molecule has bond length of 127.4 pm and a dipole moment of 1.03 debye. What is the % ionic character of the HCl bond? (Note: 1 debye =  $3.34 \times 10^{-30} \text{ C m}$ ).

Review this example on your own!!



Solution:

If the HCl bond was 100% ionic, i.e.  $\text{H}^+\text{Cl}^-$ , then we would have

$$\mu_{\text{ionic}} = (1.602 \times 10^{-19} \text{ C})(127.4 \times 10^{-12} \text{ m}) = 2.041 \times 10^{-29} \text{ C m} = 6.11 \text{ debye}$$

The observed dipole is only 1.03 debye. Therefore:

$$\% \text{ ionic} = \frac{\mu}{\mu_{\text{ionic}}} \times 100 = 17$$

Therefore, the H-Cl bond has 17% ionic character. We can think of this result another way: the H end of the HCl molecule has a charge of  $+δ = +0.17e$  and the Cl end of the molecule has a charge of  $-δ = -0.17e$ , where  $e = 1.602 \times 10^{-19} \text{ C}$ .

## 4.6 VSEPR Theory

(Valence Shell Electron Pair Repulsion Theory)

The basic premise of VSEPR theory is:

**Groups arrange themselves around an atom to minimize electron pair repulsions.**

### Did you know?

R. J. Gillespie, professor emeritus of chemistry at McMaster University in Hamilton, Ontario, is widely regarded to be the “father” of VSEPR theory.

VSEPR theory can be used as a guide to predict the geometry around an “internal” atom of a molecule. It is imperative that you **memorize the ideal VSEPR geometries and ideal molecular geometries.**

Keep in mind the following points:

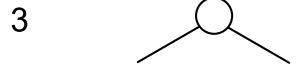
- VSEPR is a model. It is **not** perfect.
- VSEPR theory is most appropriate for predicting geometries associated with light atoms of the *p*-block. VSEPR theory is **not** appropriate for predicting the geometry of a molecule or ion whose central atom is from the *d*-block. It is also less reliable for predicting the geometry around “heavy” *p*-block atoms (e.g. Sn, Sb, Te), especially when the central atom has several bonded groups.
- Deviations from the ideal geometries generally have a destabilizing effect: the greater the deviation, the greater the destabilization.

## VSEPR geometries and related molecular geometries

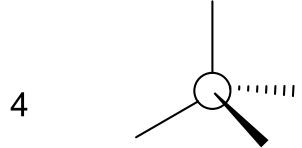
# groups      ideal VSEPR  
(electronic)  
geometry



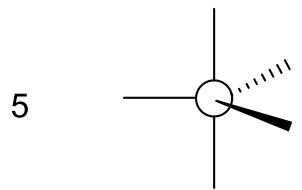
linear  
( $sp$ )



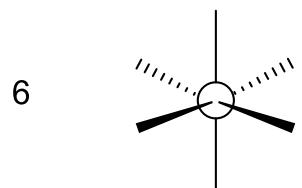
trigonal  
planar  
( $sp^2$ )



tetrahedral  
( $sp^3$ )

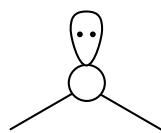


trigonal  
bipyramidal  
( $sp^3d$ )

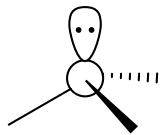


octahedral  
( $sp^3d^2$ )

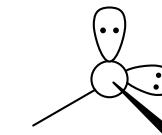
related molecular  
geometries



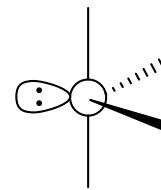
bent or  
V-shaped



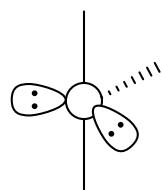
trigonal  
pyramidal



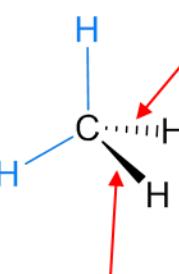
bent



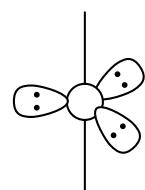
see-saw



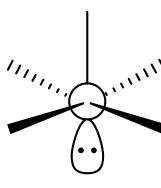
T-shaped



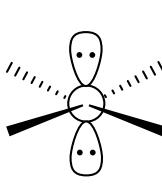
The dashed wedge  
represents a bond  
that points behind  
the plane of the  
page.



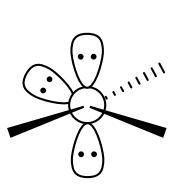
linear



square  
pyramidal



square  
planar

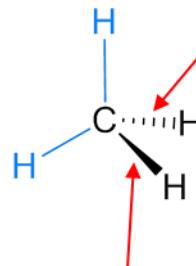


T-shaped

**Learning Tip:** The number of groups around an atom is obtained by counting the number of atoms bonded to it and the number of lone pairs.

$$\# \text{ groups} = \# \text{ bonded atoms} + \# \text{ lone pairs}$$

The dashed wedge  
represents a bond  
that points behind  
the plane of the  
page.



The solid wedge  
represents a bond  
that points out of  
the plane of the  
page.

**Example 4-9:** For each of the following: **A.** use VSEPR theory to predict the geometry and approximate bond angles. **B.** Determine whether the molecule is polar or nonpolar (i.e. Does the molecule possess a permanent dipole moment? If so, it is polar. If not, it is nonpolar.)

The underlined atom is the central atom. All other atoms are bonded directly to the underlined atom, unless stated otherwise.

- (a) H<sub>2</sub>O      (b) ClF<sub>3</sub>      (c) SO<sub>3</sub>      (d) BrF<sub>5</sub>

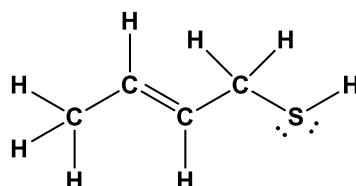


See problems 10-59 to 10-61,  
10-81 and 10-82 from  
Petrucci (11<sup>th</sup> edition).

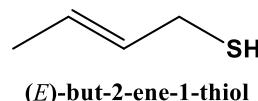
**Learning Tip:** Bond dipoles are vectors (with magnitude and direction). A molecule is nonpolar if the vector sum of the bond dipoles is zero (i.e. the bond dipoles cancel). A molecule is polar if the vector sum of the bond dipoles is not zero (i.e. the bond dipoles do not cancel). To obtain the vector sum of two vectors, we can add them "head-to-tail", without changing either the magnitude or the direction of either vector.

## 4.7 Line Structures for Organic Molecules

As the structure of molecules get more complex, it becomes time consuming (and space consuming) to draw out every single atom in a structure. Fortunately, chemists use line-angle structures to simplify the drawings of carbon-based structures. It is important for you to be able to examine the drawing of a molecule and interpret all of the information conveyed by that drawing. Examine the full and condensed structure of (*E*)-2-buten-1-thiol (a component of skunk spray) to appreciate the use of line-angle structures.



(E)-but-2-ene-1-thiol

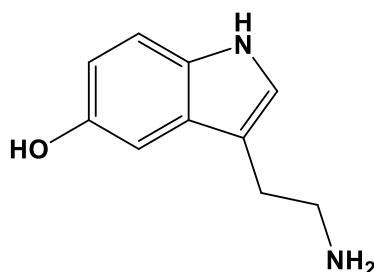


(E)-but-2-ene-1-thiol

### Guidelines for drawing and interpreting line-angle structures.

1. Carbon atoms are not explicitly shown.
  - o Each “end” of a line represents a carbon atom.
  - o Each “point” in a chain represents a carbon atom.
2. Chains of carbon atoms are drawn as a “zig-zag” pattern.
  - o Keep in mind: there is free rotation around single bonds.
3. Hydrogen atoms are not explicitly shown when bonded to carbon atoms.
  - o Look at formal charges and the presence of double or triple bonds to decide how many hydrogen atoms are bonded to each carbon atom.
  - o Neutral carbon atoms have 4 bonds. This rule will help you identify hydrogen atoms.
4. Lone pairs may or may not be explicitly shown.
  - o You will identify the number of lone pairs by the presence or absence of formal charges.

**Example 4-10:** Examine the structure below. Draw any lone pairs of electrons on the molecule. What is the condensed molecular formula for this molecule?



Total number of lone pairs of electrons:

Number of C atoms:

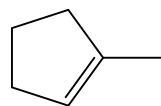
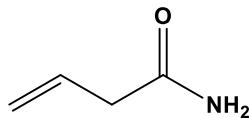
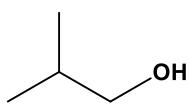
Number of H atoms:

Number of N atoms:

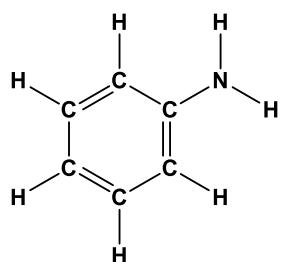
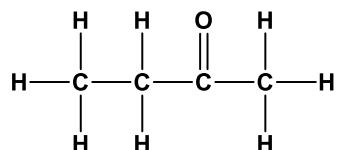
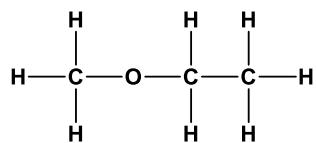
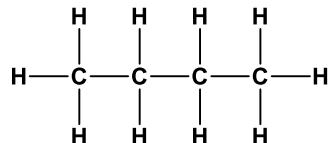
Number of O atoms:

This molecule is a neurotransmitter associated with happiness – what molecule is it?

**Example 4-11:** For each of the structures below, identify the molecular formula. Where appropriate, add lone pairs of electrons to complete the structures.



**Example 4-12:** For each of the structures below, draw the condensed line formula. Use correct bond angles according to VSPER theory, and include all lone pairs.



## 5.1 Introduction to quantum theory of chemical bonding

We will consider two different approaches for describing bonding from a quantum mechanical point-of-view. In the quantum mechanical approach to bonding, we describe bond formation in terms of “orbitals” (or orbital interactions) rather than in terms of “electron pairs”.

Before we look at the specifics of these two approaches, it is useful and instructive to compare the essential differences.

<b>VB Theory</b> a “localized orbital approach”	<b>MO Theory</b> a “delocalized orbital approach”
<ul style="list-style-type: none"><li>• We think in terms of orbitals that belong to individual atoms in the molecule.</li><li>• We imagine building a molecule <b>atom-by-atom</b> using appropriate <b>atomic orbitals</b>.  An atomic orbital helps us visualize how a single electron interacts with one nucleus.</li><li>• VB theory is useful for describing the ground-state properties of molecule (e.g. geometry).</li><li>• VB theory is used extensively in <b>organic</b> chemistry.</li></ul>	<ul style="list-style-type: none"><li>• We think in terms of orbitals that belong to the molecule.</li><li>• We imagine building a molecule <b>electron-by-electron</b> using appropriate <b>molecular orbitals</b>.  A molecular orbital helps us visualize how a single electron interacts with two or more nuclei.</li><li>• MO theory is useful for describing excited-state properties, spectroscopy, and chemical reactions.</li><li>• MO theory is used extensively in <b>inorganic</b> and <b>physical</b> chemistry, and increasingly in organic chemistry.</li></ul>

Valence bond theory has a strong connection to Lewis theory and Lewis structures.

For MO theory, we will focus on homonuclear diatomic molecules only.

## 5.2 Valence Bond Theory: The basics

A covalent bond forms when unpaired electrons on two different atoms “pair up” and are shared by both atoms. In VB theory, we describe bond formation in terms of **orbital overlap**.

There are two types of bonds/overlap to consider:

$\sigma$  bond  $\leftrightarrow$  orbitals overlap “on-axis” (i.e. along the internuclear axis)

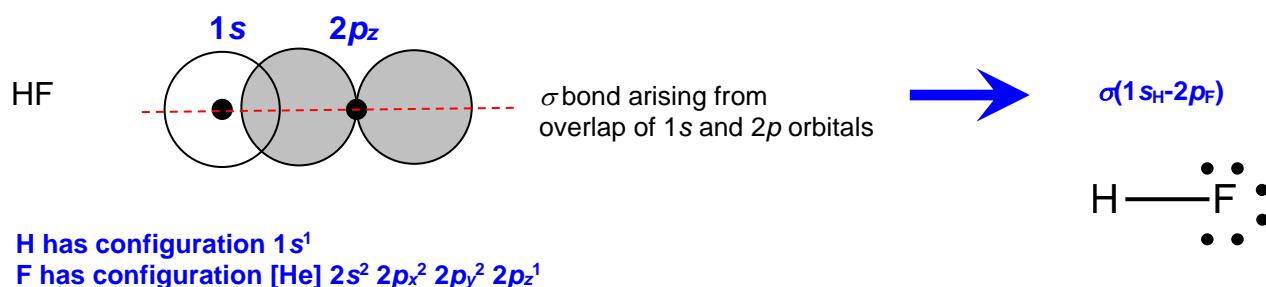
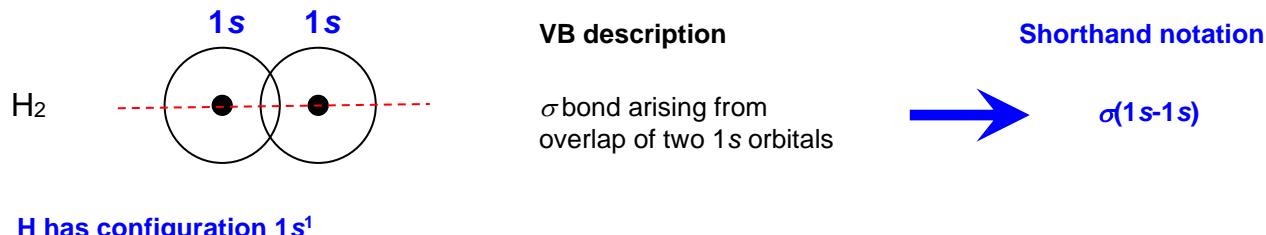
a single bond is always a  $\sigma$  bond;  
 $\sigma$  overlap is much more effective  
than  $\pi$  overlap - see O<sub>2</sub> below

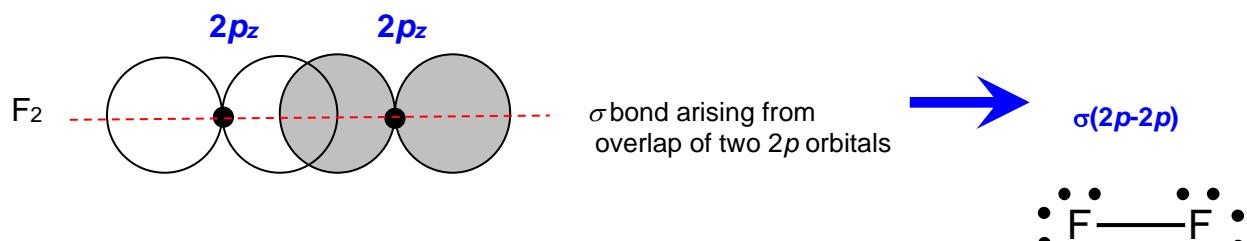
$\pi$  bond  $\leftrightarrow$  orbitals overlap “off-axis”

$\pi$  bonds are associated with  
“sideways” overlap of orbitals

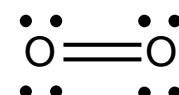
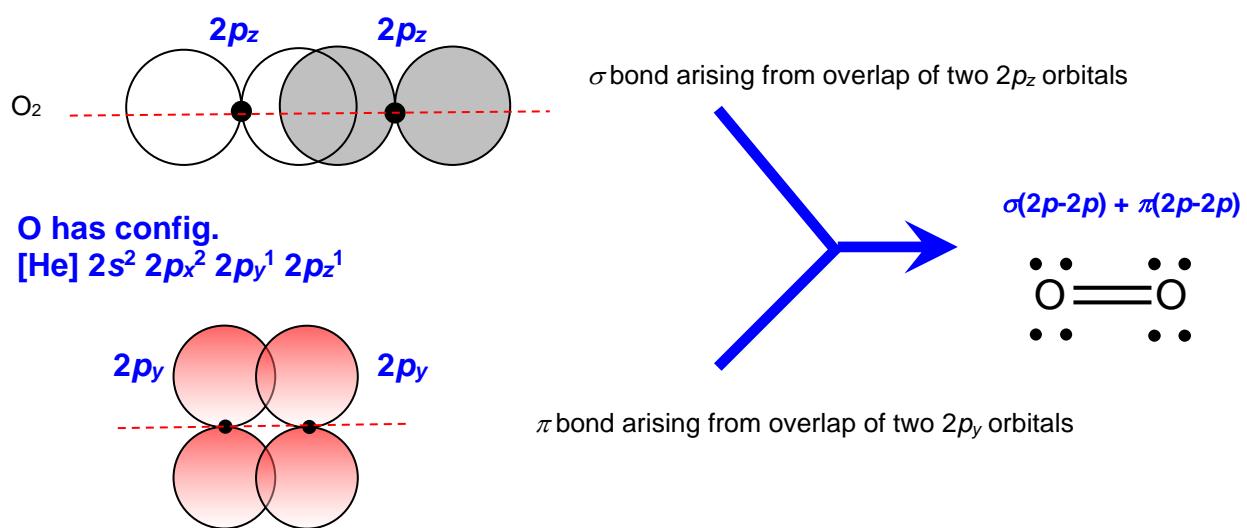
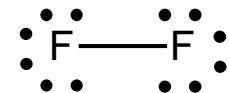
$\pi$  bonds arise only with double and triple bonds

The following examples illustrate how valence bond (VB) theory is used to describe the bonding in the H<sub>2</sub>, HF, F<sub>2</sub>, and O<sub>2</sub> molecules.





F has configuration [He]  $2s^2 2p_x^2 2p_y^2 2p_z^1$

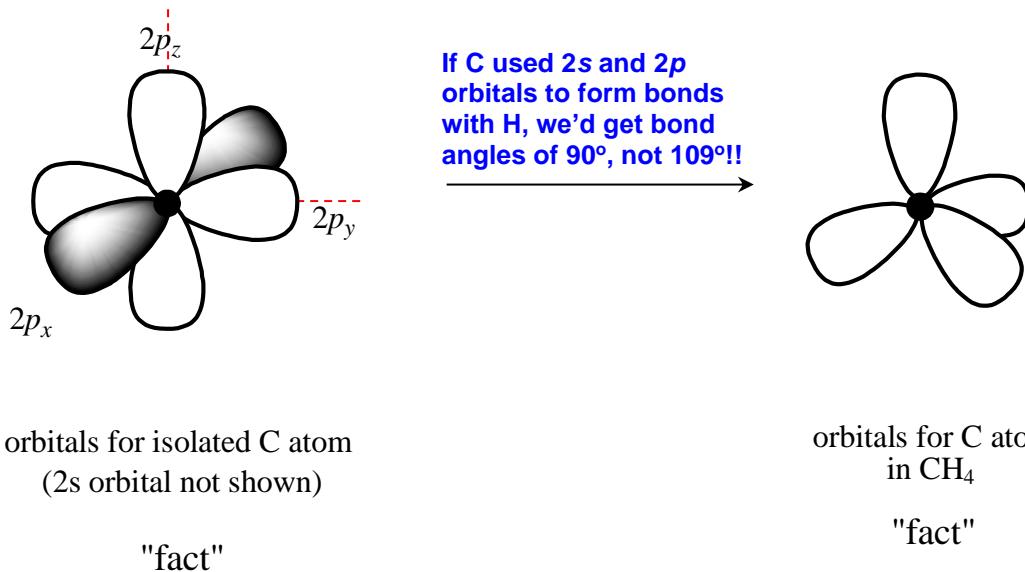


There is much better orbital overlap in a  $\sigma$  bond than there is in a  $\pi$  bond. As a result, a  $\sigma$  bond is stronger than a  $\pi$  bond. **Remember:** a double bond consists of a  $\sigma$  bond and a slightly weaker  $\pi$  bond.

However, things get much more complicated when more than two atoms are involved (e.g. CH<sub>4</sub>).

VSEPR theory  
(& experiment)  $\Rightarrow$  CH<sub>4</sub> is tetrahedral.  
The H-C-H bond angles are 109°.

**Problem?** The orbitals of a C atom do **not** point towards the corners of a tetrahedron



**Q:** How do we reconcile these two facts?

**A:** We imagine that as the H atoms are brought in towards the C atom, the valence orbitals of C are transformed into a new set of "hybrid" orbitals.  $\rightarrow$  In CH<sub>4</sub>, the hybrid orbitals on C point towards the corners of a tetrahedron.

**Orbital Hybridization**  $\Rightarrow$  Take "n" atomic orbitals and mix them to generate "n" hybrid orbitals.

$\rightarrow$  We cannot not create or destroy electrons, so we must maintain the same number of orbitals we use to describe them.

Hybrid orbitals are named according to the types and numbers of atomic orbitals used to generate the hybrid orbitals. Common hybridization schemes are listed below.

$s + p_z \Rightarrow$  **two  $sp$  orbitals**  $180^\circ$  apart

$s + p_y + p_z \Rightarrow$  **three  $sp^2$  orbitals** pointing towards the corners of an equilateral triangle

$s + p_x + p_y + p_z \Rightarrow$  **four  $sp^3$  orbitals** pointing towards the corners of a tetrahedron

$s + p_x + p_y + p_z + d \Rightarrow$  **five  $sp^3d$  orbitals** pointing towards the vertices of a trigonal bipyramidal

$s + p_x + p_y + p_z + d + d \Rightarrow$  **six  $sp^3d^2$  orbitals** pointing to the vertices of an octahedron

Memorize the correlations between the various hybridization schemes and the VSEPR geometries.

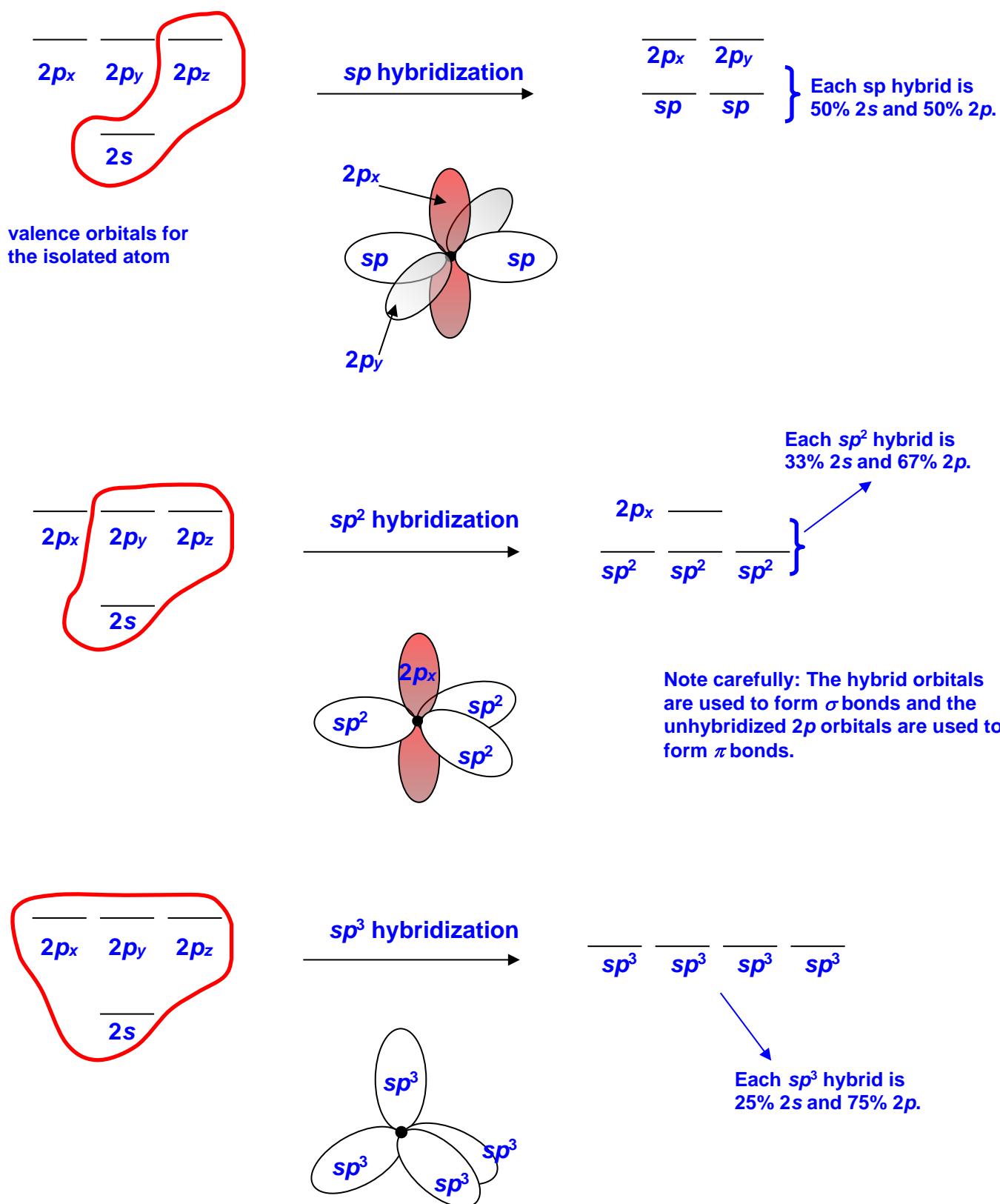
e.g.    2 groups  $\leftrightarrow$  linear  $\leftrightarrow sp$   
          3 groups  $\leftrightarrow$  trigonal planar  $\leftrightarrow sp^2$   
          4 groups  $\leftrightarrow$  tetrahedral  $\leftrightarrow sp^3$

### Did you know?

Theoretical investigations suggest that  **$d$  orbitals** do NOT participate in bond formation. Consequently, the use of  $sp^3d$  or  $sp^3d^2$  hybridization schemes has fallen out of favour with most chemists.

### 5.3 The “energetics” of $sp$ , $sp^2$ and $sp^3$ hybridization

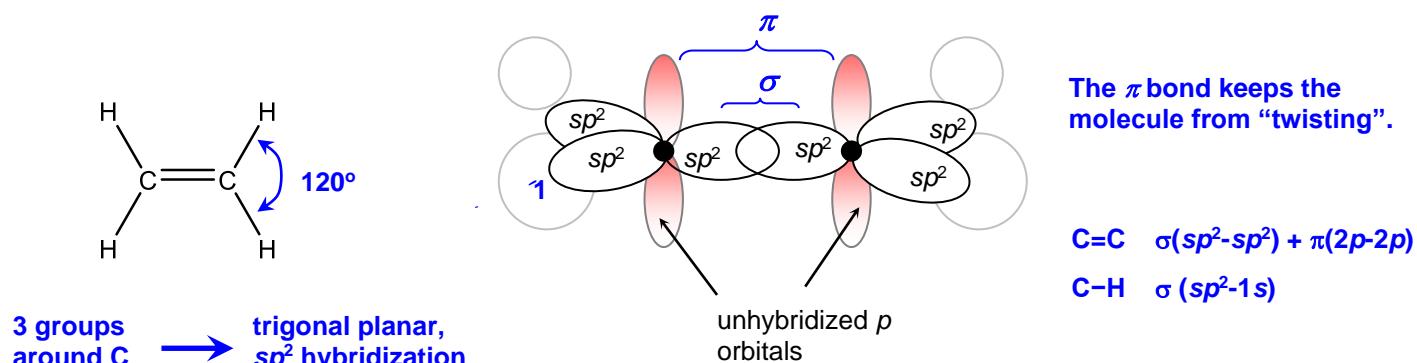
illustrated here for atoms in the second period



## 5.4 VB theory of $\sigma$ and $\pi$ bonding in polyatomics

- $\sigma$  bond
  - orbital overlap occurs along the internuclear axis
  - often involves overlap of hybrid orbitals
- $\pi$  bond
  - orbital overlap does **not** occur along internuclear axis
  - can be formed via the overlap of unhybridized  $p$  orbitals

Bonding between two  $sp^2$  hybridized C atoms (as in  $C_2H_4$ )



overlap of  $sp^2$  orbitals  $\Rightarrow \sigma$  bond

sideways overlap of  $p$  orbitals  $\Rightarrow \pi$  bond

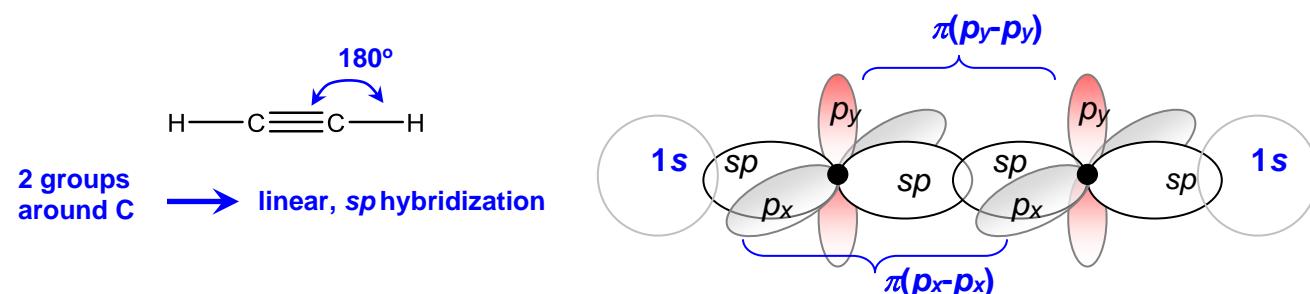
VB theory says: Each C-H bond is a  $\sigma$  bond arising from  $sp^2-s$  overlap.

The carbon-carbon double bond consists of **one  $\sigma$  bond**, arising from  $sp^2-sp^2$  overlap, plus **one  $\pi$  bond** arising from  $p-p$  overlap.

Note: **double bond = 1  $\sigma$  bond + 1  $\pi$  bond**



Bonding between two  $sp$  hybridized C atoms (as in  $C_2H_2$ )



VB theory says: Each C-H bond is a  $\sigma$  bond arising from  $sp-s$  overlap.

The carbon-carbon triple bond consists of **one  $\sigma$  bond**, arising from  $sp-sp$  overlap plus **two  $\pi$  bonds** arising from  $p_x-p_x$  and  $p_y-p_y$  overlap.

**triple bond = 1  $\sigma$  bond + 2  $\pi$  bonds**



## 5.5 Using VB theory to describe bonding in a molecule

(1) Draw an acceptable Lewis structure.

An **interior atom** is one that is bonded to more than one other atom.

(2) For each **interior** atom, determine:

- the number of groups
- the geometry around each atom
- the appropriate hybridization scheme

**Memorize:**

2 groups  $\leftrightarrow$  linear  $\leftrightarrow$   $sp$

3 groups  $\leftrightarrow$  trigonal planar  $\leftrightarrow$   $sp^2$

4 groups  $\leftrightarrow$  tetrahedral  $\leftrightarrow$   $sp^3$

5 groups  $\leftrightarrow$  trigonal bipyramidal  $\leftrightarrow$   $sp^3d$

6 groups  $\leftrightarrow$  octahedral  $\leftrightarrow$   $sp^3d^2$

**single bond =  $\sigma$**

**double bond =  $\sigma + \pi$**

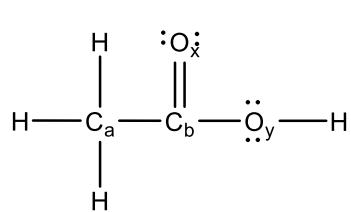
**triple =  $\sigma + 2\pi$**

(3) Identify the orbitals involved in bond formation.

(4) Classify bonds as either  $\sigma$  or  $\pi$ .

**Example 5-1:** Use VB theory to describe the bonding in acetic acid,  $\text{CH}_3\text{COOH}$ .

(Both oxygen atoms are bonded to the underlined carbon atom.)



See problems 11-7, 11-9, 11-12, 11-60 and 11-64 from Petrucci (11<sup>th</sup> edition), as well as problem B16 from the Extra Problems for CHEM 121.

The letters "a", "b", "x" and "y" on the atoms are used to identify them.

Solution:

- $\text{C}_a$  has 4 groups  $\Rightarrow$   $\text{C}_a$  is  $sp^3$  hybridized, tetrahedral geometry,  $109^\circ$  bond angles  
 $\text{C}_b$  has 3 groups  $\Rightarrow$   $\text{C}_b$  is  $sp^2$  hybridized, trigonal planar geometry,  $120^\circ$  bond angles  
 $\text{O}_y$  has 4 groups  $\Rightarrow$   $\text{O}_y$  is  $sp^3$  hybridized, tetrahedral geometry,  $109^\circ$  bond angles

Therefore:



But what about  $\text{C}_b=\text{O}_x$ ? That's an interesting question. There are **two** acceptable descriptions.

**Description #1 (assuming  $\text{O}_x$  is  $sp^2$  hybridized):**  $\text{C}_b=\text{O}_x$  consists of a  $\sigma$  bond arising from the overlap of an  $sp^2$  orbital on  $\text{C}_b$  and an  $sp^2$  orbital on  $\text{O}_x$  and a  $\pi$  bond arising from the overlap of  $2p$  on  $\text{C}_b$  and  $2p$  on  $\text{O}_x$ . In short,  $\text{C}_b=\text{O}_x$  is  $\sigma(\text{sp}^2-\text{sp}^2) + \pi(2p-2p)$ .

**Description #2 (assuming  $\text{O}_x$  is not hybridized):**  $\text{C}_b=\text{O}_x$  consists of a  $\sigma$  bond arising from the overlap of an  $sp^2$  orbital on  $\text{C}_b$  and a  $2p$  orbital on  $\text{O}_x$  and a  $\pi$  bond arising from the overlap of  $2p$  on  $\text{C}_b$  and  $2p$  on  $\text{O}_x$ . In short,  $\text{C}_b=\text{O}_x$  is  $\sigma(\text{sp}^2-2p) + \pi(2p-2p)$ .

Either description is acceptable because experimental measurements cannot tell us about the geometry around  $\text{O}_x$ . So, we don't know which description is better. Some chemists prefer the first description and others prefer the second.

**So you think you know your stuff, eh? Then try out this example.**

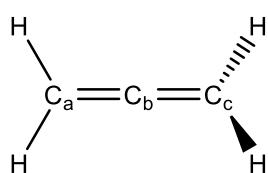
**Example 5-2:** Draw the Lewis structure for the allene molecule,  $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ .

Then answer the questions below.

- Classify each bond as  $\sigma$  or  $\pi$  and identify the orbitals involved.
- What is the H-C-C bond angle? What is the C-C-C bond angle?
- Explain why the four H atoms cannot all lie in the same plane.

Solution:

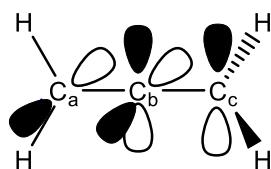
a)



bond	classification?	orbitals involved?
H-C	$\sigma$	$\text{C}(sp^2) - \text{H}(1s)$
$\text{C}_a=\text{C}_b$	$\sigma + \pi$	$\sigma: \text{C}_a(sp^2)-\text{C}_b(sp)$ $\pi: \text{C}_a(2p_x)-\text{C}_b(2p_x)$
$\text{C}_b=\text{C}_c$	$\sigma + \pi$	$\sigma: \text{C}_b(sp)-\text{C}_c(sp^2)$ $\pi: \text{C}_b(2p_y)-\text{C}_c(2p_y)$

The important point here is that  $\text{C}_b$  makes two  $\pi$  bonds using two different p orbitals that are perpendicular.

- The H- $\text{C}_a$ - $\text{C}_b$  bond angle is  $120^\circ$  because  $\text{C}_a$  is  $sp^2$ -hybridized. The  $\text{C}_a-\text{C}_b-\text{C}_c$  bond angle is  $180^\circ$  because  $\text{C}_b$  is  $sp$ -hybridized.
- The diagram below shows the unhybridized  $2p$  orbitals involved in forming the  $\pi$  bonds. In order for  $\text{C}_b$  to make two  $\pi$  bonds, the  $2p$  orbitals of  $\text{C}_a$  and  $\text{C}_c$  must be at right angles. This forces the hybrid orbitals of  $\text{C}_a$  and  $\text{C}_c$  to lie in different planes and therefore the H atoms bonded to  $\text{C}_a$  lie in a different plane than those bonded to  $\text{C}_c$ .



## 5.6 Molecular orbital (MO) theory for diatomic molecules

In molecular orbital theory, we imagine building a molecule electron-by-electron by placing the electrons in orbitals that extend over all nuclei.

molecular orbital (MO)       $\leftrightarrow$       tells us how a single  $e^-$  interacts with all of the nuclei

In principle, we could construct molecular orbitals by solving the Schrodinger equation for the “one  $e^-$  plus  $N$  nuclei” problem.

⇒ energy levels & wave functions ( $\psi$ )

► In setting up the one-electron problem for a polyatomic molecule, we would have to assume a particular geometry. Fortunately, we often know the geometry.

We would use the energy levels to construct an energy level diagram and the wave functions to construct scatter point plots, boundary surfaces and radial electron densities, just like we did for the H atom. We would then fill up the orbitals with electrons, just like we did for multielectron atoms.

In practice, we never set up or solve the Schrodinger equation for the “one electron plus  $N$  nuclei” problem. If we really wanted accurate energies and wave functions, we would set up and solve the Schrodinger equation for the entire molecule (i.e.  $n$  electrons plus  $N$  nuclei).

We use MO theory in a qualitative way to elucidate the essential features of the electronic energy level diagram and the molecular orbitals for the molecule.

## MO Theory: Key concepts

- (1) The valence electrons in a molecule occupy orbitals that extend, in principle, over all nuclei in the molecule.
  - (2) We imagine that the valence orbitals of the atoms are transformed into a set of molecular orbitals as the atoms combine to form the molecule.

*n* atomic orbitals  $\Rightarrow$  *n* molecular orbitals

- (3) Some MOs promote bonding and others don't. Sometimes, an MO makes no contribution to bonding. Consequently, MOs can be classified as **bonding**, **antibonding** or **nonbonding**.

◀ This is essentially “conservation of electrons”. If we need  $n$  atomic orbitals to describe the valence electrons of the separated atoms, then we need  $n$  molecular orbitals for describing the valence electrons of the molecule.

- Core electrons occupy nonbonding orbitals that are essentially pure atomic orbitals.

To obtain “accurate” MOs for a molecule, we’d have to set up and solve the Schrodinger equation for the molecule in question. **For most applications, we don’t need accurate MOs and so we can use an approximate (and diagrammatic) approach to deduce the MOs for a molecule.**

**Approximate MOs: The LCAO-MO Method**  
**(LCAO = linear combination of atomic orbitals)**

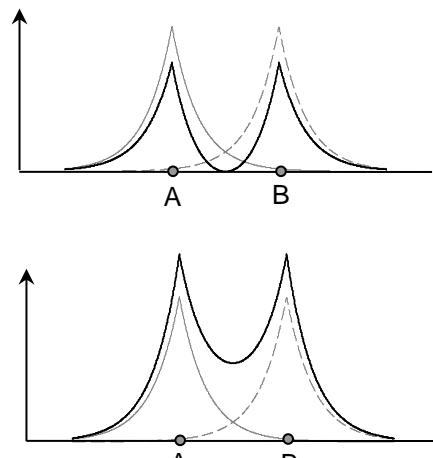
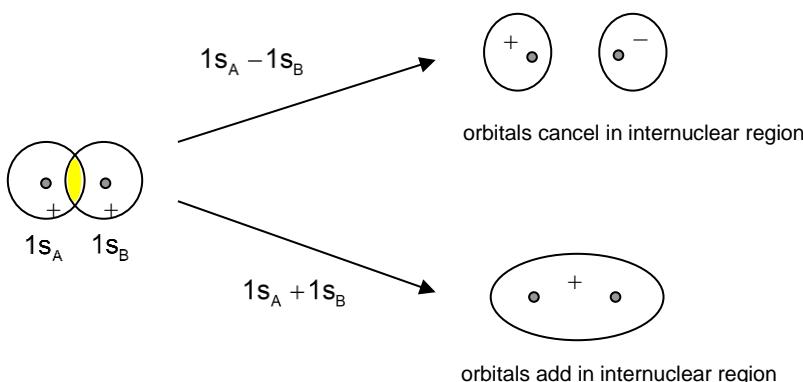
**FYI:** The LCAO-MO method tends to exaggerate the ionic character of bonds in a molecule.

We will focus on the **LCAO-MO method** of approximating the MOs for a molecule. In this method, the molecular orbitals (MOs) are obtained by taking appropriate combinations of the atomic orbitals (AOs). For a diatomic molecule AB, **we imagine transforming the atomic orbitals of A and B into a set of molecular orbitals for the AB molecule**, using the following guidelines.

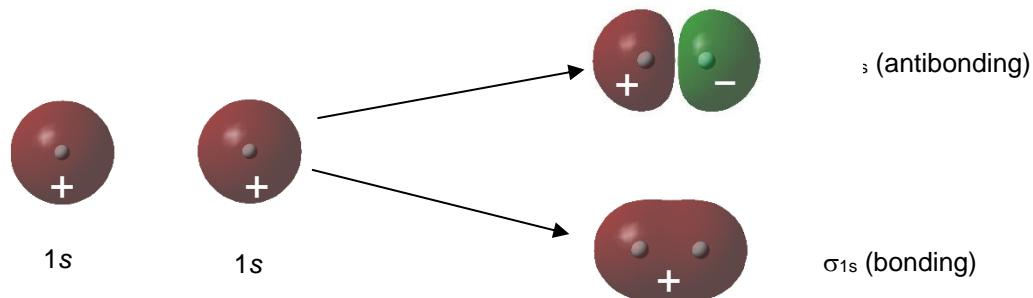
1. **Combine two AOs (one from atom A and one from atom B) to obtain two MOs (one bonding and one antibonding).**

Let's illustrate the approach using a pair of 1s orbitals, one centred on atom A and the other centred on atom B. If the two atoms are close enough that the two 1s orbitals overlap, then we must **replace the pair of AOs with a pair of MOs**. The appropriate MOs are obtained by combining the AOs in two ways: "constructively" and "destructively".

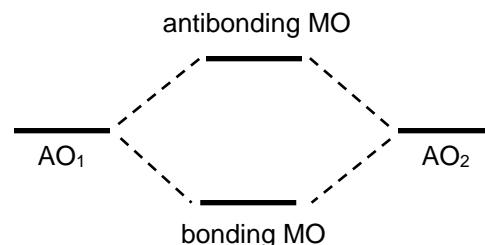
The graphs below show the probability density along the internuclear axis for the two MOs.

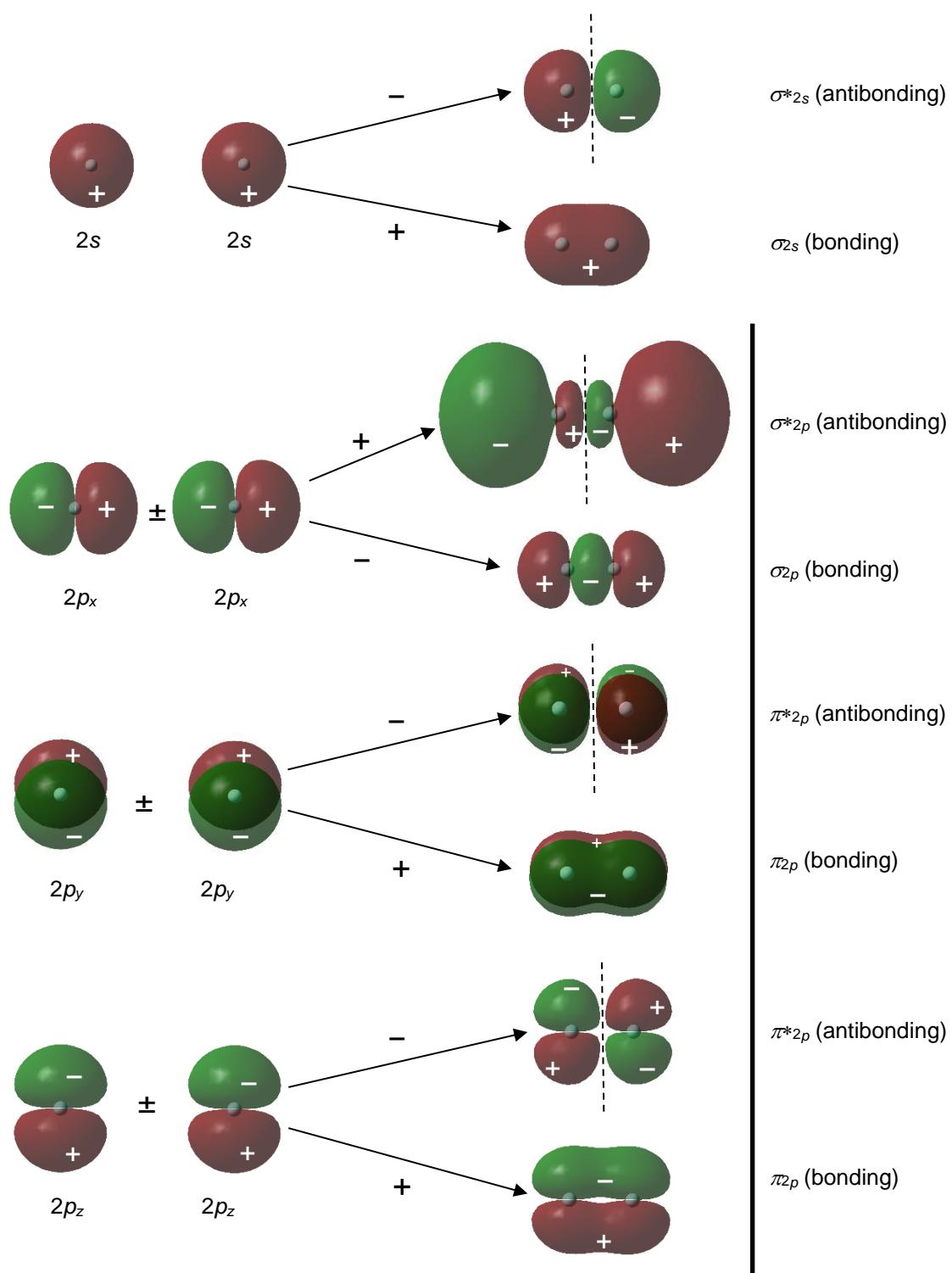


We can use colour (shading) or "+" and "-" signs, to keep track of phase, as shown below.



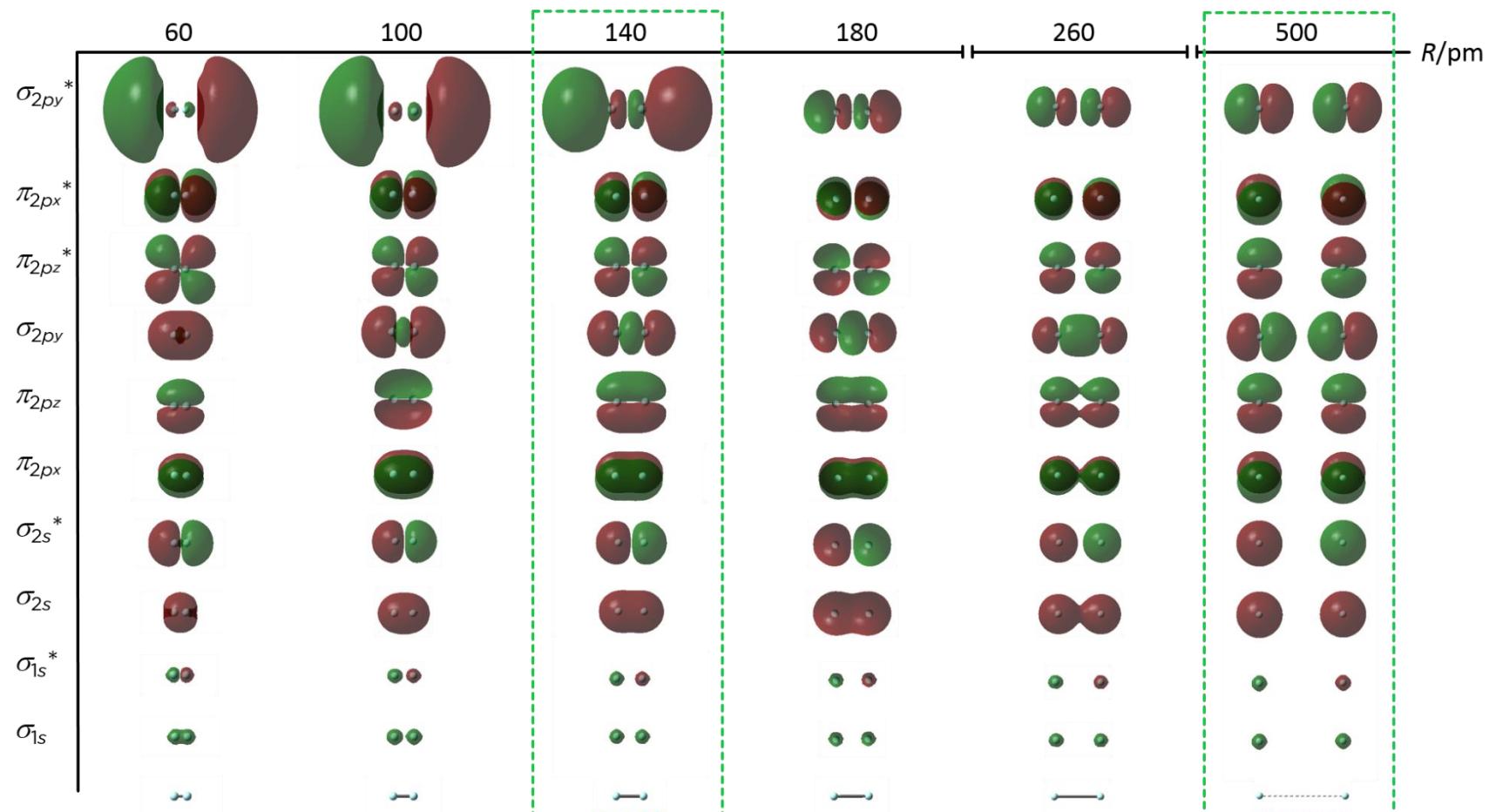
2. A bonding MO is lower in energy than the AOs from which it is derived. The antibonding MO is higher in energy than the AOs from which it is derived.



**MOs formed from 2s and 2p orbitals ( $F_2$ )**

**Digging Deeper:** For heteronuclear diatomic molecules, the energies of the AOs can be quite different, so in those cases we might have to consider other combinations (e.g.  $1s_A$  with  $2p_B$  or  $2s_A$  with  $2p_B$ ). Also, the MOs for a heteronuclear diatomic molecule are not perfectly symmetrical: the bonding orbital is “distorted” slightly towards the more electronegative atom. The antibonding orbital is distorted slightly towards the less electronegative atom. However, we will not consider these complications.

**Digging Deeper:** Read this diagram from **right to left** ( $\leftarrow$ ). When the two F atoms are very far apart (e.g. 500 pm), the valence electrons are best described using atomic orbitals that are centred on the two atoms. However, as the atoms approach each other, the valence electrons are best described using molecular orbitals that extend over both nuclei.



The experimentally determined bond length of  $\text{F}_2$  is 141 pm.

At large separation (e.g. 500 pm), the MOs of  $\text{F}_2$  are essentially just the AOs of the individual F atoms.

**Important Remarks:**

- One combination of AOs produces a BONDING ORBITAL and the other produces an ANTIBONDING ORBITAL.
- Antibonding MOs have a nodal plane perpendicular ( $\perp$ ) to the bond axis. Bonding MOs don't.
- The bonding MO is of lower energy than the AOs used to construct it and the antibonding MO is of higher energy than the AOs used to construct it.
- MOs are classified as  $\sigma$  or  $\pi$ .

$\sigma$  orbitals  $\Rightarrow$  arise from s or p orbitals that overlap along the internuclear axis.

$\pi$  orbitals  $\Rightarrow$  arise from p orbitals that overlap "off-axis"

- To deal with second-row diatomics, we need only consider the MOs formed from 1s, 2s, 2p<sub>x</sub>, 2p<sub>y</sub> and 2p<sub>z</sub>.

**Starting from diagrams of 1s, 2s, and 2p, orbitals, you should be able to deduce the shapes of all of the following MOs.**

$\sigma_{1s}$	$\sigma^*_{1s}$	$\sigma_{2s}$	$\sigma^*_{2s}$	$\sigma_{2p}$	$\sigma^*_{2p}$	$\pi_{2p}$	$\pi^*_{2p}$
---------------	-----------------	---------------	-----------------	---------------	-----------------	------------	--------------

- The energy level diagram must be memorized.** (The energy-ordering of the MOs approximately follows that of the AOs.)
- We obtain the electron configuration for the molecule by adding electrons to the molecular orbitals (starting from the lowest energy orbital). **The Pauli Exclusion Principle and Hund's Rule apply.**
- If there are a greater number of electrons in bonding orbitals than there are in antibonding orbitals, we expect the molecule or ion to be stable.

$$\text{bond order} = \frac{1}{2} \times (n_b - n_a)$$

◀  $n_b - n_a$  is the "net number" of bonding electrons. If there are more bonding electrons than there are antibonding electrons, we expect the molecule to be stable.

A long time ago (in high school?), you memorized the orbital filling order for atoms (e.g. 1s before 2s before 2p, etc. etc.). Now, you must do the same for homonuclear diatomic molecules. Fortunately, the energy-ordering of the MOs is related to the energy-ordering of the AOs, so you are really building on previous knowledge.

**For a homonuclear diatomic molecule to be stable, the bond order must be greater than zero**

(i.e., there must be a greater number of electrons in bonding MOs than in antibonding MOs).

Otherwise, the molecule is not stable.

The factor of  $\frac{1}{2}$  that appears in the definition of bond order is included because, from Lewis structures, we think of a single bond as consisting of two electrons (i.e., it requires two electrons to make one bond). To convert the "net" number of bonding electrons into a bond order, we must multiply the net number of bonding electrons by  $\frac{1}{2}$ .

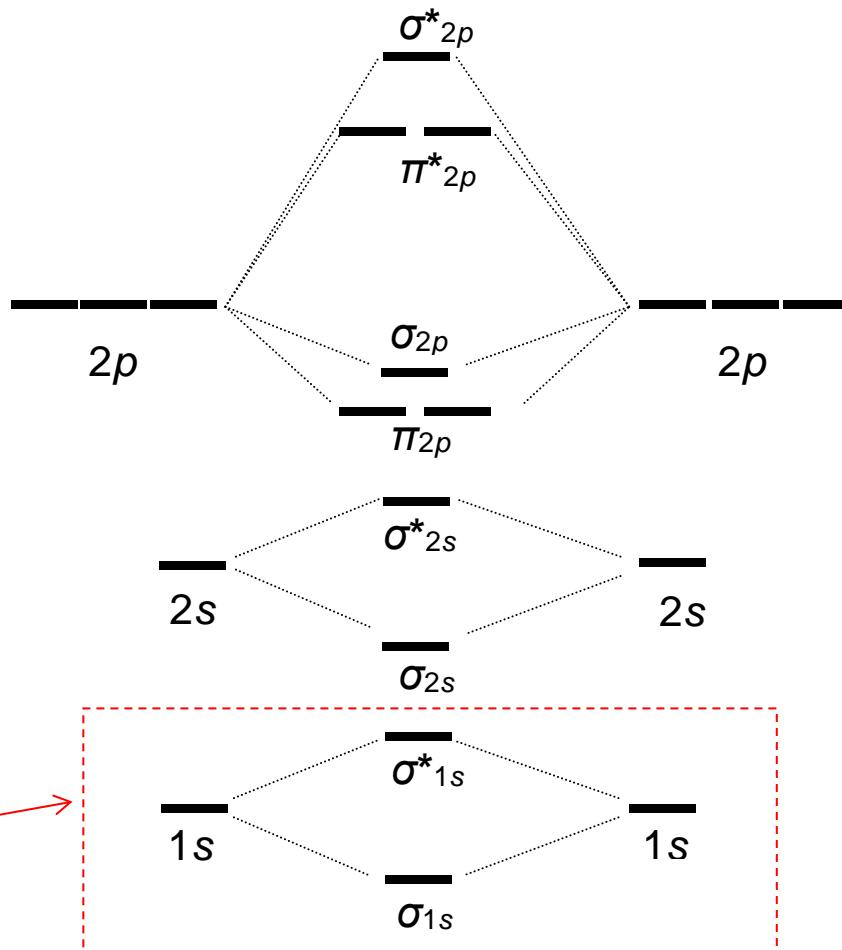
### 5.7 Electronic energy level diagrams for homonuclear diatomics

Experimental results indicate that the diagram shown below is appropriate for Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, and N<sub>2</sub>.

The MO diagram for O<sub>2</sub> and F<sub>2</sub> is shown on the next page.

#### Learning Tips:

1. This MO diagram is NOT appropriate for O<sub>2</sub> or F<sub>2</sub>. For O<sub>2</sub> and F<sub>2</sub>, use the MO diagram on the next page.
2. You must memorize this MO diagram and the one on the next page. They are NOT normally provided on exams.
3. The energy ordering of the MOs is closely related to the energy ordering of the AOs. For example, the MOs arising from 1s orbitals are lower in energy than those arising from the 2s orbitals. The MOs arising from the 2p orbitals are higher in energy than those arising from the 2s and 1s orbitals. Bonding MOs are lower in energy than the AOs from which they are derived and antibonding MOs are higher in energy.
4. It is customary to show only the MOs arising from the valence atomic orbitals. These inner or "core" orbitals are often not shown. In the Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, and N<sub>2</sub> molecules, these MOs are completely filled and make zero contribution to the overall bond order.

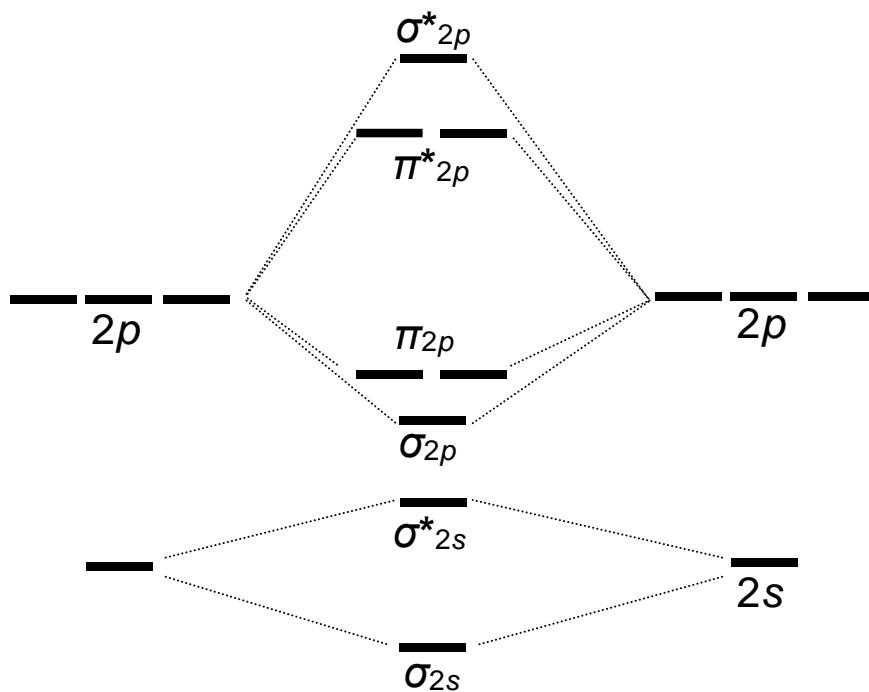


**Example 5-3:** What is the ground state electron configuration and bond order for B<sub>2</sub>? Repeat this exercise for Li<sub>2</sub>, Be<sub>2</sub>, C<sub>2</sub> and N<sub>2</sub>.



See problems 11-28, 11-30 and 11-34 (ignore the case of NO<sup>+</sup>) from Petrucci (11<sup>th</sup> edition),

The MO diagram below is appropriate for the O<sub>2</sub> and F<sub>2</sub> molecules. This diagram is essentially the same as the one given before except that **the  $\sigma_{2p}$  orbital is lower in energy than the  $\pi_{2p}$  orbitals.**



**Example 5-4:** What is the electron configuration for the O<sub>2</sub> molecule? What is the “bond order” for O<sub>2</sub> according to MO theory? Does adding an electron stabilize/destabilize the molecule? What about removing an electron? Is O<sub>2</sub> paramagnetic or diamagnetic? Is the first IE of the O<sub>2</sub> molecule greater than, less than, or equal to the first IE of the O atom?

In the previous modules, we focused on the structures of individual molecules. In this module, we extend what we have learned by considering models for describing a system containing many identical molecules, at first by neglecting the interactions between them, and then by taking into account their interactions.

By the end of this module, we will be able to describe some properties of gases and liquids in terms of the structures and interactions of the constituent molecules.

## 6.1 Kinetic Molecular Theory and the Ideal Gas Law

Structurally, gases are nature's simplest substances: a simple model and elementary calculations yield results that are surprisingly accurate. The kinetic theory of gases is an important illustration of the relation of theory and experiment, as well as the techniques that are commonly used to relate structure to properties.

The main assumptions of kinetic molecular theory are:

1. The molecules in a gas are small and very far apart. (Therefore, most of the volume which a gas occupies is empty space.)
2. The molecules are in constant random motion. (Therefore, just as many molecules are moving in one direction as in any other.)
3. Molecules collide with each other and with the walls of the container. (Collisions with the walls account for the pressure of the gas.)
4. When collisions occur, kinetic energy is conserved; that is, the collisions are "perfectly elastic". (Therefore, the total kinetic energy of all the molecules remains constant, unless there is some external influence.)
5. The molecules exert no attractive or repulsive forces on one another except during the process of collision. Between collisions, move in straight lines.
6. The average translational kinetic energy of the molecules is proportional to the kelvin temperature. The precise relationship is  $KE_{avg} = (3/2) RT$ , which brings the predicted and observed values for the gas pressure into near perfect agreement.

The motion of the molecules must be random (or chaotic) because organized motion could not be sustained for any significant length of time. Why?

At the molecular level, the walls of the container are not perfectly flat; they are full of irregularities. Even if the molecular motion was perfectly orderly (for example, with all molecules moving in parallel paths towards the left), the molecules would soon hit the wall. Any irregularity in the wall of the container would deflect some particle out of its path. The collision of the deflected particle with another particle would deflect another one, and so on. The motion inside the container would soon become chaotic and random.

The kinetic molecular theory provides a satisfactory explanation of the **ideal gas law**, which is presented on the next page. (A simplified derivation of the ideal gas law is provided in Section 6-7 of Petrucci, 11<sup>th</sup> edition. You are not responsible for the derivation.)

**The Ideal Gas Law:**

$$PV = nRT$$

► Your textbook mentions a number of gas laws (e.g., Avogadro's law, Boyle's law, and Charles' law). We expect you to remember the ideal gas law only.

In the equation above,  $R$  is a constant called the **universal gas constant**.

$$R = 8.3145 \frac{\text{kPa L}}{\text{K mol}} = 8.3145 \frac{\text{Pa m}^3}{\text{K mol}} = 0.083145 \frac{\text{bar L}}{\text{K mol}} = 0.082058 \frac{\text{atm L}}{\text{K mol}}$$

Make sure you are familiar with the various units for pressure, volume and temperature.

**Pressure,  $P$**        $\leftrightarrow$       **force per unit area**

**SI Units:**  $1 \text{ Pa} = 1 \text{ N / m}^2$

**Other units:**  $1 \text{ kPa} = 10^3 \text{ Pa}$

$1 \text{ bar} = 100 \text{ kPa} = 10^5 \text{ Pa}$

$1 \text{ atm} = 1.01325 \text{ bar} = 101.325 \text{ kPa}$

$1 \text{ Torr} = 1/760 \text{ atm} \Rightarrow 1 \text{ atm} = 760 \text{ Torr}$

**Volume,  $V$**        $\leftrightarrow$       **provides a measure of the space occupied**

**SI Units:**  $\text{m}^3$ , but  $\text{m}^3$  is too large for most applications  
Instead we use litres (L)

$1 \text{ m}^3 = 1000 \text{ L}$

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

**Kelvin temperature,  $T$**        $\leftrightarrow$       **provides a measure of the average translational kinetic energy of the molecules in a sample;  $KE_{\text{avg}} = (3/2) RT$**

$$T(\text{in K}) = t(\text{in } ^\circ\text{C}) + 273.15$$

**Note:**  $T > 0 \text{ K}$  and  $t > -273.15 \text{ } ^\circ\text{C}$

The ideal gas equation predicts the following.

**increasing  $T$**   
(keeping  $P$  and  $n$  constant)       $\Rightarrow$        $V$  increases

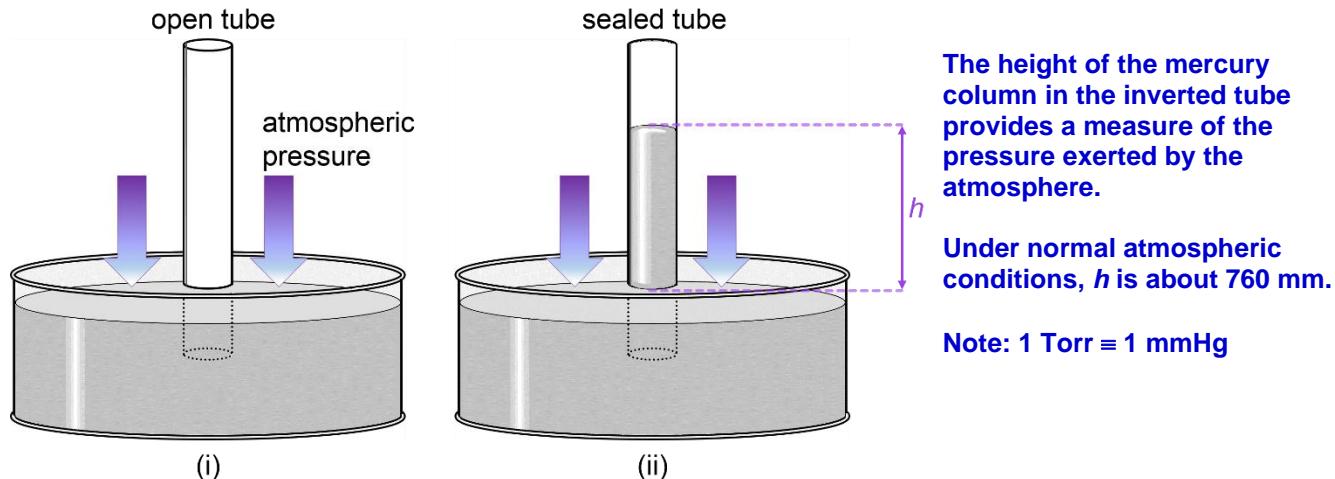
**increasing  $V$**   
(keeping  $T$  and  $n$  constant)       $\Rightarrow$        $P$  decreases

**increasing  $n$**   
(keeping  $T$  and  $V$  constant)       $\Rightarrow$        $P$  increases

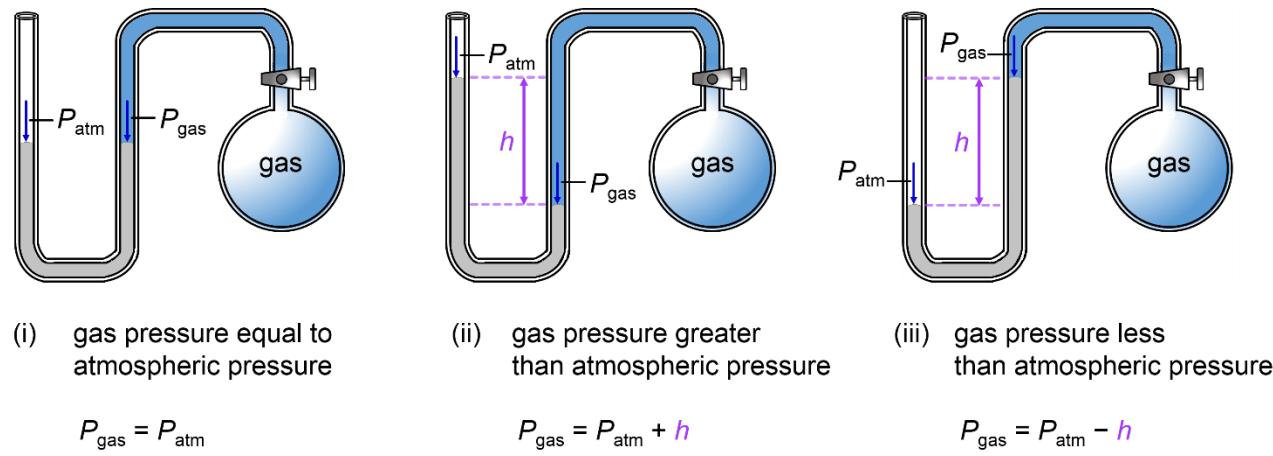
Despite its simplistic form, the ideal gas equation is remarkably realistic, provided the gas is not close to its condensation point. **Deviations from ideal behaviour are most significant when the pressure is very high or the temperature is very low.**

 **Digging Deeper: the measurement of pressure**

The pressure exerted by the atmosphere can be measured using a mercury barometer.



The pressure of exerted by a sample of gas can be measured using a mercury manometer.



**Example 6-1:** Calculate the volume of one mole of ideal gas at 0 °C and 101 kPa. What is the volume at 25 °C and 101 kPa?

**Example 6-2:** A sample of gas occupies a volume of 2.00 L at 25 °C and 101 kPa.

What is the volume at 35 °C and 151 kPa?



See problems 6-27, 6-30 and 6-32 from Petrucci (11<sup>th</sup> edition).

**Example 6-3:** A 0.474 g sample of gas occupies a volume of 0.250 L at 100 °C and 101 kPa.

What is the molar mass of this gas?



See problems 6-35 and 6-38 from Petrucci (11<sup>th</sup> edition).

It is possible to use the ideal gas equation to derive a simple relationship showing how the density ( $d$ ) of a gas is related to its molar mass ( $\mathcal{M}$ ).



See problems 6-42, 6-45 and 6-46 from Petrucci (11<sup>th</sup> edition).

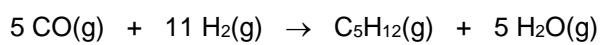
$$PV = nRT = \left(\frac{m}{\mathcal{M}}\right)RT \quad \Rightarrow \quad \mathcal{M} = \frac{(m)RT}{P} \quad \Rightarrow \quad \boxed{\mathcal{M} = \frac{dRT}{P}}$$

**Example 6-4:** An automobile airbag can be inflated by the N<sub>2</sub> gas that is produced when a solid “pellet” containing NaN<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> is detonated. What is the mass of a pellet required to inflate an automobile airbag with N<sub>2</sub>(g) at 26 °C and 735 Torr, if the airbag has a volume of 65.0 L? The reaction is given below.



See problems 6-48 through 6-52  
from Petrucci (11<sup>th</sup> edition).

**Example 6-5:** What volume of C<sub>5</sub>H<sub>12</sub> is produced if 15.0 L CO and 25.0 L H<sub>2</sub> react according to the chemical equation below? What volume of the excess reagent remains? Assume that the volumes are measured at 722 °C and 129 kPa.



See problems 6-47 and 6-54 from Petrucci (11<sup>th</sup> edition).

### Gas mixtures

Consider a mixture of gases containing  $n_A$  moles of gas A,  $n_B$  moles of gas B,  $n_C$  moles of gas C, etc. We define the partial pressure of gas A as follows. (Similar definitions hold for the other gases.)

Define:  $P_A = \left( \frac{n_A}{n_{\text{tot}}} \right) P_{\text{tot}}$  where  $n_{\text{tot}} = n_A + n_B + n_C + \dots$

$(n_A / n_{\text{tot}})$  is the **mole fraction** of A. So, if 10% of the molecules are of type “A”, then the partial pressure of gas A is simply 10% of the total pressure.

It is easy to show that **the sum of the partial pressures is equal to the total pressure**.

$$\begin{aligned} P_A + P_B + P_C + \dots &= \left( \frac{n_A}{n_{\text{tot}}} \right) P_{\text{tot}} + \left( \frac{n_B}{n_{\text{tot}}} \right) P_{\text{tot}} + \left( \frac{n_C}{n_{\text{tot}}} \right) P_{\text{tot}} + \dots \\ &= \left( \frac{n_A + n_B + n_C + \dots}{n_{\text{tot}}} \right) P_{\text{tot}} = \left( \frac{n_{\text{tot}}}{n_{\text{tot}}} \right) P_{\text{tot}} = P_{\text{tot}} \end{aligned}$$

If it is assumed that the gases in the mixture behave “ideally”, then we can apply  $PV = nRT$  to each gas separately or to the entire mixture:

$$P_A = \frac{n_A RT}{V}$$

$$P_{\text{tot}} = \frac{n_{\text{tot}} RT}{V}$$

(for fixed  $T$  and  $V$ )

$$V_A = \frac{n_A RT}{P}$$

$$V_{\text{tot}} = \frac{n_{\text{tot}} RT}{P}$$

(for fixed  $T$  and  $P$ )

If we assume ideal gas behaviour, then for fixed values of  $T$  and  $V$ , the **partial pressure of A depends on the number of moles of A** and the **total pressure depends on the total number of moles of gas**.

A quick remark about the meaning of  $V_A$ : The “partial volume” of gas A in a mixture at temperature  $T$  and pressure  $P$  represents the volume gas A would occupy on its own at temperature  $T$  and pressure  $P$ . That is, if gas A was extracted from the mixture and stored at the same  $T$  and  $P$ , it would occupy volume  $V_A$ . However, as part of the mixture, gas A occupies the total volume,  $V_{\text{tot}}$ .

**Example 6-6:** (a) Calculate the total volume of gas produced when 0.200 kg of nitroglycerin,  $C_3H_5N_3O_9$ , decomposes at 115 °C and 99.8 kPa. The decomposition reaction is given below. (b) What is the partial pressure of  $CO_2$  in the product mixture?



See problems 6-97 and 6-98  
from Petrucci (11<sup>th</sup> edition).

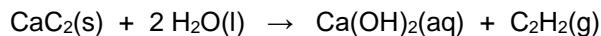
**Example 6-7:** A mixture of  $\text{N}_2(\text{g})$  and  $\text{Ne}(\text{g})$  has a mass of 2.88 g and occupies a volume of 2.50 L at 298 K and 105 kPa. What is the partial pressure of  $\text{N}_2$  in this mixture? What is the volume percent of  $\text{N}_2$ ?



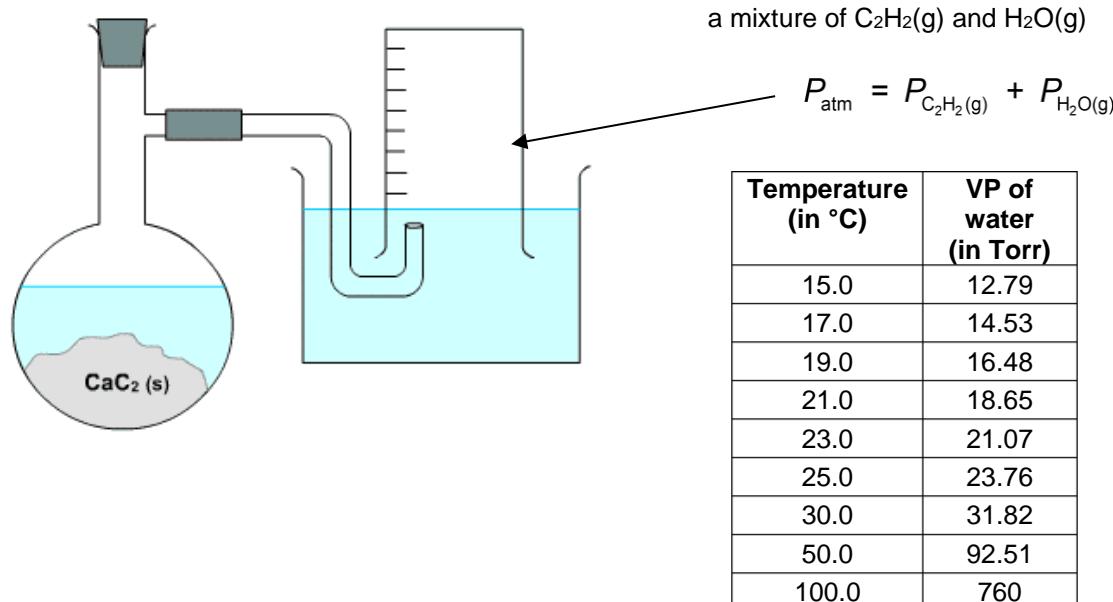
See problems 6-58, 6-66 and 6-102  
from Petrucci (11<sup>th</sup> edition).

### Collecting gases over water

An important application of the use of partial pressures arises when small amounts of gas, generated for laboratory use, are collected over water. For example, small amounts of acetylene gas,  $\text{C}_2\text{H}_2(\text{g})$ , can be generated by heating an aqueous solution of calcium carbide. The reaction is given below.



The  $\text{C}_2\text{H}_2$  gas can be collected over water using the following set up.



We adjust the inverted cylinder until the height of the water level is the same inside and out. (When the levels are equal, we know that the total pressure of gas inside the inverted cylinder is equal to the atmospheric pressure.)

The gas that is collected in the cylinder is “wet gas”, i.e. it is mixed with water vapour. This is because some water molecules escape from the surface of the water to occupy and accumulate in the inverted cylinder. Fortunately, the partial pressure of water vapour in the sample depends only on the temperature of the water. (See the table on the right.) **This method of collecting gas only works if the gas is not soluble in (or does not react with) water.**

**Example 6-8:** Calcium carbide,  $\text{CaC}_2$ , is heated gently in water to produce acetylene gas,  $\text{C}_2\text{H}_2(\text{g})$ , and calcium hydroxide,  $\text{Ca}(\text{OH})_2$ . The acetylene gas is collected over water at  $23^\circ\text{C}$  and  $1.05\text{ atm}$ . If  $2.00\text{ g CaC}_2$  yields  $524\text{ mL}$  of “wet”  $\text{C}_2\text{H}_2$  gas, then what is the % yield for the experiment?



See problems 6-68  
and 6-109 from  
Petrucci (11<sup>th</sup> edition).

## 6.2 Real gases

The ideal gas equation is valid for all gases at sufficiently low pressures. However, as the pressure on a given quantity of gas is increased, deviations from the ideal gas equation become increasingly significant. The extent of the deviations at a given pressure depends on the temperature and nature of the gas. The data below show that deviations from ideal gas behaviour are small (much less than 5%) at STP but are significant at higher pressures. Deviations from ideal behaviour are also important at lower temperatures.

### Densities, Molar Volumes and Compressibility Factors of Various Gases

Gas	Molar Mass, g mol <sup>-1</sup>	Density <sup>a</sup> at STP <sup>b</sup> g L <sup>-1</sup>	Molar Volume <sup>c</sup> at STP, L mol <sup>-1</sup>	Compressibility Factor <sup>d</sup>	
				at STP	at 300 K, 10 bar
H <sub>2</sub>	2.01588	8.87104×10 <sup>-2</sup>	22.724	1.0006	1.006
He	4.00260	0.17615	22.722	1.0005	1.005
<b>Ideal gas</b>	-	-	<b>22.711</b>	<b>1</b>	<b>1</b>
N <sub>2</sub>	28.0134	1.23404	22.701	0.9996	0.998
CO	28.0101	1.23375	22.696	0.9993	0.997
O <sub>2</sub>	31.9988	1.41034	22.689	0.9990	0.994
CH <sub>4</sub>	16.0425	0.70808	22.656	0.9976	0.983
NF <sub>3</sub>	71.0019	3.14234	22.595	0.9949	0.965
CO <sub>2</sub>	44.0095	1.95096	22.558	0.9933	0.950
N <sub>2</sub> O	44.0128	1.95201	22.550	0.9929	0.945
C <sub>2</sub> H <sub>6</sub>	30.0690	1.33740	22.483	0.9900	0.922
NH <sub>3</sub>	17.0352	0.76139	22.374	0.9852	0.887
SF <sub>6</sub>	146.0554	6.52800	22.374	0.9852	0.880
C <sub>3</sub> H <sub>8</sub>	44.0956	1.98318	22.235	0.9790	(liquid)
SO <sub>2</sub>	64.0638	2.89190	22.153	0.9754	(liquid)

<sup>a</sup> The densities are from the National Institute of Standards and Technology (NIST) Chemistry WebBook.

<sup>b</sup> **STP = standard temperature and pressure, 0 °C and 1 bar = 100 kPa.**

<sup>c</sup> The molar volume is equal to the molar mass divided by the density.

<sup>d</sup> The compressibility factor is  $Z = PV / (nRT)$ .

The ideal gas model is obviously not perfect. It neglects

- (1) the sizes of the molecules themselves
- (2) intermolecular forces

For real gases, we expect the volume ( $V$ ) to be greater than or equal to an equivalent number of moles of liquid. We also expect that the pressure ( $P$ ) will be less than the pressure predicted by the ideal gas equation because attractive intermolecular forces cause the molecules to be drawn inwards (and therefore exert less pressure on the walls of the container).

Van der Waals devised an equation of state that incorporated these ideas:

$$(P + \frac{an^2}{V^2})(V - nb) = nRT$$

In this equation,  $a$  and  $b$  are molecule-dependent constants.

- $a \leftrightarrow$  provides a measure of the strength of the intermolecular forces
- $b \leftrightarrow$  provides a measure of the sizes of the molecules

The values of  $a$  and  $b$  tend to increase with the size of the molecule, as shown in the table below.

Gas	$a$ (in $\text{L}^2 \text{ bar mol}^{-2}$ )	$b$ (in $\text{L mol}^{-1}$ )
$\text{H}_2$	0.24646	0.026665
$\text{O}_2$	1.3820	0.03186
CO	1.4734	0.039523
$\text{CO}_2$	3.6551	0.048216
$\text{C}_5\text{H}_{12}$	19.124	0.14510

Recall:  
 1 bar = 100 kPa  
 1 atm = 1.01325 bar

**Example 6-9:** Use the ideal gas equation and the van der Waals equation to estimate the pressure exerted by 1.00 mol of CO(g) in a 0.500 L container at 300 K.



See problem 6-88 from  
Petrucci (11<sup>th</sup> edition).

There are other equations that chemists use to model the relationship between  $P$ ,  $V$  and  $T$ . One of the most useful equations is the **virial equation of state**, which has the form

$$\frac{P\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \dots$$

Note:  $\bar{V} = \frac{V}{n}$

where  $\bar{V}$  is the molar volume (i.e. the volume per mole of gas). For an ideal gas,  $P\bar{V}/(RT) = 1$  and thus, the second-, third- and higher-order terms on the right hand side of the virial equation account for deviations from ideal gas behaviour. These terms become increasingly important as the volume decreases (i.e. as the pressure increases).

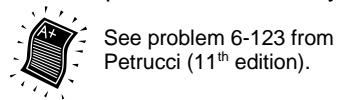
**Did you know?** Chemists prefer the virial equation over the Van der Waals equation because:

- (1) the virial equation is easily extended to include more and more correction terms to produce an equation of state that is increasingly more accurate
- (2) chemists have worked out equations that show the virial coefficients  $B$ ,  $C$ , etc. are related to the nature and strength of the intermolecular forces.

As a result, the empirical determination/measurement of the virial coefficients for a gas provides chemists an opportunity to obtain an accurate description of the nature and strength of the intermolecular interactions!!

**Example 6-10:** For  $O_2(g)$ ,  $B = -21.89 \text{ cm}^3 \text{ mol}^{-1}$  and  $C = 1230 \text{ cm}^6/\text{mol}^2$ . What is the pressure exerted by 1.00 mol  $O_2$  if it is confined to a 0.500 L flask at 273 K?

Hint: 1 L = 1000 mL = 1000 cm<sup>3</sup>



Solution:

Using the virial equation:

$$\begin{aligned} Z &= 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} \\ &= 1 + \frac{(-21.89 \text{ cm}^3 \text{ mol}^{-1})(10^{-3} \text{ L/cm}^3)}{0.500 \text{ L mol}^{-1}} + \frac{(1230 \text{ cm}^6 \text{ mol}^{-2})(10^{-3} \text{ L/cm}^3)^2}{(0.500 \text{ L mol}^{-1})^2} \\ &= 1 - 0.04378 + 0.00492 \end{aligned}$$

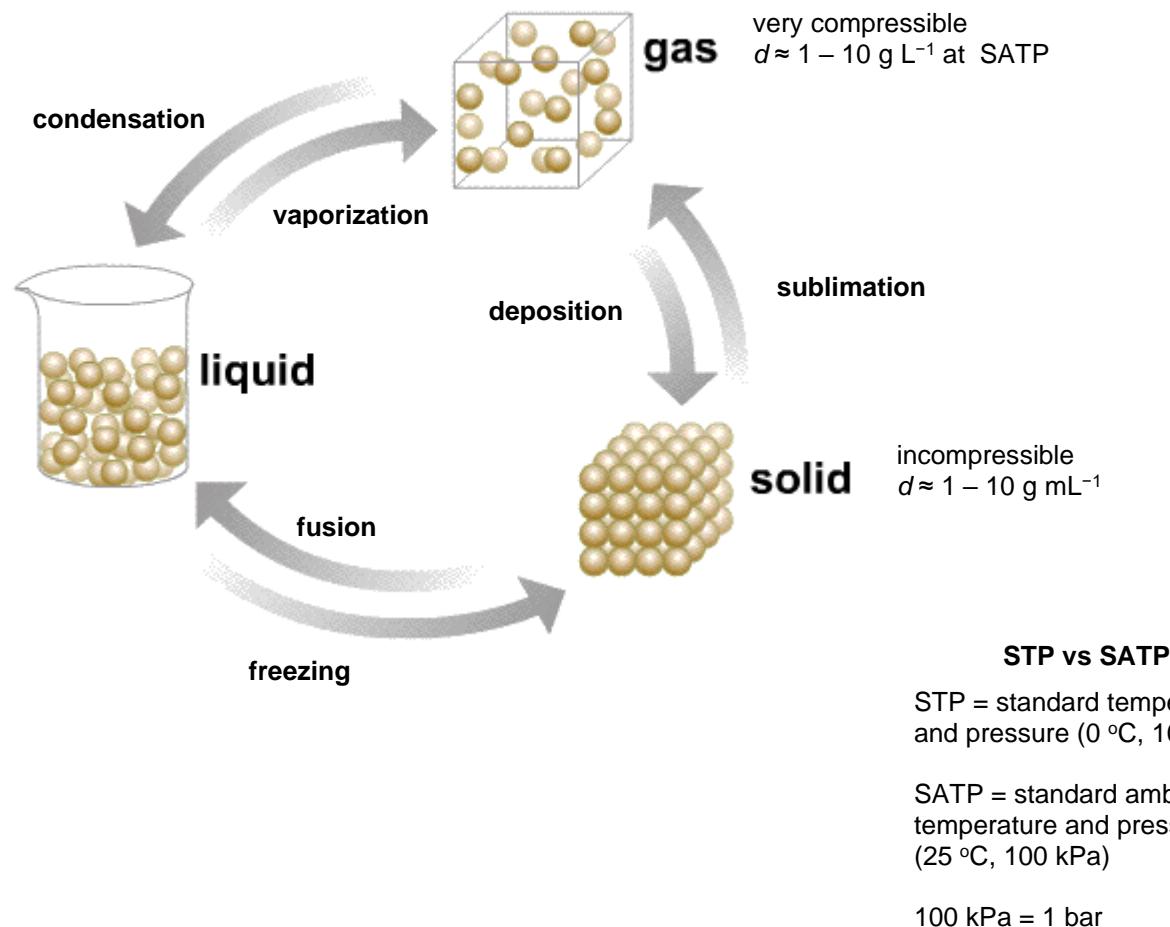
= 0.96114 (This value is only slightly smaller than the value of  $Z = 1$  for an ideal gas)

$$P = Z \times \frac{RT}{\bar{V}} = 0.96114 \times \frac{(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(273 \text{ K})}{0.500 \text{ L mol}^{-1}} = 43.6 \text{ bar} = 43.1 \text{ atm}$$

### 6.3 Intermolecular forces

In a gas, molecules move randomly and the intermolecular separations are large (i.e. most of a gas is empty space). In liquids and solids, the molecular motions are quite restricted and the intermolecular separations are small. In solids, the molecules are often, but not always, arranged in regular, repeating patterns.

Substances exist in different phases and phase changes occur because molecules exert forces on each other. (Without intermolecular forces, all substances would behave as ideal gases!!) It takes energy to overcome the attractive intermolecular forces that cause molecules to aggregate. Therefore, sublimation, fusion and evaporation are all endothermic processes.



We know that if the temperature of a gas is lowered sufficiently, the gas will condense to a liquid. Why is this? As  $T$  is lowered, the average kinetic energy of the molecules decreases. At some point, the molecules will no longer have enough kinetic energy to overcome the attractive forces that draw the molecules together. Consequently, the molecules cluster together to form a liquid.

The freezing of a liquid can be explained in the same way: If the temperature of a liquid is lowered sufficiently, the molecules will not have enough kinetic energy to overcome attractive cohesive forces that draw the molecules closer together  $\Rightarrow$  the liquid freezes.

The physical properties of a liquid depend on the strength and nature of the intermolecular forces. We will examine why the following physical properties are different from substance to substance.

**vapour pressure** = pressure of vapour that forms above a liquid in a closed container

**normal boiling point ( $T_{\text{vap}}$ )** = temperature at which the vapour pressure of the liquid equals 1 atm

**surface tension ( $\gamma$ )** = energy required to increase the surface area of a liquid

**viscosity ( $\eta$ )**  $\leftrightarrow$  provides a measure of a fluid's resistance to flow; the speed of flow through a tube is inversely proportional to the viscosity

Note: When the intermolecular forces are strong, then the molecules of the liquid do not pass by each other as easily; there is more resistance to flow and thus a higher viscosity.

**In general, the stronger the intermolecular attractions, the higher the boiling point, the greater the surface tension, the higher the viscosity, and the lower the vapour pressure.**

Our next step is to understand how molecules interact with each other and how these interactions help us to understand trends in the physical properties of compounds (e.g. boiling points, vapour pressures, viscosity and surface tensions of liquids; deviations from ideal gas behaviour, etc.)

Generally speaking, differences in the physical properties of substances can often be rationalized by considering how molecules interact with each other at the molecular level. We'll look at some of the types of intermolecular forces that act between pairs of molecules.

### Molecular properties for describing intermolecular forces

Dipole moment and polarizability are two molecular properties that are important for describing the interactions of molecules.

A molecule possesses a **dipole moment ( $\mu$ )** if the centre of positive charge does not coincide with the centre of negative charge. A dipole moment arises when bond dipoles in a molecule do not totally cancel. A non-zero dipole moment indicates that there is a separation between the centres of positive and negative charge in a molecule. As discussed on page 19 of Module 4, the magnitude of a dipole moment is charge times distance. Therefore, dipole moments are commonly expressed in C m, or debye, D. Note: 1 debye =  $3.34 \times 10^{-30}$  C m.

► In an atom, the centres of positive and negative charge coincide because the positive charge is centred on the nucleus and the electrons are symmetrically distributed around the nucleus. In a molecule, there may be an asymmetric distribution of electron density around the nuclei, and consequently, the centres of positive and negative charge may not coincide.

The **polarizability ( $\alpha$ )** of a molecule provides a measure of the extent to which its charge cloud can be distorted (polarized) by another molecule. The charge cloud of a large molecule is typically more diffuse and more easily polarized than that of a small, compact molecule. Generally speaking, **the larger the molecule, the larger the polarizability.**

Dipole moments and polarizabilities of a few molecules are given in the table below. The polarizabilities are expressed relative to that of the helium atom. (The helium atom has the smallest polarizability of all atoms and molecules.) Using data from the table below, we conclude that the H<sub>2</sub>O molecule is 7.5 times more polarizable than a helium atom and that a CCl<sub>4</sub> molecule is about 4 times more polarizable than a CH<sub>4</sub> molecule ( $53/13 \approx 4.1$ ).

**Dipole moments ( $\mu$ ) and polarizabilities ( $\alpha$ ) of a few molecules**

**Learning Tip:** The size of a molecule and the mass of a molecule are different concepts. When we speak of the size of a molecule, we are referring to the size of its electronic charge cloud, not the molecular mass. There is a correlation between size and mass (e.g. the heavier a molecule, the larger and more polarizable it is), but this correlation arises because a molecule with many atoms is not only massive but also has many electrons and therefore a large, polarizable electron cloud. **When describing intermolecular interactions, you should focus on the polarizability and polarity of the electronic charge cloud, not on the mass of the molecule.**

	$\mu$ (in debye)	$\alpha/\alpha_{\text{He}}$
H <sub>2</sub>	0	4.1
HF	1.91	3.9
HCl	1.08	13
HBr	0.80	18
CO	0.12	10
CO <sub>2</sub>	0	13
H <sub>2</sub> O	1.85	7.5
NH <sub>3</sub>	1.47	11
He	0	1
Ar	0	8.4
CH <sub>4</sub>	0	13
CCl <sub>4</sub>	0	53

### Dipole-dipole forces

Some molecules possess a permanent dipole moment,  $\mu$ , because the bond dipoles do not cancel out.

Such molecules are said to be “polar” because one end of the molecule is slightly positive and the other end is slightly negative. The charge distribution of a polar molecule can be represented by an arrow that points from the positive end to the negative end.

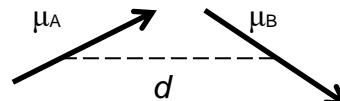
Polar molecules (i.e. dipoles) tend to orient themselves “head-to-tail”, as shown below:



The molecules are not organized into perfect straight line because the molecules are in motion (i.e. each one possesses kinetic energy) and they “jiggle” out of perfect alignment.

### Digging Deeper

For a pair of interacting polar molecules with dipole moments of  $\mu_A$  and  $\mu_B$ :

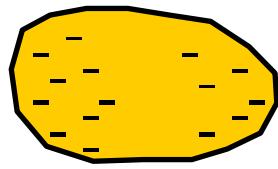


$$PE \propto -\frac{\mu_A^2 \mu_B^2}{d^6}$$

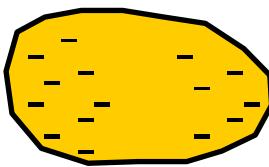
### London dispersion forces (LDFs)

The electrons in a molecule are in constant motion. At any particular instant, there may be an asymmetric distribution of electrons in the molecule (with a greater number of electrons at one end). An asymmetric distribution of electrons gives rise to an instantaneous and temporary dipole moment,  $\mu_{inst}$ , which causes (or induces) the formation of a dipole in a neighbouring molecule, as suggested below. The induced dipole moment is  $\mu_{ind}$ . (Notice the head-to-tail arrangement of the instantaneous and induced dipole moments.)

Molecule A

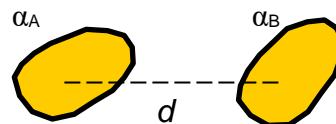


Molecule B



### Digging Deeper

For a pair of molecules with polarizabilities of  $\alpha_A$  and  $\alpha_B$ :



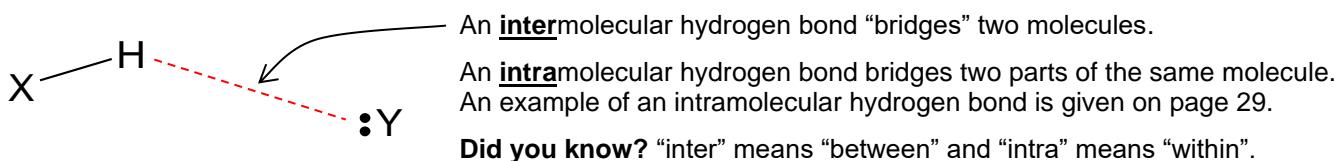
$$PE \propto -\frac{\alpha_A \alpha_B}{d^6}$$

There is an attraction between  $\mu_{inst}$  and  $\mu_{ind}$ . The strength of the interaction increases as the polarizabilities of the molecules increase. Also:

- LDFs are most attractive when the molecules are large. This is because large molecules have larger, more diffuse (more polarizable) charge clouds.
- **LDFs always contribute to the molecular interactions** because all molecules have charge clouds and are therefore polarizable to some extent.

### Hydrogen bonding forces

A special type of interaction occurs between molecules when the molecules contain a hydrogen atom bonded to N, O or F. When H is bonded to O, N or F, the H atom carries a significant positive charge and it is strongly attracted to a lone pair on another molecule. When a hydrogen atom which is covalently bonded to one atom is simultaneously attracted to the lone pair on another atom, it is “bridging” two molecules, as shown below. Such an interaction is called a **hydrogen bond**.



Note carefully:

- H is covalently bonded to X but is simultaneously attracted to a lone pair of electrons on Y.
- Typically, both X and Y are N, O, or F.
- Hydrogen bonding forces are typically stronger than dipole-dipole or London dispersion forces, but they are still weak in comparison to covalent and ionic bonding forces.

intermolecular forces		chemical bonding forces
dipole-dipole & LDFs	H bonds	covalent & ionic bonds
0.10-10 kJ mol <sup>-1</sup>	10–40 kJ mol <sup>-1</sup>	100's or 1000's kJ mol <sup>-1</sup>

The following definition was recently recommended by IUPAC (in July 2011).

**The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.**

Hydrogen bonds are important!

- H bonds between H<sub>2</sub>O molecules in ice give the solid an open structure.
- H bonds between H<sub>2</sub>O molecules in water give the liquid a high boiling point, high surface tension and a large heat capacity.
- H bonds are especially important in biology (e.g. H bonds keep the two helices of DNA together; the structures and functions of proteins and enzymes are determined by H bonds)

**FYI:** All bonding forces, as well as the atomic and molecular properties we use for describing them, have their origin in the electrostatic force between charged particles. According to Coulomb’s law, the electrostatic force,  $F$ , is proportional to the product of the charges,  $q_1 q_2$ , and inversely proportional to the square of the distance,  $d$ , between them:  $F \propto q_1 q_2 / d^2$ . Atomic and molecular properties are used to describe the interactions of atoms and molecules because it is simply not feasible or illuminating to focus on the huge number of interactions between all of the subatomic particles (electrons and protons).

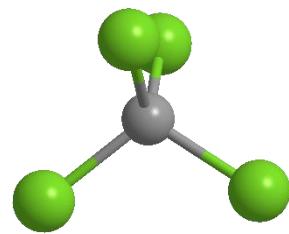
**Example 6-11:** Iodine chloride,  $\text{ICl}$ , and bromine,  $\text{Br}_2$ , have exactly the same number of electrons, and it is reasonable to assume these molecules are essentially the same size. Yet the boiling points of  $\text{ICl}(\text{l})$  and  $\text{Br}_2(\text{l})$  are quite different,  $97\text{ }^\circ\text{C}$  and  $59\text{ }^\circ\text{C}$ , respectively. Explain why  $\text{ICl}(\text{l})$  has a higher boiling point than  $\text{Br}_2(\text{l})$ .

Even though  $\text{ICl}$  and  $\text{Br}_2$  have the same number of electrons,  $\text{ICl}$  is about 1.75 times more polarizable than  $\text{Br}_2$ . The larger polarizability of  $\text{ICl}$  also contributes to making the boiling point of  $\text{ICl}$  higher than that of  $\text{Br}_2$ .



See Example 12-1, including Practice Examples A and B, from Petrucci (11<sup>th</sup> edition).

**Example 6-12:** Methane ( $\text{CH}_4$ ) and carbon tetrachloride ( $\text{CCl}_4$ ) are both nonpolar molecules. Explain why the boiling point of  $\text{CCl}_4(l)$  is much higher than that of  $\text{CH}_4(l)$ .

**vs****-162 °C****77 °C**

The C-Cl bonds are very polar, but the bond dipoles cancel. The  $\text{CCl}_4$  molecule is nonpolar.

**Example 6-13:** Use your knowledge of intermolecular forces to predict whether  $\text{CH}_3\text{COCH}_3(l)$  or  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}(l)$  has the higher boiling point.



See problems 12-1, 12-3, and 12-5 from Petrucci (11<sup>th</sup> edition).

**Example 6-14:** Which one of the liquids,  $\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$  or  $\text{CH}_3\text{CH}_2\text{OH}$ , has the highest vapour pressure at room temperature?

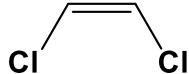


See problems 12-12 and 12-140 from Petrucci (11<sup>th</sup> edition).

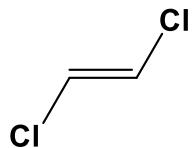
**Example 6-15:** Dichloroethene,  $C_2H_2Cl_2$ , has several isomeric forms. Use your knowledge of intermolecular forces to predict whether (*Z*)-1,2-dichloroethene or (*E*)-1,2-dichloroethene has the higher boiling point. Lewis structures are given below.



See problems 12-15, 12-17, and 12-140 from Petrucci (11<sup>th</sup> edition).



(*Z*)-1,2-dichloroethene, also called *cis*-1,2-dichloroethene



(*E*)-1,2-dichloroethene, also called *trans*-1,2-dichloroethene

**Example 6-16:** Use your knowledge of intermolecular forces to predict the order of boiling points for H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te.



See Example 12-6, including Practice Examples A and B, from Petrucci (11<sup>th</sup> edition).

**Solution:**

Each of these molecules is V-shaped, or bent, and polar.

H<sub>2</sub>O molecules form hydrogen bonds amongst themselves but the other molecules do not. Therefore, H<sub>2</sub>O(l) has the highest boiling point.

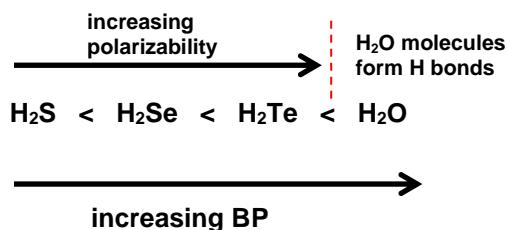
How do we rank the remaining substances? The most important consideration is not the difference in polarities but the difference in size. H<sub>2</sub>Te is much larger and more polarizable than H<sub>2</sub>Se and H<sub>2</sub>Se is much larger and more polarizable than H<sub>2</sub>S.

Therefore, the LDF's between a pair of H<sub>2</sub>Te molecules are much more attractive than between a pair of H<sub>2</sub>Se molecules or a pair of H<sub>2</sub>S molecules.

Putting all of these ideas together, we can put the substances in order of increasing boiling point.



◀ When comparing atoms in the same group, differences in electronegativities are generally small but the differences in size are quite significant.



The boiling points are as follows:

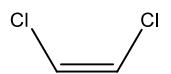
Compound	Boiling Point
H <sub>2</sub> S	-60 °C
H <sub>2</sub> Se	-41 °C
H <sub>2</sub> Te	-2 °C
H <sub>2</sub> O	100 °C

It should be noted that **similar arguments can be applied to the hydrides of group 17 elements**. Thus, in order of increasing BP, we have: HCl < HBr < HI < HF

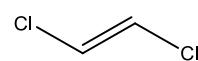
[ Digging Deeper ... Using intermolecular forces to explain differences in the properties of isomers ]

**Comparing isomers of 1,2-dichloroethene,  $\text{ClCH}=\text{CHCl}$**

In the example on page 26, you are asked to predict which compound, *cis*-1,2-dichloroethene or *trans*-1,2-dichloroethene, has the higher boiling point. The molecules are isomers: they have the same molecular formula ( $\text{C}_2\text{H}_2\text{Cl}_2$ ) but different structures. If the compounds have different boiling points, the difference must arise because of differences in the way that the molecules interact with each other in the liquid phase. So, you must consider how the differences in their structures affect the way they interact.



*cis*-1,2-dichloroethene



*trans*-1,2-dichloroethene

You know that molecules always interact with each other through London dispersion forces (LDFs). However, because the *cis* and *trans* isomers of 1,2-dichloroethene are essentially the same size and equally polarizable (they both have two C atoms, two H atoms and two Cl atoms), a difference in boiling points is probably not caused by a difference in the strength of the LDFs. Stated another way, you should expect that the LDFs between a pair of *cis* molecules should be about as attractive as they are between a pair of *trans* molecules. So, you must look beyond LDFs to explain any significant difference in the boiling points of these two compounds. You must also look beyond hydrogen bonding forces because neither one of these molecules is able to form hydrogen bonds with neighbouring molecules.

The difference in boiling points can be explained in terms of dipole-dipole forces. Since *cis*-1,2-dichloroethene is a polar molecule, dipole-dipole interactions will contribute to the attraction amongst *cis* molecules. On the other hand, *trans*-1,2-dichloroethene is a nonpolar molecule: dipole-dipole interactions do not contribute to the attraction amongst *trans* molecules. For *cis*-1,2-dichloroethene, London dispersion forces and dipole-dipole forces contribute to the intermolecular attractions whereas for *trans*-1,2-dichloroethene, only London dispersion forces contribute. Thus, you can predict that the *cis* compound will have a higher boiling point. And indeed it does: the boiling point of *cis*-1,2-dichloroethene is 60 °C and that of *trans*-1,2-dichloroethene is 48 °C. So, as this example illustrates, a subtle difference in structure can have a pronounced effect on physical properties.

In the present example, the *cis* compound has a higher boiling point than the *trans* compound. However, as the next example illustrates, we cannot generalize this result: **the *cis* isomer of a compound will not always have a higher boiling point!**

**Learning Tip:** When considering trends in boiling points, vapour pressure, etc. always focus on the ways in which the molecules interact with each other and the factors that affect those interactions (e.g. dipole moments, polarizabilities, presence of H atoms bonded to O, N or F atoms).

### Comparing isomers of but-2-enedioic acid, HOOCH=CHCOOH

It would be a mistake to assume that the *cis* isomer of a compound always has the higher boiling point. When comparing compounds, **we must always focus on the structures of the molecules and the ways in which they molecules interact in order to predict which compound has a higher boiling point.**

It is important to remember the following.

**The stronger the intermolecular attractions, the greater the:**

- boiling point
- viscosity
- surface tension
- enthalpy of vaporization

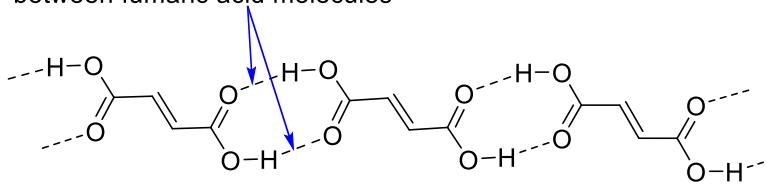
**The stronger the intermolecular attractions, the lower the:**

- vapour pressure

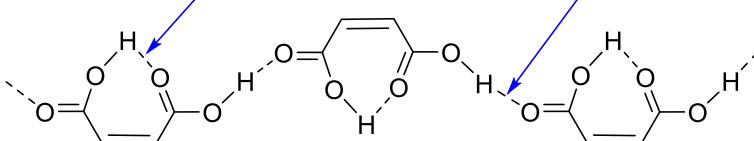
Let's return to the example of fumaric acid and maleic acid and try to predict which compound has a higher melting point. (Both compounds are solids at room temperature.)

As shown below, fumaric acid molecules form **bidentate** intermolecular H bonds, whereas maleic acid molecules form **monodentate** intermolecular H bonds and **intramolecular** H bonds. The attractions between maleic acid molecules are weaker than between fumaric acid molecules because maleic acid molecules form intramolecular H bonds (i.e. they interact less strongly with neighbouring molecules) and also because monodentate H bonds are weaker than bidentate H bonds. Consequently, maleic acid (the *cis* isomer) has a lower melting point than fumaric acid (the *trans* isomer).

bidentate intermolecular H-bonds  
between fumaric acid molecules



intramolecular H-bond within  
each maleic acid molecule



monodentate intermolecular H-bond  
between maleic acid molecules

**FYI:** The term bidentate means "having two teeth". In the bidentate H bond between a pair of fumaric acid molecules, there are actually two intermolecular H bonds arising from two binding sites.

You have already probably guessed that monodentate means "having one tooth". In the monodentate H bond between a pair of maleic acid molecules, there is only one H bond arising from one binding site.

# CHEM 120 DATASHEET

<b>1</b>	<b>2</b>											<b>18</b>	
1 H 1.008	2 Be 9.012											2 He 4.003	
3 Li 6.94												10 Ne 20.18	
11 Na 22.99	12 Mg 24.31	3 Sc 44.96	4 Ti 47.88	5 V 50.94	6 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7
55 Cs 132.9	56 Ba 137.3	(57-71) La-Lu	72 Hf 178.5	73 Ta 180.9	74 W 183.9	75 Os 186.2	76 Re 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2
87 Fr (223)	88 Ra 226	(89-103) Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl
													115 Mc
													116 Lv
													117 Ts
													118 Og

## Constants:

$$\begin{aligned}
 R &= 8.3145 \text{ kPa L K}^{-1} \text{ mol}^{-1} & N_A &= 6.022 \times 10^{23} \text{ mol}^{-1} & R_H &= 2.179 \times 10^{-18} \text{ J} \\
 &= 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} & m_e &= 9.109 \times 10^{-31} \text{ kg} & c &= 2.998 \times 10^8 \text{ m s}^{-1} \\
 &= 0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1} & e &= 1.602 \times 10^{-19} \text{ C} & h &= 6.626 \times 10^{-34} \text{ J s} \\
 &= 0.082058 \text{ atm L K}^{-1} \text{ mol}^{-1} & & & \pi &= 3.141592654
 \end{aligned}$$

## Conversion factors:

$$\begin{array}{llll}
 1 \text{ atm} = 101.325 \text{ kPa} & 1 \text{ kPa L} = 1 \text{ J} = 1 \text{ Pa m}^3 & 1 \mu\text{m} = 10^{-6} \text{ m} & 0^\circ\text{C} = 273.15 \text{ K} \\
 1 \text{ atm} = 1.01325 \text{ bar} & 1 \text{ atm L} = 101.325 \text{ J} & 1 \text{ nm} = 10^{-9} \text{ m} & 1 \text{ m}^3 = 1000 \text{ L} \\
 1 \text{ atm} = 760 \text{ Torr} & 1 \text{ bar L} = 100 \text{ J} & 1 \text{ pm} = 10^{-12} \text{ m} & \\
 1 \text{ atm} = 760 \text{ mmHg} & 1 \text{ cal} = 4.184 \text{ J} & 1 \text{ amu} = 1.6605 \times 10^{-27} \text{ kg} &
 \end{array}$$

## Key equations:

$$\begin{array}{llll}
 PV = nRT & (P + an^2/V^2)(V - nb) = nRT & c = \lambda v & \lambda = h/p \quad p = mv \\
 \Delta x \Delta p \geq h/(4\pi) & E = h\nu & E_n = -R_H/n^2 & \mu = \delta r \quad \text{B.O.} = \frac{1}{2}(n_b - n_a) \\
 KE = \frac{1}{2}mv^2 & v_{\text{avg}} = \sqrt{8RT/(\pi M)} & v_{\text{rms}} = \sqrt{3RT/M}
 \end{array}$$