INTENSE CHEM 121 Review

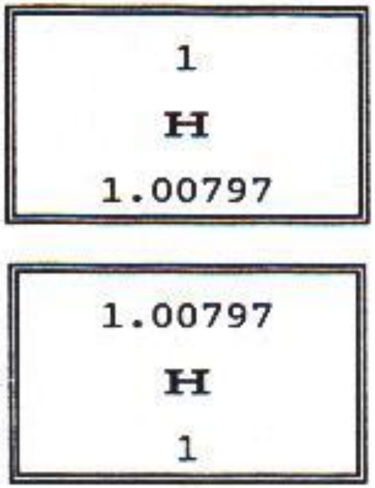
Elements and Isotopes

- Every element consists of a mixture of its isotopes.
- Isotopes are atoms which are identical in atomic number and electronic configuration, but different in atomic mass.
- The difference between the two is in the number of neutrons.

One example of an isotope is Cl.
It has an atomic number of 17.
There are two isotopes of chlorine:

Isotope	Number of Neutrons
^{35}Cl	18
^{37}Cl	20

Again, note that the difference is in neutron number.



1 = Atomic Number; 1.00797 = Atomic mass; H = hydrogen

The atomic mass of an element reflects the abundance of all isotopes of that element. There are three times as much ^{35}Cl as ^{37}Cl. We can determine the average atomic mass of chlorine in the following manner:

$$\begin{aligned} 3 \times 35 &= 105 \ for\, 35Cl \\ 1 \times 37 &= \ \ 37 \ for 37Cl \\ 4 \qquad &= 142 \end{aligned}$$

$$Avg atomic\ mass = \frac{142}{4} = 35.5$$

Since there are 3 parts ^{35}Cl and 1 part ^{37}Cl, simply multiply each isotope's mass by the ratio observed in nature.

Add up both the parts (4) and the total masses due to those parts (142).

Divide the total mass (142) by the total parts (4) and the average atomic mass is obtained (35.5).

We can do the same thing with ^{79}Br and ^{81}Br.

Both are present in nature in equal parts.

The average atomic mass is determined as follows:

$$\begin{aligned} 1 \times 79 &= 79 \\ 1 \times 81 &= 81 \\ 2 \qquad &= 160 \end{aligned}$$

$$Avg mass = \frac{160}{2} = 80$$

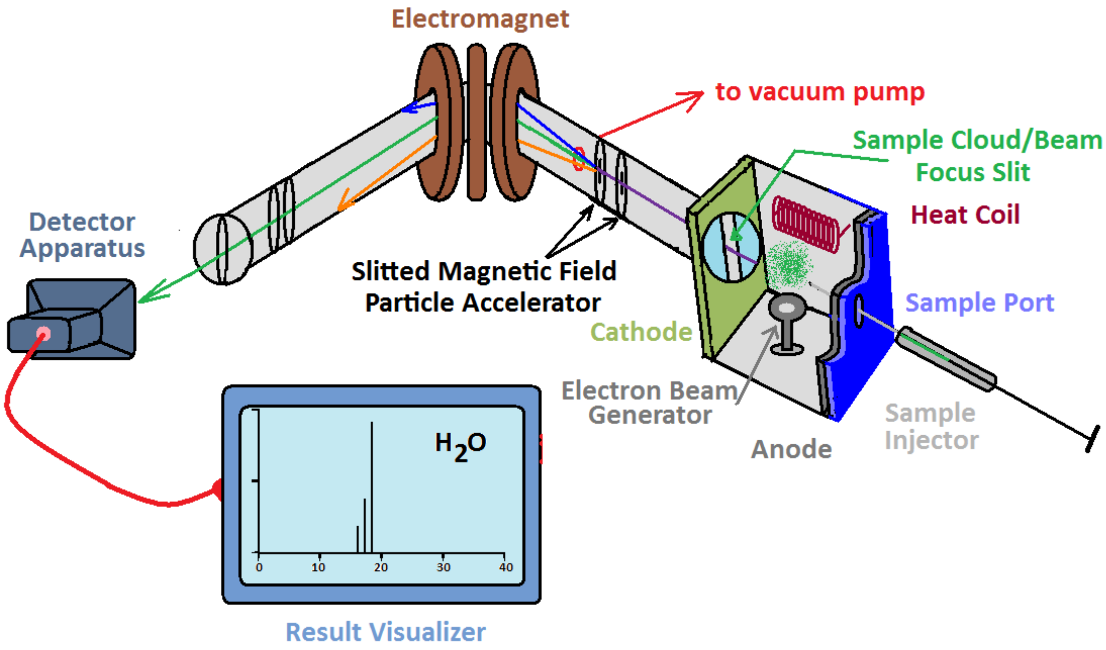
The operation is carried out just as before with the chlorine.

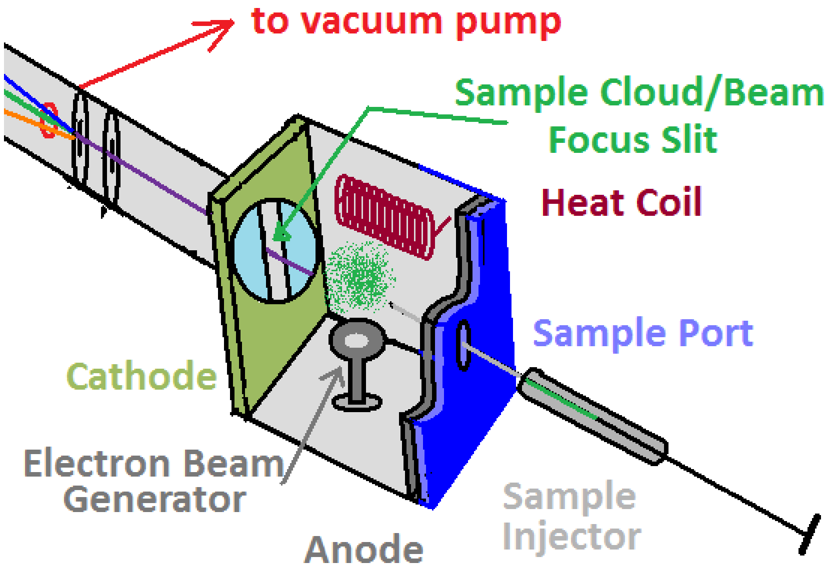
How Do We Know About (Or Measure) the Presence of Isotopes?

- Isotopes (be they radioactive or not) are relative new-comers to Chemistry and Physics.
- Isotopes were first studied following the initial development of the mass spectrometer by Wilhelm Wien in 1899, improved upon by J.J. Thomson ca 1912.
- Ca 1912, Thomson proved the presence of the first isotopes known to man: ^{22}Ne and ^{20}Ne.
- The concept/existence of "isotopes" was first proposed by Frederick Soddy, another eventual Nobel Prize winner.

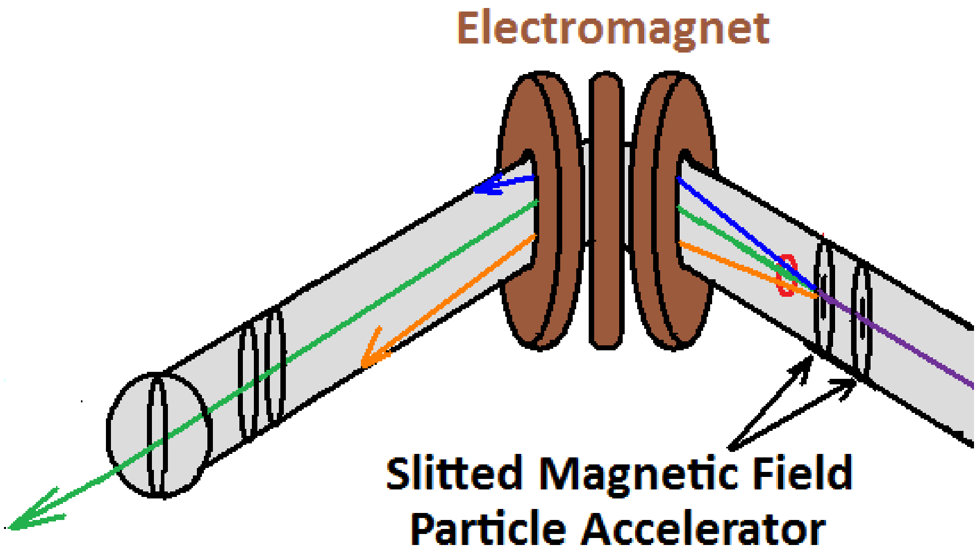
Why Discuss Mass Spectromtery?

- Mass Spectrometry makes determining chemical formulas and structures fairly simple.
- Mass Spectrometry makes determining isotope presence and abundance fairly simple.





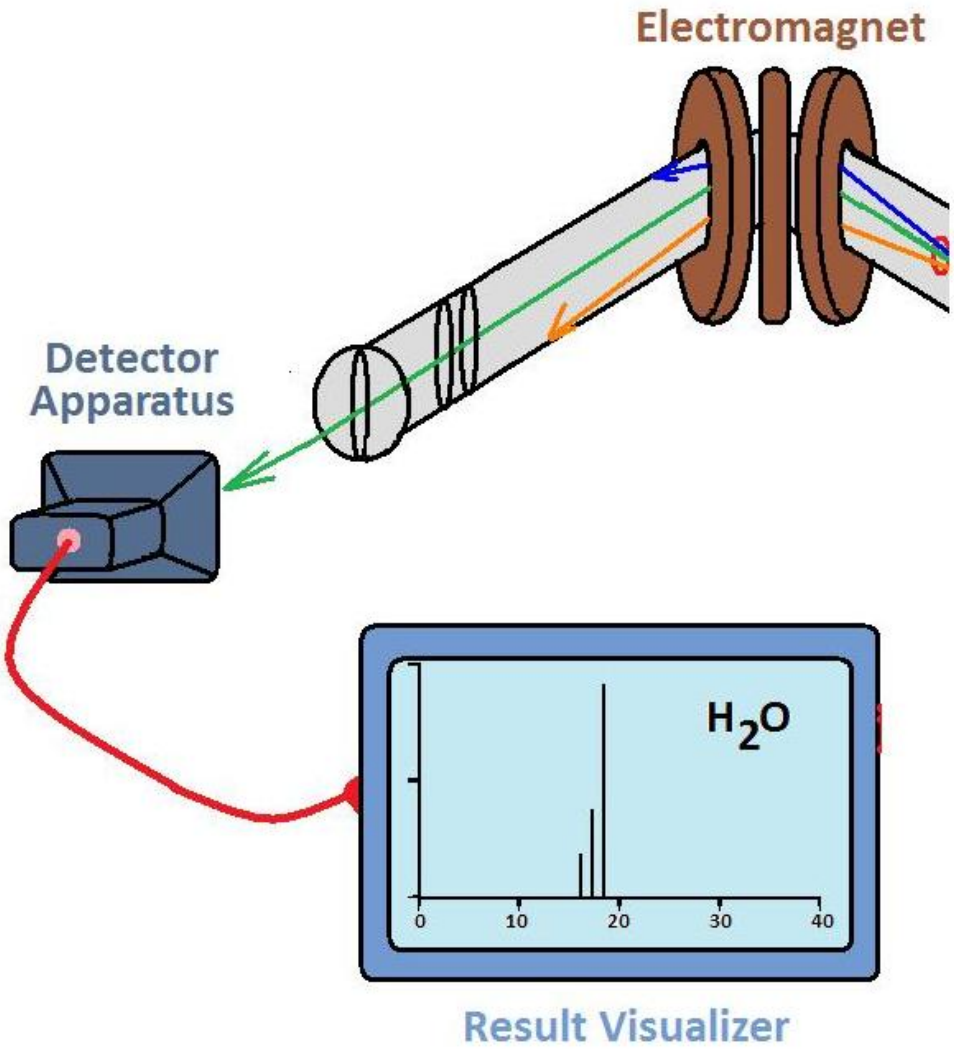
- Sample injected into sample holder/chamber
- Sample vaporized by heat coil
- Sample bombarded by electrons from electron beam generator (some folks call this an electron “gun”)
- Excess electrons boil off generator and are attracted to the Anode (positively charged)
- Remainder of electrons interact with (bombard) the sample cloud to generate sample cations
- Cations attracted to cathode (negatively charged) and are partially focused into a beam to enter the MS Tube



- Sample beam travels under vacuum to the slitted magnetic field particle accelerators – further focuses the beam of the sample cations and prepares the beam to “slingshot” around the tube bend.

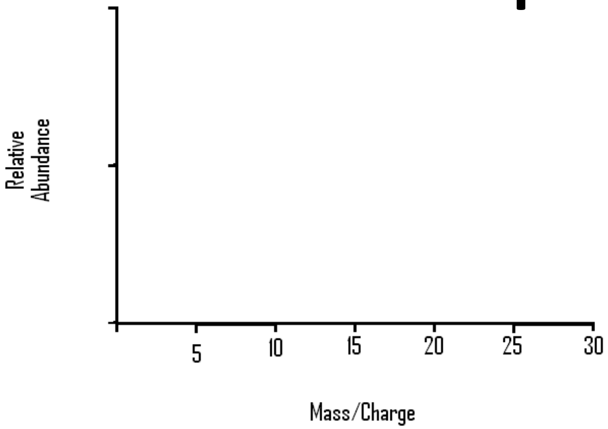
- As the beam approaches the electromagnet, the magnetic field causes the beam to split into “three” beams:
  - Heavy beam (**blue beam**)
  - “Correct beam” (**green beam**)
  - Light beam (**orange beam**)

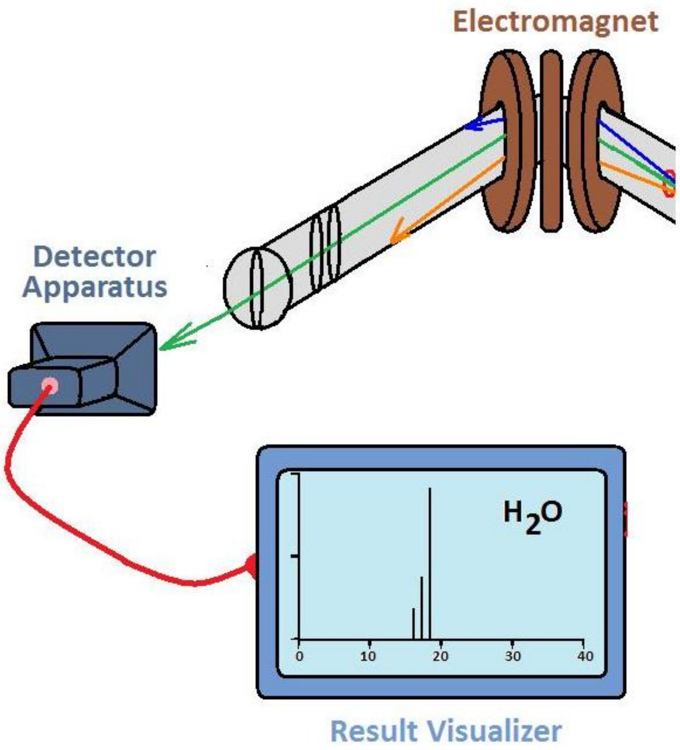
- “Correct beam” of fragments and/or molecules and/or ions hits the detector apparatus where it’s digitized for read-out on the result visualizer.
- The mass spectrum on the visualizer is that of water: tallest peak is 18/1 (m/z; for water, itself); second highest is 17/1 (for OH fragment); third highest is 16/1 (for atomic oxygen).



Mass Spectrometry: Some Examples

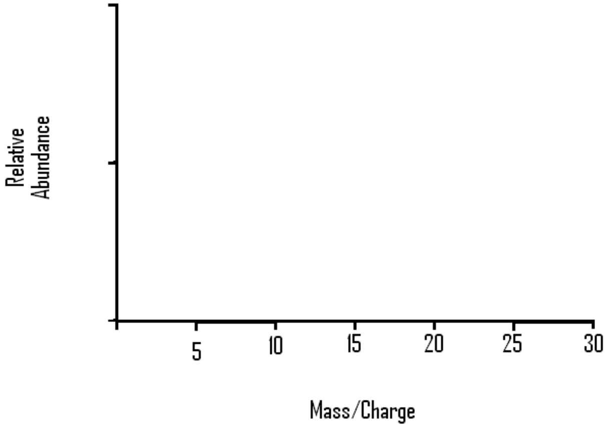
- The mass spectrum identifies molecular mass and molecular particle/fragment masses of a parent compound.
- When a mass spectrum is visualized, it is a “bar/line” graph set on a set of axes as at upper right.
- The mass spectrum for water, BTW, is lower right for an illustration of the “bar/line” graph.
- Newer MS’ seem, in some instances, to be using “peaks” in some instances, rather than “lines”.

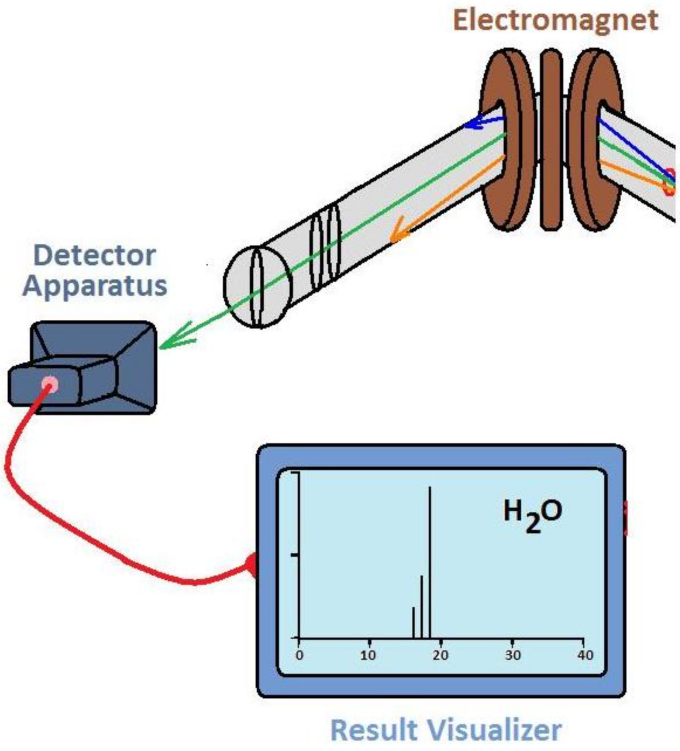




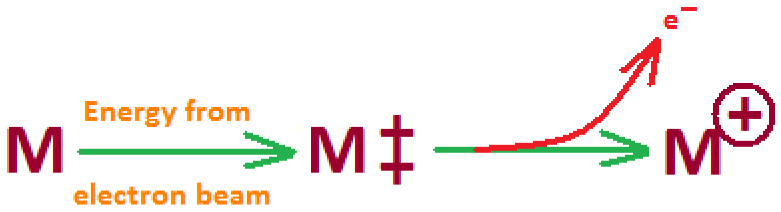
- The vertical axis is Relative Abundance – usually the highest peak is given the value of “100”.

- The horizontal axis is the mass/charge ratio, often expressed as m/z or m/e.





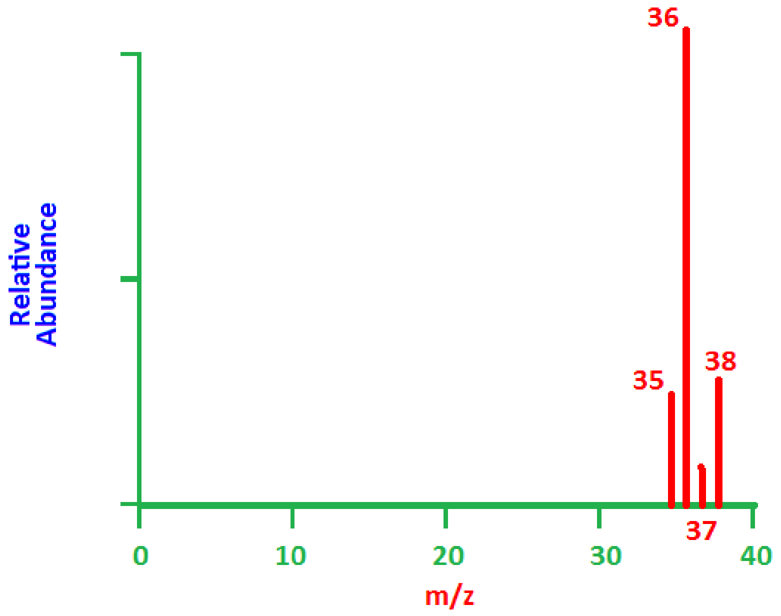
- How does one obtain the mass spectrum of a compound or a mixture of isotopes, barring the techno-mechanical portion of this activity?



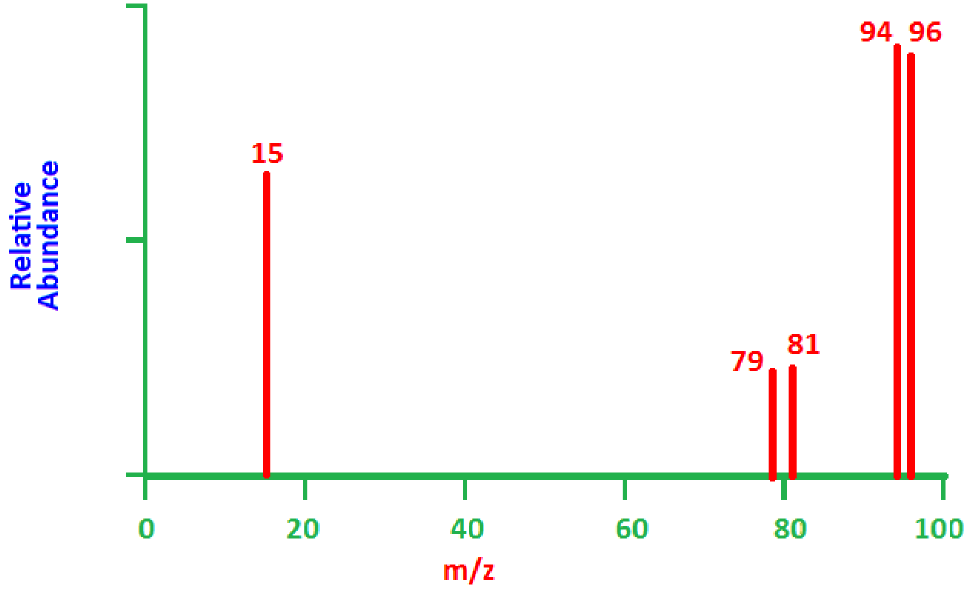
- “Circle +” = radical ion

Mass Spectrometry Used to Determine Abundance of Isotopes in Nature

- Sample contains HCl – what's the proportion of ^{35}Cl to ^{37}Cl in nature?
- 35 peak is ^{35}Cl
- 37 peak is ^{37}Cl
- Ratio of peak heights = 3:1, hence 3X as much ^{35}Cl as there is ^{37}Cl
- 36 peak is from H ^{35}Cl
- 38 peak is from H ^{37}Cl
- 35 peak called "A" peak
- 37 peak called "A+2" peak since is 2 mass units heavier/beyond the 35 peak



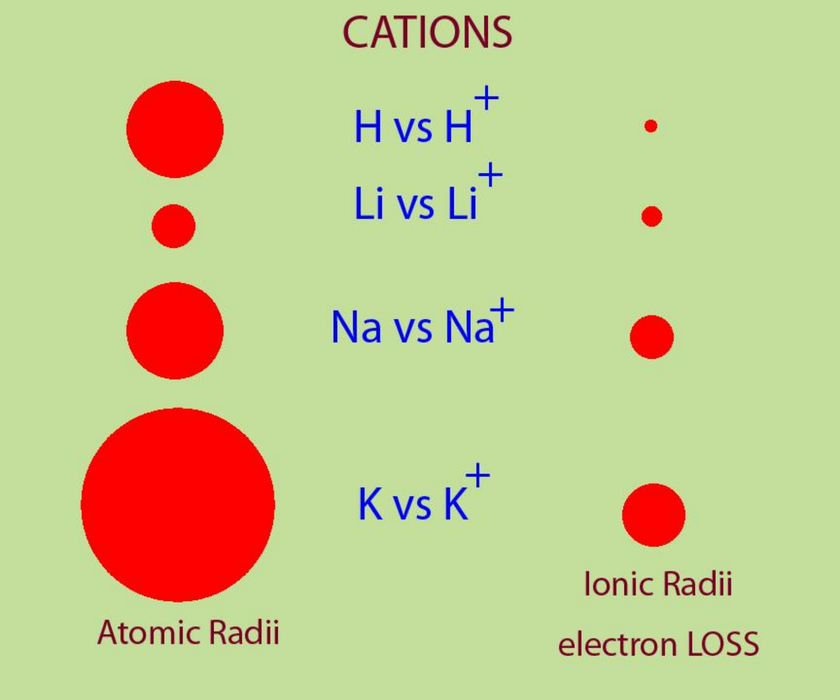
Mass Spectrometry Used to Determine Abundance of Isotopes in Nature

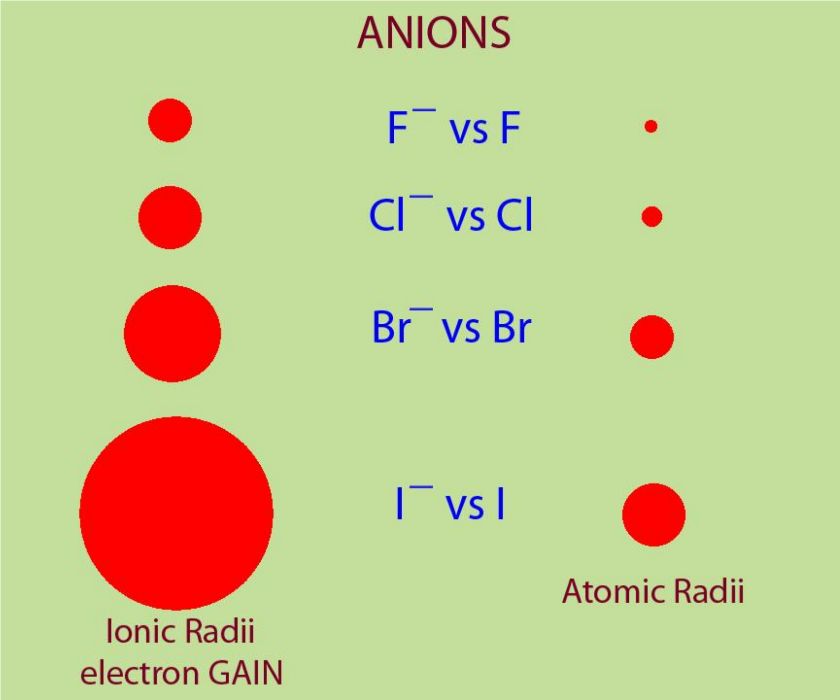


- Sample contains methyl bromide (bromomethane) – what's the proportion of ^{79}Br and ^{81}Br in nature?
- 15 peak is CH_3 peak
- 79 and 81 peaks in almost equal amounts – big clue
- Hence almost equal – one can actually calculate the numbers based on the actual peak heights
- 94-79 = 15 for the methyl
- 96-81 = 15 for the methyl
- Since the 94 and 96 peaks differ only by methyl, the peak heights are also another clue as to the abundance of the two isotopes.

Ionization: Atoms, Ions and Their Radii

- In order for most metals and non-metals to be reactive, they must find a way to be charged, i.e., they must either lose electrons (and be positively charged) or gain electrons (to be negatively charged).
- When this occurs, they are said to ionize. Ions are charged particles.
- **Cations are positively charged ions.**
- **Anions are negatively charged ions.**





CATIONS

- Elements in Groups I, II and III have less than 4 electrons in their outer shells (specifically, they have 1, 2 and 3 electrons, respectively).
- In order for these elements to be most stable when they ionize, i.e., to attain the electronic configuration of the previous noble gas, they must lose 1,2 and 3 electrons, respectively.
- This will yield charges of +1, +2 and +3, respectively.
- The positive charges are due to the excess of protons left in the nucleus after the electrons are removed

ANIONS

- Elements in Groups V, VI and VII have more than 4 electrons in their outer shells (specifically, the have 5, 6 and 7 electrons, respectively).
- In order for these elements to be most stable when they ionize, i.e., to attain the electronic configuration of the following noble gas, the must gain 3, 2 and 1 electrons, respectively.
- In other words, the outer shell, unlike that of the cations, must fill up with electrons to make a total of 8 electrons in the outer shell.
- When this happens, the charges obtained are -3, -2 and -1, respectively.
- The negative charges are due to the accumulation of electrons which out number the protons in the nucleus.

Electrolytes

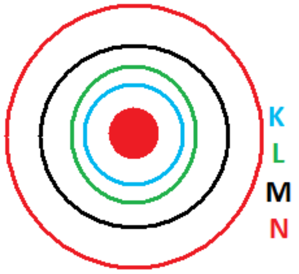
- Cations and anions are collectively known as electrolytes: charged particles that conduct an electrical current in aqueous solution.
- Biological Application???
- When looking at the periodic table and remembering the electron shells from discussions, the periodic table tells you very valuable information about how those elements in the representative group will ionize.
- We first have to accept that when an element's **outer most shells** are **filled or are empty** is when that element is **most stable**.

Group IV Elements

- One issue that was not discussed in earlier discussion was that of what happens when the atom is in Group IV?
- Elements in this group will gain or lose electrons depending on the reaction conditions.

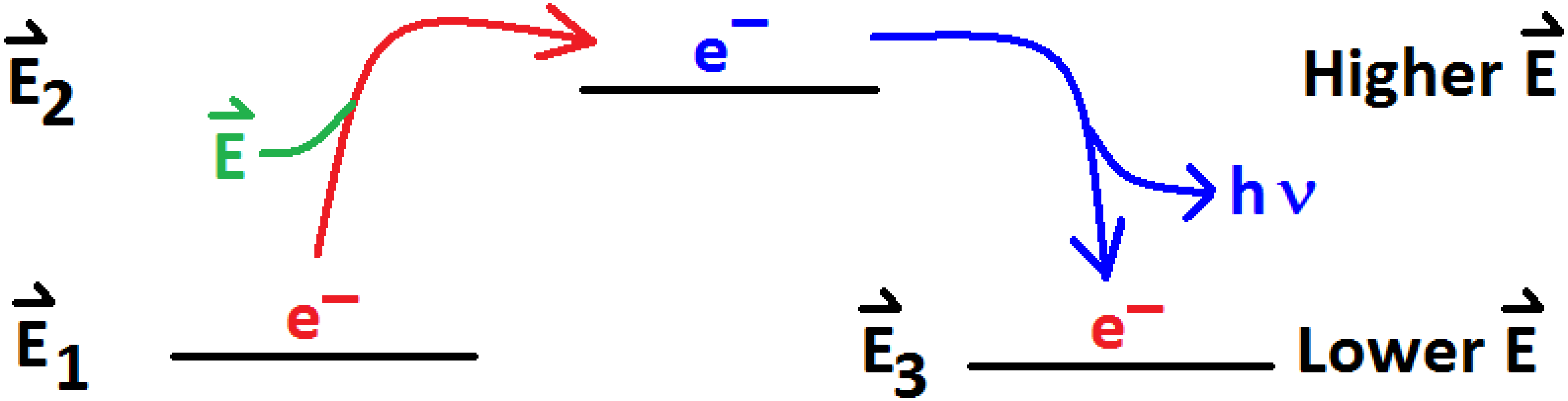
Electronic Configuration of Atoms

We start with the nucleus and work outward from there. Each element has a unique electron configuration. It is this uniqueness that determines the chemical properties of each element. Every element has a different electron arrangement that requires placement of electrons from the inner shell thence to the next shell, thence to the next shell. The innermost shell (K shell) must fill first. It holds a maximum of 2 electrons. Once the K shell is filled, the L shell begins to fill. The L shell holds a maximum of 8 electrons. When the L shell is filled, the M shell begins to fill. The M shell holds a maximum of 8 or 18 electrons. The reason for this will become apparent in a short while. Once the M shell is filled, the N shell begins to fill. The N shell holds a maximum of 8 or 32 electrons. As with the M shell, this will become clearer in a bit.



	Nucleus	K	L	M	N
H	$1p^+$	$1e^-$			
He	$2p^+$ $2n$	$2e^-$			
Li	$3p^+$ $4n$	$2e^-$	$1e^-$		
Na	$11p^+$ $12n$	$2e^-$	$8e^-$	$1e^-$	
Sc	$21p^+$ $24n$	$2e^-$	$8e^-$	$9e^-$	$2e^-$

- These energy shells (I use orbitals interchangeably) do not explain, though, how electrons move between energy levels,



- When electrons become excited, they "jump" to a higher level.
- As they relax, they give off energy in the form of heat or light energy (hυ in the graphic).
- There must, therefore, be another way to examine this phenomenon.

Black Body Radiation

- In the 19th century, classical physics (includes mechanics, thermodynamics, electricity, magnetism and light) failed to explain line spectra.
- People watched "red hot" pokers emit red light; when the temperature was raised to 1200° C, the poker emitted white light as more yellow and blue light were emitted and mixed with the red light.
- This sort of radiation that depends on the ***<u>solid's</u>*** temperature and NOT on what elements make up the solid is called black body radiation.

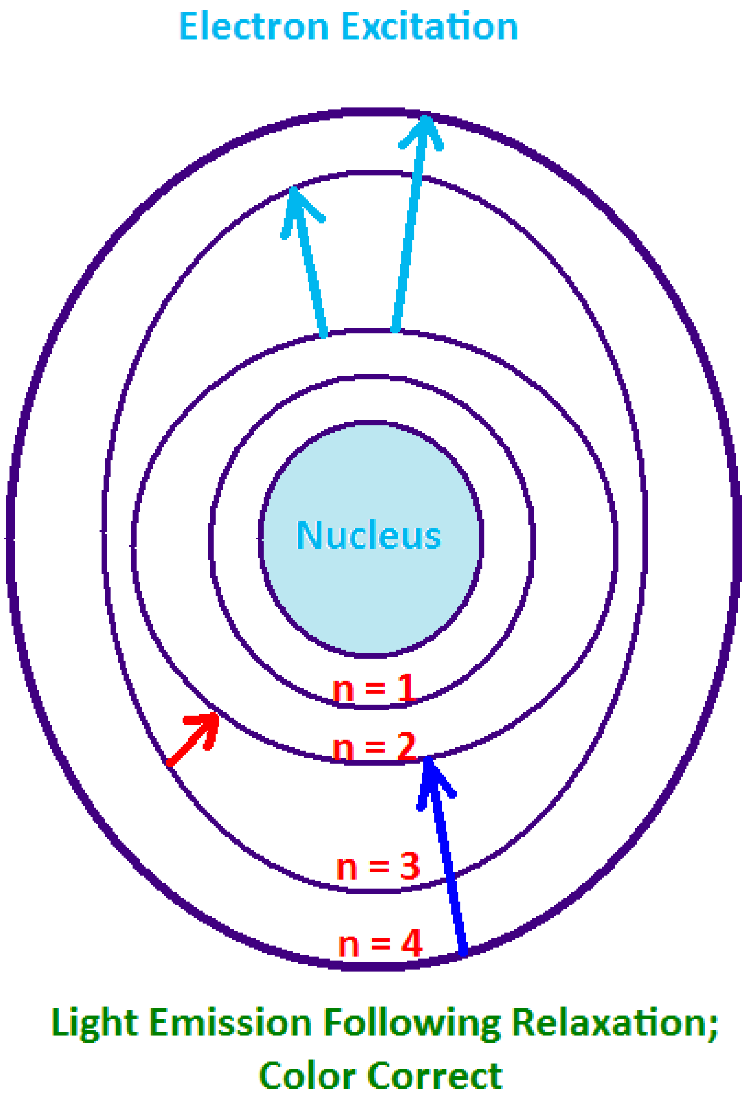
- To explain black body radiation, Max Planck in 1900 developed a revolutionary theory to cover all aspects of black body radiation:
  - the energy of vibrating atoms in a system of unique atoms is fixed
  - EME emitted by these vibrating atoms corresponds ONLY to the difference between 2 permitted energy levels
  - The quantum, or smallest packet, of energy that can be emitted is expressed by Planck's equation, $E = h \upsilon$, where
- E = energy emitted
- h = Planck's constant
- υ = frequency of radiated light
- emitted light is emitted as a single quantum that has energy that is EXACTLY an integral multiple of the simplest quantum (packet): $h \upsilon$, i.e., $h \upsilon$, $2h \upsilon$, $3h \upsilon$,$4 h \upsilon$, $5h \upsilon$,$6h \upsilon$, $7h \upsilon$ and NOT $0.5 h \upsilon$, $2.4h \upsilon$, $3.7h \upsilon$, $7.65h \upsilon$.
- Each integral multiple emits a “line” of color and contributes to a “line spectrum” or a “discrete spectrum” which is an element’s (and its ion[s’]) “fingerprint”.

- A useful analogy to understanding this is to think of vending machines, stamp machines that increase in exact nickel or quarter increments and NOT in penny or 3 cents increments.

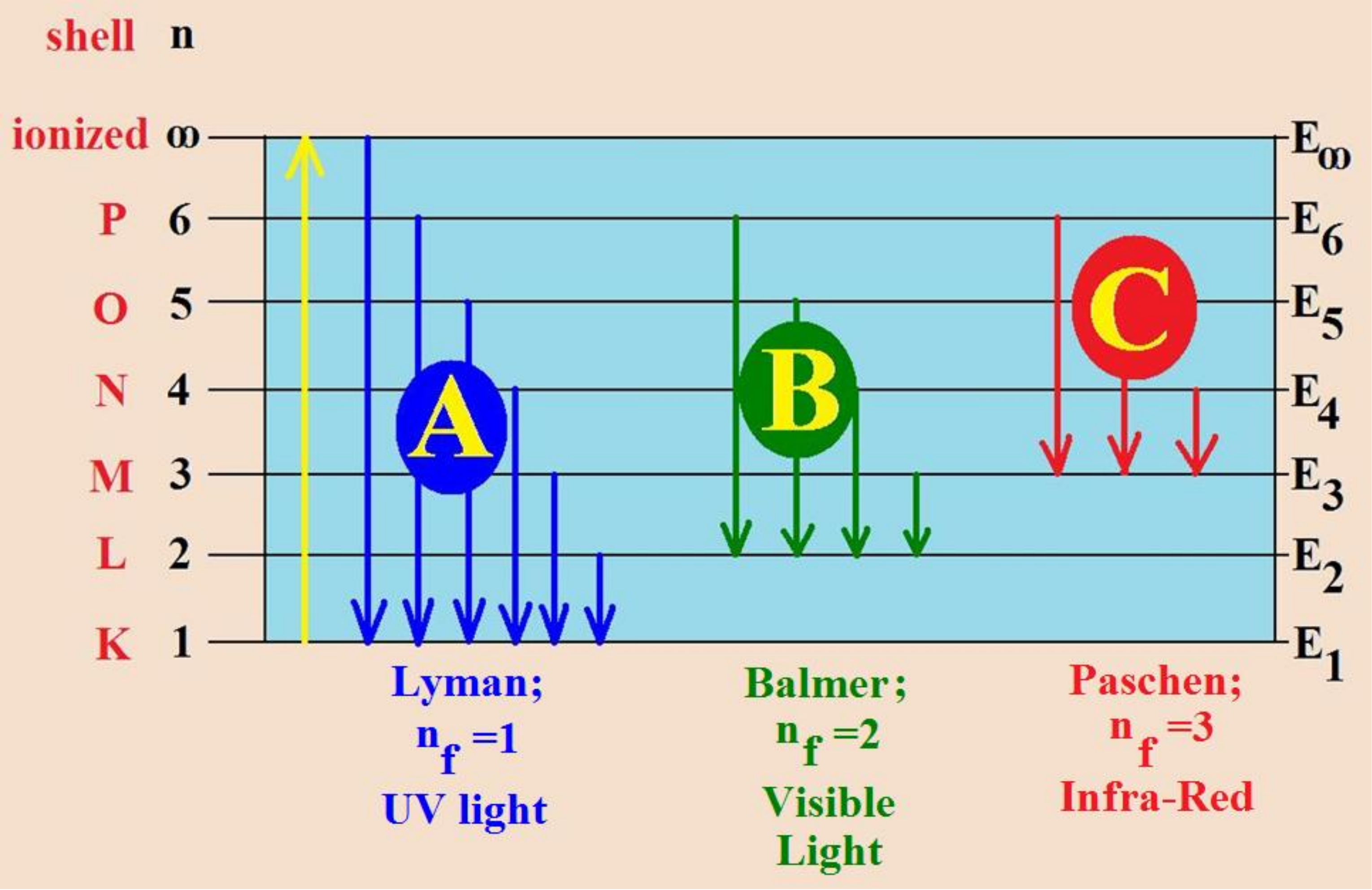
- The importance of the structure of atoms as applied to line spectra became apparent in 1913 when Bohr discovered how to explain the line spectrum of hydrogen.
- He first derived an equation to explain the energy of electrons [E_n].
- Each energy value (E_1, E_2, E_3, E_4, E_5, E_6, ...) is called an <u>energy level</u>.
- The ONLY permitted values for E_n are, below:
  - Where E_n = electron energy at level "n"
  - B = a constant based on Planck's constant and the mass and charge of an electron; = 2.2×10^{-18}J
  - N = an integer and corresponds to the primary quantum number; may also = “n”. More on this later.
  - The negative sign on B (-B) is there to remind us that energies of attraction are negative (this is due to nuclear and electron co-attraction).

$$E_n = \frac{-B}{n^2}$$

- Bohr felt that the hydrogen atom was similar to the solar system:
- Meaning that all energy levels were present with electrons in a specific level on numerous quantum mechanical explanations.
- "n" on graphic stands for energy level or orbital

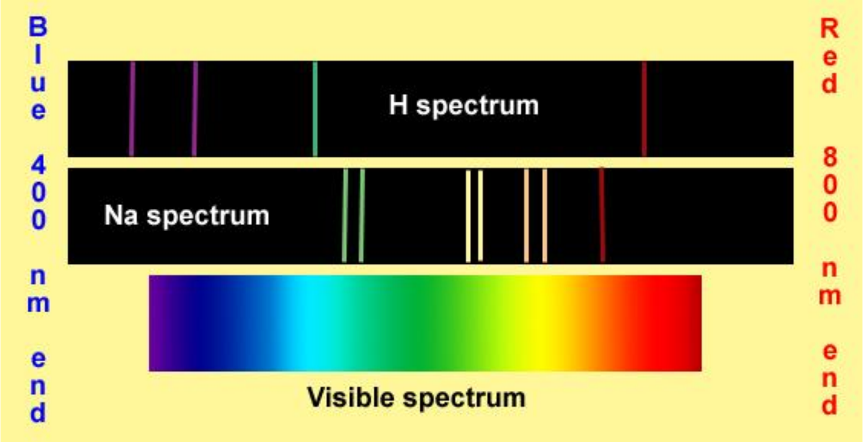


- **When discussing line spectra -- particularly of that Nobel-prize-winning element, hydrogen -- it is necessary to understand that emission spectra consist of several SERIES of lines.**
- **The usual series is observed are IR, visible and UV.**



- Why are atoms important in understanding colored light?
- Raindrops split visible sun light into a familiar continuous spectrum we know as a rainbow (42° for red and 40° for blue; 52 ° and 54.5°, respectively, for a second rainbow; “double rainbow” and colors are reversed).
- Specific elements, however, do not give continuous spectra when light released from a gas discharge tube (a light "bulb" with a specific element in it) is sent through a slit and viewed.
- The light emitted by the gas discharge tube consists of discrete wavelengths (colors) of light, e.g., light from a hydrogen discharge tube appears fuschia and consists of light of 4 specific wavelengths: 410.1 nm, 434.0 nm, 486.1 nm and 656.3 nm or violet, violet, indigo and carmine (next slide).
- When viewed, this spectrum has ONLY 4 LINES of light (at the above wavelengths) -- this set of spectral data is called a LINE spectrum or an emission spectrum.
- The line spectrum of an element is its fingerprint and is unique to itself.

Continuous and Discrete (Line) Spectra



Some elements can be forced to emit light quite simply by placing them in a fire (bunsen burner) and allowing them to burn, e.g.,

Element	Flame	Element	Flame
Na	Bright yellow	Rb	Red
Sr	Carmine	Ba	Green
K	Violet	Cu	Greenish blue
Cs	Blue	Ca	Brick red to orange

These are called flame tests and are used to qualitatively identify compounds containing these elements. We shall see later why the line spectra of the element and its ion are identical.

- In order to understand line spectra, we must look at energy changes or differences (ΔE):
- $\Delta E = E_f - E_i$
- ΔE = difference in energy between 2 states
- E_f = final energy state
- E_i = initial energy state

- **We can apply this concept to the Bohr equation, as well, below.**

$$\Delta E = \frac{-B}{n_f^2} - \frac{-B}{n_i^2} = B\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

- ***KEY:***
- **If $n_f > n_i$: the electron ABSORBS energy and goes from a lower level to a higher energy level (also called an excited state)**
- **If $n_i > n_f$: the electron releases energy and goes from a higher level to a lower level (gives off light at specific frequencies and, hence, colors)**
- **In ALL movements (transitions) electrons move all at once, i.e., the move from n_i to n_f ALL AT ONCE without stopping at n_x in between the two (n_i and n_f).**
- **Every movement to a lower level causes a spectral line.**
- **All the spectral lines give the emission spectrum for each element.**
- **E.g., Determine the energy difference for an electron that starts in n=6 and relaxes to n=2:**

$$\Delta E = B\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$$

$$\Delta E = 2.2 * 10^{-18}\left(\frac{1}{6^2} - \frac{1}{2^2}\right)$$

$$\Delta E = 2.2 * 10^{-18}(-0.2222) = -4.86 * 10^{-19}\,J$$

- Calculate the frequency in Hz of the EME released by the above electron energy-level change. Calculate the wavelength of this light, as well.
- First, lose the negative sign on the energy -- it's not useful, here
- E = h υ
- Now, solve for υ :

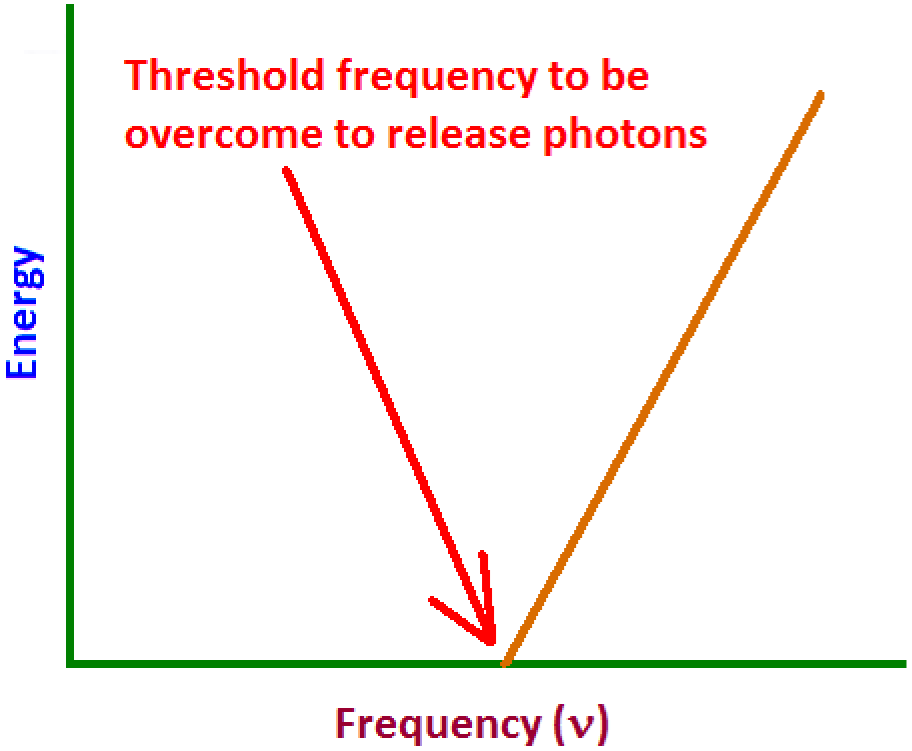
$$\nu = \frac{E}{h} = \frac{4.89 * 10^{-19} J}{6.63 * 10^{-34} Js} = 7.38 * 10^{14} Hz$$

$$\lambda = \frac{c}{\nu} = \frac{3.0 * 10^{8}\ m/s}{7.38 * 10^{14}\ Hz} * \frac{10^{9}\ nm}{1m} = 406.5\, nm$$

This is at the "edge" of the violet portion of the spectrum. This is one line of a complete line spectrum for hydrogen.

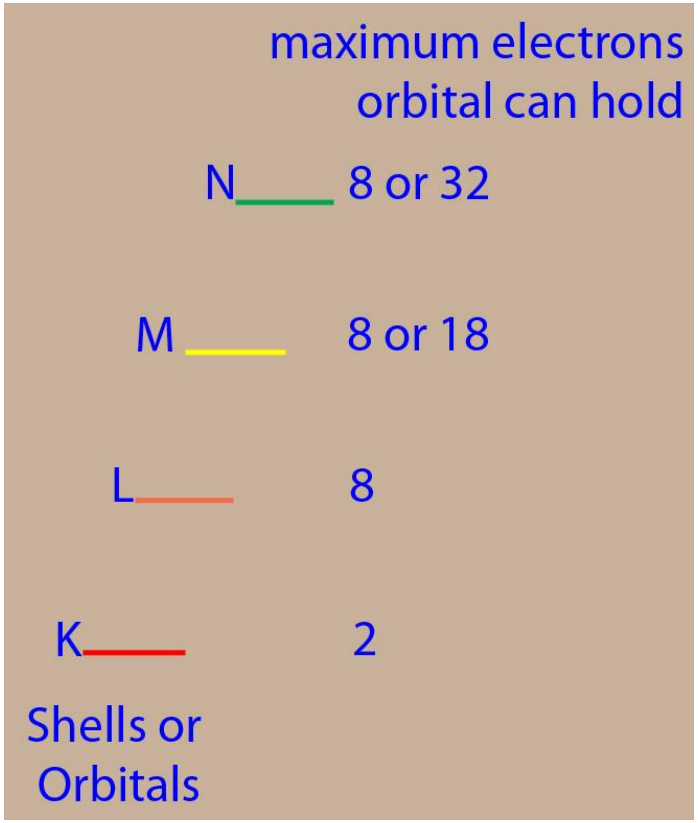
- Bohr's work only explains the single electron atom, H, and does not work with atoms that are larger than H.
- It does, however, tell us that, although not all are occupied by electrons, all energy levels are present in all atoms.

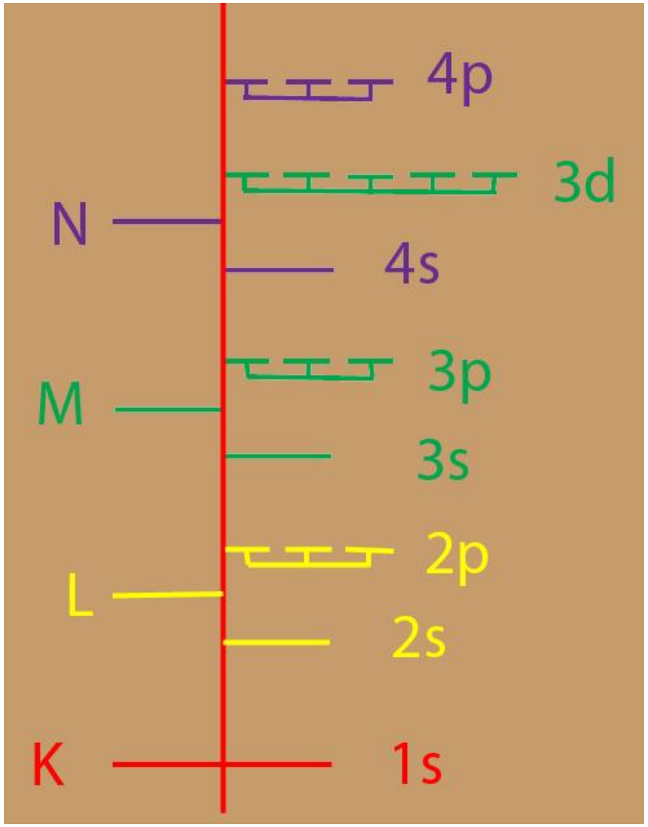
- Einstein expanded on Planck's quantum theory to explain the photoelectric effect.
- The photoelectric effect is defined as occurring when a beam of light that is shining on certain metals causes the release of a beam of electrons.
- The photoelectric effect is dependent on the frequency (color) of the light: weak blue light releases photoelectrons with higher energy than does bright red light.
- In addition, if the frequency is less than a minimal value (defined as the threshold frequency) no photoelectric effect is observed:



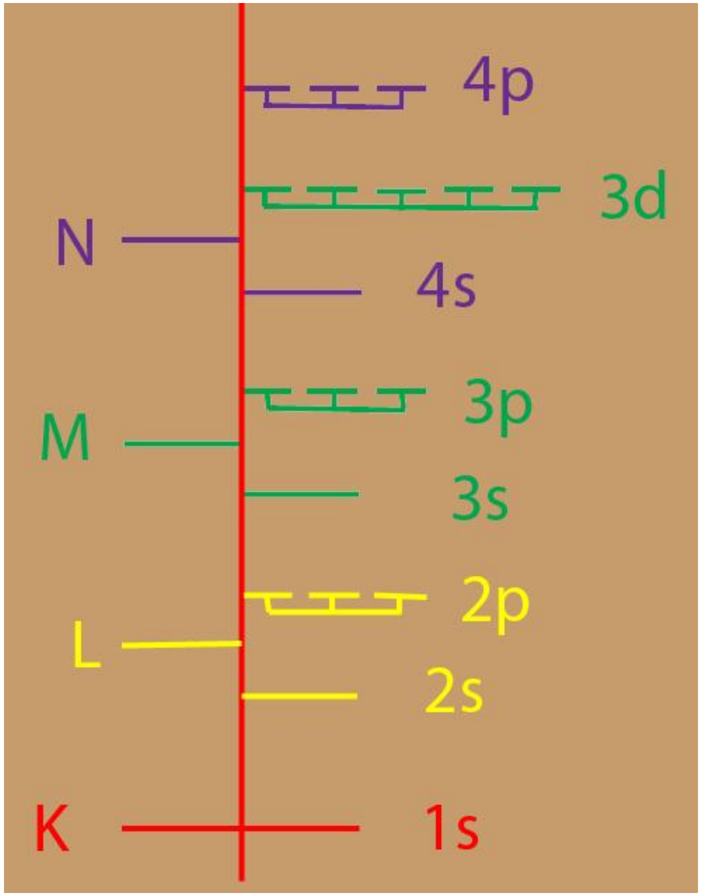
- When the photoelectric effect occurs, the release of light is quanta called photons.
- Analogy: VW stuck in mud: lot's of people can push one at a time to no avail -- a tractor can pull it out and give extra energy (kinetic energy) to it.
- Planck's equation allows us to also calculate the energy of these photons.

It turns out that each energy shell (orbital) has sub-shells within it, much like how trees grow in layers or laminates, with one exception: the K shell. The K shell has one and only one subshell in it. It is called the 1s subshell. **All s subshells hold a maximum of only 2 electrons.** Once the 1s subshell is filled (at element #2, He), the next electron has to go into the L shell.

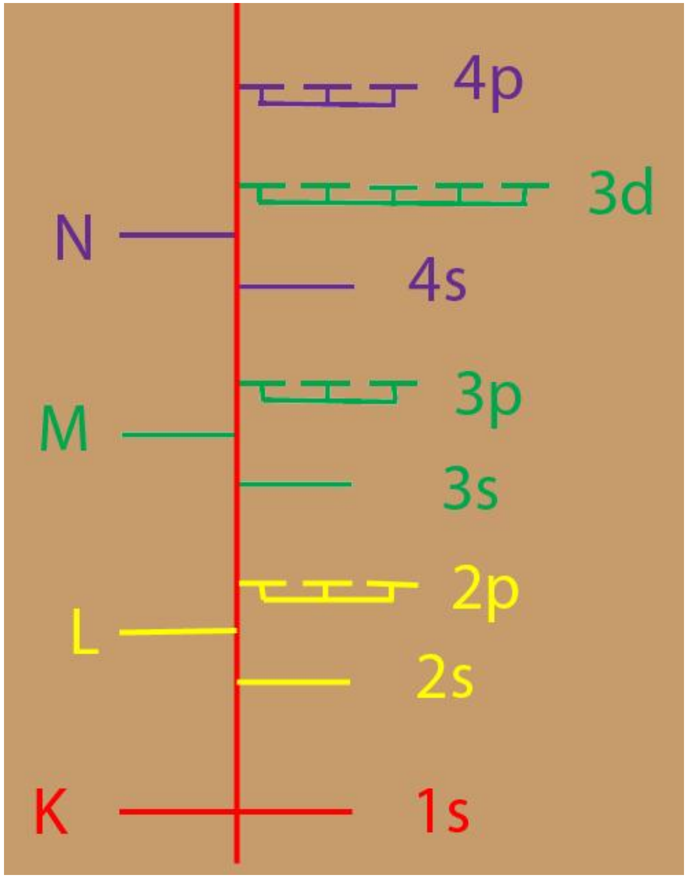




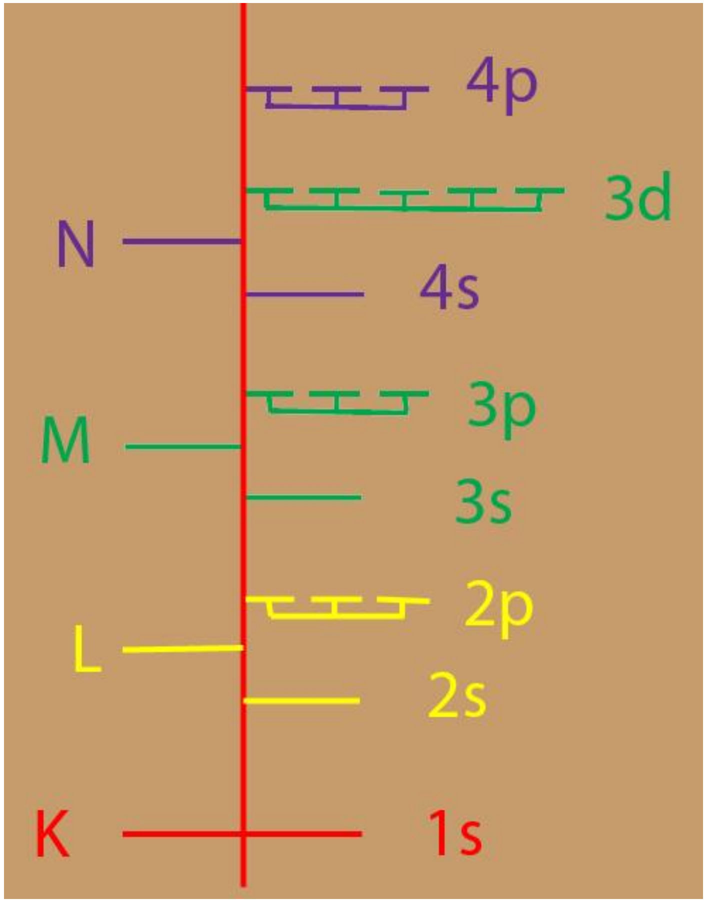
The L shell consists of 2 subshells: the 2s and the 2p subshells. The third electron goes into the 2s subshell. Once the 4th electron has filled the 2s subshell, the 5th electron has to go into the 2p subshell. Here's where it gets a bit messy. The 2p subshell consists of 3 sub-subshells. All subshells and sub-subshells hold a maximum of 2 electrons. Since the 2p subshell consists of 3 sub-subshells, it actually holds a maximum of 6 electrons. Remember that **the L shell holds a maximum of 8 electrons.** 2 + 6 = 8. The 8 electrons come from the two 2s and six 2p electrons when that shell is filled. When the last 2p electron is in place (element 10, Ne), the 11th electron must begin to fill the M shell.



The M shell, remember, is sort of strange: **it holds a maximum of 8 or 18 electrons.** How does it do that? The M shell consists of the 3s and 3p subshells. A third subshell is also available as necessary: the 3d subshell. We already know that s subshells hold a maximum of 2 electrons and that p subshells hold as maximum of 6 electrons by virtue of having 3 sub-subshells, apiece. What about the 3d subshell? All d subshells hold a maximum of 10 electrons. Since electrons prefer to pair up, that tells us that there are 5 sub-subshells in any d subshell. Since we already know that 8 electrons come from the 3s and 3p subshells, and we now know that their may be 10 more from the 3d subshell, it follows that 8 + 10 = 18. Even though the 3d shell is a part of the M shell, energy-wise, it begins to fill AFTER the N shell (4s subshell) begins to acquire electrons. You'll see why in a bit.

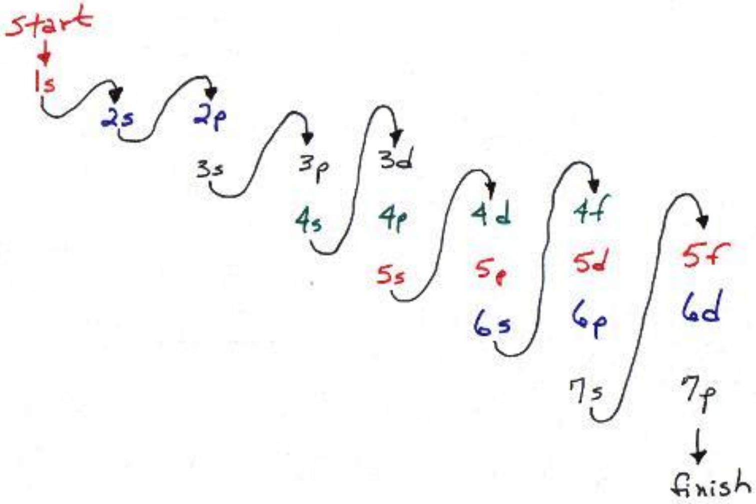


The N shell, remember, **may hold 8 or 32 electrons**, maximally. It may hold this many electrons because not only does it contain 4s, 4p and 4d subshells, it also contains a 4f subshell. The total number of electrons that an f subshell may hold is 14. Again, since electrons like to pair up, this says that there are 7 sub-subshells in the 4f subshell. Hence, 2 + 6 + 10 + 14 = 32 total electrons.

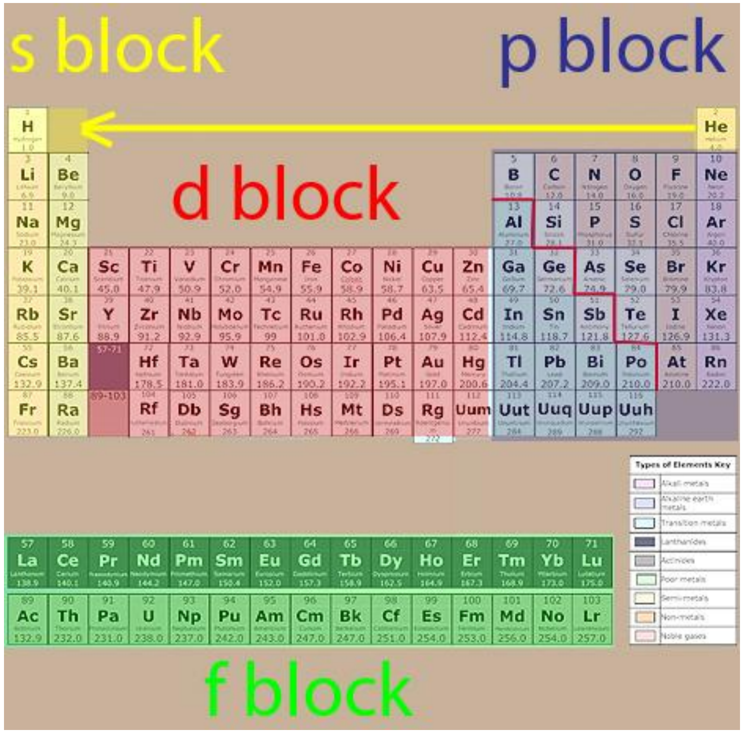


Groups I and II	Transition elements	Groups III through VIII	Lanthanides and Actinides
These elements make up the "s" block elements.	These elements make up the "d" block elements.	These elements make up the "p" block elements.	These elements make up the "f" block elements.

Once we look at the periodic table, sub-shell filling becomes elementary



The subshells have a specific order in which they fill



The periodic table is, bar none, the best "cheat sheet" any chemist has available to him or her.

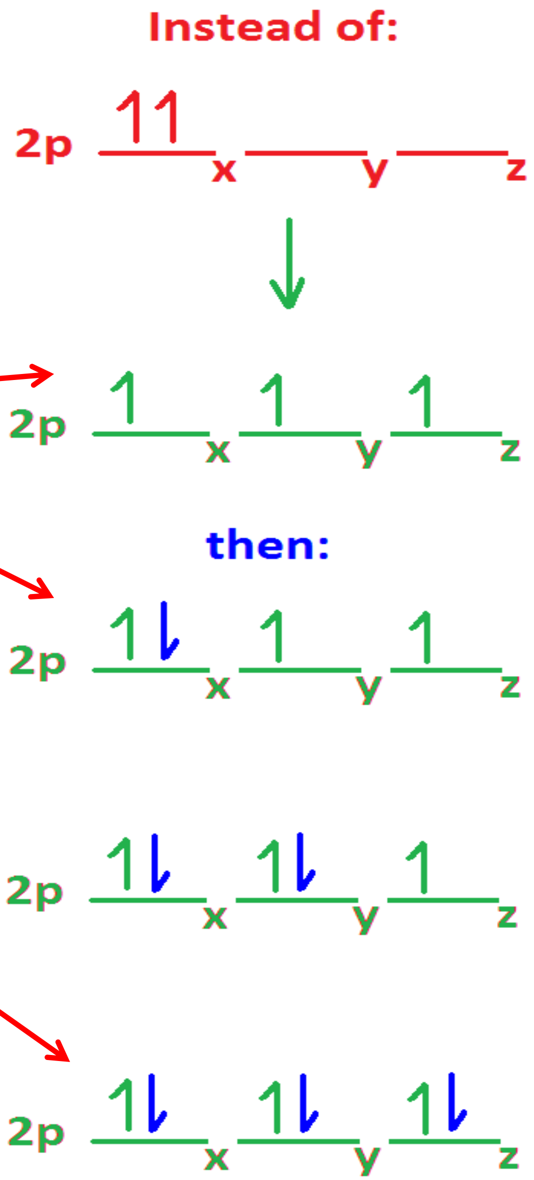
- This means that every element in a specific Group has electrons, successively, in a specific subshell that is easily identifiable.
- In terms of periods, this is even easier.
- Off the left of the periodic table are Arabic numbers that run from top to bottom, starting at 1.
- Since periods go horizontally across the periodic table, every element in a specific period starts with that number.
- Let's look at some examples.

- Hydrogen is the first element on the periodic table.
- It is in Group I and period 1.
- Put the period number first and follow it with the block letter: 1s.
- That means that this element has an electron in the 1s subshell.
- We also have to put in how many electrons there are.
- This is done by inserting the number in the subshell as a superscript.
- Since there is only one electron, the electronic configuration of H is $1s^1$.
- Again, this says that there is one electron in the 1s subshell.
- Let's look at helium, now.
- He is in period 1.
- It is element number 2.
- It's electronic configuration is $1s^2$ -- period 1, s block and has 2 electrons.
- The 1s subshell is now full.
- Note: He is the exception to the p block elements -- it has no p electrons.
- The next element on the periodic table is Li.
- Note that it is in group I and period 2.
- In order to write the electronic configuration for Li, you MUST start at H and go all the way through to Li: $1s^2 2s^1$.
- This takes into account all of the electrons necessary to make up Li.

- The 4th element is Be.
- It is in group II and period 2.
- Its electronic configuration is $1s^2 2s^2$.
- For this period, this closes out the s block elements.
- Boron (B) is the 5th element on the periodic table.
- It is in group III and period 2.
- Its electronic configuration is $1s^2 2s^2 2p^1$.
- The 6th element is carbon (C).
- It has one more electron than B: $1s^2 2s^2 2p^2$.
- Nitrogen's (N) electronic configuration is $1s^2 2s^2 2p^3$.
- At this point, the 2p subshell is half full.

Hund’s Rule

- There is a specific rule dealing with the order in which sub-subshells fill.
- This rule is Hund's Rule. Hund's Rule says that the electrons enter each sub-orbital of a given type singly and with identical spins before any pairing of electrons of opposite spin occurs within those orbitals:
- This graphic shows that each sub-subshell (p, d or f -- p in the graphic) must half fill, first, with electrons of one spin before the sub-subshells can completely fill with electrons having opposite spin.
- In other words, for a p subshell, all three sub-subshells must half fill with one electron each before the 4th electron can fill the first sub-subshell, the 5th electron can fill the second sub-subshell and the 6th electron can then fill the last sub-subshell.



- Oxygen (O) has one more electron: $1s^2 2s^2 2p^4$;
- while fluorine (F) has one more than O: $1s^2 2s^2 2p^5$.
- Neon (Ne) fills up the p subshell and closes out the second period: $1s^2 2s^2 2p^6$.
- The 11th element is sodium (Na).
- It starts out the third period and has one more electron than Ne: $1s^2 2s^2 2p^6 3s^1$.
- There is another way in which to write this electronic configuration that is a sort of shorthand: rather than going through all of the electronic configuration, use the previous noble gas as a core and add to it, e.g., for Na, then, the electronic configuration can be written as $[\mathrm{Ne}]3s^1$.
- For Mg, the electronic configuration is $[\mathrm{Ne}]3s^2$.

The remainder of the third period elements' electronic configuration are tabulated below in both formats:

Element	Traditional notation	Shorthand notation
Al	**$1s^22s^22p^63s^23p^1$**	**$[Ne]\ 3s^23p^1$**
Si	**$1s^22s^22p^63s^23p^2$**	**$[Ne]\ 3s^23p^2$**
P	**$1s^22s^22p^63s^23p^3$**	**$[Ne]\ 3s^23p^3$**
S	**$1s^22s^22p^63s^23p^4$**	**$[Ne]\ 3s^23p^4$**
Cl	**$1s^22s^22p^63s^23p^5$**	**$[Ne]\ 3s^23p^5$**
Ar	**$1s^22s^22p^63s^23p^6$**	**$[Ne]\ 3s^23p^6$**

Potassium (K) starts out period 4 in Group I. In this case, the shorthand method for its electronic configuration is $[Ar]4s^1$. The last element for which we will consider electronic configuration is Ca. Its configuration is $[Ar]4s^2$.

Periodic Law

Short periods		
Period	Contents	Orbitals
First period	H → He (2 elements)	1s
Second period	Li → Ne (8 elements)	2s2p
Third period	Na → Ar (8 elements)	3s3p
Long periods		
Fourth period	K → Kr (18 elements)	4s3d4p
Fifth period	Rb → Xe (18 elements)	5s4d5p
Sixth period	Cs → Rn and Lanthanides (32 elements)	6s5d4f6p
Seventh period	Fr → Ac and Actinides (Incomplete; holds 16 elements)	7s6d5f7p

- Let's start examining atoms with some of their ions.
- Figure, below, illustrates the difference between elemental lithium and the monovalent lithium cation utilizing electron configuration.
- Note that in order for Li to ionize that it loses the single 2s electron. I left the empty 2s shell in that figure to illustrate where the electron used to be.
- It is not necessary to write out the empty orbitals.

$$Li^0 = 1s^2\,2s^1$$

$$Li^+ = 1s^2\,2s^0$$

- Likewise, the figure, below, illustrates what happens when elemental chlorine is ionized to the monovalent chloride anion.
- In this case, an extra electron is gained in the 3p shell, filling it.
- What's important, here, is to remember which electron shells contain which orbitals/sub-shells.
- The reason this is important goes right back to our earlier discussion that explained that atoms will gain or lose sufficient electrons to achieve an outer electron arrangement identical to the preceding or following noble gas.
- **This means that the K shell wants to be full at 2 electrons; the L shell at 8 electrons; the M shell at 8 electrons -- these correspond to He, Ne and Ar, respectively.**

$$Cl^0 = 1s^2\,2s^2\,2p^6\,3s^2\,3p^5$$

$$Cl^- = Cl^{-1} = Cl^{1-} = 1s^2\,2s^2\,2p^6\,3s^2\,3p^6$$

Elemental states to their respective ionic states using electronic configuration:

$$Na = 1s^2 2s^2 2p^6 3s^1$$

$$Na^{+1} = Na^{1+} = Na^{+} = 1s^2 2s^2 2p^6 3s^0$$

$$Na \bullet \rightarrow Na^{+} + e-$$

$$Ca = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

$$Ca^{2+} = Ca^{+2} = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^0$$

$$Al = 1s^2 2s^2 2p^6 3s^2 3p^1$$

$$Al^{+3} = Al^{3+} = 1s^2 2s^2 2p^6 3s^0 3p^0$$

$$S = 1s^2 2s^2 2p^6 3s^2 3p^4$$

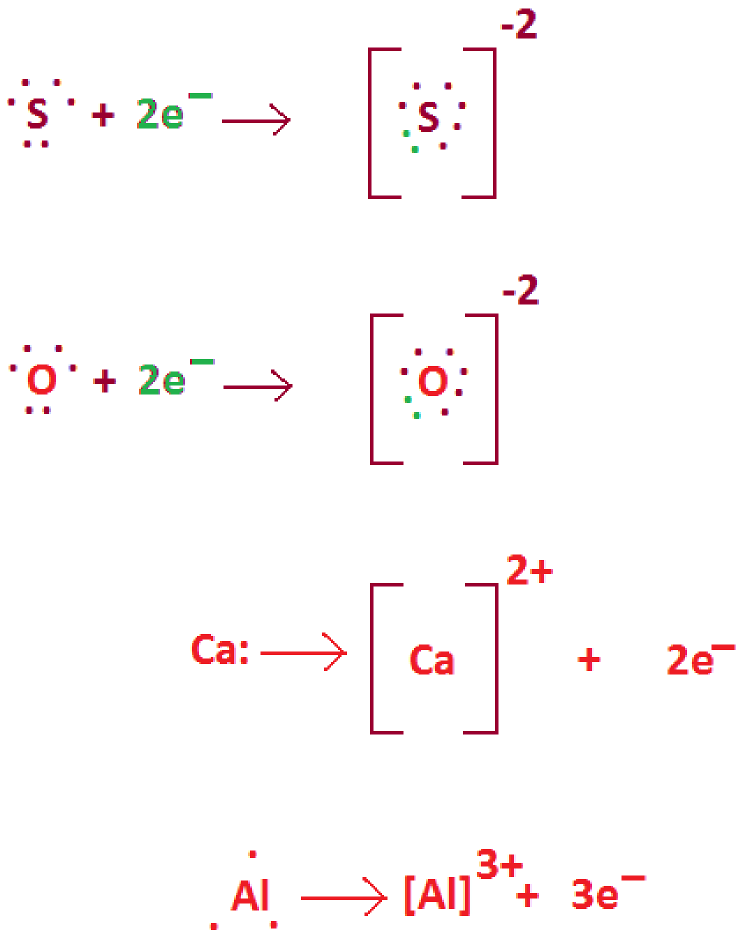
$$S^{-2} = S^{2-} = 1s^2 2s^2 2p^6 3s^2 3p^6$$

$$O = 1s^2 2s^2 2p^4$$

$$O^{-2} = O^{2-} = 1s^2 2s^2 2p^6$$

There is another method in which to approach this concept, as well.
It is called Lewis Structures.

- Lewis Structures, for all intents and purposes, utilize different symbols, e.g., dots, squares, "x's", triangles, ad nauseum, to represent the electrons in the outer valence shell of the atoms.
  - Remember that it takes 2 electrons to make a single bond
  - Whenever possible, you need to place 8 electrons around your atoms (= octet rule)
  - At times you will only get 2 electrons around some atoms, e.g. H, Li, Na, K and that fulfills the octet rule, too
- Fortunately for us, the representative elements are the easiest and the ones we'll focus on.
- Remember that these groups are in numerical order from I to VIII.
- The number of the group tells you exactly how many electrons are in the outer valence shell of the atom with which you are working.
- Thus, we may draw the ionization of each of the elements described above in the figure at right.
- Note that cations lose their outer shell electrons and anions gain electrons in their outer shells.
- All of these are examples of simple ions: atoms that have acquired a net positive or negative charge by losing or gaining electrons, respectively.



Ions and atoms with identical electronic configuration are called isoelectronic:

$$Al^{3+} = 1s^2 2s^2 2p^6$$

$$Ne = 1s^2 2s^2 2p^6$$

- The last Group, Group VIII, has 8 electrons in its outer shell -- with the exception of He which only has 2 (in the 1s subshell).

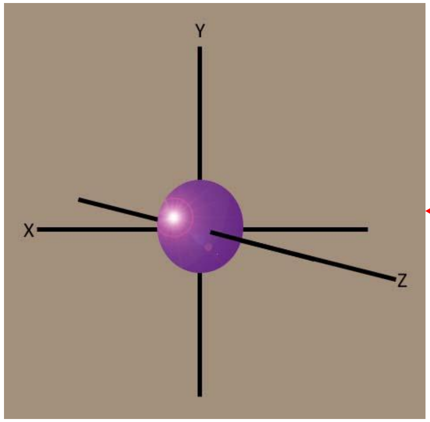
Wave Mechanics: An Introduction

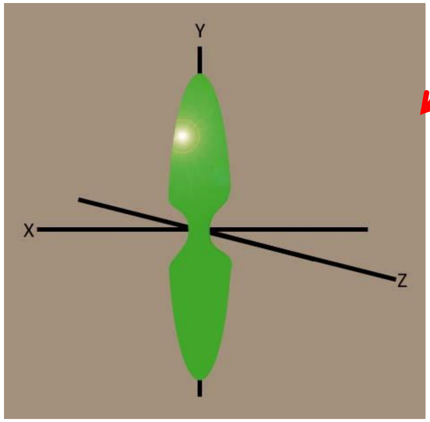
- Remember that light has dualistic properties.
- Louis DeBroglie looked at matter and wondered if matter had wave-form properties, i.e., does matter vibrate at its own unique frequency?
- DeBroglie's theory revolutionized the mathematical description of atoms and matter.
- DeBroglie's theory proposes that a particle moving has some sort of wave nature that allows for the calculation of its wavelength-equivalence:
- $\lambda = (h/mv)$
  - λ = wavelength-equivalence
  - h = Planck's constant
  - m = mass of the particle
  - v = velocity (speed) of the particle
- Remember that $p = mv$
- This work resulted in the manufacture and technology behind the electron microscope.

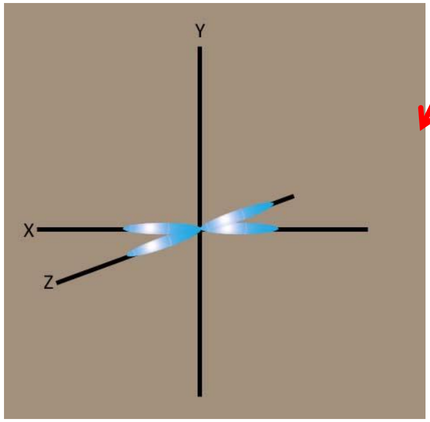
- Two other scientists took DeBroglie's work and applied to the wave-like properties of sub-atomic particles.
- Werner Heisenberg developed his uncertainty principle at the same time.
- His equation allows for the determination of the degree of uncertainty when measuring a particle's location and momentum simultaneously.
- By virtue of his equation, if the particulate mass is large, the uncertainties in both variables are incredibly small.
- At best, his equation tells us where an electron might have been, but not where it will be.
- Heisenberg's Uncertainty Principle predicts the probability of finding electrons within each electron's energy affinity, i.e., close to the nucleus, farther out, etc, i.e., the atomic orbital.

- Erwin Schrödinger derived his wave equation that requires the utilization of the quantum numbers of each electron in an element.
- His equation changed the view of electron orbitals from concrete, solar system-type to "fuzzy" regions with mathematical restrictions.
- Solutions to Schrödinger's Wave Equations give 3 parameters called quantum numbers.
- Each set of quantum numbers describes an electron cloud wave function called an orbital.
- Orbitals are 3-D, geometric regions.

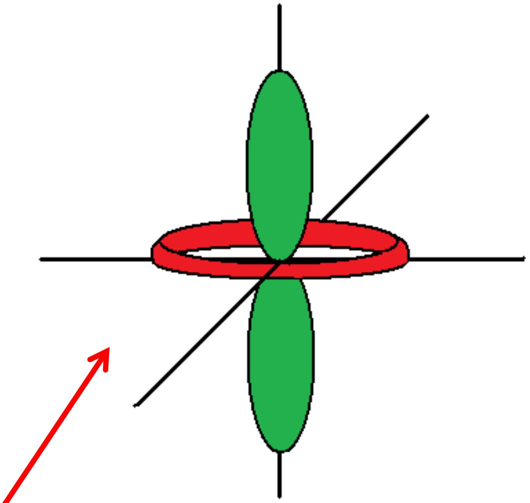
- Shown on the following slide are some representative orbital shapes -- the schematics are not inclusive, merely representative.
- These orbitals came about as a result of Schrödinger's Wave Equations.

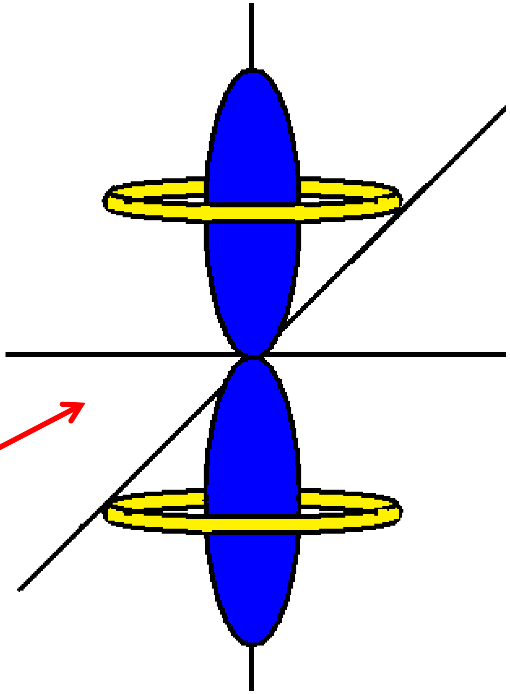






- s subshell: spherical
- p subshell: “dumb-bell” shaped
- d subshell: cloverleaf shaped
- d subshell: single-ringed dumb-bell
- f subshell: double ringed dumb-bell





Quantum Numbers

- The motions of the electrons about the nucleus can be described in terms of 4 (not just three as we've been discussing) quantum numbers:
  - Principal Quantum Number = "n"
  - Subsidiary Quantum Number; Secondary Quantum Number; Angular Momentum Quantum Number = "*l*"
  - Magnetic Quantum Number = "m"
  - Spin Quantum Number = “s”

ASIDE: Quantum Numbers in Brief

1°	2°	shape	subshell	3°
n	*l*			m
1	0	Sphere	s	0
2	1	Dumbbell	p	-1,0,1
3	2	Ringed dumbbell; clover leaf	d	-2,-1,0,1,2
4	3	Ringed dumbbell	f	-3,-2,-1,0,1,2,3

Principal Quantum Number = "n"

Principal Quantum Number = "n":
designates the effective volume of the space in which the electron moves;
increased "n" means increased energy with the shell;
values vary theoretically between 1 and infinity (∞)

Shell	"n"
K	1
L	2
M	3
N	4
O	5
P	6

Secondary Quantum Number = “*l*”

Subsidiary Quantum Number;
Secondary Quantum Number;
Angular Momentum Quantum Number = "*l*":
designates the shape of the region which the electron occupies;
values vary from 0 to ("n"-1):
If "n" = 1, *l* = 0 ONLY
If "n" = 2, *l* = 0,1
ETC:

"n"	*l*
1	0
2	0,1
3	0,1,2
4	0,1,2,3
5	0,1,2,3,4
6	0,1,2,3,4,5

Secondary Quantum Number: Application

l	Electron designation
0	s
1	p
2	d
3	f
4	g
5	h
6	i

Magnetic Quantum Number = "m"

Magnetic Quantum Number = "m":
designates in a general way the orientation of the electron path in space; values vary from -*l*, 0, +*l*:

"n"	*l*	"m"
1	0	0
2	0	0
	1	-1,0,+1
3	0	0
	1	-1,0,+1
	2	-2,-1,0+1,+2
4	0	0
	1	-1,0,+1
	2	-2,-1,0,+1,+2
	3	-3,-2,-1,0,+1,+2,+3

Spin Quantum Number = “s”

- The fourth quantum number, "s", or Spin Quantum Number is independent of the Schrödinger wave equation.
- The first three quantum numbers describe the orbitals in which the electrons may be; the last quantum number describes the electrons, specifically, that are in these orbitals.
- There are two values for this number: ± ½.
- This value specifies the direction of spin of the electron about its own axis as the electron moves around the nucleus.
- Spin is clockwise or counter-clockwise (+ or -, respectively) and is designated the ½ arbitrarily -- probably due to Hund's rule.

Hund’s Rule

- ≡ every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.
- This means that in each "sub" subshell, there are only 2 electrons with equal BUT OPPOSITE SPIN once they begin to fill:
- E.g.: 2p: ⇑⇓x⇑⇓y⇑⇓z

- This fourth quantum number came about when Stern and Gerlach (in 1921) "shot a beam" of vaporized Ag atoms through a strong electromagnet and the vapor beam split into two.
- This indicated that electrons behaved like tiny magnets (remember the induced magnetic field, earlier) and deflected towards the opposite, or attracting, pole.
- This same sort of pattern also occurs with the mono-electronic atom, H, suggesting that each atom's electron has its own spin, i.e., there is no 100% identical spin of electrons even in H.

PAULI EXCLUSION PRINCIPLE

- The PAULI EXCLUSION PRINCIPLE says: No two electrons in a particular atom can have the same set of 4 quantum numbers, i.e., each electron has its own quantum number "fingerprint".
- I.e., each electron is unique.

Shell	"n" or "N" **Primary Quantum Number**	ℓ (ranges from zero to n-1) **Secondary Quantum Number**	Subshell	"m" (ranges from zero to ±ℓ) **Magnetic Quantum Number**	Shape	"s" (arbitrarily assigned as ±½; independent of Schroedinger's Wave Equation) **Spin Quantum Number**
K	1	0	1s	0	Spherical	±½
L	2	0	2s	0	Spherical	±½
		1	2p	-1,0,+1	Dumb-bell	±½
M	3	0	3s	0	Spherical	±½
		1	3p	-1,0,+1	Dumb-bell	±½
		2	3d	-2,-1,0+1,+2	Clover-leaf and ringed dumbbell	±½
N	4	0	4s	0	Spherical	±½
		1	4p	-1,0,+1	Dumb-bell	±½
		2	4d	-2,-1,0,+1,+2	Clover-leaf and ringed dumb-bell	±½
		3	4f	-3,-2,-1,0,+1,+2,+3	Ringed and Double-ringed dumb-bell	±½

Summary & Application

1) n or N does NOT mean the number of electrons. It means that Schroedinger came up with a way to give each shell in an atom a number, hence the K shell’s “number” is “1” – much like we humans have a name AND a social security number.

2) “n” or “N” only tells us which shell a single electron has been in.

3) ℓ tells us the subshell that the electron has been in, e.g., s or p or d or f and it is dependent on the value of “n” or “N”, e.g., ℓ varies from zero to n-1, e.g., if “n” is 3, then ℓ varies from 0 to 1 to 2 (which is its maximum value because 3-1 =2).

4) “m” depends upon the value of ℓ, and varies from – ℓ to 0 to + ℓ. This means that if m = 2, then ℓ equals -2, -1, 0, +1, +2. Among other things, the value of “m” is that the number of “m” values you get essentially tells you what subshell the electron was in, in addition to the shape of that subshell.

5) The spin quantum number does not depend on ANY of these 3 quantum numbers, I.e., it’s independent of the Schroedinger Wave Equation. Its numerical value is ½. To determine if the spin of the electron is clockwise, we assign a “+” sign; counterclockwise, we assign a “-“; this is arbitrarily assigned unless we actually ran the experiment in the lab to confirm it.

So, if we were given the following set of quantum numbers, 2,0,0,+½, we can now give an electron an “address” of sorts that would describe where it had been:

the quantum number series is ALWAYS in the order n,l,m,s, so we can identify the electron from or data.

N = 2; this means that we’re looking at an electron that was in the L shell.

ℓ = 0; this means that we’re looking at an electron that was in the s subshell.

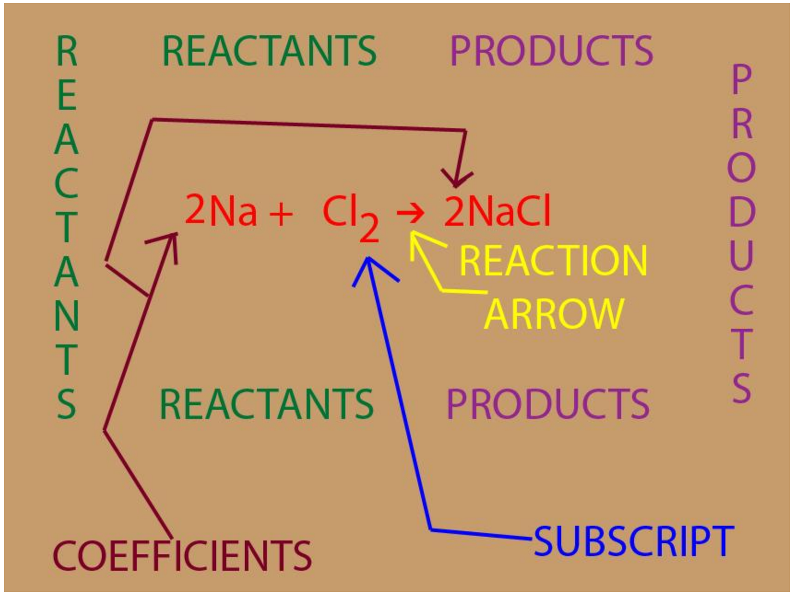
m = 0; this confirms that we’re looking at an electron that is in a spherical subshell (orbital), which is an s subshell.

s = +½; this means that the electron we’re working to identify spins in a clockwise manner.

Succinctly, then, this is quantum address for an L shell electron in a spherical s subshell that’s spinning clockwise.

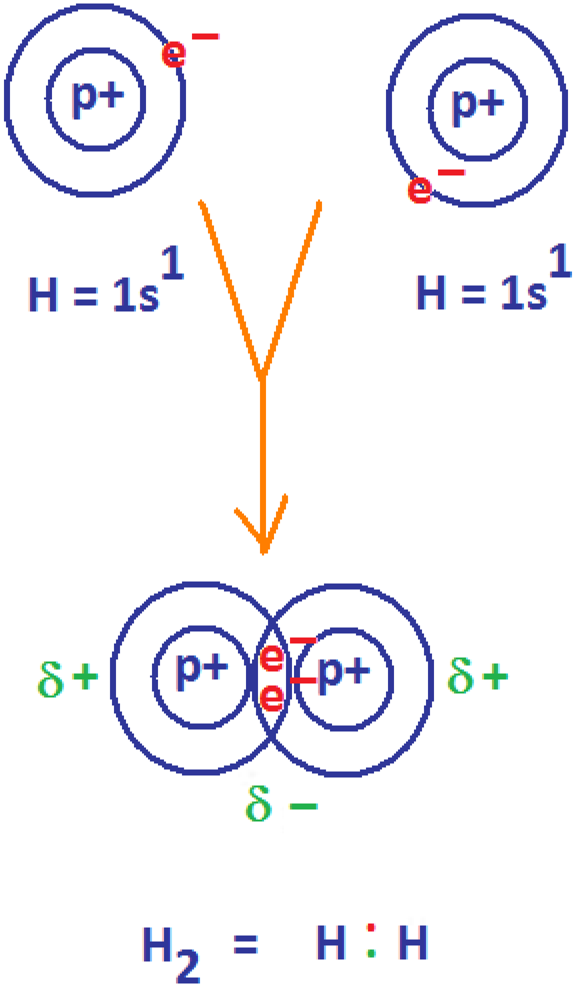
Molecular Geometry and Orbital Hybridization

Chemical Bonding & Reactions

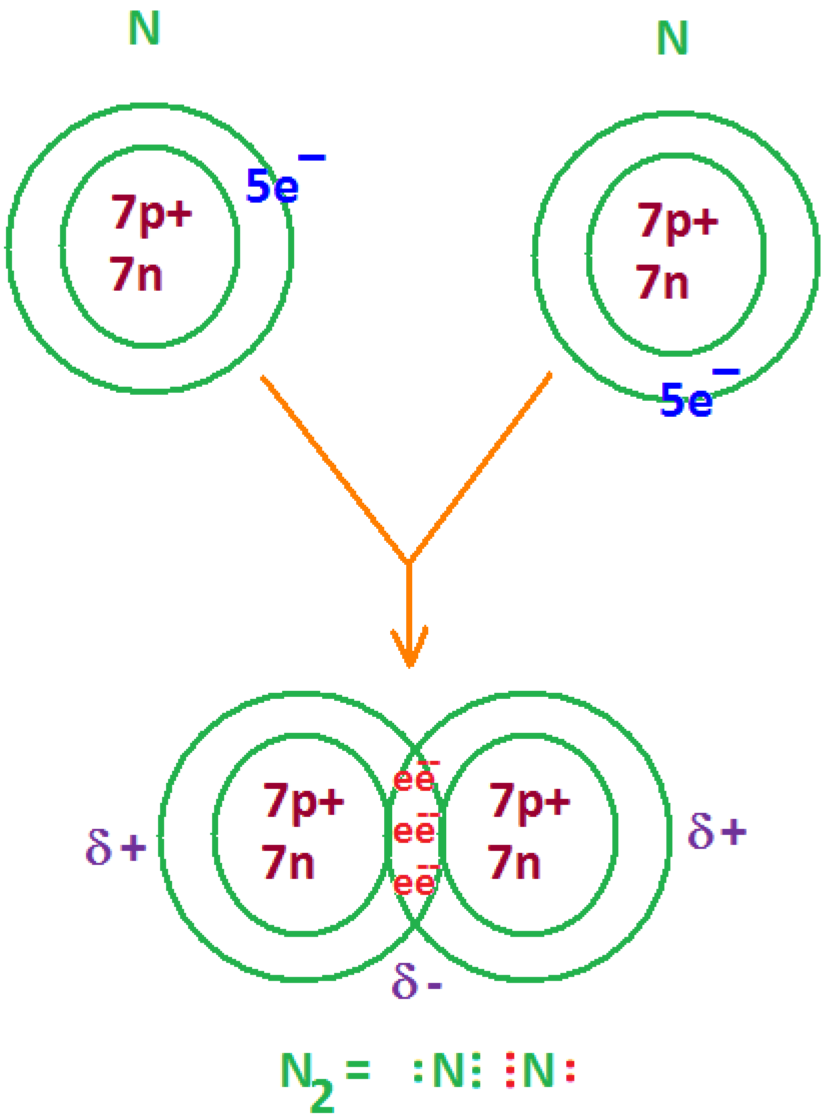


Covalent Compounds

- Covalent compounds are formed by a chemical bond that occurs between two atoms by sharing electrons -- NOT gaining or losing.
- The Figure illustrates a simple covalent bond between two atoms of hydrogen (NOTE: hydrogen, nitrogen, oxygen, fluorine, chlorine, bromine and iodine prefer to function as molecules in their elemental states held together by covalent bonds).
- Note that at the bottom of the graphic that there are three distinct regions about the molecular hydrogen: there are 2 regions that are electron deficient and 1 region that is electron dense due to the electron overlap/sharing.
- The region that is deficient in electrons is said to be partially positive (δ+; electropositive) and the region that is electron dense is said to be partially negative (δ-; electronegative).
- This covalent bond still follows the octet rule.



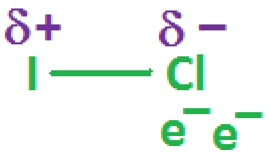
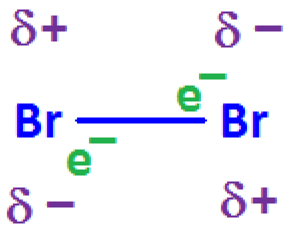
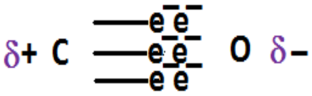
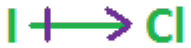
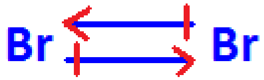
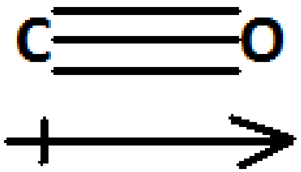
- The Figure shows the covalent bonds between two atoms of nitrogen to form molecular nitrogen.
- Note that there is a triple bond present -- note also that it takes 2 electrons to make each single bond.



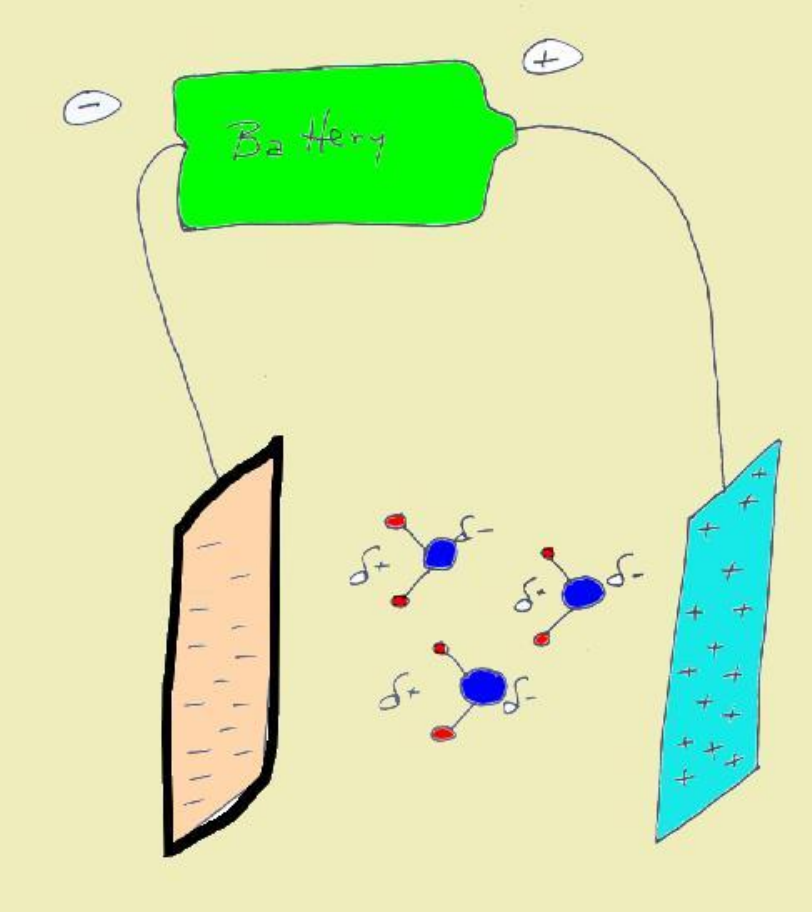
When discussing covalent molecules, there are several terms one must know in order to fully appreciate the diversity of these molecules. These terms are summarized in the table, below:

Nonpolar covalent bond	**A covalent bond in which the bonding pair of electrons is shared equally by the bonded atoms.**
Polar covalent bond	**A covalent bond that shows bond polarization (bonding electrons are not shared equally).**
Bond polarization	**The attraction of the shared electrons to the more electronegative atom of a bonded pair of atoms.**
Electronegativity	**The tendency of an atom to attract shared electrons of a covalent bond.**
Dipolar force	**The attractive force that exists between the positive end of one polar molecule and the negative end of the same molecule.**
Polar molecule	**A molecule with polarized bonds which results in asymmetrical distribution of charge.**
Nonpolar molecule	**Molecules with nonpolarized bonds which results in symmetrical distribution of charge.**

- Remember from previous discussions that the most electronegative element on the periodic table is fluorine; the most electropositive element is Francium.
- Utilizing the above definitions and the previous statement, let's see if we can determine by two methods if a molecule contains a polar or non-polar covalent bond.
- The first method is the "eyeball" method.
- Let's consider three molecules: ICl, Br_2 and CO.
- Let's set them side-by-side in the table, next slide, and walk through this method a step at a time.

	ICl	Br_2	CO
Step 1: identify most electronegative atom	**Cl**	**Br and Br**	**O**
Step 2: draw electrical orientation			
Step 3: draw direction of polarization			
Step 4: identify type of bond (not James, either)	**Polar covalent bond**	**Non-polar covalent bond**	**Polar covalent bond**

- Another way in which to think of polar molecules is to think of water with two electrodes suspended in it attached to a battery.
- Polar molecules align themselves electronically, i.e., by charge, in an electrical field:
  - the partially positive part of the molecule (red hydrogens) is aligned with the negative electrode and
  - the partially negative part of the of the moleceule (blue oxygens) is aligned with the positive electrode -- "in essence" closing the circuit.



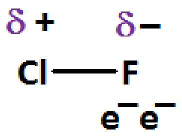
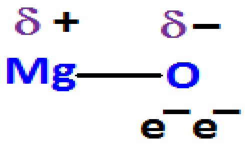
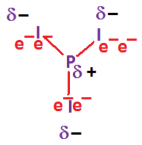
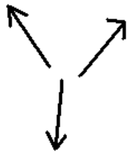
The second method requires the utilization of a chart of known electronegativities:

		H **2.1**					
Li **1**	**Be** **1.5**		**B** **2**	**C** **2.5**	**N** **3**	**O** **3.5**	**F** **4**
Na **0.9**	**Mg** **1.2**		**Al** **1.5**	**Si** **1.8**	**P** **2.1**	**S** **2.5**	**Cl** **3.0**
K **0.9**	**Ca** **1.0**		**Ga** **1.6**	**Ge** **1.8**	**As** **2.0**	**Se** **2.4**	**Br** **2.8**
Rb **0.8**	**Sr** **1.0**		**In** **1.7**	**Sn** **1.8**	**Sb** **1.9**	**Te** **2.1**	**I** **2.5**
Cs **0.7**	**Ba** **0.9**						

- The chart is not complete; it will suffice for this discussion.
- As far as I'm concerned, the units are unimportant.
- It's the concept that I want you to get.
- The value of this method is that the extent of bond polarization is proportional to the difference in electronegativity (ΔEN) between the bonded atoms.
- When computed, a number is obtained that fits into one of the three ranges tabulated, below:

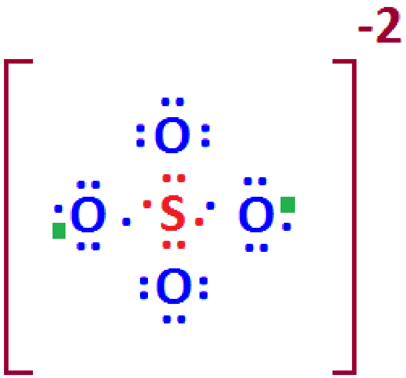
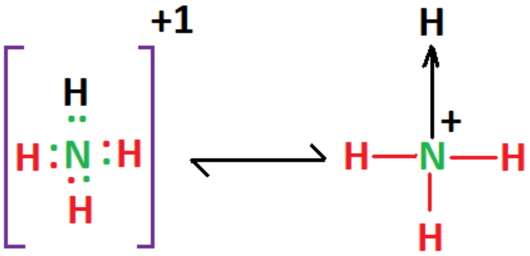
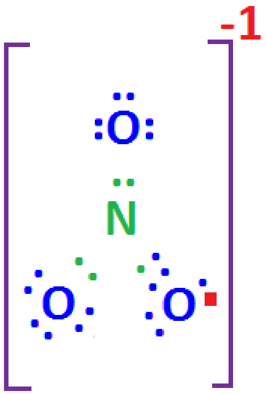
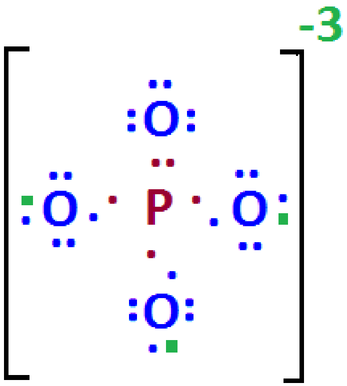
Range	Bond type
0	Non-polar covalent
0 - 2.0	Polar covalent
>2.0	Ionic

Let's run three examples as we did, before,
only this time compare the "eyeball" method with this electronegativity method.
We'll use ClF, MgO and PI_3 as our examples.
As before, links are below, as well to illustrate the process.

	ClF	MgO	PI_3
Most electronegative atom	**F**	**O**	**I**
Electrical orientation			
Polarization direction			
Bond type by eyeball	**Polar covalent**	**Polar covalent**	**Polar covalent**
Δ EN	**4-3=1**	**3.5-1.2=2.3**	**(2.5-2.1)*3=1.2**
Correct bond-type	**Polar covalent**	**Ionic bond**	**Polar covalent**

- Binary compounds are pretty simple.
- Not all covalent substances are as simple.
- Polyatomic ions are ions that are bound covalently to each other with a net charge.
- Most polyatomic ions are negatively charged.

Examples of polyatomic ions are tabulated, below:

Name	**Formula**	**Name**	**Formula**
	SO_4^{2-}		NH_4^+
Sulfite	SO_3^{2-}	**Bicarbonate**	HCO_3^-
	NO_3^-		PO_4^{3-}
Nitrite	NO_2^-	**Arsenate**	AsO_4^{3-}
Carbonate		CO_3^{2-}	

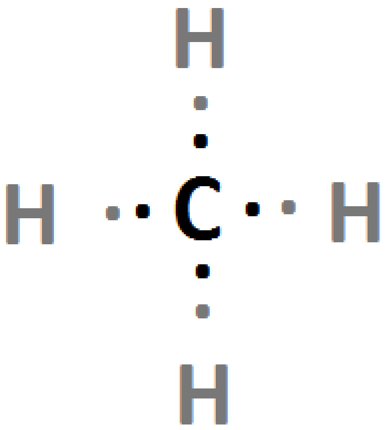
- The ammonium ion is a bit different from the other polyatomic ions -- besides being the only cation mentioned.
- It also contains a coordinate covalent bond.
- A coordinate covalent bond is a bond between 2 atoms in which one atom donates the 2 electrons (both electrons) to make the bond.
- In the case of the ammonium ion, the coordinate covalent bond occurs between the unbonded pair of electrons in nitrogen and the extra hydrogen ion (proton) to make the polyatomic cation.
- A coordinate covalent bond is drawn as an arrow going from the two electrons' source to the electron acceptor.
- Remember that ammonia is neutral; the ammonium ion has the extra charge due to an extra proton and no electron to balance it out.

- Covalent bonds share electrons, i.e., one electron from one element will be shared with one electron from another element to form the bond between the two.
- Two electrons, then, are required to make a single bond between two atoms.
- **That's concept 1 to walk away with prior to getting into this topic.**
- **The second concept to walk away with prior to going through orbital hybridization is to accept as fact that all orbitals are present around each atom.**
- Only those orbitals closest to the nucleus in sequential order fill so as to create an electron "cloud" around nucleus at optimal energies.
- The remainder of the orbitals is the topic for further discussion in another course.
- **The third concept to walk away with is that when we speak of orbital hybridization, we're talking about hybridization in the same case as if we were to cross a pure red flower with a pure white flower to obtain the hybrid, the pink flower.**
- In other words, the hybrid is somewhere in between the pure -- or elemental -- states.
- In the case of hybrid orbitals, the new orbitals will have energies that are lower than an energy-rich pure state and higher than an energy-poor state.

- With that introduction, let's get started understanding how the sharing of electrons for the formation of a covalent bond works.
- As our first example, we'll examine methane, Figure, right.
- Note that in this representation of methane, CH_4, that each bond consists of 2 electrons --

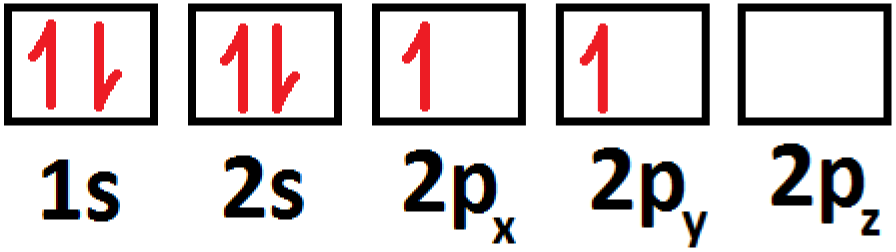
  one electron from C (●) and one electron from

  H (●).
- These electrons in the bond are shared, remember.
- So, how does this happen?

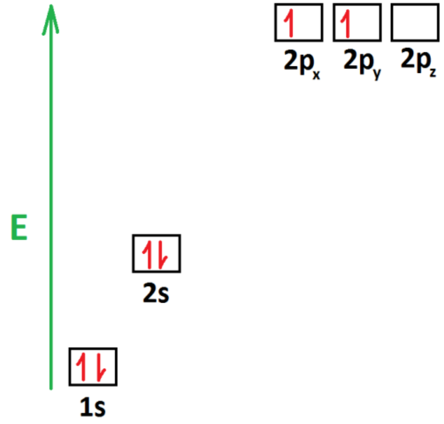


- The figure, below, illustrates the ground, or elemental, electronic configuration of carbon and of hydrogen.
- Note that, in carbon, that there are two sets of paired electrons and two sets of unpaired electrons.
- Remember that carbon is in Group IV on the periodic table and will make four bonds.
- Remember, too, that these 4 electrons have to be shared and that that will not happen until the second set of paired electrons is "split up" so that there are 4 unpaired electrons to share to make 4 single bonds with 4 hydrogen atoms.

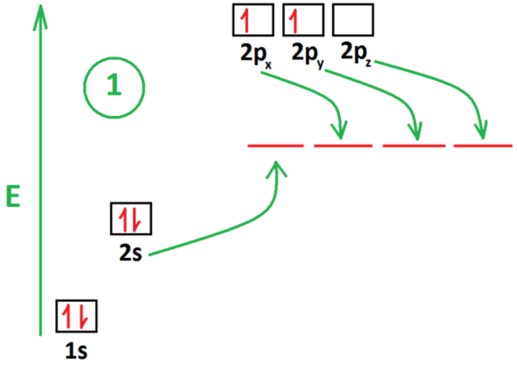
$$C = 1s^2 2s^2 2p^2$$

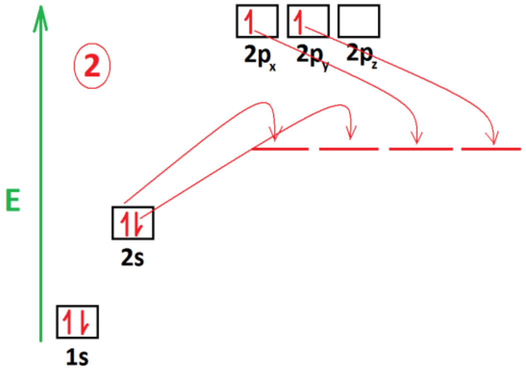


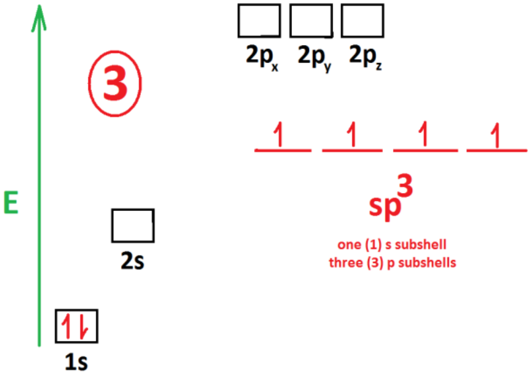
Figure, right, shows a representation of the ground state orbitals in terms of energy moving away from the nucleus (bottom of graphic) out (top of graphic).



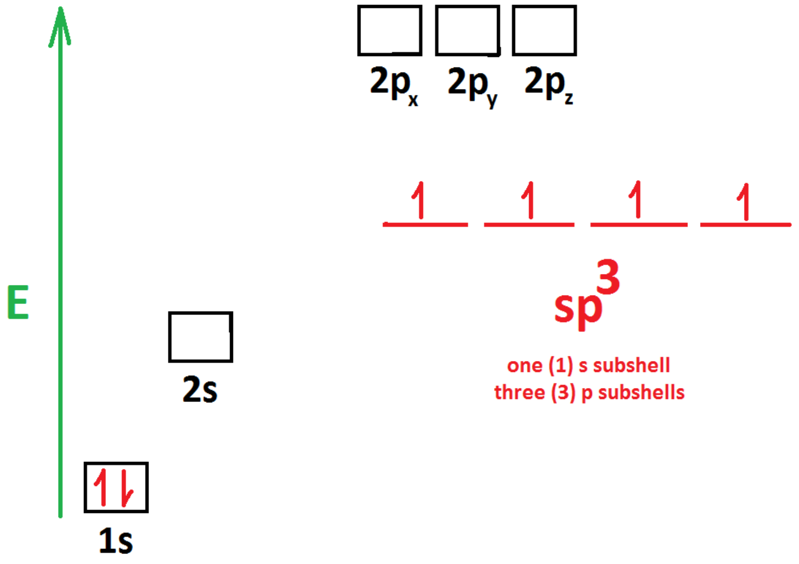
- Figures, below, shows what has to happen for the two 2s electrons to separate.
- In brief, the 2s and all three 2p sub-orbitals must gain and lose, respectively, energy **(1)** in order to force the separation of the two 2s electrons into unpaired electrons at the same energy as the two 2p electrons.
- In order for this to happen, the three 2p orbitals give up energy to drop down **(2)**; the 2s orbital gains the energy to come up a bit and to split the two 2s electrons up **(3)**.



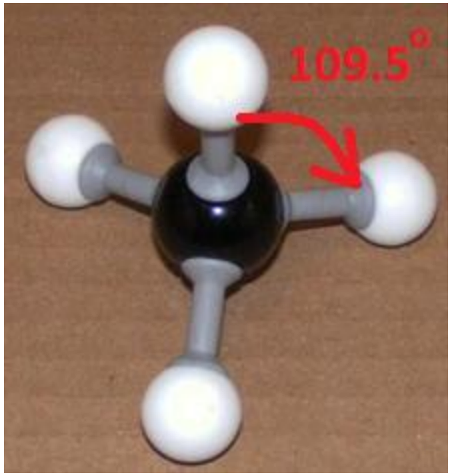


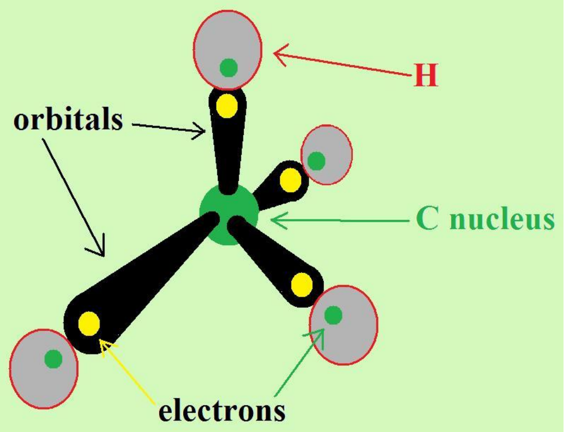


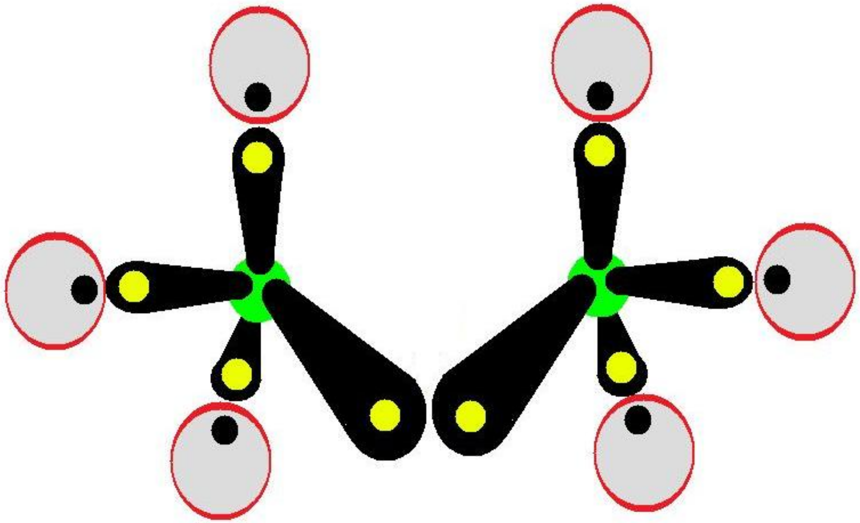
- The result is seen at right
- While the 2s and 2p orbitals are shown as empty, the key is to remember that they are no longer "around" and that there is a new hybrid orbital.
- That new orbital contains all 4 electrons, unpaired, and is called an sp^3 hybridization.
- An sp^3 hybridized orbital is so called because one of the s orbitals and three of the p orbitals underwent energy differences (hybridization) to accommodate the splitting up of the elemental 2s electrons.
- This is the hybridization that carbon undergoes when it has 4 single bonds around it.



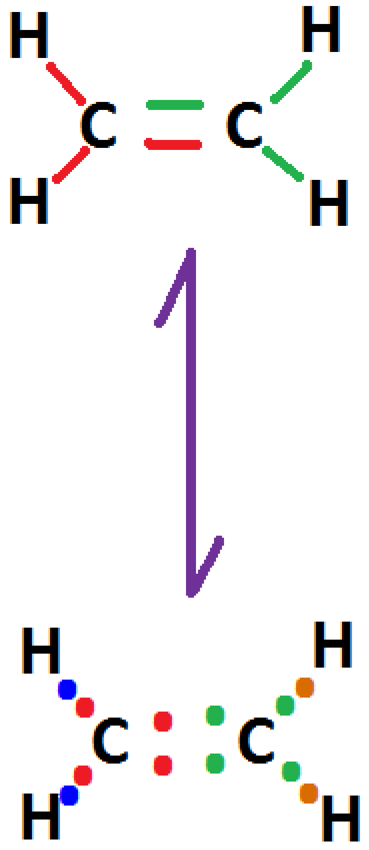
- Once we alter the orbitals, the shape (geometry) changes, as well.
- The shape of one **sp^3** orbital is teardrop.
- Carbon has four of them.
- When they are arranged around the carbon nucleus, there are 109.5° between each orbital.
- What this means is that the actual shape of an sp^3 hybridized atom is that of a tetrahedron -- a three-legged milking stool with a flag-pole.
- Note, too, that another way in which to remember the geometry is to add up one s shell with three p shells to get four total shells.
- These four shells correspond to the placement for 4 individual electrons at the top, more or less, of each inverted teardrop-shaped orbital.
- BTW: I use the terms shells and orbitals interchangeably.



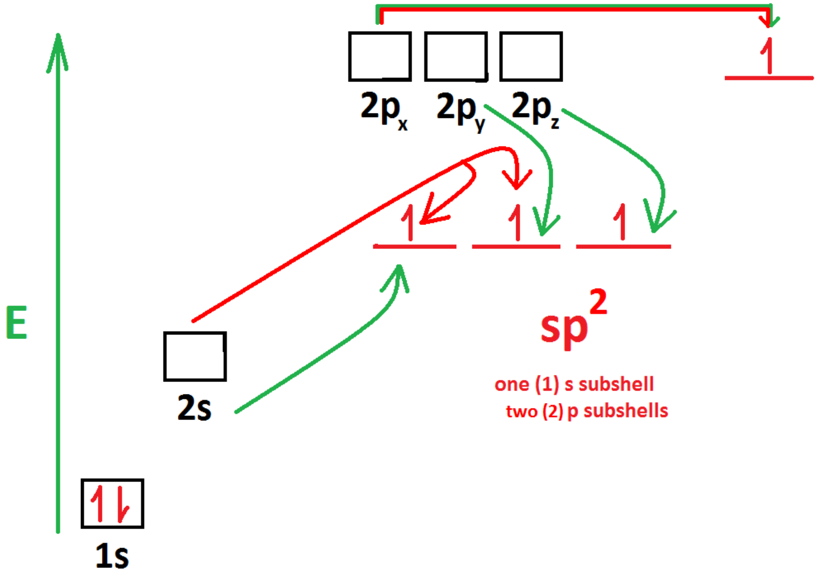




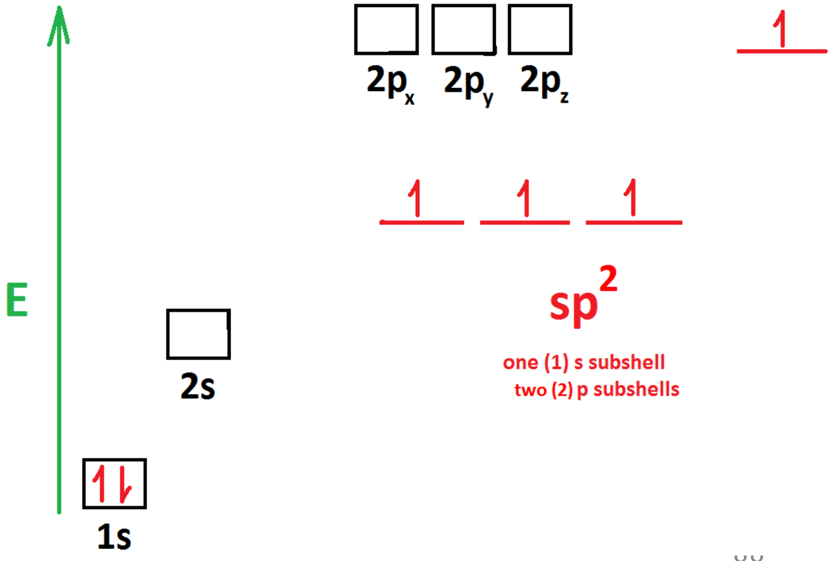
- Not all carbon compounds have all single bonds about the carbon atoms.
- Some have double bonds.
- If a single bond consists of 2 shared electrons, it follows that a double bond consists of 4 shared electrons, i.e., 2 electrons per bond still.
- The simplest carbon compound that contains a double bond between carbon atoms is ethylene (common name), right.
- In order for the carbon to form these two bonds between each carbon atom, a different hybridization has to occur.



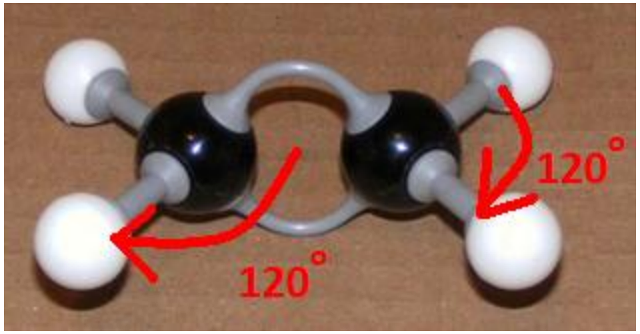
- The difference between hybridization to make four single bonds around carbon and to make a double bond and two single bonds around carbon is the rearrangement of the electrons:



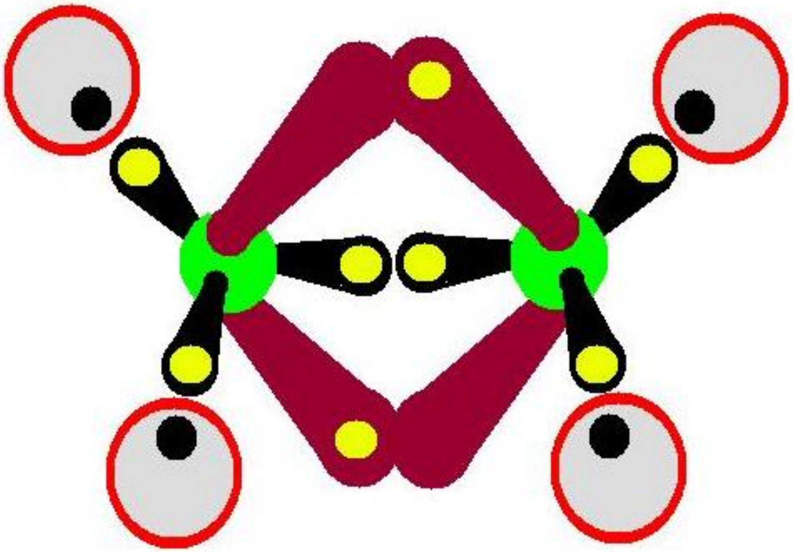
- Note that in this case, that two of the 2p orbitals give up energy so that the 2s orbital may gain it and split up the two 2s electrons. During this process, one of the 2p electrons remains in a "standard" 2p sub-shell, below. This is significant and we'll touch on that in a moment.



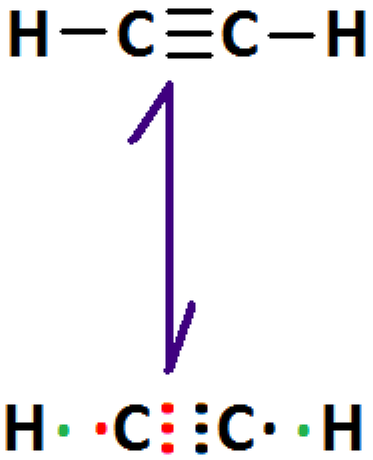
- When carbon has two single bonds and one double bond on it, it is in sp^2 hybridization.
- The shape about the carbon atoms in this hybridization, given 3 sp^2 orbitals, is triangular, planar triangular or trigonal planar, right.
- Each hybrid orbital is separated by 120° bond angles.
- As with the sp^3 hybrid, one may also derive the number of electrons from the hybridization, i.e., one s orbital and two p orbitals hybridize to separate 3 electrons.
- The fourth electron will be discussed, shortly.



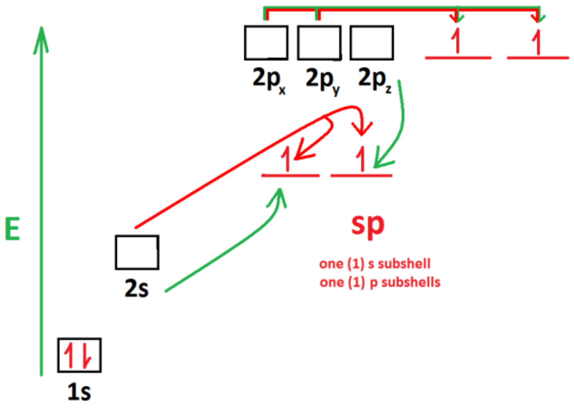
- sp^2 hybridization accounts for only one of the two bonds in the double bonds.
- The second bond in the double bond comes from the lone 2p electron.
- Here's how it works: the p orbital's geometry is dumb-bell shaped.
- When it is overlapped with the sp^2 hybrid orbitals, right, two kinds of bonds occur between the carbon atoms.
- The first is an end-to-end bond where the orbitals butt up against the other.
- This kind of bond is called a sigma (σ) bond and comes from the sp^2 hybrids.
- The second bond to make the double bond comes from side-to-side, top-to-top and bottom-to-bottom overlap of the p orbital.
- This bond is called a pi (π) bond.
- To reiterate, the first of the double bond is sp^2; the second of the double bond is p.
- In order for the second bond to form completely, there must be overlap from top and bottom.
- This becomes very important in the lectures on organic chemistry that focus on aromatic compounds.



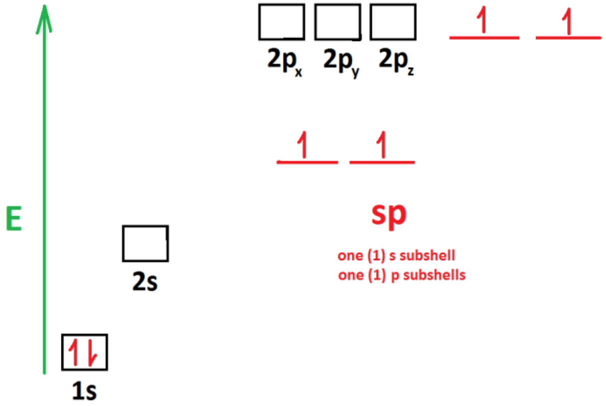
- The third, and last, carbon-based bond we'll examine is the triple bond. The simplest carbon-based compound that has a triple bond (three bonds; total of 6 electrons shared) is acetylene (common name), Figure, right.



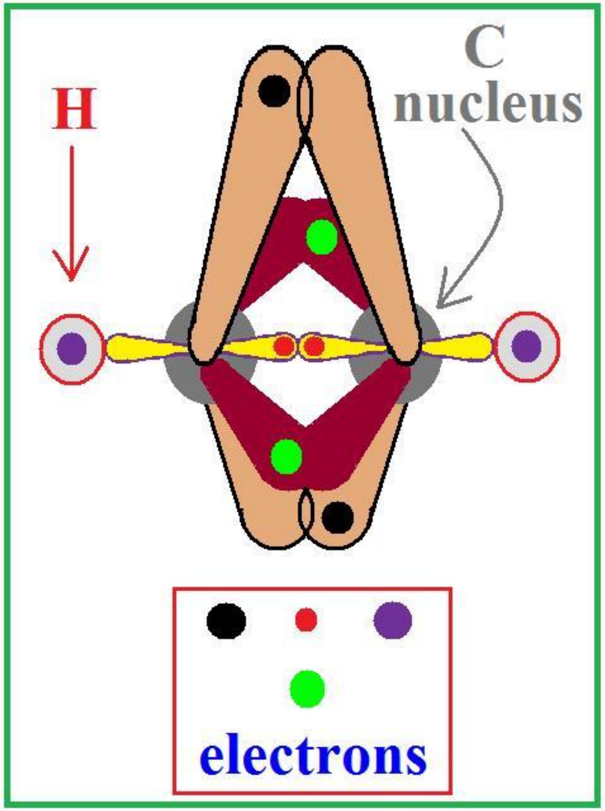
- While there are still four bonds on each carbon atom, three of those bonds are between the two carbon atoms. Figure, below, illustrates the mechanics that must occur in order for this new hybridization to actuate.



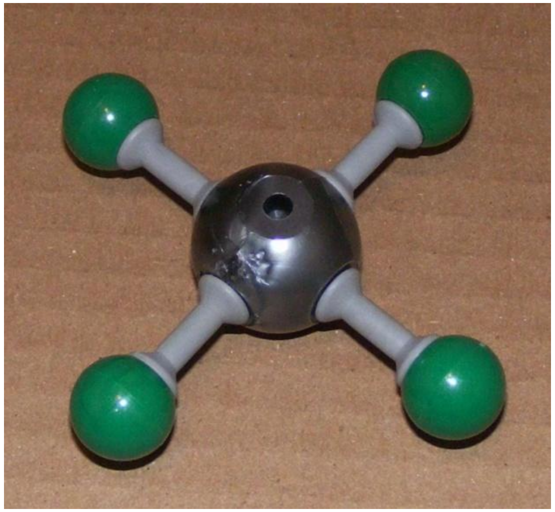
- Note that in this case, the 2s orbital absorbs the energy given off by one of the 2p orbitals to give the new hybrid, below.
- This new hybrid is called an **sp** hybrid; note that the two 2p electrons remain in "standard" 2p orbitals.
- When a carbon atom has one single bond and one triple bond about it, it is said to be in sp hybridization.
- What about the shape of the molecule?
- It is linear, i.e., the geometry about the two carbon atoms is arranged in a straight line with 180° bond angles between them.
- As the shortest distance between two points is a straight line, the sp orbital (one s shell and one p shell) may be easily remembered as 1+1 = 2.



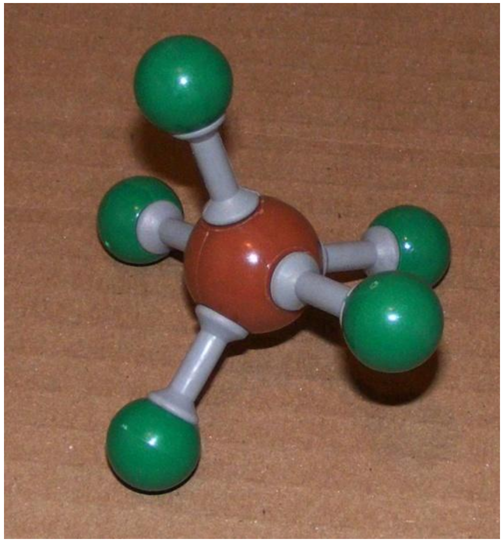
- sp hybridization accounts for only one of the three bonds about the two carbon atoms in the triple bonds.
- The actual sp hybridized orbital provides electrons for the end-to-end sigma bonds; the remaining two 2p orbitals provide the last two sets of electrons to form pi bonds to "seal it up", Figure, right.



- Carbon is not the only atom to undergo orbital hybridization in order to make bonds.
- In many cases the hybridization pattern may be concluded by examining the periodic table and counting electrons in outer shells, e.g., Be is in Group II and undergoes sp hybridization yielding linear (aka digonal) geometry, B is in Group III and undergoes sp^2 hybridization yielding trigonal planar geometry

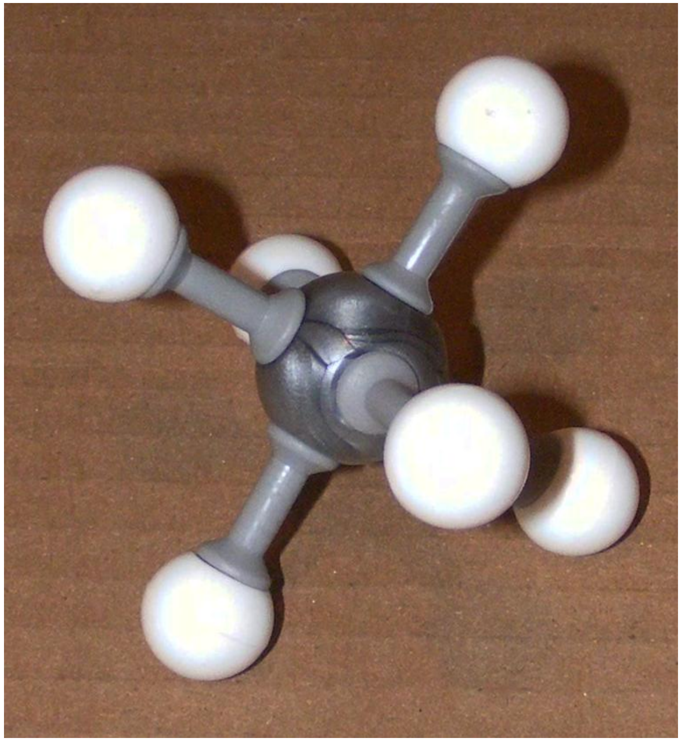


- Less obvious are Pt, Pd and Ni which undergo dsp^2 hybridization to give a square planar geometry -- note that sp^3 and dsp^2 hybrids are distinctly different hybridizations.

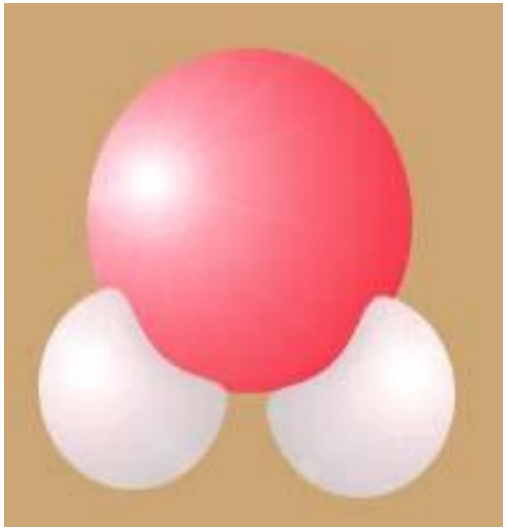


- Likewise, it's not always possible to determine that P (in a +5 state) undergoes dsp^3 hybridization to yield trigonal bipyramidal geometry, Figure, right .
- Do you see the 5 bonding sites?

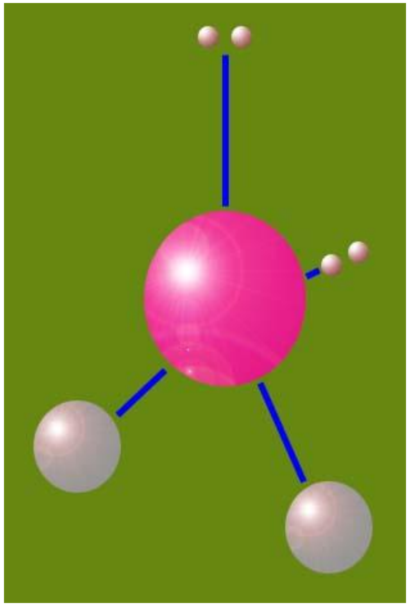
- or that S (in a +6 state) undergoes d^2sp^3 hybridization to give an octahedral geometry, Figures.
- Do you see all 6 binding sites?

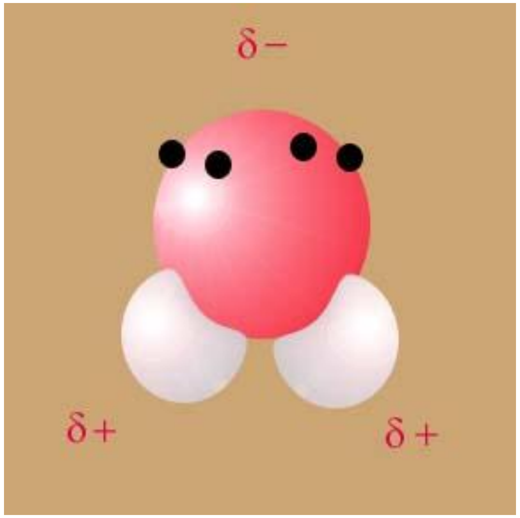


- A strange hybridization requires some additional discussion.
- This has to do with how oxygen hybridizes to form water.
- Oxygen is in group VI on the periodic table and its electronic configuration is $1s^2 2s^2 2p^4$, where there are 2 unpaired 2p electrons.
- In the older literature, oxygen was said to have undergone p^2 hybridization.
- This gave a geometry around the oxygen in water that was angular.



- The newer literature shows that oxygen undergoes a strange sp^3 hybridization.
- This is a slightly different look at sp^3 hybridization than what we have become accustomed to.
- When we examined it earlier, we saw that there were 4 unpaired electrons at each sp^3 hybrid orbital.
- In the case of oxygen in water, there are two sp^3 hybrids with an electron each and two sp^3 hybrids with one PAIR of electrons, each, giving the tetrahedral geometry, right.
- The tetrahedral geometry better explains the surface tension of water and properties of ice (floats) than does the angular geometry.
- Be aware that both explanations are still "out there", though. More coming in the lecture on water.





Water forms hydrates.
A hydrate is defined as the evaporation product
of an aqueous solution of a soluble salt.
The water with the salt is called
water of hydration or water of crystallization.
Examples of these follow in the table, below:

Name	Formula	Name
Epsom salts	$MgSO_4 \cdot 7H_2O$	Magnesium sulfate heptahydrate
Alum	$KAl(SO_4)_2 \cdot 12H_2O$	Potassium aluminum sulfate dodecahydrate
Plaster of Paris	$CaSO_4 \cdot 1/2H_2O$	Calcium sulfate hemihydrate
Gypsum	$CaSO_4 \cdot 2H_2O$	Calcium sulfate dihydrate
Glauber's salt (cathartic)	$Na_2SO_4 \cdot 10H_2O$	Sodium sulfate decahydrate
Blue vitriol	$CuSO_4 \cdot 5H_2O$	Copper sulfate pentahydrate

Hydrated compounds that lose water of hydration when exposed to air
are said to effloresce.
A substance that can remove moisture from the air is called hygroscopic.
A deliquescent substance is that substance that is hygroscopic and
removes enough water from the air to dissolve itself completely.

Hydrate Structure

There are five forms of hydrates:

1. **Water of hydroxylation. The structural unit is the hydroxide ion. Removal of this "water" leads to disruption of the crystalline structure.**
2. **Water of coordination. In this case the water is joined by the metal ion by coordinate bonds, e.g., $BeSO_4 \cdot 4H_2O$ is really $[Be(H_2O)_4]^{2+}[SO_4]^{2-}$. This water is essential to the stability of these crystals.**
3. **Anion water. In this case, the water is attached to the anion by hydrogen bonding, e.g., $CuSO_4 \cdot 5H_2O$ is really $[Cu(H_2O)_4]^{2+}$ (waters of coordination) and $[SO_4(H_2O)]^{2-}$ (anion water).**
4. **Lattice water. Water is in the crystalline lattice, but it is not attached to either cation or anion, e.g., $KAl(SO_4)_2 \cdot 12H_2O$ is really $K^+[Al(H_2O)_6]^{3+}[SO_4]_2^{2-}$ (coordination water) plus $6H_2O$ (in lattice, but not bonded with the potassium ion).**
5. **Zeolitic water. This water occupies random positions in the crystal. Loss or gain of these waters do not change crystalline structure.**

Chemical Reactions

Now that we've gone through some elementary bonding concepts,
it's time to get down to some nitty-gritty with reactions.
Chemical reactions may be subdivided into main categories: non-redox and redox.
Each of these two categories may be further sub-divided into three more categories, apiece.
The categories of reactions are illustrated, below:

Chemical Reactions					
Non-Redox			Redox		
Combination	Double Replacement (Metathesis)	Decomposition	Combination	Single Replacement (Substitution)	Decomposition

Decomposition Reactions	
In this kind of reaction, a single substance is broken down to form 2 or more simpler substances	
$X \rightarrow Y + Z$	
Redox Examples	Non-Redox Examples
$2MgO \rightarrow 2Mg + O_2$ $2Ag_2O \rightarrow 4Ag + O_2$ $ZrI_4 \rightarrow Zr + 2I_2$ $KClO_3 \rightarrow KCl + O_2$	$MgCO_3 \rightarrow MgO + CO_2$ $H_2CO_3 \rightarrow CO_2 + H_2O$ $PbCO_3 \rightarrow PbO + CO_2$

- The fastest way to identify whether a reaction is a redox or non-redox type is to look at the reaction and see if there is a change in charge or not.
- If an element is used or formed, it's probably a redox.
- If there's no charge change, it's probably a non-redox.

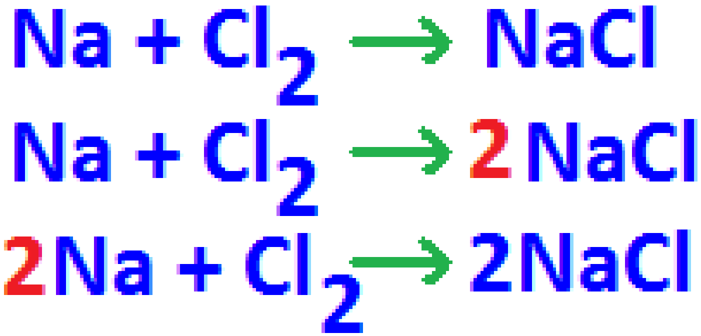
Combination Reactions	
These reactions are also known as (aka) addition or synthesis reactions. In this type of reaction, 2 or more substances react to form a single substance	
$D + E \rightarrow F$	
Redox Examples	Non-redox Examples
$2Ca + O_2 \rightarrow 2CaO$ $H_2 + Cl_2 \rightarrow 2HCl$ $4Al + 3O_2 \rightarrow 2Al_2O_3$ $Zr + 2I_2 \rightarrow ZrI_4$ $N_2 + 3H_2 \rightarrow 2NH_3$	$SO_3 + H_2O \rightarrow H_2SO_4$ $SO_2 + H_2O \rightarrow H_2SO_3$

- The fastest way to identify whether a reaction is a redox or non-redox type is to look at the reaction and see if there is a change in charge or not.
- If an element is used or formed, it's probably a redox.
- If there's no charge change, it's probably a non-redox.

Replacement Reactions	
Single Replacement	Double Replacement
Always redox; 1 element reacts with a compound and displaces another element from the compound.	aka Metathesis or neutralization reaction; **not redox**; "partner swapping"; tends to occur in aqueous solution.
$A + CX \rightarrow C + AX$	$CX + DY \rightarrow CY + DX$
Iron stripped from ore with C: $3C + 2Fe_2O_3 \rightarrow 4Fe + 3CO_2$	$KOH + HNO_3 \rightarrow KNO_3 + H_2O$

- The fastest way to identify whether a reaction is a redox or non-redox type is to look at the reaction and see if there is a change in charge or not.
- If an element is used or formed, it's probably a redox.
- If there's no charge change, it's probably a non-redox.

- Now that we've got the 6 fundamental types of reactions down, let's take a look at chemical reaction nomenclature, Figure, Below.
- Those chemicals that are on the left of the arrow are the reactants and those on the right are the products.
- Reactants under go change during the reaction and products are substances that are formed as a result of the reaction.
- A coefficient goes in front of the whole chemical formula and applies to the whole chemical formula just like an algebraic equation.
- A subscript goes beneath and behind the only element to which it applies. In the example, overall, there are 2 chlorine atoms on the reactant side and two on the product side of the reaction.
- The whole reaction in the graphic is balanced, i.e., there are the same numbers of sodium atoms on both sides of the reaction and there are the same numbers of chlorine atoms on both sides of the reaction.
- The balanced reaction is consistent with the Law of Conservation of Matter: atoms are neither created nor destroyed in chemical reactions, only rearranged.



$$Na + Cl_2 \rightarrow NaCl$$

$$Na + Cl_2 \rightarrow 2\,NaCl$$

$$2Na + Cl_2 \rightarrow 2NaCl$$

- So with this succinct introduction, let's begin balancing some simple chemical reactions.
- Probably the very best thing to remember about these is that if you make like atoms in compounds are ions and know their charges -- or can derive them quickly -- you can balance most in a short time with a little practice.
- Our first example is $Mg + O_2 \rightarrow MgO$.
- On the left side of the reaction, both elements have an individual charge of zero.
- On the right side, the Mg has an effective charge of +2 (it's in group II) and oxygen an effective charge of -2 (it's in group VI).
- The charges balance out.
- The drawback is that there are 2 oxygens on the left and one on the right.
- We'll put a 2 in front of the MgO which also gives us 2 magnesiums on the right.
- Put a 2 in front of the Mg on the left and the equation is balanced:

$$2Mg + O_2 \rightarrow 2MgO$$

- The second example is $LiOH + H_2SO_4 \rightarrow H_2O + LiSO_4$.
- In this example, the Li has an effective charge of +1.
- The hydroxide ion (OH-) has a charge of -1.
- Sulfuric acid is balanced as sulfate is -2 and there are 2 hydrogens to balance that.
- Water is balanced, charge-wise.
- Since we already knew that Li has a charge of +1 and sulfate of -2, we know that there has to be 2 lithiums to make lithium sulfate -- we'll ad that 2 as a subscript behind the Li to make Li2SO4.
- Since there are 2 lithiums on the right, we'll put a 2 in front of the LiOH to make 2LiOH.
- There are 6 oxygens on the left. To make 6 on the right, we'll put a 2 in front of the water.
- The final balanced equation is:

$$2LiOH + H_2SO_4 \rightarrow 2H_2O + Li_2SO_4$$

- The third example is $Ni(NO_3)_2 + K_2S \rightarrow NiS + KNO_3$.
- Nitrate has a charge of -1.
- There are 2 of them to balance out for the +2 charge on the nickel.
- Two potassiums neutralize the charge from the sulfide (-2).
- This equation is actually much easier than the previous one.
- We know there are 2 potassiums and 2 nitrates on the left of the reaction, hence, we'll put a 2 in front of the KNO_3 on the right.
- The balanced reaction is:

$$Ni(NO_3)_2 + K_2S \rightarrow NiS + 2KNO_3$$

- Our fourth example is:

$$AgNO_3 + BeCl_2 \rightarrow AgCl + BeNO_3$$

- Ag has a charge of +1; nitrate, -1.
- Be is in group II and has a charge of +2; chloride of -1.
- There are 2 chlorides to balance out the charge with the Be.
- Let's start by putting a 2 in front of the AgCl to balance out the chlorides on each side of the reaction.
- When we do that, we have to put a 2 in front of the $AgNO_3$.
- Since we've done that, we've got to put parentheses around the NO_3 in $BeNO_3$ to make $Be(NO_3)_2$.
- The balanced equation is:

$$2AgNO_3 + BeCl_2 \rightarrow 2AgCl + Be(NO_3)_2$$

- The fifth example is $Al + H_2SO_4 \rightarrow AlSO_4 + H_2$.
- Al on the left has zero charge -- it's an element.
- Sulfate is -2 and hydrogen is +1 on the left side; on the right, hydrogen has zero charge -- another element.
- On the right, Al has a +3 charge. Let's focus on the $AlSO_4$.
- Al has a charge of +3; SO_4 has a charge of -2.
- In order for these two to balance, there has to be some lowest number common to them.
- In this case, it's 6 (2*3=6).
- The balanced form, then is $Al_2(SO_4)_3$.
- This means that a 2 goes in front of the Al on the left and a 3 goes in front of the sulfuric acid; a 3 goes in front of the elemental hydrogen on the right.
- The balanced reaction is:

$$2Al + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2.$$

- The last reaction is $C_2H_6 + O_2 \rightarrow H_2O + CO_2$.
- In this instance, it's actually easier to forget charges and focus on absolute numbers.
- There are 2 carbons on the left.
- We need to put a 2 in front of the carbon dioxide on the right.
- There are 6 hydrogens on the left.
- We need to put a 3 in front of the water on the right.
- There are 7 oxygens on the right, now.
- To make 7 on the left, we put a 31/2 in front of the O_2.
- It's actually balanced this way.
- The issue, though, is that most chemists hate using fractions in balanced reactions.
- Hence, we'll just double every coefficient and obtain the following as the balanced reaction:

$$2C_2H_6 + 7O_2 \rightarrow 6H_2O + 4CO_2$$

- And this is exactly how easy it is as long as you remember to keep track of the charges.

The Mole

- When you go to the bakery to buy 12 rolls, you are also buying a dozen rolls.
- When you go to the feed store and buy a ton of corn, you are also buying 2000 pounds of corn.
- When you buy a lot that measures about 44,000 square feet, you are also buying an acre.
- All of these are just another way of saying the same thing.

- Chemists do the same thing: when speaking about the number of particles contained in a sample of element or compound with its atomic or molecular mass expressed in grams, they are also speaking about a mole of that substance.

- For example, if you look at sulfur on the periodic table, you see that it has a mass of 32.1.
- Since we've discussed the mole, we can now put units on it that are better than atomic mass units: grams per mol (g/mol).
- That means that one mole of sulfur has a mass of 32.1 grams.
- If we were to look at chlorine on the periodic table, we now know that it has a mass of 35.5 grams per mole.
- That means that if we have 35.5 grams of chlorine, we have one mole of chlorine -- just another way of saying something in another way.

Let's look at some numerical examples.

Example 1:

Determine the mass in grams of 1.35 mol S.
Solution:

$$(1.35\,mol\,S)\,\frac{(32.1\,g\,S)}{1\,mol\,S} = 43.34\,g\,S$$

Example 2:

Determine the mass in grams of 1.5 mol Cu.

Solution:

$$(1.5\,mol\,Cu)\frac{(63.55\,g\,Cu)}{1\,mol\,Cu} = 95.33\,g\,Cu$$

Example 3:

Determine the mass in grams of 0.5 mol Ca.

Solution:

$$(0.5\,mol\,Ca)\frac{(40.1\,g\,Ca)}{1\,mol\,Ca} = 20.05\,g\,Ca$$

Example 4:

Determine the mass in grams of 0.10 mol HCl.

Solution: This one is slightly different: it involves a compound instead of just an element. Go to the periodic table and look up the atomic masses of H and Cl. Add them up (1 + 35.5 = 36.5 g/mol).

NOW it's just like the other problems:

$$(0.1 mol\ HCl)\frac{(36.5\ g\ HCl)}{1 mol\ HCl} = 3.65\ g\ HCl$$

Example 5:

Determine the mass in grams of 0.4 mol acetic acid ($HC_2H_3O_2$).

Solution: Do just like the previous example.

Go to the periodic table and look up the atomic masses for H, C and O (1, 12 and 16 g/mol).

Multiply the mass of H by 4, C by 2 and O by 2 – there are 4-H, 2-C and 2-O.

Add the totals up (4 + 24 + 32 = 60 g/mol). Do it just like the previous problem:

$$(0.4\ mol\ HC_2H_3O_2)\left(\frac{60\ g\ acetic\ acid}{1 mol\ acetic\ acid}\right) = 24\ g\ acetic\ acid$$

Example 6:

15 g HCl is how many mol HCl?

Solution: This is just a variation on a theme we've already done:

$$(15\,g\,HCl)\,\frac{(1\,mol\,HCl)}{36.5\,g} = 0.411\,mol\,HCl$$

Example 7:

30 g H_2SO_4 is how many mol H_2SO_4?

Solution: Go to the periodic table and
find the atomic masses for H (1), S (32.1) and O (16).
The molecular weight of sulfuric acid is 98 g/mol.

$$(30\,g\,H_2SO_4)\,\frac{(1\,mol\,H_2SO_4)}{98\,g\,H_2SO_4} = 0.306\,mol\;Sulfuric\;Acid$$

Example 8:
You have been given 49 g H_2SO_4.
You were told that this was 0.5 mol.
What is the molecular weight of sulfuric acid?
Solution: This is easier than it looks.
As long as you remember that the units on molecular weight are g/mol, you'll always be able to do this sort of problem:

$$Molecular\ weight = \frac{grams}{mol} = \frac{49\ grams\ H_2SO_4}{0.5 mol} = 98\ g / mol$$

Avagadro's Number

- One mole is not only equal to the gram-formula weight of a compound, but it is also equal to Avagadro's number (N_{Av}).
- This number is a constant and has many different units.
- For now, this number is $6.023*10^{23}$ atoms/mol.

Examples and Applications

Example 1:

$1*10^{23}$ atoms of NaOH is how many g NaOH?

Solution: Look up the atomic mass of Na (23), O (16) and H (1).

Add 'em up (40 g/mol) for the molecular weight of NaOH.

$$(1\times10^{23}\,atoms\,NaOH)\left(\frac{1\,mol}{6.023*10^{23}\,atoms}\right)\left(\frac{40\text{ g }NaOH}{1\,mol\,NaOH}\right)=6.64\,g\,NaOH$$

Example 2:

$4*10^{23}$ atoms of $NaC_2H_3O_2$ is how many g $NaC_2H_3O_2$?

Solution: Look up the atomic mass of Na (23), C (12), H (1)

and O (16) on the periodic table.

Add 'em up (82 g/mol) for the molecular weight of sodium acetate.

$$(4*10^{23}\,atoms\,NaC_2H_3O_2)\left(\frac{1\,mol\,NaC_2H_3O_2}{6.023*10^{23}\,atoms\,NaC_2H_3O_2}\right)\left(\frac{82\text{ g }NaC_2H_3O_2}{1\,mol\,NaC_2H_3O_2}\right)=54.46\text{ g }NaC_2H_3O_2$$

Example 3:
18.25 g of HCl is how many atoms of HCl?
Solution: Just run it backwards:

$$(18.25\,g\,HCl)\left(\frac{1\,mol\,HCl}{36.5\,g\,HCl}\right)\left(\frac{6.023*10^{23}\,atoms\,HCl}{1\,mol\,HCl}\right)=3.012*10^{23}\,atoms\,HCl$$

Example 4:
49 g H_2SO_4 is how many atoms of H_2SO_4?
Solution:

$$(49\,g\,H_2SO_4)\left(\frac{1\,mol\,H_2SO_4}{98\,g\,H_2SO_4}\right)\left(\frac{6.023*10^{23}\,atoms}{1\,mol\,H_2SO_4}\right)=3.012*10^{23}\,atoms\,H_2SO_4$$

That subject has been pretty well beaten to death.
Let's move onto another type of calculation: percent composition.
For any compound, XY,
the per cent composition of X or Y in XY is as follows:

$$\%X = \frac{X}{X+Y} \times 100 = \frac{molecular\ weight\ of\ X}{molecular\ weight\ of\ X + molecular\ weight\ of\ Y} \times 100$$

The per cent composition of Y in XY is as follows:

$$\%Y = \frac{Y}{X+Y} \times 100 = \frac{molecular\ weight\ of\ Y}{molecular\ weight\ of\ X + molecular\ weight\ of\ Y} \times 100$$

Example 1:

Calculate the per cent composition of N in $(NH_4)_2CO_3$:
Solution: Go to the periodic table and look up the
masses of N (14), H (1), C (12) and O (16). Add 'em up (96 g/mol):

$$\% N = \frac{28\, grams\, of\ nitrogen}{96\, grams\, (NH_4)_2CO_3} \times 100 = 29.17\%\ nitrogen$$

Example 2:

Calculate the per cent composition of carbon in CaC_2O_4.
Solution: as before. Ca's atomic mass is 40.1 g/mol.

$$\% C = \frac{24\, grams\, C}{128.1\, g\, CaC_2O_4} \times 100 = 18.74\%\, C$$

Example 3:
Calculate the % S in Fe_2S_3.
Solution: Same as before.

$$\% S = \frac{96\, g\, S}{207.7\, g\, Fe_2S_3} \times 100 = 46.22\% S$$

Review example:
How many atoms of S are in the previous example?
Solution:

$$(96\, g\, S) \frac{1 mol\, S}{32\, g\, S} \frac{6.023 * 10^{23}\, atoms S}{1 mol\, S} = 1.807 * 10^{24}\ Atoms$$

Empirical Formulas

- The empirical formula of a compound is defined as the "simplest whole number ratio of the atoms" in a compound.
- The best way to learn how to determine the empirical formula of a compound is to see the mechanics involved with the arithmetic manipulation of data:
- **E.g. 1: A compound contains 92.3% carbon and 7.7% hydrogen. Calculate the empirical formula of the compound.**

To solve this problem, there are four steps:

- 1) "Convert" % to grams.

92.3 g + 7.7 g = 100 g sample

- 2) Determine the number of moles of each atom in the sample.

$$92.3\,g\,C * \frac{1 mol}{12\,g\,C} = 7.69\,mol \approx 7.7\,mol$$

$$7.7\,g\,H * \frac{1 mol}{1 g\,H} = 7.7\,mol$$

- 3) Divide both numbers of moles by the smallest number of moles (this step reduces the numbers to usable amounts).

$$For\ C: \frac{7.7}{7.7} = 1$$

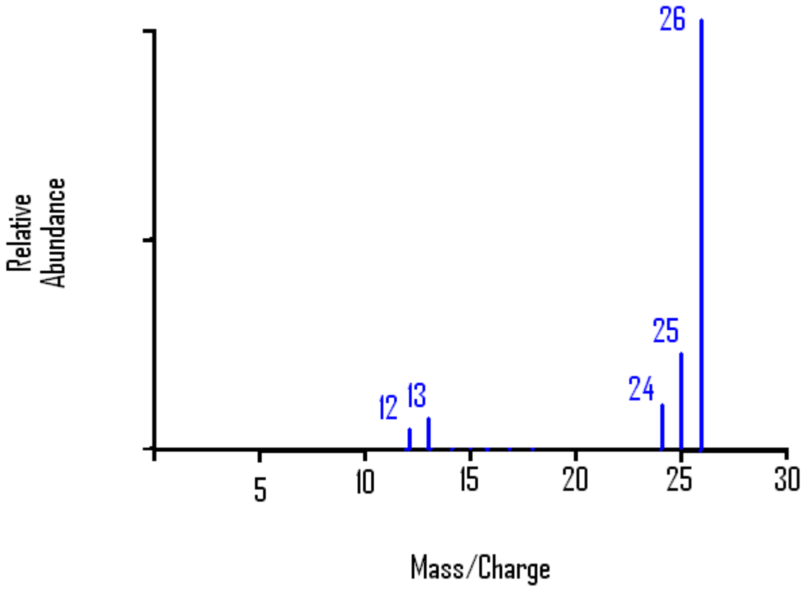
$$For\ H: \frac{7.7}{7.7} = 1$$

- 4) Write the empirical formula.
- C_1H_1 or CH
- What, though, would you do if you were told that the compound had a molecular weight of 26 and you needed to calculate the molecular formula?
- The simplest is to divide the molecular weight (26) by the empirical weight (13) and see that it is 2 (or twice as heavy as the empirical formula).
- Double the formula and you get: C_2H_2 or acetylene (ethyne).
- We take advantage of this knowledge when we perform mass spectroscopy.

Acetylene (Ethyne) Mass Spectrum

- Sample contains C and H.
- There is another way to determine the compound. That's to look at the smaller fragments and work forward.

- The smallest peak is 12 m/z
- The next smallest peak is 13 m/z
- 12 is pretty clear to be C
- 13 is equally as clear because there is only one element with a mass of 1: H, therefore, 13 must be for CH
- The peak with the highest MW is 26.
- 26/13 = 2, hence, the compound must be C_2H_2, or ethyne.



- The 25 peak is C_2H and the 24 peak is C_2

Percent Composition

That subject has been pretty well beaten to death.
Let's move onto another type of calculation: percent composition.
For any compound, XY,
the per cent composition of X or Y in XY is as follows:

$$\%X = \frac{X}{X+Y} \times 100 = \frac{\textit{molecular weight of } X}{\textit{molecular weight of } X + \textit{molecular weight of } Y} \times 100$$

The per cent composition of Y in XY is as follows:

$$\%Y = \frac{Y}{X+Y} \times 100 = \frac{\textit{molecular weight of } Y}{\textit{molecular weight of } X + \textit{molecular weight of } Y} \times 100$$

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Solution: Go to the periodic table and look up the masses of N (14), H (1), C (12) and O (16). Add 'em up (96 g/mol):

$$\% N = \frac{28\, grams\, of\ nitrogen}{96\, grams\, (NH_4)_2 CO_3} \times 100 = 29.17\%\, nitrogen$$

Example 2:

Calculate the per cent composition of carbon in CaC_2O_4.

Solution: as before. Ca's atomic mass is 40.1 g/mol.

$$\%\,C = \frac{24\ grams\,C}{128.1\,g\,CaC_2O_4} \times 100 = 18.74\%\,C$$

Example 3:

Calculate the % S in Fe_2S_3.

Solution: Same as before.

$$\%\,S = \frac{96\,g\,S}{207.7\,g\,Fe_2S_3} \times 100 = 46.22\%\,S$$

Chemical Reactions and the Mole

An earlier lecture dealt with the mole at the end of that section.

This discussion combines what you have already learned about the mole with what you've just learned about chemical reactions.

Example 1:
For the balanced chemical reaction
$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$,
determine the following: if 1 mole of $AgNO_3$ reacts with 1 mole of NaCl, how many moles of AgCl will be formed?
Solution: ALWAYS start by looking at the equation and making sure that it's balanced.
It's the chemical version of a recipe and is very important in these types of questions.
Secondly, always start with what you KNOW.

$$(1\,mol\ AgNO_3)\left(\frac{1\,mol\ AgCl}{1\,mol\ AgNO_3}\right) = 1\,mol\ AgCl\ formed$$

Note that we started with the 1 mol of $AgNO_3$
that we knew about and then using factor labeling,
built in the stoichiometry (atomic book keeping) from the balanced equation
and solved the problem.

Example 2: For the following balanced chemical reaction $2Ag_2O \rightarrow 4Ag + O_2$, determine the following: if 1.5 mol Ag_2O are heated to decomposition, how many mol Ag are formed? Solution: Just as we did, above:

$$(1.5\,mol\;Ag_2O)\left(\frac{4\,mol\;Ag}{2\,mol\;Ag_2O}\right) = 3\,mol\;Ag\;formed$$

Example 3:

For the following balanced chemical reaction $2HCl + Ba(OH)_2 \rightarrow BaCl_2 + 2H_2O$, determine the following: if you have 36.5 g HCl, how many mol $BaCl_2$ will be produced? Solution: This is just a variation on an earlier theme:

$$(36.5\,g\;HCl)\left(\frac{1\,mol\;HCl}{36.5\,g\;HCl}\right)\left(\frac{1\,mol\;BaCl_2}{2\,mol\;HCl}\right) = 0.5\,mol\;BaCl_2$$

Follow-up: How many grams is this?

$$(0.5\,mol\;BaCl_2)\left(\frac{(208.3\,g\;BaCl_2}{1\,mol\;BaCl_2}\right) = 104.2\,g\;BaCl_2$$

Example 4:
For the following balanced chemical reaction
$N_2 + 3H_2 \rightarrow 2NH_3$,
determine the following:
If you have 14 g nitrogen,
how many grams of NH_3 will be formed?
Solution: As before:

$$(14\ g\ N)\left(\frac{1 mol\ N}{14\ g\ N}\right)\left(\frac{1 mol\ N_2}{2\ mol\ N}\right)\left(\frac{2\ mol\ NH_3}{1 mol\ N_2}\right)\left(\frac{17\ g\ NH_3}{1 mol\ NH_3}\right) = 17\ g\ NH_3$$

Note that it was necessary to convert from atomic nitrogen to molecular nitrogen.

Chemical Reactions and Molarity

By definition, molarity (M) is the number of moles of solute (the substance[s] in lesser amounts) per liter of solution.

Example 1:
36.5 g HCl are dissolved in enough water to make
1 liter of solution.
What is the molarity of the solution?

$$M = \frac{mol\,HCl}{L} = \frac{(36.5\,g\,HCl)\dfrac{1mol\,HCl}{36.5\,g\,HCl}}{1L} = 1M$$

Example 2: 18.25 g HCl are dissolved in enough water to make 250 mL of solution. What is the molarity of the solution? Solution:

$$M = \frac{mol\ HCl}{L} = \frac{(18.25\,g\ HCl)\,\frac{1\,mol\ HCl}{36.5\,g\ HCl}}{(250\,mL)\,\frac{1\,L}{1000\,mL}} = \frac{0.5\,mol}{0.25\,L} = 2\,M$$

Example 4: How many mL of 2M HNO_3 are required to react with 5.61 g KOH as follows: $HNO_3 + KOH \rightarrow KNO_3 + H_2O$

Solution:

$$(5.61\,g\ KOH)\left(\frac{1\,mol\ KOH}{56.1\,g\ KOH}\right)\left(\frac{1\,mol\ HNO_3}{1\,mol\ KOH}\right)\left(\frac{L}{2\,mol\ HNO_3}\right)\left(\frac{1000\,mL}{1\,L}\right) = 50\,mL$$

Example 3: How many mL of 0.5M H_2SO_4 are required to react with 4 g NaOH from the following reaction?

$H_2SO_4(aq) + 2NaOH(s) \rightarrow Na_2SO_4 + 2H_2O$

Solution: Don't get hung up the small stuff.

Use what you know and factor labeling.

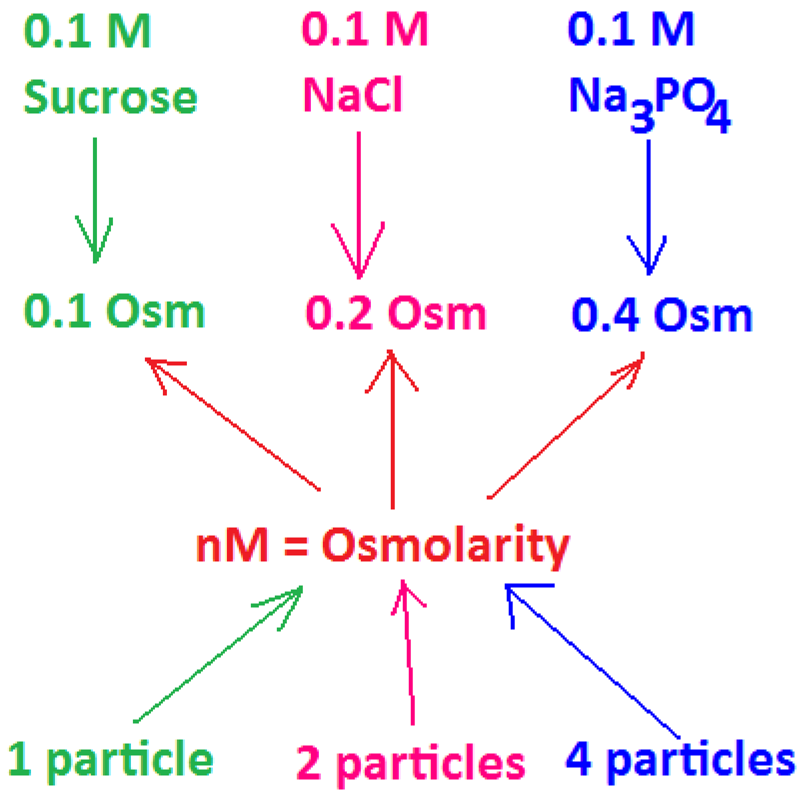
$$(4\,g\ NaOH)\left(\frac{1\,mol\ NaOH}{40\,g\ NaOH}\right)\left(\frac{1\,mol\ H_2SO_4}{2\,mol\ NaOH}\right)\left(\frac{L}{0.5\,mol\ H_2SO_4}\right)\left(\frac{1000\,mL}{1\,L}\right)=100\,mL$$

Note how grams were converted to moles and how the reaction stoichiometry played its role, here, too.

Also note that the molar concentration of the sulfuric acid was inverted to get the units (and, hence, the answer) correct, as well.

Osmolarity

- Osmolarity equals the product of the number of particles of the solute after dissociation times the molarity of the solution (nM).
- π = nMRT



0.1 M Sucrose

0.1 M NaCl

0.1 M Na_3PO_4

0.1 Osm

0.2 Osm

0.4 Osm

nM = Osmolarity

1 particle

2 particles

4 particles

Example: calculate the osmotic pressure of a solution that is 0.25 M in sucrose at 27°C. R = 62.4 torr-L/mol-K. Solution:

$$\pi = n\,M\,RT = (1 mole)\left(\frac{0.25 mole}{L}\right)\left(\frac{62.4 torr - L}{mole - K}\right)\left(\frac{1 mm Hg}{torr}\right)\left(\frac{1 atm}{760 mm Hg}\right)*300 K = 6.16 atm$$

Sucrose is a non-electrolyte and has an "n" of 1. Torr are converted to atm. The osmolarity of this sucrose solution is: n M = Osm or 1 * 0.25 = 0.25 Osm

Example: calculate the osmotic pressure of a solution that is 0.25 M in $CaCl_2$ at 27° C. Solution: $CaCl_2$ is an electrolyte and dissociates into 3 particles. "n" = 3.

$$\pi = n\,M\,RT = (3 mols) * \frac{0.25 mol}{L} * \frac{62.4 torr - L}{mol - K} * \frac{1 mm Hg}{1 torr} * \frac{1 atm}{760 mm Hg} * 300 K = 18.5 atm$$

The osmolarity of this solution is 3 * 0.25 or 0.75 Osm.

Example: calculate the molecular weight of a solute that is a non-electrolyte in aqueous solution.
The solution contains 14 g of the solute.
The osmotic pressure is 2 atm and R is 62.4 torr-L/mol-K and the temperature is 27°C.
Solution: this is a non-electrolyte, hence "n" = 1.
M, remember, is the molarity of the solution,
which is the number of mols of solute per liter of solution (mol/L).
To get the number of mols, the mass of the solute is divided by the molecular weight (grams/MW).
We'll substitute, then, grams/MW*L, for M:

$$\pi = n\,M\;R\,T = M\;R\,T = \frac{grams}{MW * L} * R\,T$$

Rearranging:

$$MW = \frac{grams * R * T}{\pi * L} = \frac{(14\,grams) * 62.4\,torr - L * 300\,K}{(mol - K) * (2\,atm) * (\frac{760\,torr}{1\,atm})} = 172.42\,g\,/\,mol$$

Limiting Reagents

- Now that we've explored moles, chemical reactions and moles and molar concentration and reactions, it is time to explore the concept of limiting reagents (reactants).
- A limiting reagent (reactant) is the reactant (reagent) present in the smallest amount based on stoichiometry and molecular weight.

Example -- 1

- Example 1: For the following chemical reaction, $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, determine which reactant is the limiting reagent if you have 20 g CH_4 and 100 g oxygen.
- Solution: ALWAYS pick the same product for the multiple parts to this question. It doesn't matter if it's the carbon dioxide or the water -- just make sure you pick and use the same one for each problem as you solve it.
- Solution on next slide

Step 1: Determine the amount of carbon dioxide produced from the 20 g CH_4:

$$(20\,g\,CH_4)\left(\frac{1\,mol\,CH_4}{16\,g\,CH_4}\right)\left(\frac{1\,mol\,CO_2}{1\,mol\,CH_4}\right)\left(\frac{44\,g\,CO_2}{1\,mol\,CO_2}\right)=55\,g\,CO_2$$

Step 2: Determine the amount of carbon dioxide produced from the 100 g of oxygen:

$$(100\,g\,O_2)\left(\frac{1\,mol\,O_2}{32\,g\,O_2}\right)\left(\frac{1\,mol\,CO_2}{2\,mol\,O_2}\right)\left(\frac{44\,g\,CO_2}{1\,mol\,CO_2}\right)=68.6\,g\,CO_2$$

As the methane caused the production of the least amount of CO_2, it is the limiting reagent, i.e., no matter how much oxygen is available, this reaction will produce no more than 55 g CO_2.

Example 2: For the following balanced reaction,

$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$,

if you have 4 g CH_4 and 15 g chlorine, which is the limiting reagent?

Solution: Step 1:

Determine the amount of CCl_4 (carbon tetrachloride or "carbon tet" as it's known) produced by the 4 g CH_4:

$$(4\,g\,CH_4)\left(\frac{1\,mol\,CH_4}{16\,g\,CH_4}\right)\left(\frac{1\,mol\,CCl_4}{1\,mol\,CH_4}\right)\left(\frac{153\,g\,CCl_4}{1\,mol\,CCl_4}\right)=38.25\,g\,CCl_4$$

Step 2: Determine the amount of carbon tet produced by the 15 g of molecular chlorine:

$$(15\,g\,Cl_2)\left(\frac{1\,mol\,Cl_2}{71\,g\,Cl_2}\right)\left(\frac{1\,mol\,CCl_4}{4\,mol\,Cl_2}\right)\left(\frac{153\,g\,CCl_4}{1\,mol\,CCl_4}\right)=7.45\,g\,CCl_4$$

The smallest amount of carbon tet produced is with the 15 grams of molecular chlorine.
The molecular chlorine is the limiting reagent.

Reaction Yield

The last topic for this lecture is reaction yield, i.e., relative to how much pen and paper say you're "supposed" to get how much did you really get? To do this we have to calculate per cent yield, which is defined as the per cent of the theoretical amount of product actually produced by a reaction:

$$\%\,yield = \frac{Actual\ yield}{Theoretical\ yield} * 100$$

Example: For the following reaction,

$CO_2 + 2NH_3 \rightarrow CH_4N_2O + H_2O$,

if you started with 6 g of ammonia and obtained 5 g urea (CH_4N_2O), calculate the percent yield.

Solution:

Step 1: Calculate the theoretical yield:

$$(6\,g\,NH_3)\left(\frac{1\,mol\,NH_3}{17\,g\,NH_3}\right)\left(\frac{1\,mol\,urea}{2\,mol\,NH_3}\right)\left(\frac{60\,g\,urea}{1\,mol\,urea}\right)=10.6\,g\,urea\,,theoretically$$

Step 2: Calculate the percent yield:

$$\%\,yield=\frac{actual\,yield}{theoretical\,yield}*100=\frac{5\,g}{10.6\,g}*100\approx 50\%\,yield$$

Gas Laws

- The gas laws give us arithmetic relationships which tell us about the gases when
  - they are mixed (Dalton's Law),
  - the temperature is altered (Charles' Law), when
  - the pressure is changed (Boyle's Law),
  - they diffuse (Graham's Law) and
  - they are under pressure over a liquid (Henry's Law).

- Before we get into the specific laws, let's remember that a standard atmosphere of pressure is 1 atmosphere.
- This is also equal to
  - 760 mm Hg,
  - 29.92 inches Hg and
  - 14.7 psi.
- This standard atmosphere is the pressure needed to support a 760 mm column of mercury in a barometer tube.
- Pressure, remember, is the force exerted upon a substance per unit area.

- Example: Express 1600 psi as
  - a) atm,
  - b) torr,
  - c) mm Hg and
  - d) inches Hg.
- Solution: First, 1 Torr = 1 mm Hg. The Torr was named for the developer of the barometer, Torricelli.

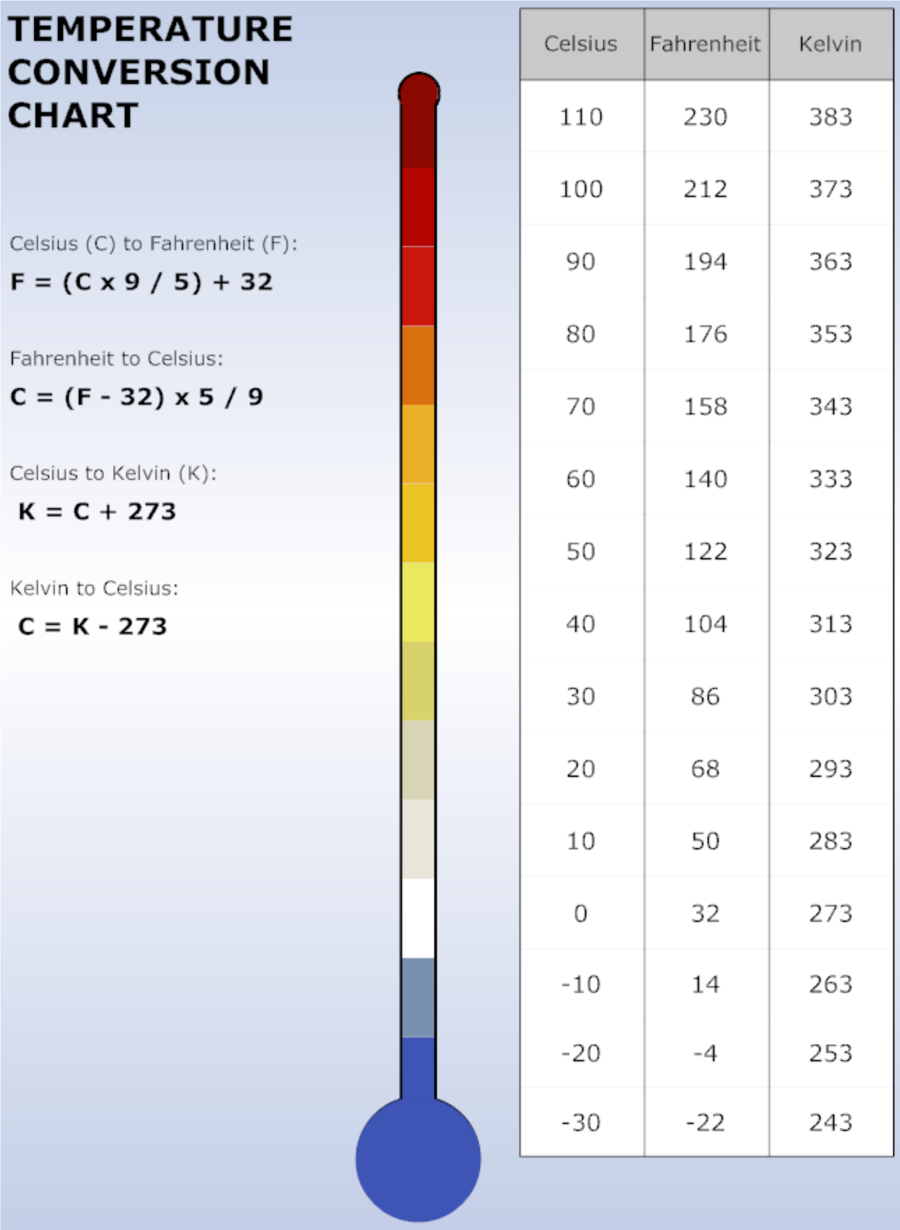
$$(1600\,psi)*\frac{1\,atm}{14.7\,psi}=108.8\,atm$$

$$108.8\,atm*\frac{760\,torr}{1\,atm}=82721\,torr \Leftrightarrow 82721\,mm\,Hg$$

$$(82721\,mm\,Hg)*\frac{1\,inch}{25.4\,mm\,Hg}=256.7\,inches\,Hg$$

Remember, also, your temperature conversions and the points of boiling and freezing on all three temperature scales.

Body temperature (on average) = 98.6°F; 37°C; 310K



TEMPERATURE CONVERSION CHART

Celsius (C) to Fahrenheit (F):

F = (C x 9 / 5) + 32

Fahrenheit to Celsius:

C = (F - 32) x 5 / 9

Celsius to Kelvin (K):

K = C + 273

Kelvin to Celsius:

C = K - 273

Celsius	Fahrenheit	Kelvin
110	230	383
100	212	373
90	194	363
80	176	353
70	158	343
60	140	333
50	122	323
40	104	313
30	86	303
20	68	293
10	50	283
0	32	273
-10	14	263
-20	-4	253
-30	-22	243

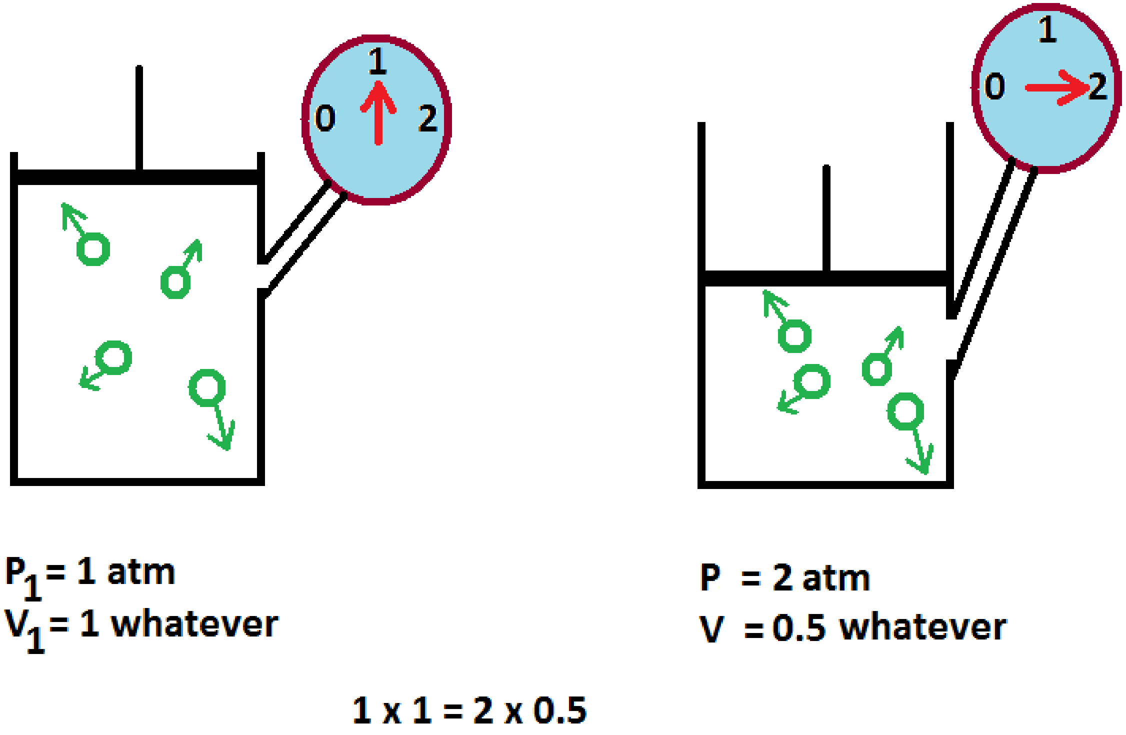
Boyle's Law

- The first gas law we'll examine is Boyle's Law.
- Boyle's Law says that the product of the pressure (P_1) and volume (V_1) of a gas under a first set of conditions is equal to the product of the pressure (P_2) and volume (V_2) it occupies under a second set of conditions:

$$P_1V_1 = P_2V_2$$

In order for Boyle's Law to work,
the temperature must remain a constant.

- When the pressure is increased on a gas in a cylinder fitted with a frictionless piston, the volume is proportionately reduced.
- The converse is equally as true.
- Note that if P_1 = 1 atm and V_1 = 1 whatever volume label that the product is 1.
- The same holds true for a P_2 of 2 atm and a V_2 of 0.5 whatever volume label.
- Even in this day and age of new math, 1 still equals 1.



Example: How many liters of air at 1 atm need to be pumped into a bicycle tire with a 1 liter volume at a pressure of 65 psi?
Solution: First, set up Boyle's Law equation:

$$P_1V_1 = P_2V_2$$

P_1 equals 1 atm; V_1 equals "X", P_2 equals 65 psi and V_2 equals 1 L. Remember, though, that you may not mix units. To bypass this fiasco, convert the 65 psi into atm (4.42 atm) Rearrange the equation and solve for "X":

$$V_1 = X = \frac{(4.42\,atm)\,(1\,L)}{1atm} = 4.42\,L\,of\;air$$

Charles' Law

Charles' Law says that the volume of a gas is directly proportional to the absolute temperature of that gas while the pressure is held constant.

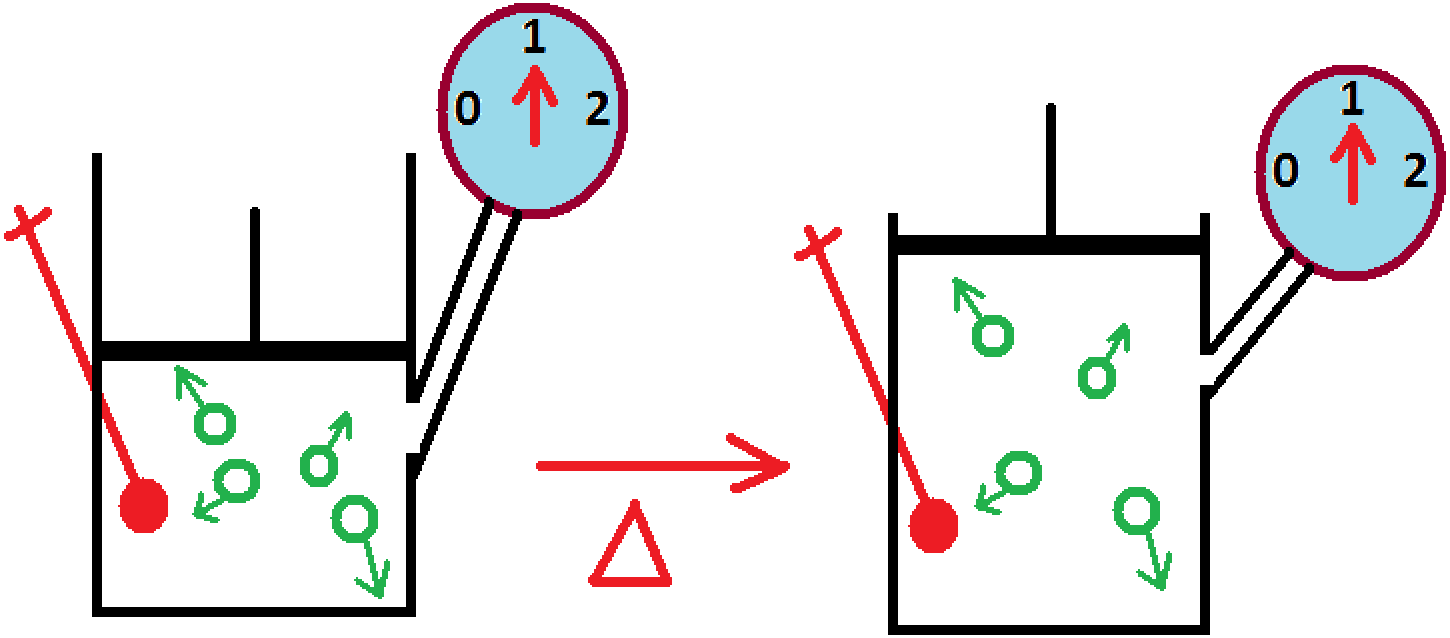
You've all seen this when you watch a hot air balloon fill with air.

Arithmetically, Charles' Law may be expressed in a manner similar to that of Boyle's Law:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Where the first volume of a gas divided by a first absolute temperature of that gas is equal to the second volume of the gas divided by its second absolute temperature.

- Note that the pressure never changes when a gas in a cylinder kept at constant pressure is heated and its volume expands.



Example: A gas occupies 350 mL at 27° C.
The gas is heated until it occupies 700 mL.
What is the new temperature of the gas?
Solution: First set up Charles' Law as above.
Second assign values to each variable:
V_1 equals 350 mL, T_1 equals 300 K (How'd I get this?),
V_2 equals 700 mL and T_2 equals "X".
Rearrange, plug in and solve for "X":

$$\frac{T_1 V_2}{V_1} = \frac{(700\,mL)*(300\,K)}{350\,mL} = 600\,K \Leftrightarrow 327^{\circ}\,C$$

Gay-Lussac’s Law

- If volume is held to a constant,
- Then pressure and absolute temperature vary directly

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

The Combined Gas Law

The combined gas law is just that: combined.
It is Boyle's, Charles‘ and Gay-Lussac’s Laws combined:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Remember, too, that the temperature
MUST be the absolute temperature.
Note the Boyle's part and the Charles' part
and the Gay-Lussac’s part of this law.

Example: 250 mL of oxygen is collected at 30° C at 740 Torr.
What volume will the gas fill at STP?
STP is standard temperature (0° C) and pressure (760 torr).
Solution: rearrange the combined gas law to solve for V_2.
Plug the numbers in and calculate:

$$V_2 = \frac{T_2 P_1 V_1}{T_1 P_2} = \frac{(273\,K)*(740\,Torr)*(250\,mL)}{(303\,K)*(760\,torr)} = 219.3\,mL$$

Second Example: 4 L of helium are at STP.
The He is compressed into 0.5 L at 50° C.
What pressure is the He under?
Solution: As before, rearrange the equation.
Solve for P_2:

$$P_2 = \frac{T_2 P_1 V_1}{T_1 V_2} = \frac{(323\,K)*(1\,atm)*(4\,L)}{(273\,K)*(0.5\,L)} = 9.5\,atm$$

The Ideal Gas Law, aka Universal Gas Law

This equation is easily expressed:
PV = nRT,
where P is pressure (in atm),
V is volume (in liters),
n equals the number of moles of the gas present,
T is the absolute temperature and
R is the universal gas constant
(with the units described just above, R = 0.0821 L*atm/mol*K.
R is determined by substituting standard values
into the rearranged equation:

$$R = \frac{PV}{nT} = \frac{(1atm)*(22.4\,L)}{(1mol)*(273\,K)} = 0.0821\frac{L*atm}{mol*K}$$

In other words,
1 mol of any gas at 1 atmosphere of pressure
and 273 K will occupy 22.4 liters.

Example: Calculate the volume of a gas in an enclosed container if 0.525 mol of this gas exerts a pressure of 3 atm at 10° C? Rewrite the equation and plug the numbers into it:

$$V=\frac{nRT}{P}=\frac{(0.525\,mol)*(0.0821\,L*atm)*(283\,K)}{3\,atm*(mol*K)}=4.07\,L$$

Example: Calculate the number of mols of a gas that fills a cylinder of 500 mL at 100° C and pressure of 720 torr. Solution: convert torr to atmospheres (720/760) = 0.95 atm. Rearrange the equation and solve for n:

$$\frac{PV}{RT}=n=\frac{(0.95\,atm)*(0.5\,L)*(mol*K)}{(0.0821\,L*atm)*(373\,K)}=0.016\,mol\ of\ the\ gas$$

Example: A sample of diethyl ether has a mass of 16.5 g and occupies a volume of 5 L at STP.

What is the molecular weight (MW) of the diethyl ether?

Solution: There is no "n" term in this question.

Remember that the mols of something may be determined by dividing the mass of the substance by its MW and substitute this into the universal gas law equation for "n" after rearrangement:

$$MW = \frac{(16.5\,g)*(0.0821 L*atm)*(273\,K)}{(1 atm)*(5\,L)*(mol*K)} = 74\,g/mol$$

Dalton's Law

- Dalton's Law is defined as "the pressure of a mixture of gases is equal to the sum of the pressure of each individual gas (partial pressure)", i.e., $P_T = P_1 + P_2 + P_3 + P_4 + ... + P_n$,
  - where P_T is the total pressure of the gaseous mixture,
  - P_1 is the partial pressure of gas 1,
  - P_2 is the partial pressure of gas 2,
  - P_3 is the partial pressure of gas 3, ad nauseum.

- Example: A sample of air is collected at a pressure of 745 mm Hg. The partial pressure of nitrogen (pN_2) is 600 mm Hg and the pO_2 is 50 mm Hg. If water vapor is the only other gas present, what is the pH_2O vapor?
- $P_T = P_1 + P_2 + P_3$;
  - P_T is 745 mm Hg,
  - P_1 is 600 mm Hg,
  - P_2 is 50 mm Hg and
  - P_3 is to be determined:
- $745 = (600 + 50) + P_3$
- $P_3 = 745 - 650 = 95$ mm Hg $= pH_2O$

- Example: A container has a gas mixture of nitrogen, oxygen and carbon monoxide. The total pressure is 2500 torr. The pN_2 is 800 torr, the pO_2 is 500 torr. What is the pCO?
- Solution: $P_T = P_1 + P_2 + P_3$
- $2500 = (800 + 500) + P_3$
- $P_3 = 2500-1300 = 1200$ torr

Continuation: if 1 mole of CO is present, what volume does the gas fill at 0° C?

Solution: use the universal gas law equation and solve with rearrangement for V:

$$V = \frac{nRT}{P} = \frac{(1\,mol)*(0.0821\,L*atm)*(273\,K)}{(1.6\,atm)*(mol*K)} = 14\,L$$

Graham's Law

Graham's Law says that the rate of diffusion or effusion of 2 gases is inversely proportional to the square root of the molecular masses of the gases:

$$\frac{Rate\ of\ A}{Rate\ of\ B} = \sqrt{\frac{MW_B}{MW_A}}$$

Effusion is defined as gas "leaking" out of a container through a small hole.

Diffusion is defined as gases mixing on their own when brought together.

Example: Compare the rate of diffusion of molecular chlorine with molecular hydrogen:

$$\frac{Rate\ of\ H_2}{Rate\ of\ Cl_2} = \sqrt{\frac{MW_{Cl_2}}{MW_{H_2}}} = \sqrt{\frac{71}{2}} \approx 6$$

Therefore H_2 diffuses 6 times faster than does Cl_2.

Example: Compare the rate of diffusion of molecular oxygen with molecular iodine:

$$\frac{Rate\ of\ O_2}{Rate\ of\ I_2} = \sqrt{\frac{MW_{I_2}}{MW_{O_2}}} = \sqrt{\frac{254}{32}} \approx 3$$

O_2 diffuses 3 times faster than iodine.

Example: Compare the rate of diffusion of molecular nitrogen with molecular oxygen:

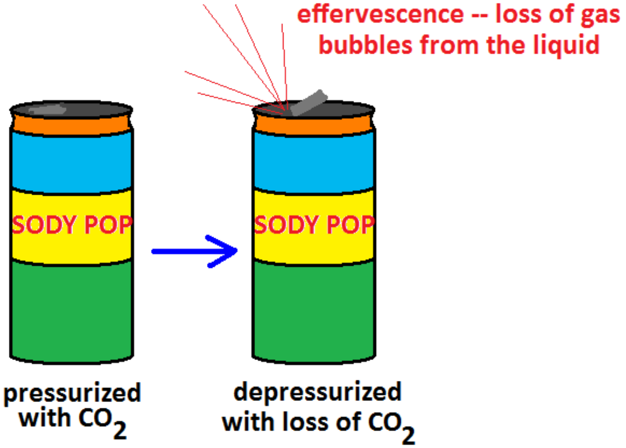
$$\frac{Rate\ of\ N_2}{Rate\ of\ O_2} = \sqrt{\frac{MW_{O_2}}{MW_{N_2}}} = \sqrt{\frac{32}{28}} \approx 1.07$$

Nitrogen and oxygen diffuse at about the same rate.

Gases are Soluble in Water

As mentioned shortly,
Henry's Law says that the greater the pressure of a gas over a solution,
the greater the amount of gas dissolved in the solution.
The table, below summarizes the solubilities of 3 gases in water:

Gas	Solubility per 100 g water at 20° C
O_2	4.3 mg
CO_2	169 mg
NH_3	10.6 grams



Henry's Law

- Henry's Law says that the greater the pressure of a gas over a solution, the greater the amount of that gas dissolved in the solution.
- Consider a soda.
- When you first open it, the can is under pressure that is greater than atmospheric pressure, hence, the "pffffffttttttt" when you open it.
- Sodas are canned under pressure with CO_2 to make the "fizz".
- At sea level, it takes longer for the soda to go flat than it does at Lake Tahoe simply because of pressure differences.
- If you don't entirely believe this, go to San Francisco, buy a soda and put it in your car.
- Drive to Lake Tahoe and open it fast.
- Do this part outside your car and aim the can away from yourself or other people :-)

- Henry's Law is also responsible for people getting the "bends".
- When people dive deeply using compressed air, they MUST slowly come back up so that the nitrogen bubbles that are driven into tissues at deep levels (and, hence, with high pressures) may slowly be released and breathed out.
- If the person comes up too rapidly, these bubbles expand and can cause death as they compress tissues.
- Helium is less soluble than nitrogen and is used when deep diving is expected and a bit more rapid ascent is expected and reduces the instances of getting the bends.

Gas	Solubility Coefficient
CO_2	0.57
O_2	0.024
N_2	0.012
He	0.005±

- Note that oxygen, relatively speaking, isn't very soluble in aqueous systems while carbon dioxide is.
- As a general rule, the greater the temperature, the lower the solubility, which explains why warm soda goes "flat" faster than does cold soda.

Elements of Thermochemistry

- Thermodynamics is the study of the change of energy from one form to another.
- Energy is the ability to do work.
- Work is the change in kinetic energy of the object.
- Kinetic energy is the energy of motion.

Potential Energy

- Stored energy
- Energy of position
- If object is above the ground

= gravitational potential energy

- Since Wt = m g, then,

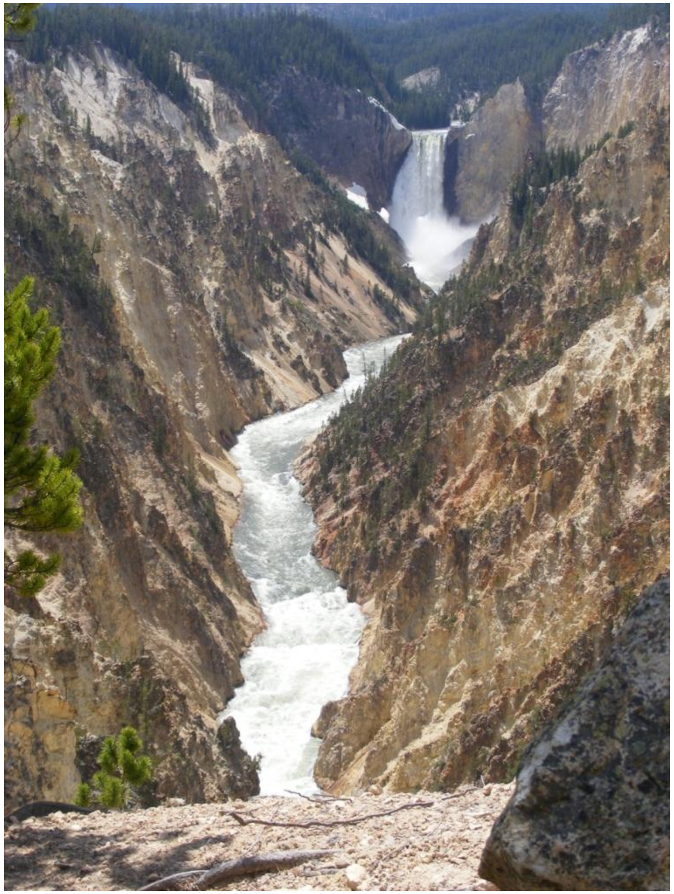
$PE_{grav} = m\ g\ h$,

where m = mass, g = gravity, h = height above ground

Kinetic Energy

- Energy of motion:

$$KE = \frac{1}{2} m v^2$$



Practical Kinetic Energy

The Yellowstone River in the Grand Canyon of the Yellowstone, 23 June 2008.

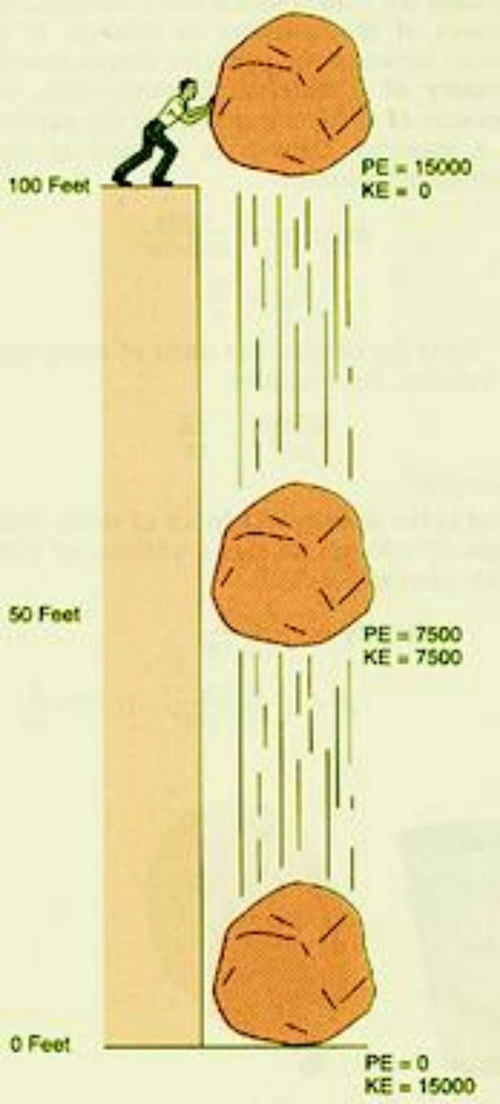
Law of Conservation of Energy

- Is the relationship between PE and KE:

- The total energy is always conserved

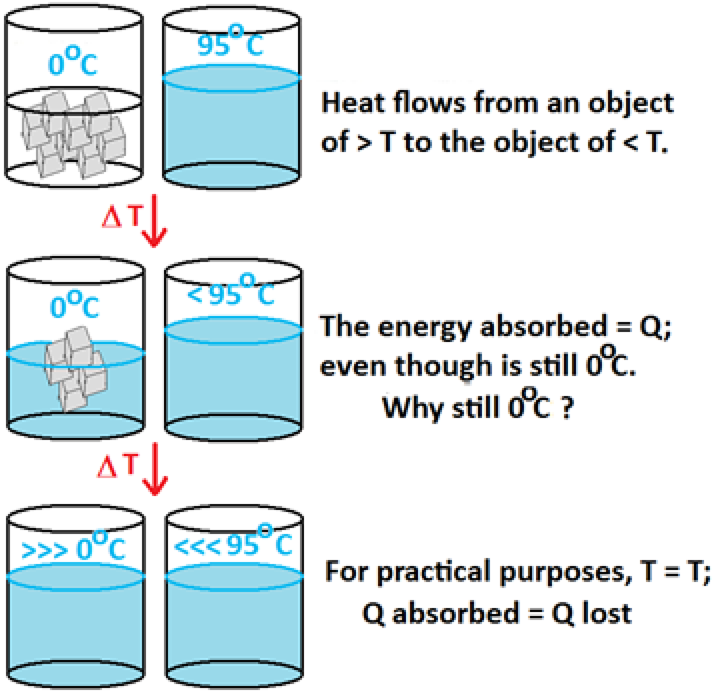
or

- Energy is neither created nor destroyed – merely transformed



Heat

- Heat flows from an object of hotter temperature to an object of cooler temperature. The absorbed energy we represent by "Q".



Heat flows from an object of > T to the object of < T.

The energy absorbed = Q; even though is still 0°C. Why still 0°C ?

For practical purposes, T = T; Q absorbed = Q lost

When talking about heat, it would be helpful to have some terms defined that will allow us to quantitatively determine just how much heat has been transferred between objects or between systems.

The first term for discussion is heat capacity (C).

Heat capacity is defined as the amount of energy transferred per change in absolute temperature or:

$$C = \frac{Q}{\Delta T}$$

C is in units of Joules per mole per Kelvin.

- This term (heat capacity) is all fine and dandy -- it doesn't, though, give us a measure in terms of mass and/or amount.
- To that end we use the term specific heat capacity (c).
- Specific heat capacity is equal to the heat capacity divided by the molecular weight and is in units of joules per Kelvin per gram.
- Joules aren't as widely known as are calories.
- One calorie is equal to 4.184 Joules.
- One calorie (cal) is defined as the amount of heat necessary to raise the temperature of 1 gram of water by 1° C -- a little less than a perfect definition, yet close enough for our purposes.
- One Calorie (Cal or kcal) is 1000 calories or 1 kilocalorie (kcal).
- The kcal is the unit we use for "food calories".

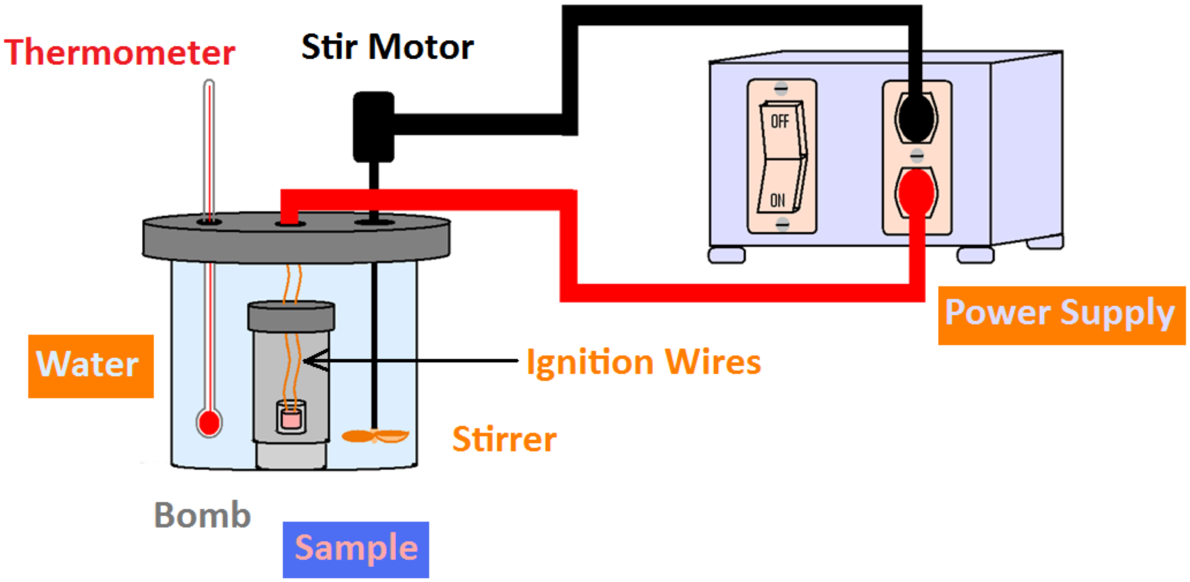
How could we use this information to determine the amount of heat, Q, that has been transferred between two objects? We use a simple equation:

$$Q = m c \Delta T$$

Where Q = the amount of heat in calories or Joules,
m = the mass in grams,
c = the specific heat in joules per Kelvin per gram OR calories per Kelvin per gram, and
ΔT = the change in temperature in Kelvins (also in °C, Δsince the difference is numerically equivalent -- remember, Δthough, to keep your units straight).

The table, below, summarizes the
specific heat capacity of some representative substances:

Substance	Specific Heat Capacity (J/K/g)
Water	4.169
Al	0.898
Diamond	0.518
Fe	0.443
Pb	0.130



- Specific heat capacities are measured in a "bomb calorimeter":
- The way this works is that sample is placed in the sample holder in the “bomb" and two wires are set in the substance through the water-tight lid.
- The lid is sealed, the wires are attached to a power supply, water is poured around the bomb and the stirrer rotates to mix the water.
- When the temperature of the water is equilibrated, the power is turned on, the sample is ignited and the temperature increase from the sample combustion is measured by an increased water temperature.

The challenge is that you have to remember that the calorimeter also absorbs some heat, so we have to take that into account:

$$\Delta Q_c = m_c \, c_c \, \Delta T$$

Where the "c" subscript represents the calorimeter –
heat absorbed by it, mass of it, specific heat capacity of it
and the change in absolute temperature of the calorimeter.
So, when figuring the whole heat transfer,
we must write the equation as follows:

$$\Delta Q_{Total} = Q_{Substance} + Q_{Calorimeter}$$

We can then re-write the equation thusly:

$$\Delta Q_{Total} = mc \, \Delta T + m_c \, c_c \, \Delta T$$

The key to this equation and its application is to remember that:

$$\Delta T = T_{final} - T_{initial}$$

Example 1: 50 g of coal are placed in a calorimeter at 20° C. The calorimeter has a mass of 100 g and is made of Fe. 950 J of heat increases the temperature of the calorimeter to 35° C. What is the specific heat capacity of the coal?

We know the specific heat capacity of the Fe from the table above: 0.443 J/g/K.

The change in temperature = 35° C - 20° C = 15° C which is equivalent to 15 K.

Set up the equation:

$$\Delta Q_{Total} = mc\,\Delta T + m_c\,c_c\,\Delta T$$

Manipulate it:

$$\Delta Q_{Total} - m_c\,c_c\,\Delta T = m\,c\,\Delta T$$

Rearrange and isolate "c":

$$\frac{\Delta Q_{total} - m_c\,c_c\,\Delta T}{m\Delta T} = c = \frac{950 - (100)(0.443)(15)}{(50)(15)} = 0.407\ J/g/K$$

0.407 J/g/K is equivalent to 0.097 cal/g/K.

Example 2: 100 g tar are placed in a calorimeter at 10° C.
The calorimeter has a mass of 200 g and is made of diamond.
10,000 Joules (J) of heat increases the temperature of the calorimeter to 95° C.
What is the specific heat capacity of the tar?
We already know the specific heat capacity of the diamond from the table, above: 0.518 J/g/K.
The temperature difference is equal to 95° C - 10° C, which equals 85° C -- this is equivalent to 85 K.
Set up the equation as before and solve for "c":

$$\frac{\Delta Q_{total} - m_c c_c \Delta T}{m \Delta T} = c = \frac{10000 - (200)(0.518)(85)}{(100)(85)} = 0.140 J/g/K$$

This is equivalent to 0.0336 cal/g/K.

Example 3: 75 g aspirin are placed in a calorimeter at 20° C.
The calorimeter has a mass of 125 g and is made of lead (Pb).
850 J of heat increases the temperature of the calorimeter to 22° C.
What is the specific heat capacity of aspirin?
We know the specific heat capacity of Pb from the table: 0.130 J/g/K.
The change in temperature is 2K.
Set up the equation, isolate and solve for "c", as before:

$$\frac{\Delta Q_{total} - m_c c_c \Delta T}{m \Delta T} = c = \frac{850 - (125)(0.130)(2)}{(75)(2)} = 5.45\,J/g/K$$

This is equivalent to 1.303 cal/g/K.

We saw that the combination of both the substance and the calorimeter contributed to the ΔQ. What about the ΔQ BETWEEN 2 different containers or systems? In that case,

$$\Delta Q_1 = \Delta Q_2$$

Since one is absorbing heat, the other must be losing heat. We can use this set up to determine the final temperature of 2 systems mixing.

Example 1: a Pb pipe of 300 g is at 25° C.
If the ends of the pipe are plugged after 300 g water at 90° C
are poured into it, what is the final temperature of the new system?
Key to this is that the lead pipe is going heat up and
the water is going to cool down.
The 2 equations, then for the temperature differential are as follow:
$\Delta T_{Pb} = T_f - 25$ and $\Delta T_{H2O} = 90 - T_f$
The heat capacities of Pb and water are as follow,
respectively: 0.130 J/K/g and 4.169 J/K/g
Set up the formula and solve for T_f:

$$Q_{Pb} = Q_{H2O}$$

$$(300)(0.130)(T_f - 25) = (300)(4.163)(90 - T_f)$$

$$39T_f - 975 = 112563 - 1251T_f$$

$$1290T_f = 113538$$

$$T_f = 88^o C \, or \, 361K$$

In other words, as we discussed before,
lead heats up and water cools down.

Example #2: A gold container at 30° C has 400 g water at 100° C poured into it. The gold container has a mass of 500 g. What is the T_f? (the specific heat capacity (c) of Au is 0.130 J/g/K).

Key to this is that the gold container is going heat up and the water is going to cool down.

The 2 equations, then, for the temperature differential are as follow:

$\Delta T_{Au} = T_f - 30$and $\Delta T_{H2O} = 100 - T_f$

The heat capacities of Au and water are as follow, respectively:

0.130 J/K/g and 4.169 J/K/g

Set up the formula and solve for T_f:

$$Q_{Au} = Q_{H2O}$$

$$(500)(0.130)(T_f - 30) = (400)(4.163)(100 - T_f)$$

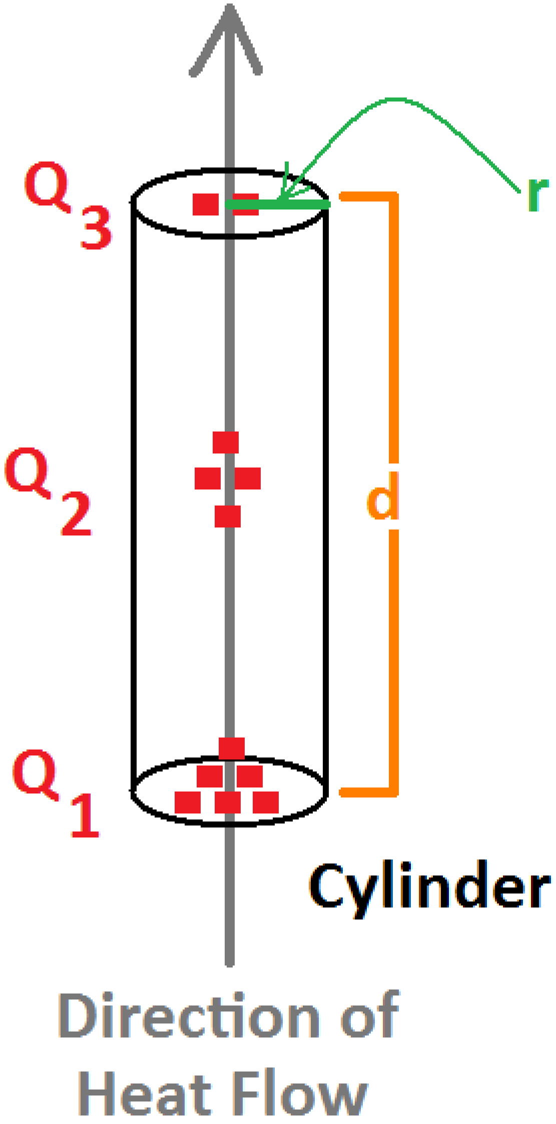
$$65T_f - 1950 = 166760 - 1668T_f$$

$$1733T_f = 168710$$

$$T_f = 97.35^\circ C \; or \; 370K$$

Flow of Heat

- When discussing heat, it's important to actually comprehend how heat flows.
- Among other reasons to comprehend heat flows, we can eventually fold a discussion on the flow of heat into a discussion of how gases traverse membranes in the body to provide oxygen to the cells and CO_2 transport out of the body.
- To begin the discussion, let's examine Fick's Law.
- Fick's Law says that **the rate of diffusion of heat per unit area through a cylinder in a direction perpendicular to the area is proportional to the heat gradient through the cylinder in that direction**



The heat gradient is defined as:

$$\frac{\Delta Q}{volume \times d} \Leftrightarrow \frac{H}{d}$$

And the area of the face of the cylinder is <u>π r^2</u>.
If we combine these two equations with one more:

$$\frac{Q}{t} = Flow\ of\ heat$$

We get the following:

$$\frac{Q}{t} = D\,A\,\frac{H}{d}$$

Where Q is the amount of heat,
t is time,
D is a constant,
$A = \pi r^2$,
H is the heat per unit volume
d is distance or thickness of the cylinder.

This cylinder for heat diffusion may be likened to a semipermeable membrane, therefore, the heat flow is analogous to diffusion of a solute. The rate of diffusion of a solute per unit area in a direction perpendicular to the area is proportional to the concentration gradient in that direction. By substituting mass (m) for amount of heat (Q) and concentration gradient (∆ [C]) for H, then, the mass of solute diffusing per unit time may be expressed as below:

$$\frac{m}{t} = D\,A\,\frac{\Delta[\,C\,]}{d}$$

Again, "m" is mass diffusing,
"t" is the time in which diffusion is occurring,
and ∆ [C] is the concentration gradient.
The remainder of the terms are as defined before.

Diffusion is analagous to the flow of gas through semipermeable membranes:

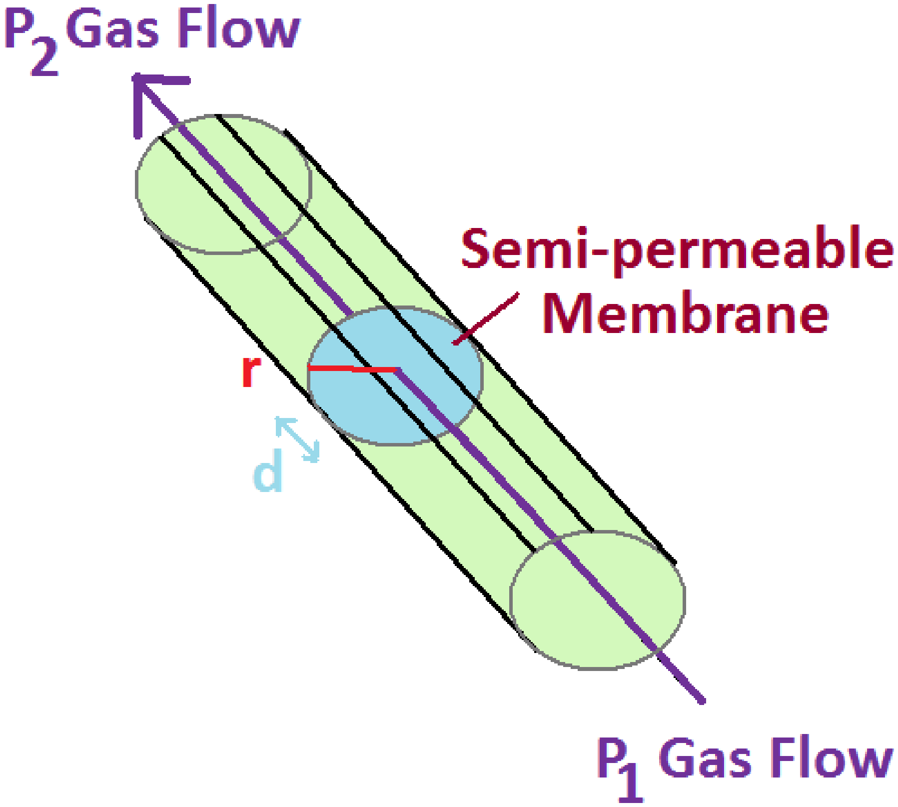
$$\frac{\Delta d}{\Delta t} \propto \frac{A \Delta P}{d}$$

or

$$\frac{\Delta d}{\Delta t} = D\,\frac{A \Delta P}{d}$$

Where Δ d is the difference in thickness of the membrane,
Δ t is the time it takes to cross the membrane (time difference) and
Δ P is the pressure gradient or pressure difference across the membrane.

- This last equation tells us that the speed of a gas through a semi-permeable membrane is directly proportional to the cross sectional area of that membrane and the pressure gradient ($P_1 - P_2 = \Delta P$) between the two sides of the membrane.
- It also tells us that flow is inversely proportional to the thickness (d) of the membrane.
- This is illustrated at right where a semi-permeable membrane is placed in a tube with gas flowing in one direction through the membrane.



From our previous equation, note that that the distance difference per time difference is simply velocity. We can re-write the equation, now, as follows:

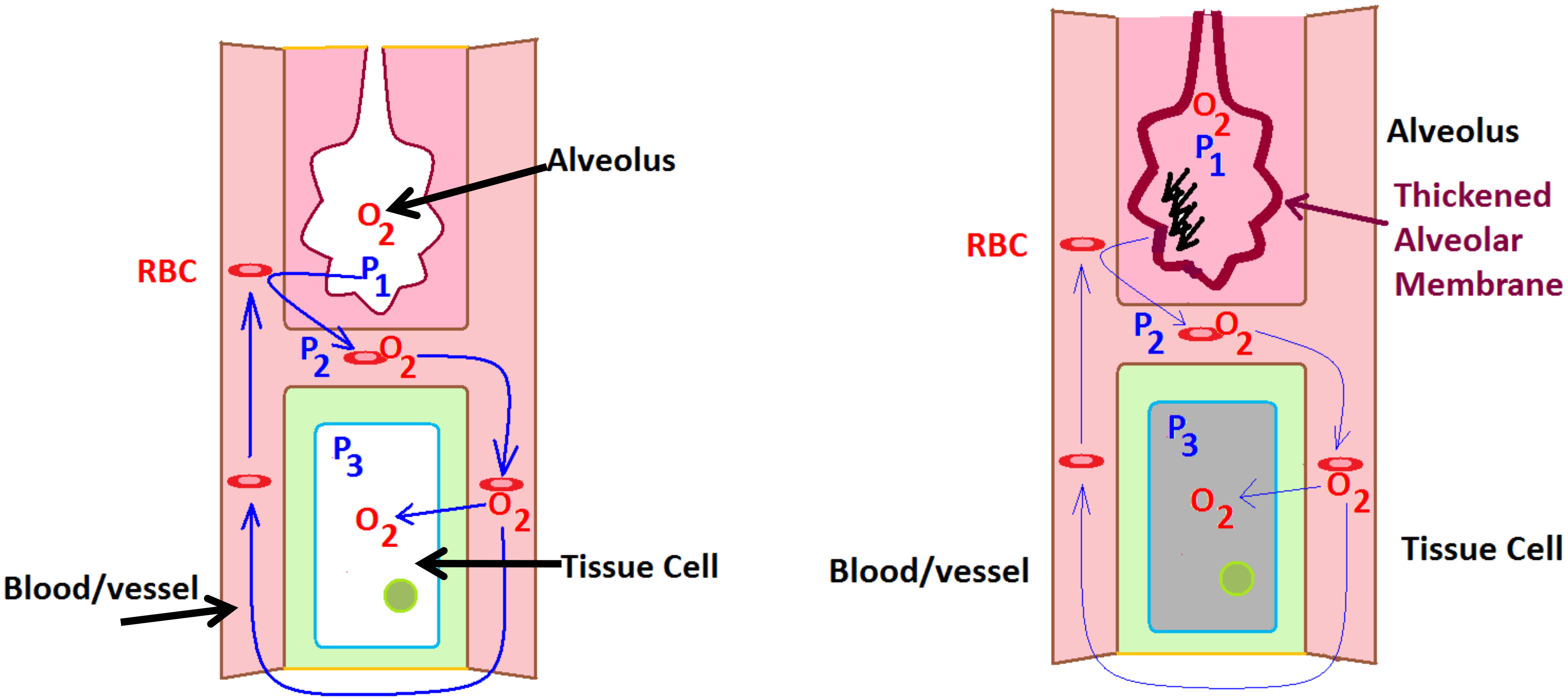
$$\frac{\Delta d}{\Delta t} = v = D\frac{A \Delta P}{d}$$

Where the only new variable is "v": velocity (or speed). We may, thus, write the equation as follows:

$$v = D\frac{A \Delta P}{d}$$

If d reduces by half, v increases by two-fold. If d increases its thickness by 3 fold, then v reduces to one third its original value. Hence, the thicker the membrane, the slower the diffusion of the gas. Can we apply this in a clinical perspective? Yes, we can.

Normal Gas Exchange Across Alveolar Membranes



Normal Gas Flow, left; Reduced Gas Flow, right.

- If, though, one develops pulmonary edema through heart failure, chemical inhalation, mountain sickness or pulmonary frostbite, then the alveolar membranes thicken as in the figure, right, that makes it very difficult to get gases across the membranes and cause the cells to begin to consider the possibility of their death without treatment as long as the body can function (have you seen "Vertical Limit"?) .

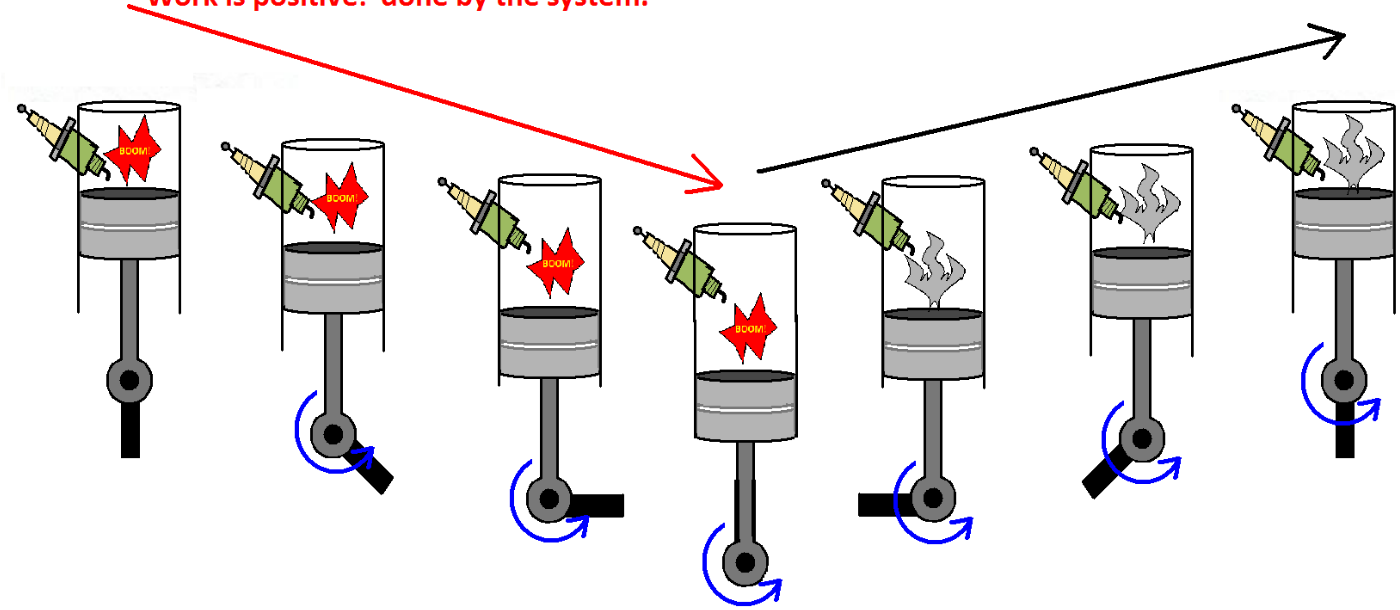
- **REFERENCE**: MacDonald, S. and Burns, D. : Physics for Life and Health Sciences. (Addison-Wesley: London) © 1975.

Introduction to The Laws of Thermodynamics

First Law

- Represented as ΔH
- Heat of Reaction
- Enthalpy

The First Law of thermodynamics says that when heat is added to a system at rest, the system will perform work due to the change in internal energy of the system.
A car engine is a good example of this.
When gas fills the cylinder and the spark jumps across the plug, the gasoline ignites and explodes, forcing the piston down.
This is positive heat, i.e., it is donated to the system.
There are internal energy changes and work is positive, i.e., work is done by the system -- the car moves when in gear.



Internal Energy Change

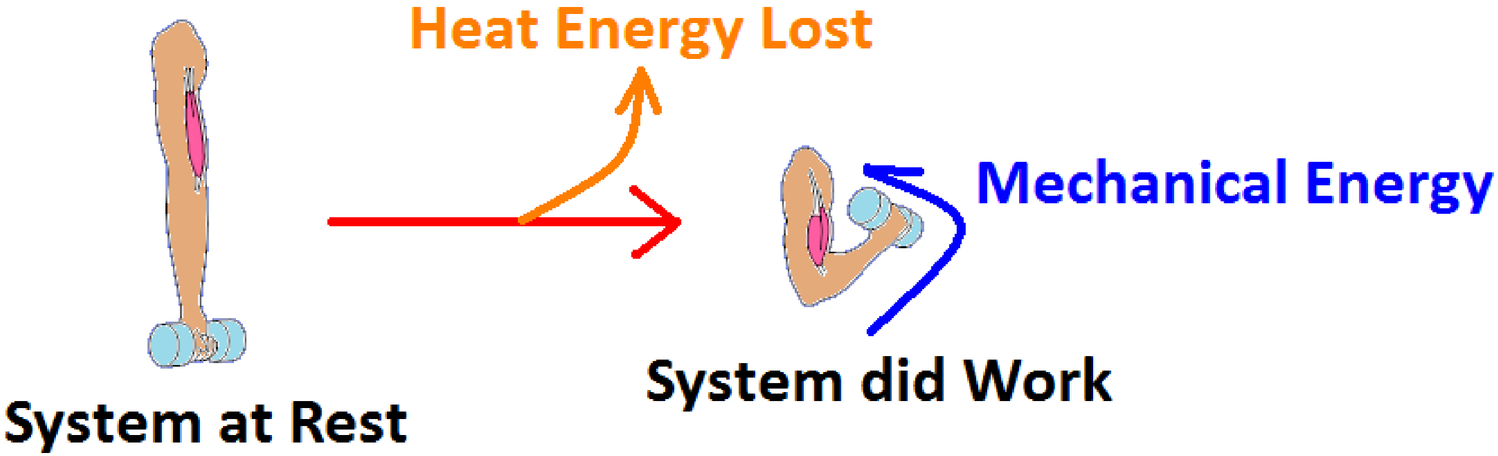
Fuel + Air + Spark = BOOM!
Positive heat: heat donated to the system.
Work is positive: done by the system.

Alternatively, the First Law may be stated as follows: work done BY a system is equal to the change in mechanical energy PLUS the energy that LEAVES the system.

Weight lifting is a good example of that.

When a system is at rest (e.g., the biceps brachii), nothing happens.

When the biceps contracts, the system did work, heat energy is lost and there is a change in mechanical energy.



Another perspective on the First Law is that energy is neither created nor destroyed, but changed from one form to another.

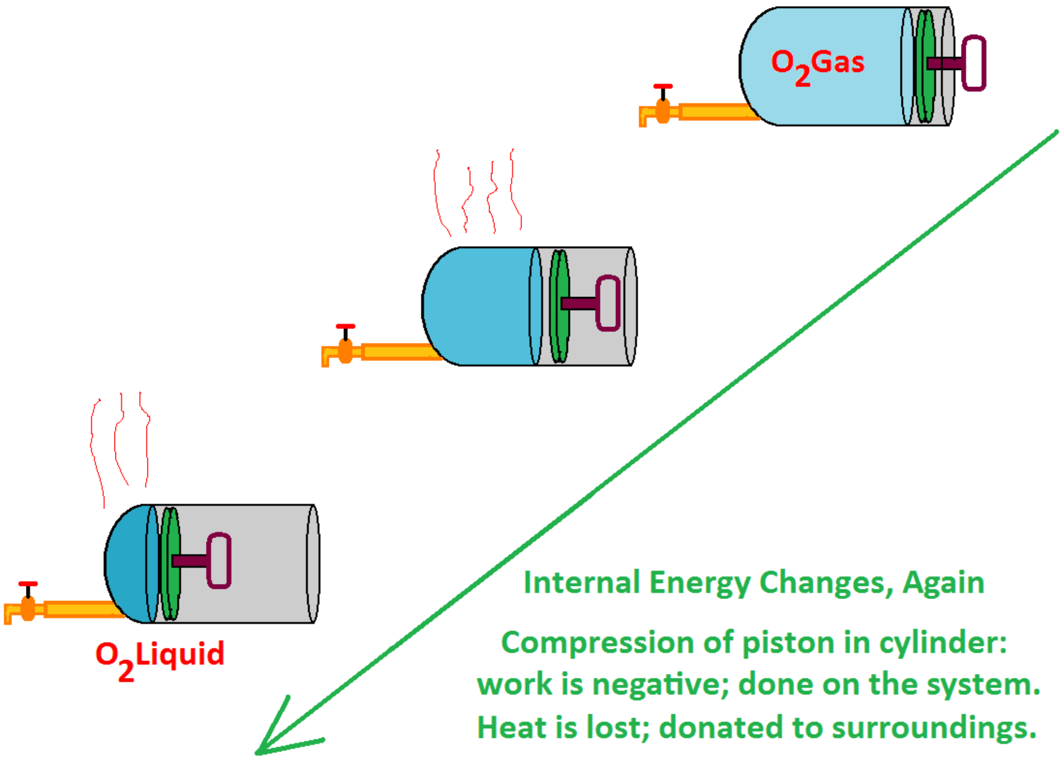
The converse First Law says that work done on a system is equal to the change in mechanical energy PLUS the energy that is absorbed BY the system.

A good example of this is compressing a gas to a liquid.

When a gas that is compressible is placed inside a cylinder with a piston and the piston is compressed, the work is negative.

In other words, work is done ON the system.

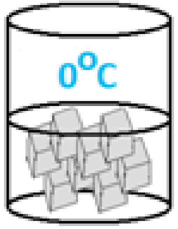
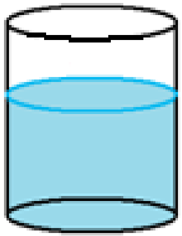
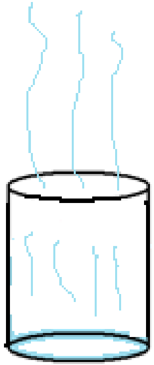
Heat is lost and donated to the surroundings.



Internal Energy Changes, Again

Compression of piston in cylinder:
work is negative; done on the system.
Heat is lost; donated to surroundings.

The Second Law of Thermodynamics says that spontaneous changes in the universe are accompanied by increasing entropy in the universe, i.e., chaos is always increasing.

 	$\Delta S>0$ → $\Delta S<0$ ←		$\Delta S>0$ → $\Delta S<0$ ←	
Solid ice: highest order and least entropy		Liquid Water		Water vapor (gas): most disorder and highest entropy

ΔS = ENTROPY = the amount of disorder, chaos, randomness of a system

- The Second Law of thermodynamics says that systems prefer a sense of chaos (entropy), i.e., chaos is more probable than an ordered system.
- For example, in poker, there are only a few hands, e.g., royal flush, with high points.
- This says, then, that there are MORE hands with NO value.
- This is entropy.
- Another example of entropy comes to us from family structure and dynamics: in dysfunctional families there is a high degree of entropy and a low degree of order.
- In functional families, there is some entropy and more order.
- Entropy is ALWAYS increasing -- or at least equals zero.
- In processes that are reversible, the change in entropy equals zero and chaos equals a constant.
- In processes that are IRreversible, which includes most natural processes, the change in entropy is greater than or equal to zero always and chaos increases.

- Thermodynamics predicts whether a reaction will go as written or not.
- Thermodynamics does NOT predict how fast the reaction will go -- that's the function of kinetics.
- How is it possible to predict whether or not a reaction will go?
- By studying Gibbs Free Energy (G).
- In general,
  - When the change in Gibbs Free energy (ΔG) is NEGATIVE, the reaction GOES as written.
  - When the ΔG is POSITIVE, the reaction does NOT go as written.

Another state function is the free energy change, aka **GIBB'S FREE ENERGY** = ΔG ⇔ dG.

This free energy change is equivalent to expressing arithmetically the difference between a state of minimum energy (-ΔH) and maximum chaos (+ΔS) that occurs when possible for a chemical reaction to proceed spontaneously, i.e., as written.

dG says NOTHING about reaction rate!

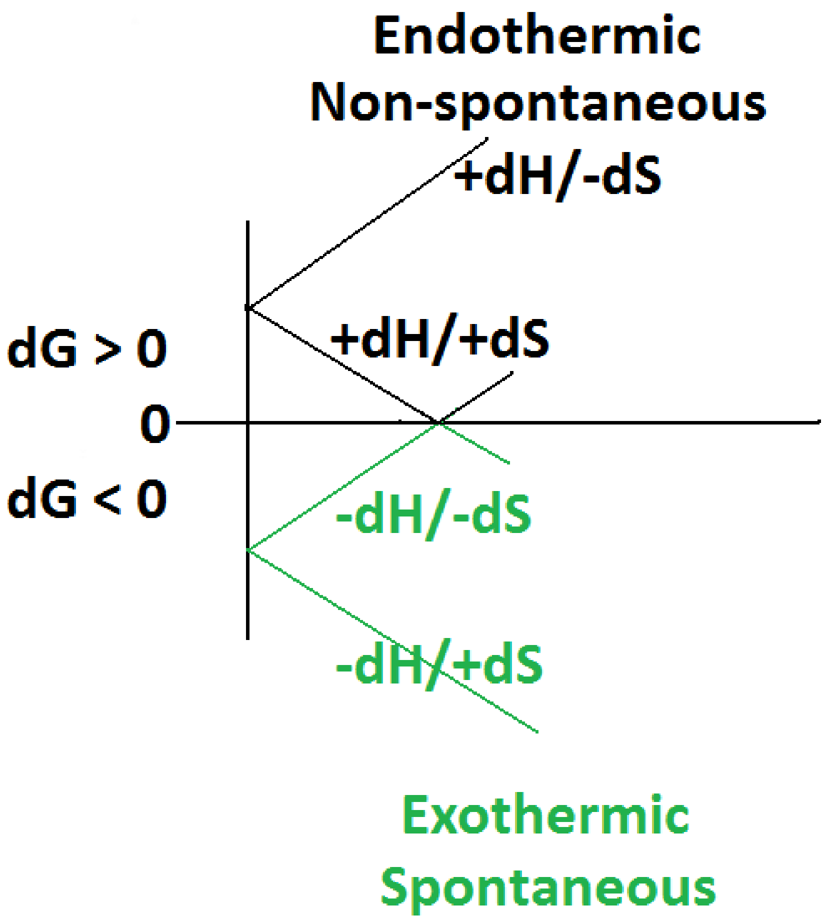
The arithmetic expression is:

$$\Delta G = \Delta H - T\Delta S,$$

where the "T" is the absolute temperature of the system.

When ΔG<0, the reaction goes as written.

When ΔG>0, the reaction does NOT go as written, see graphic:



- There is a relationship between 1st law, 2d law and Gibbs free energy:

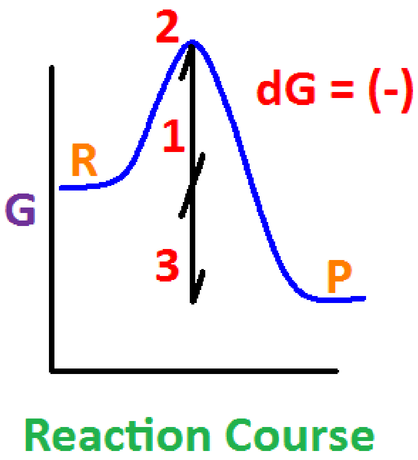
$$\Delta G = \Delta \text{1st law} - T\Delta \text{2d law}$$

- or the change in free energy (Δ G) is equal to the change in the first law (enthalpy or Δ H) minus the absolute temperature (T) times the change in the 2d law (entropy or Δ S). This, then, may be re-written as

$$\Delta G = \Delta H - T \Delta S$$

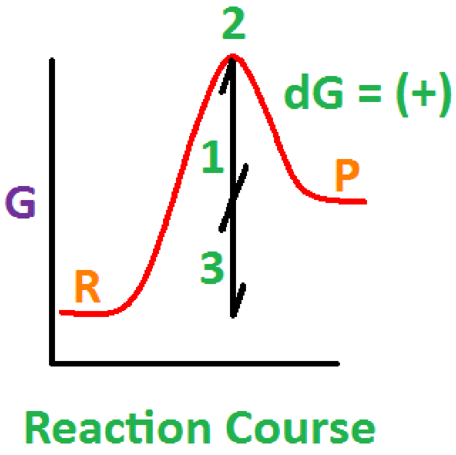
- In other words, the change in free energy is equal to the change in enthalpy less the change in entropy at some absolute temperature, T. The difference in this equation is sometimes called the Third Law of thermodynamics and may be stated as follows: as the energy of a reaction is changed from one form to another, entropy changes -- if the difference at a fixed absolute temperature is negative, the reaction goes spontaneously as written; if it is positive, it does NOT go spontaneously as written.

- The following graphic illustrates this concept.
- Each graphic has ΔG on the vertical axis and the reaction course (reactant [R] to product [P]) on the horizontal axis.
- Note that in an exergonic reaction that the energy level for the reactants is higher than for the products.
- Note that for an endergonic reaction that the energy level for the reactants is lower than for the products.
- The region labeled #1 in each plot is the energy of activation, sometimes labeled $\Delta G'$ or E_a; #2 is the transition state -- where the energy is so high the bonds make-n-break -- if this energy is not reached, no bonds make-n-break; #3 is the free energy difference (ΔG).



$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Exergonic reaction



α-D-glucose → β-D-glucose

Endergonic Reaction

Is it possible to decrease the energy of activation?

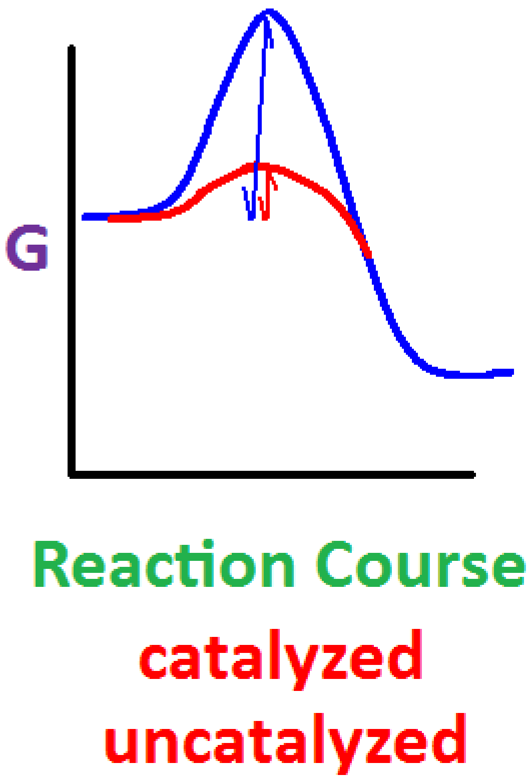
Yes!

With a catalyst.

A catalyst is something that speeds up the rate of the reaction without being consumed during the course of the reaction.

Note in the graphic that the difference between the solid line ("regular" reaction) and the asterisked line (catalyzed reaction) is the decrease in E_a.

This decrease in E_a is caused by the catalyst.



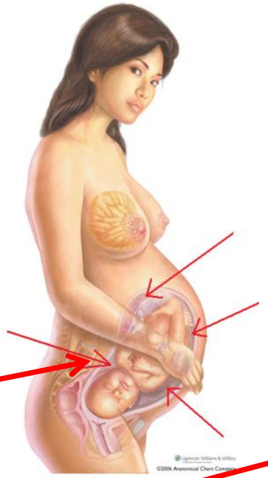
- The Third Law of Thermodynamics says that the entropy of ANY pure, perfect crystalline element or compound at 0 K is ZERO: there is NO molecular movement.
- Impure substances also have NO molecular movement at 0 K, but since the impurity is not equally distributed, this causes an increasing entropy, i.e., entropy does not equal zero in impure substances at 0 K.

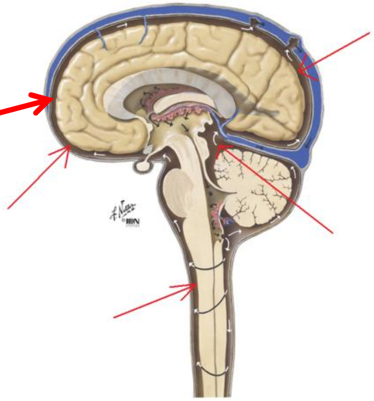
Liquid Laws

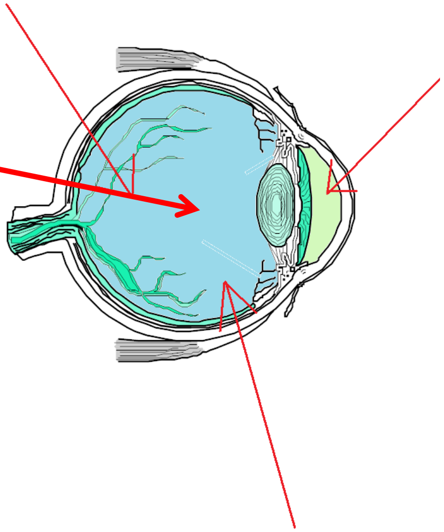
- Whether it be in topical product development or in health care, knowledge of how fluids function (flow) is critical.
- To understand fluids, a number of laws must be examined.

Pascal's Law

- Pascal's Law says that when a pressure is applied to a confined liquid, the pressure is spread out over the liquid.
- Three really good examples of this are illustrated in the Figure.
- These examples are amniotic fluid, fluid in the eye and cerebrospinal fluid.
- Keep in mind that these fluids are wonderful shock absorbers at low pressure, but that at high pressure, they become a "weapon", i.e., these fluids are double edged swords.

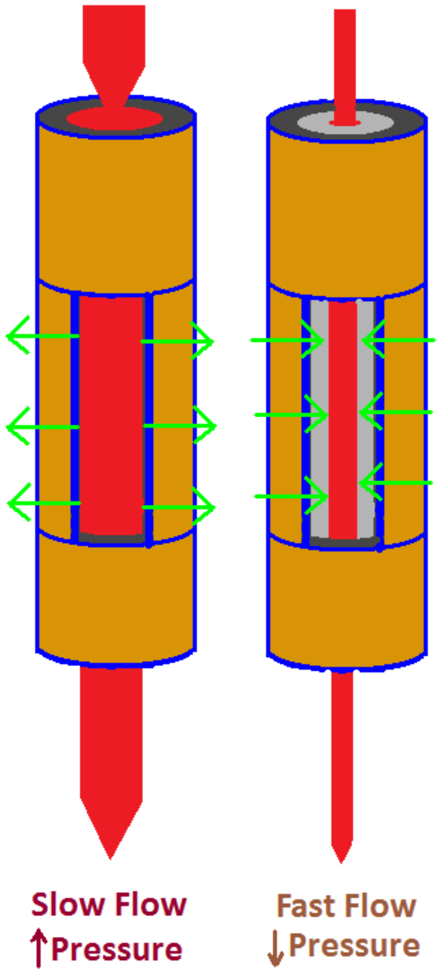




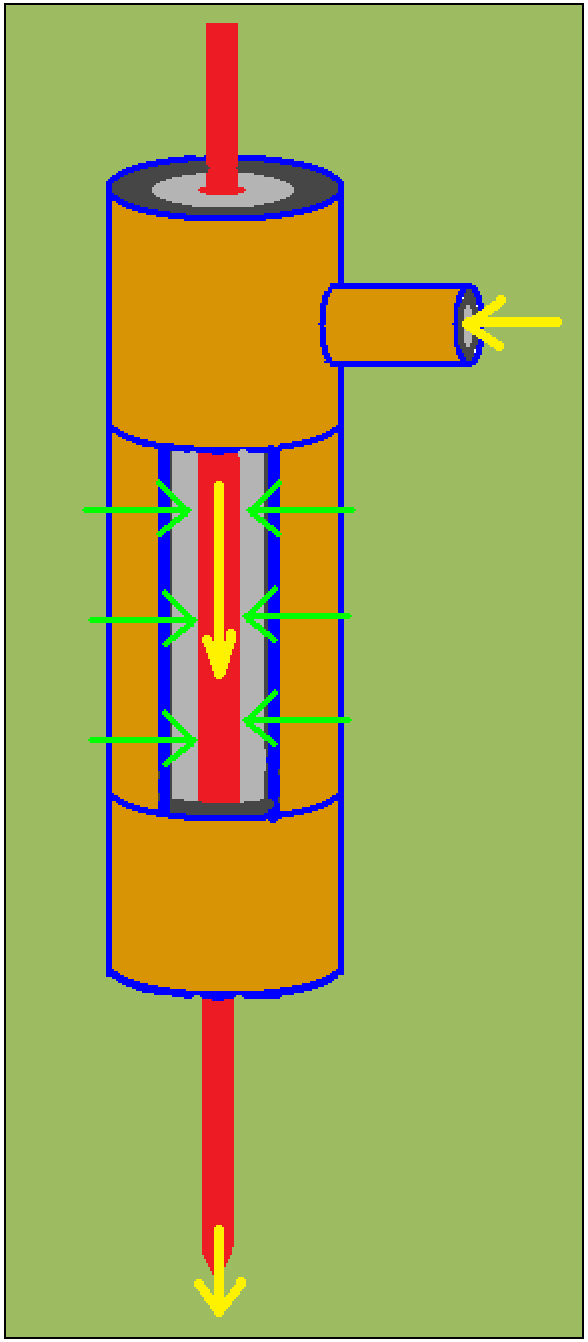


Bernoulli's Law

- Bernoulli's Law says that the faster a liquid flows through a tube, the less pressure that liquid exerts on the sides of the tube :



- It is this concept by which aspirator "pumps" work on sink faucets, Figure, right.
- Note that in the aspirator that with rapid flow, the pressure on the sides of the tube are reduced (a vacuum) and air rushes into the aspirator to make a suction.
- A modification on this law is the Venturi effect for gases and liquids.

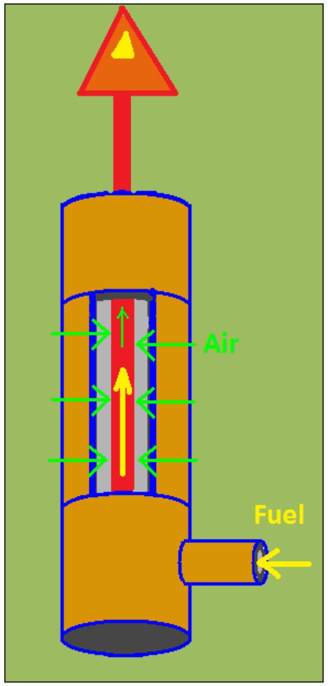


Venturi Effect

- The Venturi effect happens because fluid pressure drops around the fluid as the fluid speed increases.
- If a fluid is forced (for example: air or water) down a tube with a narrowing in it, the fluid will move faster through the narrow part.
- When it starts to move faster the pressure drops.

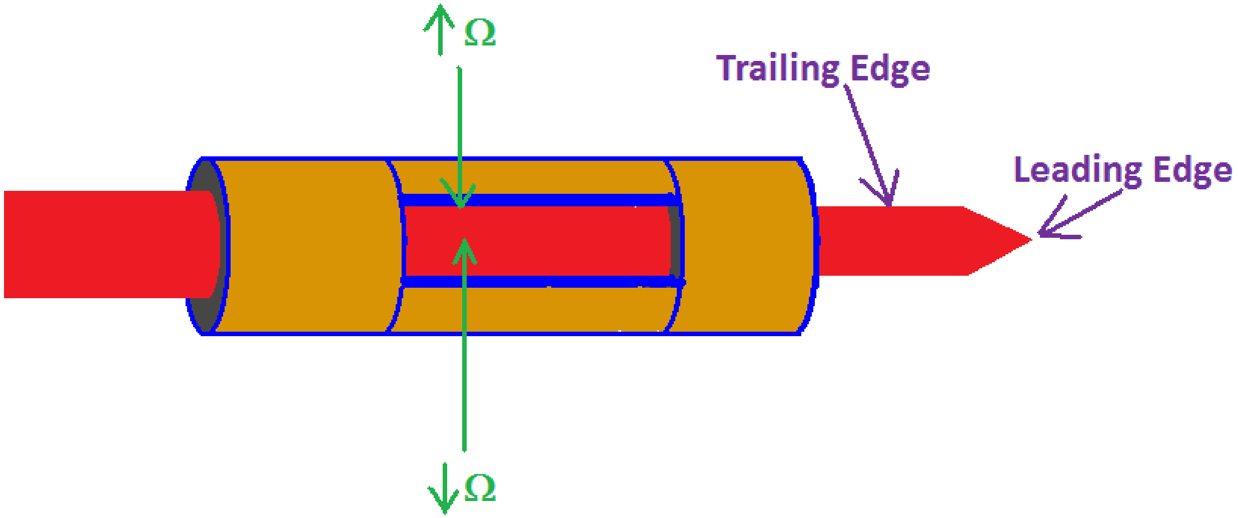
- When the pressure drops below the pressure of the air outside the "jet" (the nozzle, so to speak; the needle valve), other fluids, e.g., fuel, perfume, mixing with the fluid are sprayed into the air, creating a mixture that travels through the intake manifold of a car, Bunsen burner or bulb atomizer where it is burnt for energy or sprayed onto oneself.

- The Venturi effect doesn't really help the gas move faster, but it does encourage fuel and air to mix better giving a more useful and productive fuel burn, as does a bulb atomizer with perfumes give a more uniform spray through which to walk.



The Flow of Fluids

- Although my personal fluid preference is blood, this next section pertains to most fluids, specifically, those water based. Fluids tend to flow in one of two manner: laminar flow or turbulent flow. In laminar flow, a fluid, or fluids, flows in streamlines and in concentric layers through a tube.
- In the graphic, note that there are two obvious portions of the fluid flowing through the tube: the leading edge that has the least resistance to flow and the trailing edge that has the most resistance to flow and, hence, sort of "sticks" more to the sides of the tube.



- If you looked down the barrel of the tube, you would see the fluid coming out of the tube at you with a sort of "bullet" shape.

Turbulent flow occurs when the fluid, or fluids, is flowing in all directions and continuously mixing in a crosswise flow pattern.

The whorls observed in the figure are called Eddy currents and are very much like what one sees in rivers at blockages or obstructions.

The tendency to turbulent flow may be measured in terms of a number called the Reynold's number (R_e). This number is used for the prediction of turbulent flow.

The R_e may be determined as below:

$$R_e = \frac{v\,d\,\rho}{\eta}$$

Where R_e is the Reynold's number,
v is the velocity of the fluid flow,
d is the diameter of the vessel and
η is the viscosity of the fluid, whether it be blood, fuel, or perfume.

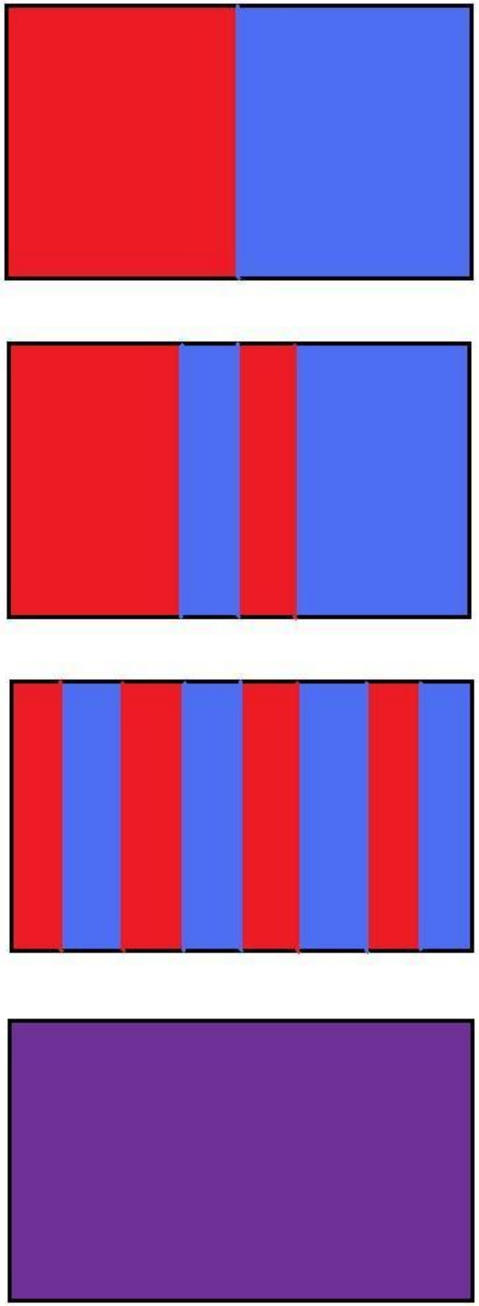
- A Reynold's number between about 200-400 indicates that turbulent flow occurs at branches of vessels (tubes) but NOT along the length of the vessels or tubes.
  - In the human body this tends to be in the large arteries where they branch off.
- A Reynold's number greater than 2000 indicates that turbulent flow occurs even in straight, smooth lengths of vessels or tubes.
  - In the human body this would occur in ventricles of the heart (the larger, lower chambers in the heart) during blood ejection.
  - It was this very problem, coupled with the rough surface that eventually caused Barney Clark to have either a stroke or pulmonary embolus that eventually lead to his death after having an artificial heart implanted in himself.
  - As the blood flowed turbulently over the rough surface of the artificial heart, the blood began falling on itself and began clotting.

Solutions, Dilutions and Colloids

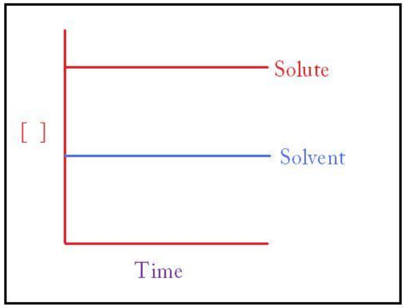
Solutions and Colloids

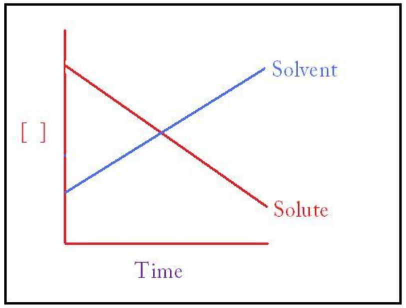
- A solution is a homogeneous mixture of 2 or more substances in which the components are present as atoms, molecules or ions.
- A solvent is the substance present in a solution in the largest amount.
- Solutes consist of one or more substances present in a solution in an amount lesser than that of the solvent.
- Dissolving describes the process of forming a solution when the solvent and solute[s] make a homogeneous mixture,e.g., sugar water.

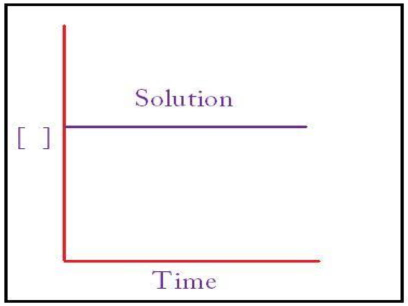
Diffusion



The movement of a solute from a region of higher concentration to a region of lower concentration until the solute is uniformly distributed in solution.

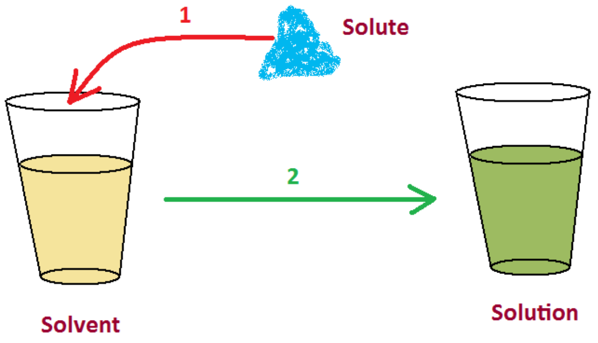




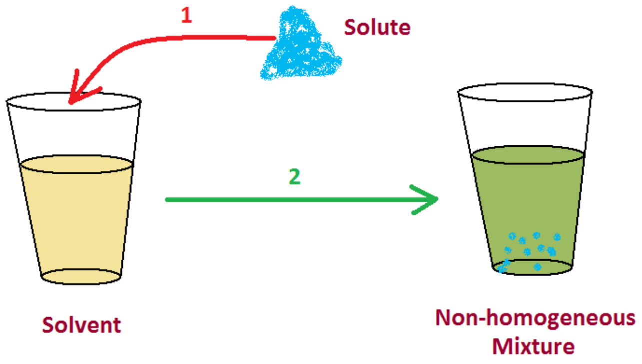


Concentration Gradient

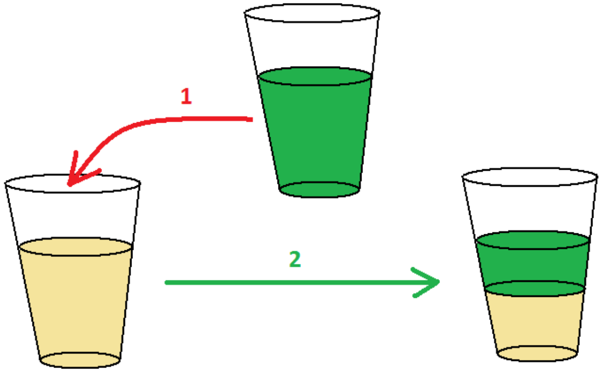
Soluble substances are substances that dissolve to a significant extent in the solvent.



An insoluble substance is the opposite of a soluble substance, i.e., makes a non-homogeneous mixture.



Immiscible is used to describe liquids that are insoluble in each other, e.g., oil and water.



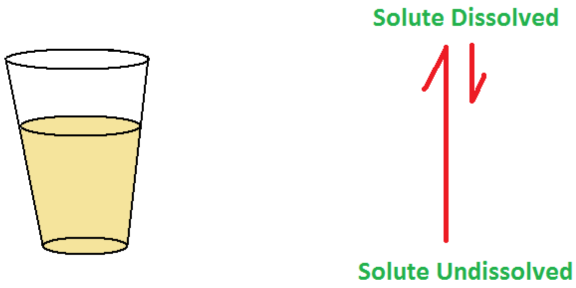
Solubility

- Solubility is defined as the maximum amount of a substance dissolved in a specified volume of solvent at a specific temperature and pressure

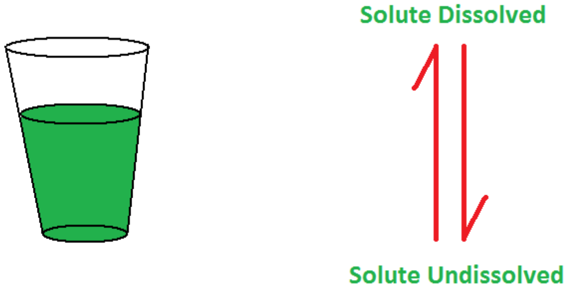
In very rough terms,
Solubility may be defined as summarized in the table, below:

Solubility in grams/0.1 L	Definition
< 0.1	Insoluble
0.1 - 1	Slightly soluble
1 - 10	Soluble
> 10	Very soluble

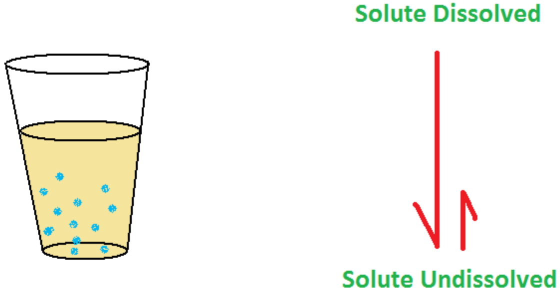
Unsaturated solutions contain less solute dissolved per unit volume of a solvent. All of the solute in an unsaturated solution is dissolved with excess solvent "caging" the solute.



Saturated solutions are solutions where dissolved solutes are in equilibrium with undissolved solutes, i.e., micro-precipitation occurs but is not observed by the naked eye (dissolved, but at the solubility limit).



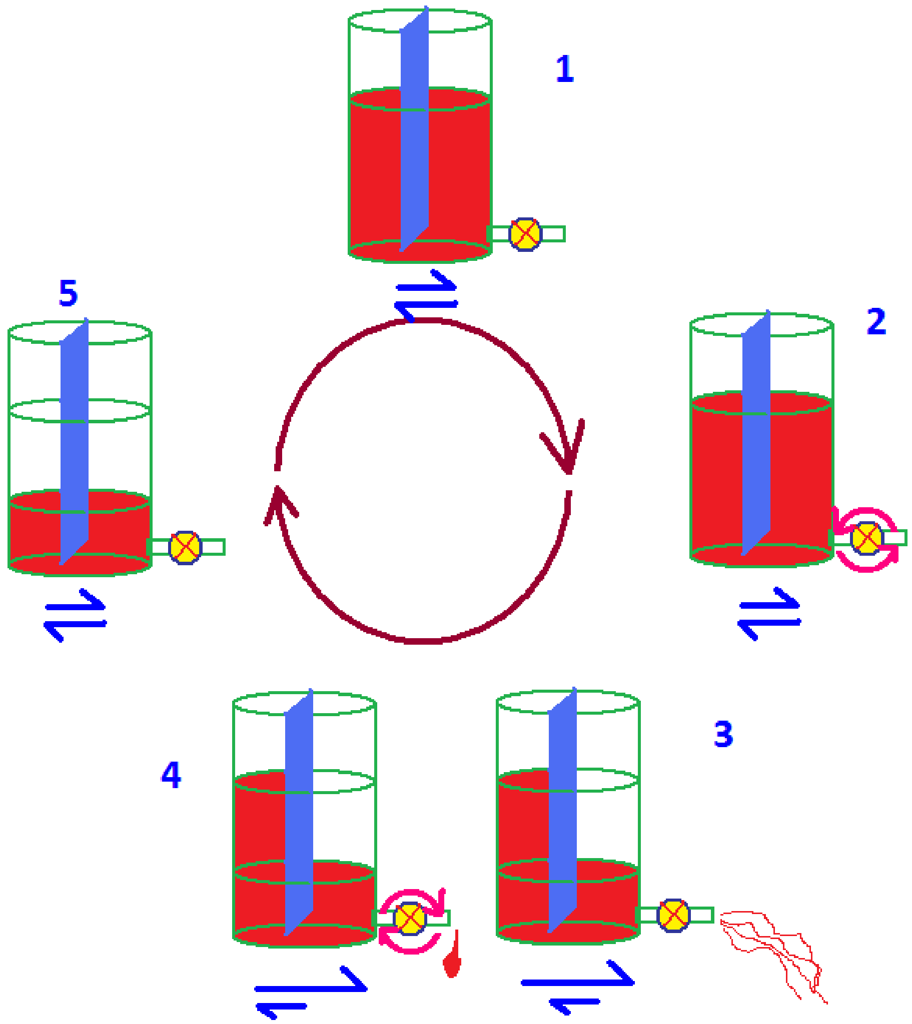
Supersaturated solutions are really mixtures. In these solutions, the solution contains more solute in the undissolved state at equilibrium, i.e., precipitate at bottom of container.



- Solutions undergo dynamic equilibrium.
- Dynamic means lots of activity.
- Equilibrium means no net change.
- Unsaturated, saturated and super-saturated solutions are constantly "changing".
- In the case of the first, more solute is dissolved than undissolved;
- The second, the dissolved/undissolved solute is at equilbrium;
- In the third solution, more solute is undissolved than is dissolved.

LeChatelier’s Principle

- Any shift to the equilibrium of a system may be brought about by outside forces.
- Le Chatelier's Principle says simply, yet eloquently, when a system at rest is acted upon by an outside force, the system responds by moving in a direction to reach equilibrium, again.
- Le Chatelier's Principle may be illustrated using a container that has two joining reservoirs with one external valve.
- At equilibrium, the reservoirs have the same volume.
- Once the outside valve has been turned on (outside force), the reservoir closest to it loses volume more and faster than the one farther away.
- Once the valve is closed (outside force), the two reservoirs balance out, again.



Chemical Properties of Water

- Water is very stable in the presence of high heat.
- At 2727° C, only 11.1% of water decomposes to form hydrogen and oxygen gases.

Water auto-ionizes, i.e., it "separates" or dissociates in itself:

$$2H_2O \Leftrightarrow H_3O^+ + OH^-$$

- The H_3O^+ ions are called hydronium ions and are acidic -- they form the basis for determining the pH of solutions, mixtures and colloids.

- The OH^- ions are the hydroxide ions and are alkaline or basic.

Auto-ionization of Water

Let's for a moment forget about acids and bases and focus on water. Water auto-ionizes in itself:

$$2H_2O \rightarrow H_3O^+ + OH^-$$

The reaction is NOT favored as written, although the ratio of protons to hydroxide ions is unity.

At 25° C, the concentration of both ionic species is $1*10^{-7}$ M.

Now, let's go back to the acids and bases.

H_3O^+ is acidic.

OH^- is alkaline.

In ACIDIC solutions, the molar concentration of H_3O^+ ($[H_3O^+]$) is greater than the molar concentration of OH^- ($[OH^-]$.

In NEUTRAL solutions, they are equal to each other.

In ALKALINE solutions, $[OH^-]$ is greater than $[H_3O^+]$.

In any dilute solution of water, the product of the hydronium ion concentration and hydroxide ion concentration is a constant, regardless of the solute.

This constant is called the dissociation constant of water and is represented by K_w.

We can determine the K_w based off of the equilibrium expression for the dissociation of water as follows:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Note that the coefficient "2" in the equilibrium reaction became the exponent "2" in the equilibrium expression.
By rearranging, the equation takes on a slightly different look:

$$K [H_2O]^2 = [H_3O^+] * [OH^-]$$

The molar concentration of water is around 55 M -- compared to the small amount that ionizes, it doesn't really change. Since it doesn't really change to any significance, the product of the constant, K, and the square of the $[H_2O]$ are equal to the K_w and the equation takes on the following look:

$$K_w = [H_3O^+] * [OH^-]$$

At 25° C, the K_w is equal to the square of $1*10^{-7}$, or $1*10^{-14}$.

How do we use this information to determine the acidity or alkalinity of a solution? From:

$K_w = [H_3O^+] * [OH^-]$, we substitute the numerical values:

$$1*10^{-14} = (1*10^{-7}) * (1*10^{-7})$$

Next, we take the logs of each side:

$$\log (1*10^{-14}) = \log[(1*10^{-7}) * (1*10^{-7})]$$

which rearranges to:

$$\log (1*10^{-14}) = \log (1*10^{-7}) + \log (1*10^{-7})$$

This gives us:

$$-14 = -7 + -7$$

Take the negative of both sides and we get:

$$14 = 7 + 7$$

Taking the negative log (-log) of this equation may be re-written as "p":

pK_w = pH + pOH

or:
14 = pH + pOH, where $[H^+] = [H_3O^+]$

Another way to look at this is that:

$[H_3O^+] = 1*10^{-pH}$

At neutrality where the hydronium and hydroxide ion concentrations are equal, the pH is 7 ($-\log[1*10^{-7}]$).

When the pH is less than 7, the solution is acidic.
When pH equals 7, is neutral.
When the pH is greater than 7, the solution is alkaline or basic.

Acids and Bases

Centuries ago, certain substances were recognized for:

Sour taste	Turned vegetable blues to red	Solvent power	Ability to neutralize alkalies to form salts

These were called "acids" from "ac" which means sharp, as in *acetum*.

Other substances were recognized for:

Soapiness	Cutting grease	Having the reverse effect of acids

These were called "alkalies" which is from Arabic for plant ashes.
They are also called bases.

Most Significant Properties

1) Their effect on acid/base indicators.
The table, below, summarizes the acid and base forms of
6 different acid/base indicators:

Acid Form (color)	Indicator	Base Form (color)
Red	**Litmus**	**Blue**
Clear	**Phenolphthalein**	**Pink**
Yellow	**Bromocresol green**	**Green**
Yellow	**Phenol red**	**Red**
Red	**Methyl red**	**Yellow**
Yellow	**Bromocresol purple**	**Purple**

2) Their ability to react with each other to produce salts.
3) Their catalytic action.
4) Their ability to displace weaker acids or bases.
5) Aqueous solutions conduct an electrical current.

Acid-Base Titrations

- Knowing now what we know about acids, how may we apply this information to the lab?
- By studying acid/base titrations.
- Acids and hydroxide bases react to form water and a salt.
- This sort of reaction is called a neutralization reaction.
- Bases that contain bicarbonate or carbonate in them also produce carbon dioxide in addition to the water and the salt.
- Examples of these sorts of [neutralization] reactions are summarized, below, in the table:

$HCl + NaOH \rightarrow NaCl + H_2O$
$H_2SO_4 + 2\ KOH \rightarrow K_2SO_4 + 2H_2O$
$2HNO_3 + Ba(OH)_2 \rightarrow Ba(NO_3)_2 + 2H_2O$
$H_3PO_4 + Al(OH)_3 \rightarrow AlPO_4 + 3H_2O$
$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2\uparrow + H_2O$
$6HNO_3 + Al_2(CO_3)_3 \rightarrow 2Al(NO_3)_3 + 3CO_2\uparrow + 3\ H_2O$
$H_2SO_4 + MgCO_3 \rightarrow MgSO_4 + CO_2\uparrow + H_2O$

Normality

In reactions, thus far, we've looked at grams and moles. Sometimes, though, we need to express units in terms of protons, hydroxide ions or charges.

When we do this we use a unit called EQUIVALENTS.

By definition, an equivalent (Eq) of base is that amount of base that contributes or provides 1 mol of hydroxide ion (OH^-):

$NaOH \rightarrow$ 1 mol OH^- which is 1 Eq

$Ba(OH)_2 \rightarrow$ 2 mol OH^- which is 2 Eq

$Al(OH)_3 \rightarrow$ 3 mol OH^- which is 3 Eq

By definition, an equivalent (Eq) of acid is that amount of acid that contributes or provides 1 mol of hydronium (H_3O^+) or hydrogen (H^+) ion:

$HCl \rightarrow$ 1 mol H^+ which is 1 Eq

$H_2SO_4 \rightarrow$ 2 mol H^+ which is 2 Eq

$H_3PO_4 \rightarrow$ 3 mol H^+ which is 3 Eq

By definition, an equivalent (Eq) of salt is that amount of salt that will contribute or provide 1 mol of positive (OR negative) charges when dissolved or dissociated:

$KCl \rightarrow K^+ + Cl^-$ which gives 1 Eq

$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$ which gives 2 Eq

$AlCl_3 \rightarrow Al^{3+} + 3Cl^-$ which gives 3 Eq

Remember that we can calculate Molecular Weight by dividing the mass of X mol of substance (in grams) by the number of mols ("X") to get molecular weight in g/mol.

Using equivalents, we can calculate EQUIVALENT WEIGHT, as well:

Let's calculate the equivalent weight of $AlCl_3$ -- this has a molecular weight of 133.5 g/mol

$$\frac{133.5\,g}{mol} * \frac{1\,mol\,AlCl_3}{3\,Eq} = \frac{44.5\,g}{Eq}$$

Notice that we used the total number of positive charges (OR negative charges: 3 * 1 = 3) for our equivalents.

Let's calculate the equivalent weight of sulfuric acid:

$$\frac{98\,g\,H_2SO_4}{mol} * \frac{1 mol\,H_2SO_4}{2\,Eq} = \frac{49\,g}{Eq}$$

Let's calculate the equivalent weight of LiCl:

$$\frac{42.5\,g\,LiCl}{mol} * \frac{1 mol\,LiCl}{1 Eq} = \frac{42.5\,g}{Eq}$$

Let's calculate the equivalent weight (Eq Wt) of $Mg(OH)_2$

$$\frac{58.3\,g\,Mg(OH)_2}{mol} * \frac{1 mol\,Mg(OH)_2}{2\,Eq} = \frac{29.15\,g}{Eq}$$

Clinically, the unit milli-equivalent is used (mEq) when measuring serum concentrations of electrolytes, e.g., sodium and potassium ions.

When we first learned about the mole, we extended our knowledge by studying a concentration term called molarity (M = Molar). This is a unit that expresses how many mols of a substance are dissolved in one liter of solution.

We can use equivalents to do a similar concentration term: normality (N = Normal). Normality is defined as the number of equivalents of a substance that is dissolved in one liter of solution (Eq/L).

Let's begin by calculating the normality of a solution that has 40 g NaOH dissolved in 1 L of water:

$$(40\,g\,NaOH)*\frac{1mol}{40\,g\,NaOH}*\frac{1\,Eq}{1mol}*\frac{1}{1liter}=1\,N=1\frac{Eq}{L}$$

Notice how the units cancel out.

Let's calculate the normality of a solution of 29.15 g $Mg(OH)_2$ that is dissolved in 500 mL of water.

$$(29.15\,g\,Mg(OH)_2*\frac{1mol}{58.3\,g\,Mg(OH)_2}*\frac{2\,Eq}{1mol}*\frac{1}{0.5\,L}=2\,N=2\frac{Eq}{L}$$

Acid Formation and Dissociation

The formation of protonic acids may occur by 6 different mechanisms. These mechanisms and examples are summarized in the table, below:

Acid Formation Mechanism	Representative Reactions
Direct union of elements	$H_2 + Cl_2 \rightarrow 2\ HCl$ $H_2 + S \rightarrow H_2S$ $H_2 + Br_2 \rightarrow 2\ HBr$ $H_2 + F_2 \rightarrow 2HF$ $H_2 + I_2 \rightarrow 2HI$
Action of water on non-metal oxides	$CO_2 + H_2O \rightarrow H_2CO_3$ $SO_3 + H_2O \rightarrow H_2SO_4$ $P_4O_{10} + 6\ H_2O \rightarrow 4H_3PO_4$ $SO_2 + H_2O \rightarrow H_2SO_3$
Heating salts of volatile acids with NON-volatile or SLIGHTLY volatile acids	$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl\uparrow$ $NaBr + H_3PO_4 \rightarrow NaH_2PO_4 + HBr\uparrow$
By the action of salts with other acids producing a precipitate	$H^+ + Cl^- + Ag^+ + NO_3^- \rightarrow AgCl + H^+ + NO_3^-$ $2H^+ + SO_4^{2-} + Ba^{2+} + 2ClO_3^- \rightarrow BaSO_4 + 2H^+ + 2ClO_3^-$
By hydrolysis	$PBr_3 + 3\ H_2O \rightarrow H_3PO_3 + 3\ HBr$ $PCl_5 + 4\ H_2O \rightarrow H_3PO_4 + 5\ HCl$
By oxidation-reduction reactions	$H_2S + I_2 \rightarrow 2HI + S$ $2HNO_3 + 2SO_2 + H_2O \rightarrow 2H_2SO_4 + NO\uparrow + NO_2\uparrow$

- If the acid has one ionizable proton, it is called a mono-protic acid.
- If it has 2, a di-protic acid.
- If it has three ionizable protons, it is called a triprotic acid.
- The significance has to with eventually using this information in reaction-type calculations.
- Each proton has its own dissociative step, i.e., the protons don't just "fall off" the acids all at once.
- They are removed a proton at a time.

Monoprotic Dissociation -- 1 H^+	**Diprotic Dissociation -- 2 H^+**	**Triprotic Dissociation -- 3H^+**
$HCl + H_2O \rightarrow H_3O^+ + Cl^-$	$H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$ $HCO_3^- + H_2O \rightarrow H_3O^+ + CO_3^{2-}$	$H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$ $H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$ $HPO_4^{2-} + H_2O \rightarrow H_3O^+ + PO_4^{3-}$
$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$	$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ $HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$	
$HCN + H_2O \rightarrow H_3O^+ + CN^-$		

Base Formation

There are 5 mechanisms by which hydroxides are formed.
These mechanisms and representative reactions are summarized in the table, below:

Base Mechanism	**Representative Reaction**
Alkali metals or alkaline earth metals react with water	$2\ K + 2\ H_2O \rightarrow 2\ K^+ + 2\ OH^- + H_2\uparrow$ $Ca + 2\ H_2O \rightarrow Ca^{2+} + 2\ OH^- + H_2\uparrow$ $2\ Na + 2\ H_2O \rightarrow 2\ Na^+ + 2\ OH^- + H_2\uparrow$
Water reacting with oxides of alkali/alkaline earth metals	$Na_2O + H_2O \rightarrow 2\ Na^+ + 2\ OH^-$ $CaO + H_2O \rightarrow Ca^{2+} + 2\ OH^-$ $MgO + H_2O \rightarrow Mg^{2+} + 2\ OH^-$
Salts with other bases with a resulting precipitate	$2\ Na^+ + CO_3^{2-} + Ca^{2+} + 2\ OH^- \rightarrow CaCO_3\downarrow + 2\ Na^+ + 2\ OH^-$
Electrolysis	$2\ Na^+ + 2\ Cl^- + 2\ H_2O + \text{Electrolysis} \rightarrow 2\ Na^+ + 2\ OH^- + H_2\uparrow + Cl_2\uparrow$
Dissolving NH_3 in water	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Acids and Bases Dissociate in Water

Fortunately for us, acids and bases dissociate in water:

$HA + H_2O \rightarrow H_3O^+ + A^-$

Where HA is any acid and A^- is the anion left behind after the proton has separated from the acid.

We may determine the acid dissociation constant (like we did for water) as follows, left:

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

$$K * [H_2O] = K_a = \frac{[H_3O^+] * [A^-]}{[HA]}$$

The water concentration doesn't change as we saw in the K_w determination, so we'll rearrange the equation as above, right:

Where K_a is the acid dissociation constant.

The K_a is equal to the arithmetic relationship between the undissociated and dissociated acid:

$HA \Leftrightarrow H^+ + A^-$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

and notice that the K_a is directly proportional to $[H^+]$ -- more on this later.

Acids like H_2A and H_3A have multiple dissociation steps.

Each step is represented by its own K_a or K_b:

$H_2A \Leftrightarrow HA^- + H^+$

$HA^- \Leftrightarrow A^- + H^+$

where

$$K_{a1} = \frac{[HA^-][H^+]}{[H_2A]}$$

and

$$K_{a2} = \frac{[A^-][H^+]}{[HA^-]}$$

The total K_a for this reaction is equal to the product of the two dissociation constants:

$$K_{a1} \bullet K_{a2} = \frac{[HA^-][H^+][A^-][H^+]}{[H_2A][HA^-]}$$

and

$$K_{a-TOTAL} = \frac{[H^+]^2[A^-]}{[H_2A]}$$

A tri-protic acid has three dissociations, hence the total K_a is equal to the products of the three dissociation constants.
Likewise, the K_b's for bases are calculable in the same manner; an exception for bases is that you are focusing on the OH-'s instead of the protons.

We can do the same for a base:

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

The equilibrium expression is as follows:

$$K = \frac{[NH_4^+]*[OH^-]}{[NH_3]*[H_2O]}$$

Again, since the water concentration doesn't change, we'll rearrange and manipulate:

$$K*[H_2O] = K_b = \frac{[NH_4^+]*[OH^-]}{[NH_3]}$$

Where K_b is the base dissociation constant.

Note that in all cases, these equilibrium expressions are the quotient of the product concentrations and the reactant concentrations.

Would you suspect, then, that there is some sort of relationship between K_a, K_b and K_w? Let's see.

Remember that:

$$K_w = [H_3O^+]*[OH^-]$$

and that:

$$K_a = \frac{[H_3O^+]*[OH^-]}{[HA]}$$

and that:

$$K_b = \frac{[HA]*[OH^-]}{[A^-]}$$

Let's multiply K_a by K_b and see what happens:

$$K_a * K_b = \frac{[H_3O^+]*[HA]*[A^-]*[OH^-]}{[HA]*[A^-]}$$

Note that all we're left with after canceling is:

$$[H_3O^+]*[OH^-] = K_aK_b = K_w$$

So that we now know that the product of the acid and base dissociation constants for the same compound is equal to the K_w.
Since $K_aK_b = 1*10^{-14}$, if the K_a or the K_b is in a reference table in a textbook or online, the other can easily be calculated.

Additionally, we can also use this same method with conjugate acid-base pairs, e.g. HF and F^- and NH_4^+ and NH_3:

$$K_w \overset{?}{=} K_a\{HF\} * K_b\{F^-\}$$

$$K_w \overset{?}{=} \frac{[H_3O^+]*[HF]*[F^-]*[OH^-]}{[HF]*[F^-]}$$

$$K_w \overset{yes}{=} [H_3O^+]*[OH^-]$$

and:

$$K_w \overset{?}{=} K_a\{NH_4^+\} * K_b\{NH_3\}$$

$$K_w \overset{?}{=} \frac{[H_3O^+]*[NH_3]*[NH_4^+]*[OH^-]}{[NH_3]*[NH_4^+]}$$

$$K_w \overset{yes}{=} [H_3O^+]*[OH^-]$$

Why is all of this important? How would you know if a salt solution or any solution from an acid and/or a base will be acidic, alkaline or neutral with both H^+ and A^- present?

Method 1:
Eyeball the pH of Solutions of Acids and Bases

A **strong acid** and a **strong base** mixed together yields a neutral solution, e.g., hydrochloric acid with sodium hydroxide.

A **strong acid** and a **weak base** yields an acidic solution, e.g., hydrochloric acid and ammonia.

A **weak acid** plus a **strong base** yields a basic solution, e.g., acetic acid and sodium hydroxide.

A **weak acid** and a **weak base** mixed together can be complex. **BUT**! If they are equal in strength they will yield a neutral solution, e.g., acetic acid and ammonia.

Determining the pH of A Solution

If a solution of 0.3M HOAc dissociates in water by the following reaction:
$HOAc + H_2O \rightarrow H_3O^+ + OAc^-$,
What is the pH of the solution? K_a for HOAc is $1.8*10^{-5}$
Solution: Always write out the equation, first, in these types of questions as laid out below:

	HOAc	**+**	**H_2O**	**→**	**H_3O^+**	**+**	**OAc^-**
[Before reaction]	**0.3M**				**0M**		**0M**
[After reaction]	**- x**				**+ x**		**+ x**
Total concentration of species	**0.3 - x**				**x**		**x**

Note that the concentrations change in proportion to the amount (number of mols) of reactants and products, i.e., 1 mol of HOAc begets 1 mol of hydronium ion and 1 mol of acetate ion.

Write the equilibrium expression, substitute and rearrange and solve:

$$K_a = \frac{[H_3O^+]*[OAc^-]}{[HOAc]} = \frac{X*X}{0.3-X} = \frac{X^2}{0.3-X} \approx \frac{X^2}{0.3}$$

$$(K_a)*(0.3) = X^2$$

$$\sqrt{(1.8*10^{-5})*(0.3)} = X = 0.0023\,M$$

$$X = 0.0023\,M = [H_3O^+]$$
$$pH = -\log 0.0023 = 2.64$$

What is the pOH for this aqueous solution?

Since pH + pOH = 14, it follows that 14 - 2.64 = 11.36 is the pOH.

Example #1: What is the pH of a solution that is 0.8M in ammonia? K_b for NH_3 = $1.8*10^{-5}$.
Solution: Set up as before:

	NH_3	+	H_2O	→	NH_4^+	+	OH^-
[Before reaction]	0.8M				0M		0M
[After reaction]	- x				+ x		+ x
Total concentration of species	0.8 - x				x		x

$$K_b = \frac{[NH_4^+]*[OH^-]}{[NH_3]} = \frac{X*X}{0.8-x} \approx \frac{X^2}{0.8}$$

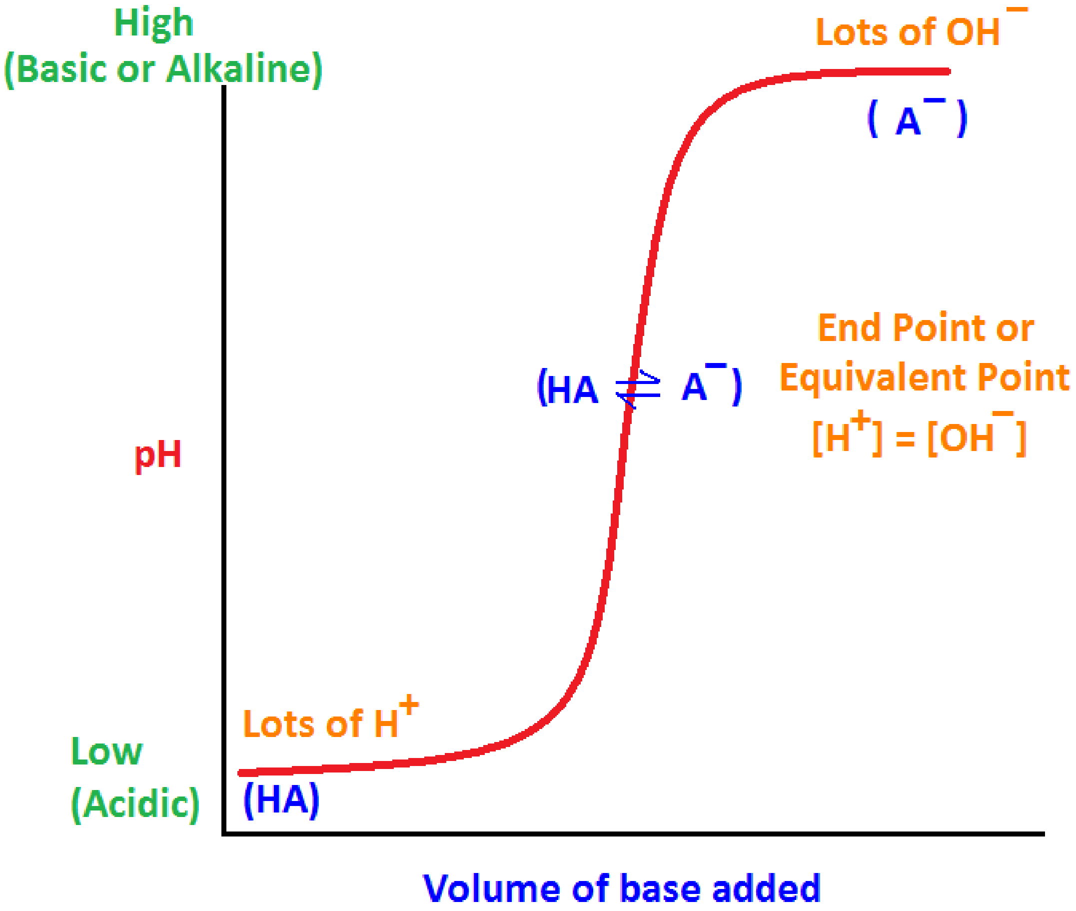
$$\sqrt{(1.8*10^{-5})*(0.8)} = X = 0.0038\,M$$

$$pOH = -\log 0.0038 = 2.42$$

$$pH = 14 - 2.42 = 11.58$$

Acid-Base Titrations: In General:

Titrations of acids and bases follow a general sigmoid-shaped curve for a mono-protic acid:



Acid-Base Titrations

$HA \leftrightarrow H^+ + A^-$

Or

$HA + MOH \leftrightarrow HOH + MA$

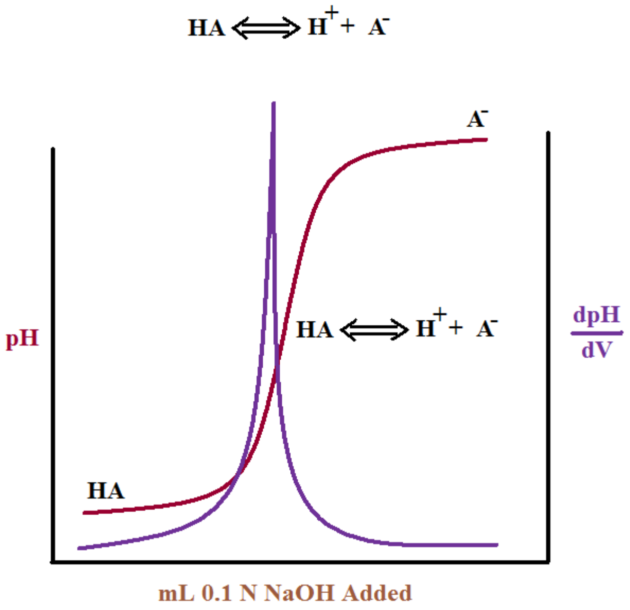
Mono-protic Acid

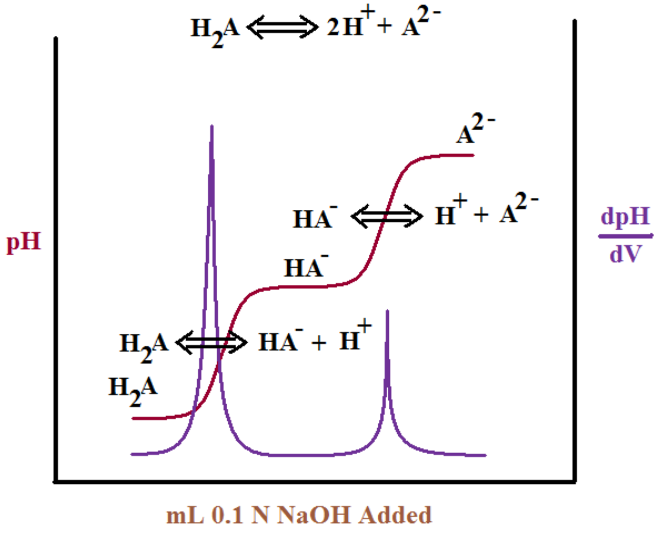
$H_2A \leftrightarrow 2H^+ + A^{-2}$

Or

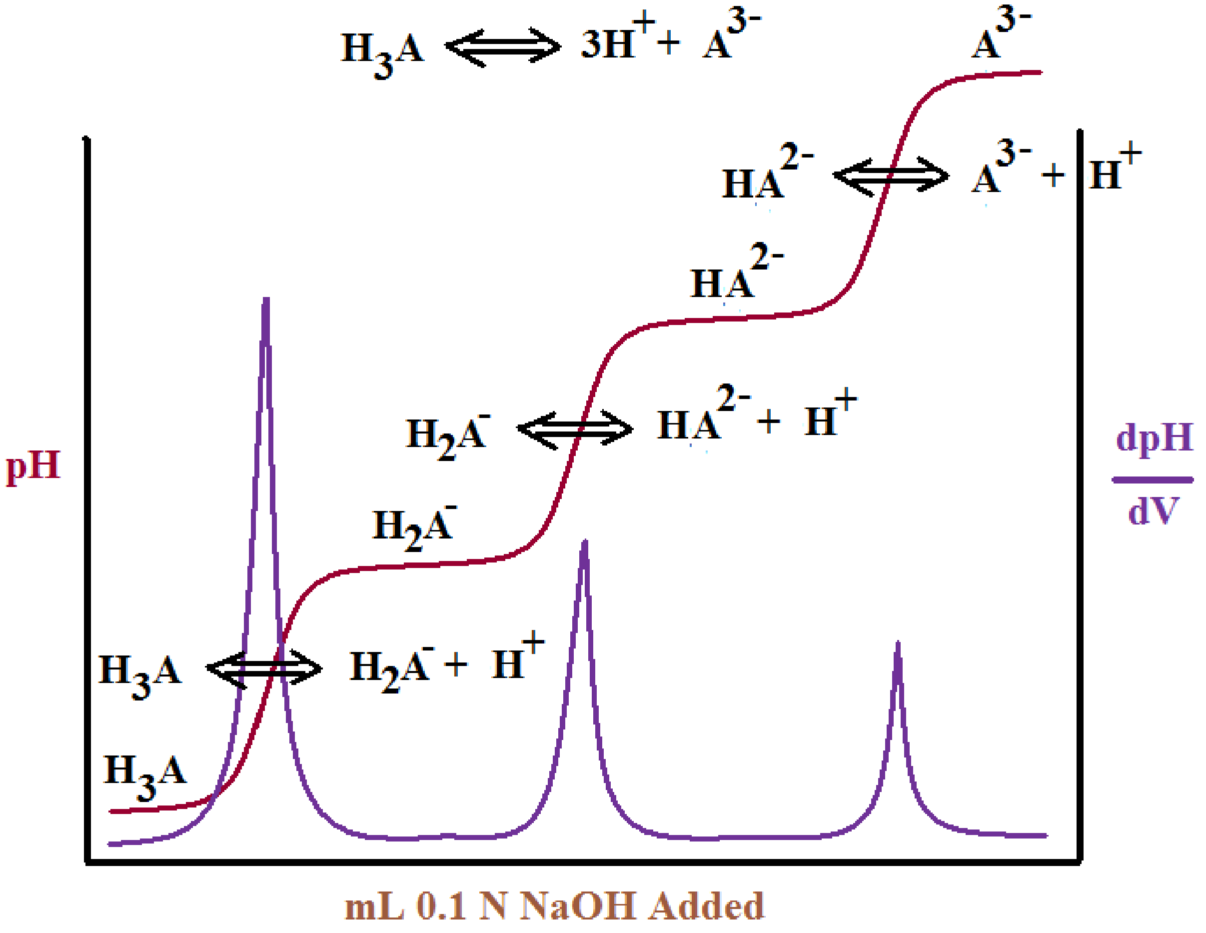
$H_2A + 2MOH \leftrightarrow 2HOH + M_2A$

Di-protic Acid

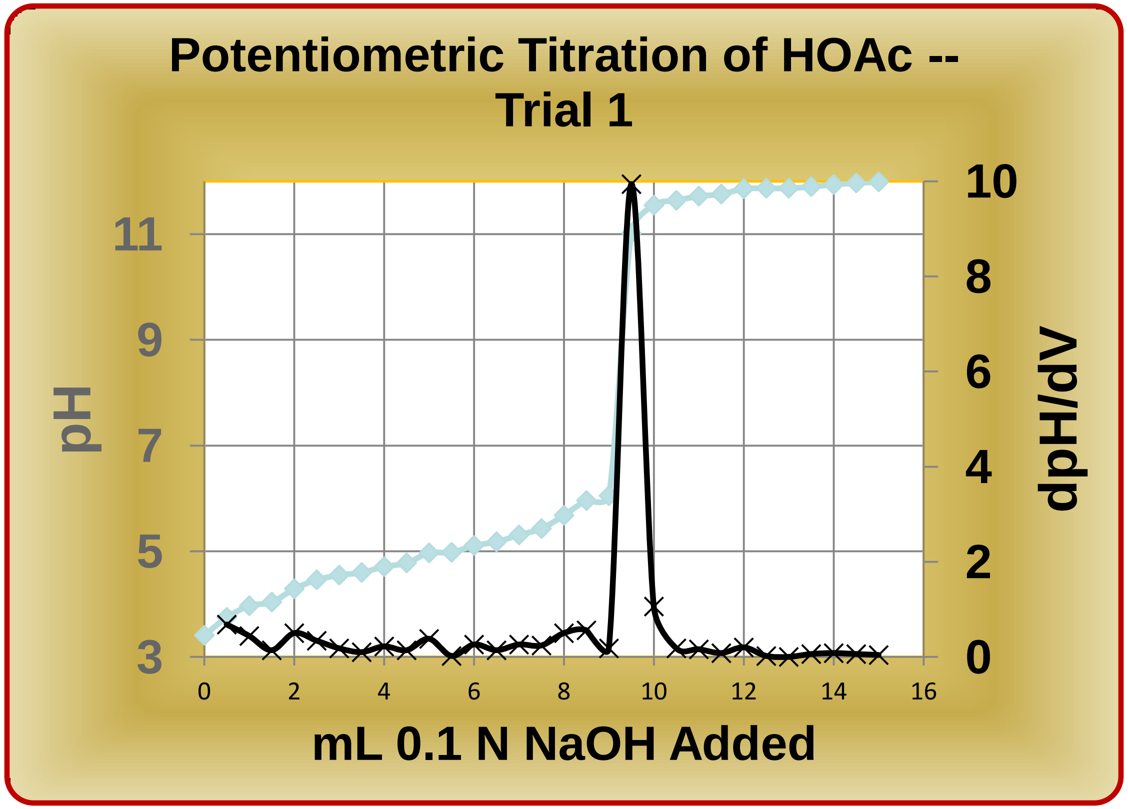




Tri-Protic Acids have THREE Endpoints

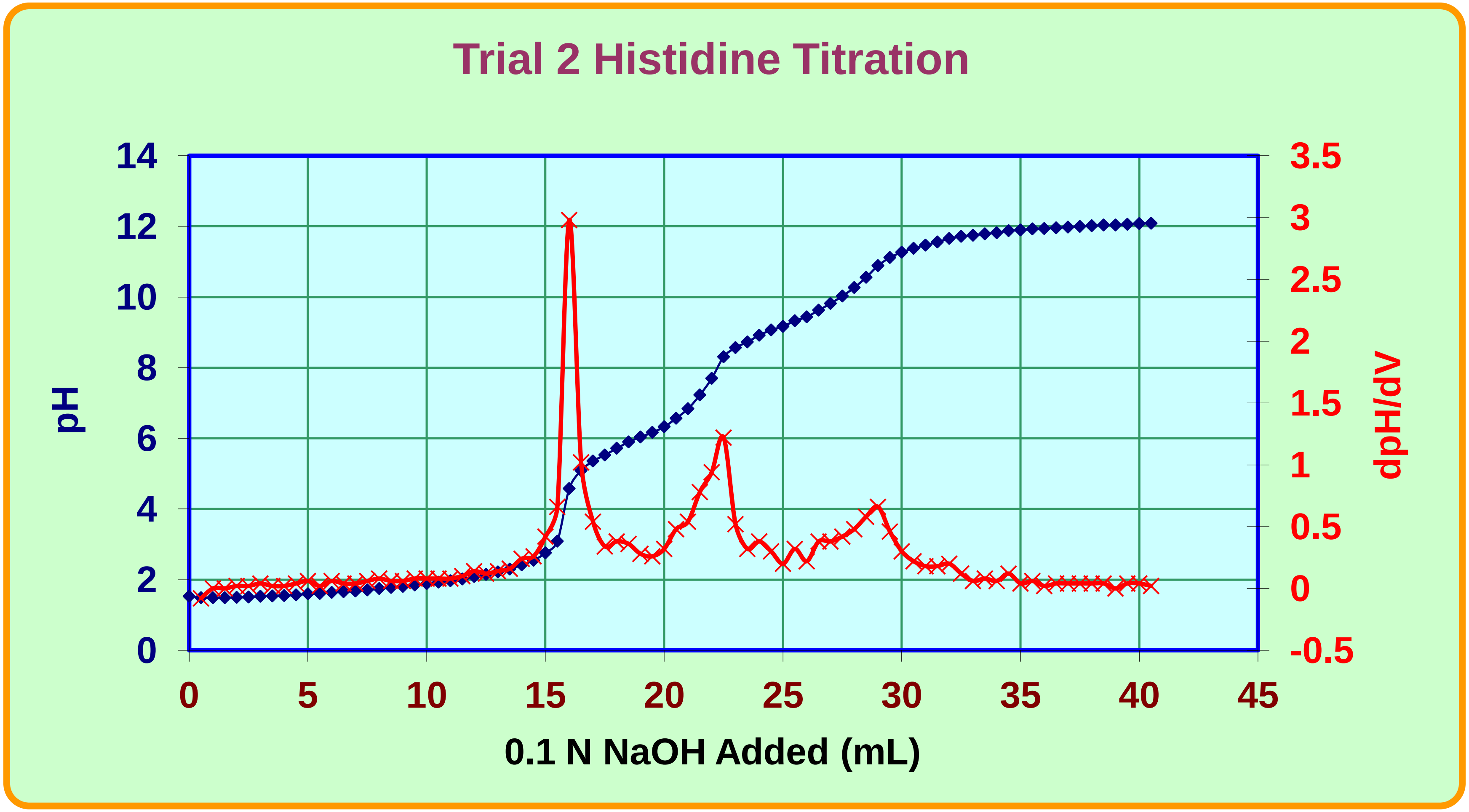


When using a pH meter to keep track of the titration, the equivalent point/end point are not obvious. Typically a technique called "taking the first derivative" of the pH curve (the sigmoid shaped curve) is used to determine these points. Without going into detail, this involves manipulating the sigmoid curve data to take on a sort of "backwards, inside out parabolic shape".



The value of the equivalence point is that it is the pH at which the $[H^+] = [OH^-]$. At that point, divide the volume at the endpoint in half, read from that volume up onto the sigmoid-shaped curve, then over to the pH curve and you will be at the numerical value for the negative log of the acid dissociation constant (pK_a)

Amino Acid Titration: 3 Endpoints



Henderson-Hasselbalch Equation for Calculating the pH of a Weak Acid

- The derivation of this equation is a rather lengthy one and is summarized, below.
- Note that it starts from the very simple mono-protic acid dissociation that we've pretty much beaten to death.
- The salt concentration is equivalent to the anion concentration.
- This equation is very useful in biomedical research when making buffers.

$$HA \Leftrightarrow H^{+} + A^{-}$$

$$K_a = \frac{[H^{+}]*[A^{-}]}{[HA]}$$

$Rearranging, sequentially:$

$$\frac{[HA]}{[A^{-}]} * K_a = [H^{+}]$$

$$-\log\left(\frac{[HA]}{[A^{-}]} * K_a\right) = -\log[H^{+}]$$

$$-\log\left(\frac{[HA]}{[A^{-}]}\right) - \log K_a = pH$$

$$-\log\left(\frac{[HA]}{[A^{-}]}\right) + pK_a = pH$$

$$\log\left(\frac{[A^{-}]}{[HA]}\right) + pK_a = pH \Leftrightarrow pKa + \log\left(\frac{[salt]}{[acid]}\right)$$

Example #1: Find the pH of a solution that is 0.05M in carbonic acid and 0.025M in bicarbonate ion.

The K_{a1} for carbonic acid is $4.4*10^{-7}$.

Solution: First get the pK_a

$$pK_a = -\log(4.4*10^{-7}) = 6.357$$

Secondly, set up, manipulate and plug into the equation:

$$pH = pK_a + \log\left(\frac{[salt]}{[acid]}\right) \Leftrightarrow pK_a + \log\left(\frac{HCO_3^-}{H_2CO_3}\right)$$

$$pH = 6.357 + \log\left(\frac{0.025}{0.05}\right) = 6.357 + \log 0.5$$

$$pH = 6.357 - 0.301 = 6.056$$

Example #2: If a solution of carbonic acid was at a pH of 7.35 and was 0.03M in carbonic acid, what molar concentration of bicarbonate ion is present?
Use the same K_{a1} as in Example 1, above.
Solution: Manipulate the equation right off the bat and substitute right into it:

$$pH = pK_a + \log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right)$$

$$pH - pKa = \log\left(\frac{[HCO_3^-]}{H_2CO_3}\right)$$

$$pH - pK_a = \log[HCO_3^-] - \log[H_2CO_3]$$

$$pH - pK_a + \log[H_2CO_3] = \log[HCO_3^-]$$

$$anti\log(pH - pK_a + \log[H_2CO_3]) = [HCO_3^-]$$

$$anti\log(7.35 - 6.357 + (\log 0.03)) = [HCO_3^-]$$

$$anti\log(-0.530) = [HCO_3^-] = 0.295M$$

Redox Reactions: Oxidation-Reduction Reactions

- Reduction ALWAYS occurs with oxidation -- you can not have one without the other.
- One substance is oxidized and the other is reduced.

Three Definitions of Oxidation

- 1) A substance is oxidized when it GAINS oxygen atoms, e.g.:
  - $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2\uparrow + 6H_2O$
- 2) A substance is oxidized when it LOSES hydrogen atoms, e.g.:
  - Methanol (CH_3OH) → formaldehyde (CH_2O) + $H_2\uparrow$
- 3) A substance is oxidized when it LOSES electrons, e.g.:
  - $Mg + Cl_2 \rightarrow Mg^{2+} + 2Cl^-$ (equivalent to $MgCl_2$ -- Mg has to undergo electron loss, first)

Three Definitions of Reduction

- 1) A substance is reduced when it LOSES oxygen atoms, e.g.:
  - $2\ KClO_3$ + heat → $2KCl + 3O_2\uparrow$
- 2) A substance is reduced when it GAINS hydrogen atoms, e.g.:
  - $CO + 2H_2$ + Pt, Pd or Ni catalyst → CH_3OH (methanol)
- 3) A substance is reduced when it GAINS electrons, e.g.:
  - $Cu^{2+} + 2e^- \rightarrow Cu$

Redox Reactions -- More Terms

- When a redox reaction occurs, one substance is reduced and another oxidized.
  - The substance that is reduced is the OXIDIZING AGENT.
  - The substance that is oxidized is the REDUCING AGENT, e.g.:

$$CuO + H_2 \rightarrow Cu + H_2O$$

- The **CuO is the oxidizing agent** as the Cu in the CuO is reduced from the +2 state on the left side of the arrow to the elemental state on the right side of the arrow.
- The **H_2 is the reducing agent** as the H_2 goes from the elemental state on the left side of the arrow to a +1 state on the right side of the arrow.
- This reaction also demonstrates another way in which to remember reduction.
- Reduction of something occurs when its charge is further reduced.
- This means that if Cu is in a +2 state that it is reduced to Cu in a +1 state in the appropriate reaction.
- Likewise, Br in the elemental state (I'm using atomic -- not molecular Br_2) may be reduced to Br in the -1 state.
- As long as electrons may be GAINED, the substance will be reduced in its charge.

Oxidation Number/Oxidation State Defined

- We now have some introductory terms and ideas about redox reactions.
- The next step is to learn how to use this information with new skills so that we may balance redox reactions.
- Before we begin, though, understand that oxidation number and oxidation state mean the same thing.

- The oxidation number of a covalently bonded element is the charge the element would have if all the shared pairs of electrons in the Lewis structure for the species were transferred to the more electronegative atoms.
  - The oxidation number of covalently bound elements are not real charges like the charges on ions. Hence, they may not be experimentally measured.
  - Only for simple mono-atomic ions such as Ba^{2+}, Na^{+}, S^{2-} and for elements such as N_2, O_3, are oxidation numbers real numbers that are easily obtained in the lab.
  - In binary ionic compounds, the bonding electrons are already on the more electronegative atom because ionic bonds result from electron transfer, therefore, the oxidation number of mono-atomic ions equals the ionic charge.

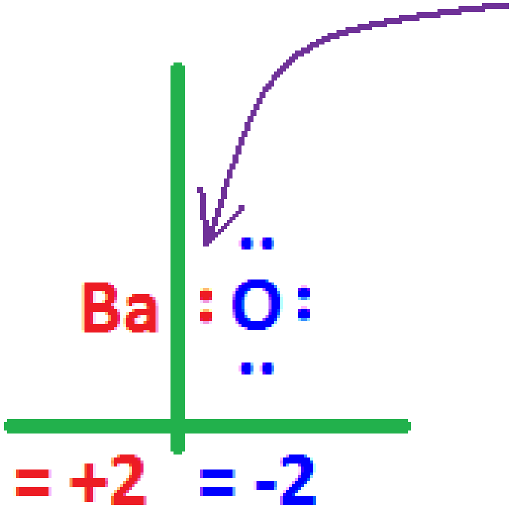
1. electrons shared between 2 unlike atoms are counted with the more electronegative atom and
2. electrons shared between 2 like atoms are divided between the sharing atoms.

E.g., determine the oxidation number of N_2:

- Three (3) electron pairs are shared by two (2) identical atoms, hence, by #2, above, half the electrons are counted with each atom.
- The nitrogen nucleus has a +7 charge (7 protons) and with 7 negative charges (7 electrons), the apparent charge is 0. Therefore, the oxidation number of N_2 is zero (0).

E.g., determine the oxidation numbers of Ba and O in BaO:

- **Oxygen is more electronegative and so, by #1, above, the shared electrons are counted with oxygen as shown right:**
- **The line shows the SHIFTING of electrons.**
- **Since oxygen has 6 protons and APPEARS to have 8 electrons, the oxidation state of oxygen is -2.**
- **Note the movement of the 2 electrons away from the Ba and towards the O (arrows pointing to).**
- **Ba APPEARS to have "lost" 2 electrons and its oxidation state is +2 since its nucleus now has an excess of 2 protons relative to the number of electrons left behind.**



Oxidation Number Rules

1) All elements have an oxidation number of zero (0):

E.g.	H_2	O_2	N_2	Ca
Oxidation Number	0	0	0	0

2) Monoatomic ions' charges equal the oxidation number of that monoatomic ion:

E.g.	Na^+	K^+	Sr^{2+}	F^-
Ionic Charge	+1	+1	+2	-1
Oxidation Number	+1	+1	+2	-1

3) Cations from Groups I and II have oxidation numbers equal to +1 and +2, respectively:

E.g.	Na^+	Ba^{2+}	K^+	Mg^{2+}
Ionic Charge	+1	+2	+1	+2
Oxidation Number	+1	+2	+1	+2

4) With only a few exceptions, the oxidation number of H is +1:

E.g.	H^+	H^-
Ionic Charge	+1	-1
Oxidation Number	+1	-1 (as the HYDRIDE ion)

5) The oxidation number of O is -2; exception: when it's in a peroxide, it's oxidation number is then -1:

E.g.	O^0	H_2O	H_2O_2 (hydrogen peroxide)	NaOH
Ionic Charge of O	0	-2	-1	-2
Oxidation Number of O	0	-2	-1	-2

6) The sum of all the oxidation numbers in a compound is equal to zero (0):

E.g.	$KMnO_4$	K^+	Mn^{+7}	O^{-2}
Oxidation Numbers	0	+1	+7	-2
TOTAL Oxidation Numbers	0	+1	+7	-8 (4 of them in the compound)
Sum of TOTAL Oxidation Numbers	0			

- Arithmetic example:

$$1(\text{ox \# of } K^{+}) + 1(\text{ox \# of } Mn^{+7}) + 4(\text{ox \# of } O^{-2})$$

$$= (1*1) + (1*7) + (4*-2) = 0$$

7) The sum of all the oxidation numbers in an ion is equal to the charge on the ion:

E.g.	$Cr_2O_7^{-2}$	Cr^{+6}	O^{-2}
Oxidation Numbers	-2	+6	-2
TOTAL Oxidation Numbers	-2	+12 (2 of them in the ion)	-14 (7 of them in the ion
Sum of TOTAL Oxidation Numbers	-2		

- Arithmetic example:

$$2(\text{ox \# of } Cr^{+6}) + 7(\text{ox \# of } O^{-2})$$

$$= (2*6) + (7*-2) = -2$$

Three Methods of Balancing Redox Reactions

Method 1	Method 2	Method 3
Oxidation Number Method	Oxidation Number Method for Aqueous Solutions	Half-Reactions for Aqueous Solutions Method

EXAMPLE

- For this example for ALL three methods (after you get through the homework, I don't care which method you utilize as long as you can do it), we'll use the following UNBALANCED equation:

- $Cr_2O_7^{2-} + HNO_2 + H^+ \rightarrow Cr^{3+} + NO_3^- + H_2O$

Method 1: Oxidation Number Method

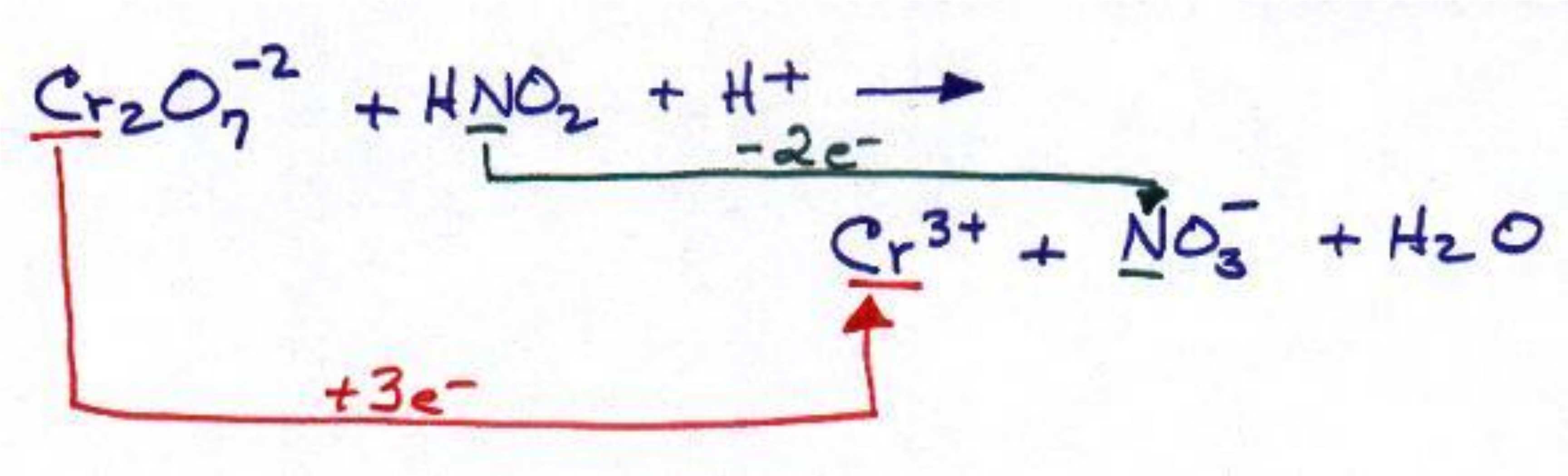
- Step Number One: Assign oxidation numbers.
- Do this just as I set up the rules for oxidation numbers, above, in the multiple tables.
- Keep track of your charges.

$$(Cr_2O_7)^{-2} = 2Cr + 7O$$
$$-2 = 2x + -14$$
$$(7 \cdot -2)$$
$$\frac{-2+14}{2} = x = +6$$

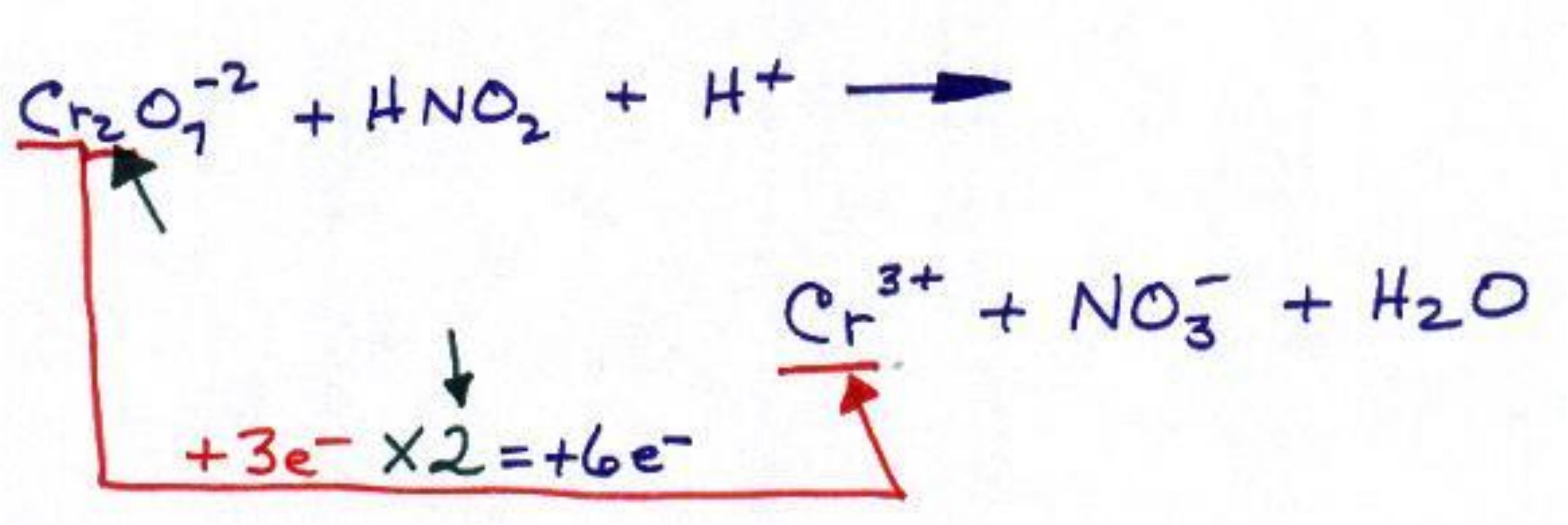
$$HNO_2 = 1H + 1N + 2O$$
$$0 = (1 \cdot 1) + x + (2 \cdot -2)$$
$$0 = 1 + x + (-4)$$
$$0 - 1 + 4 = x = +3$$

$$\overset{+6}{Cr}_2\overset{-2}{O}_7{}^{2-} + \overset{+1}{H}\overset{+3}{N}\overset{-2}{O}_2 + H^+ \longrightarrow Cr^{3+} + \overset{+5}{N}\overset{-2}{O}_3{}^- + \overset{+1}{H}_2\overset{-2}{O}$$

- Step Number Two: You need to determine which reactant gains (oxidizing agent) or loses (reducing agent) electrons and identify how many electrons are lost per individual atom ONLY at this point.



- Step Number three: Determine the gain or loss of electrons per formula unit -- this reaction is a great example: dichromate ion ($Cr_2O_7^{2-}$) has 2 Cr's.
- That means that EACH Cr (formula unit) gains 3 electrons as it's reduced for a total of 6 electrons gained (2 formula units times 3).



- Step Number Four: Balance the left side of the reaction for gain and loss of electrons.

$$Cr_2O_7^{2-} + 3HNO_2 + H^+ \longrightarrow Cr^{3+} + NO_3^- + H_2O$$

- Step Number Five: Balance the redox pair, now, by balancing the right side of the reaction.

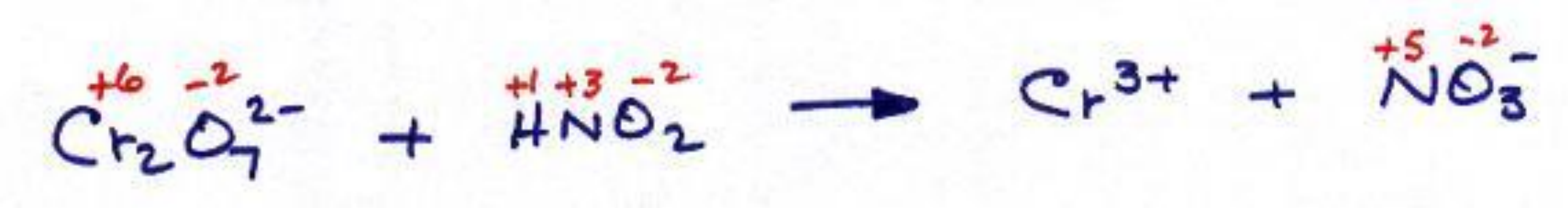
$$Cr_2O_7^{2-} + 3HNO_2 + H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + H_2O$$

- Step Number Six: Balance everything EXCEPT oxygen and hydrogen.
- Step Number Seven: Balance the oxygens.
- Step Number Eight: Balance the hydrogens.
- Step Number Nine: Write the balanced equation/reaction.

$$Cr_2O_7^{-2} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

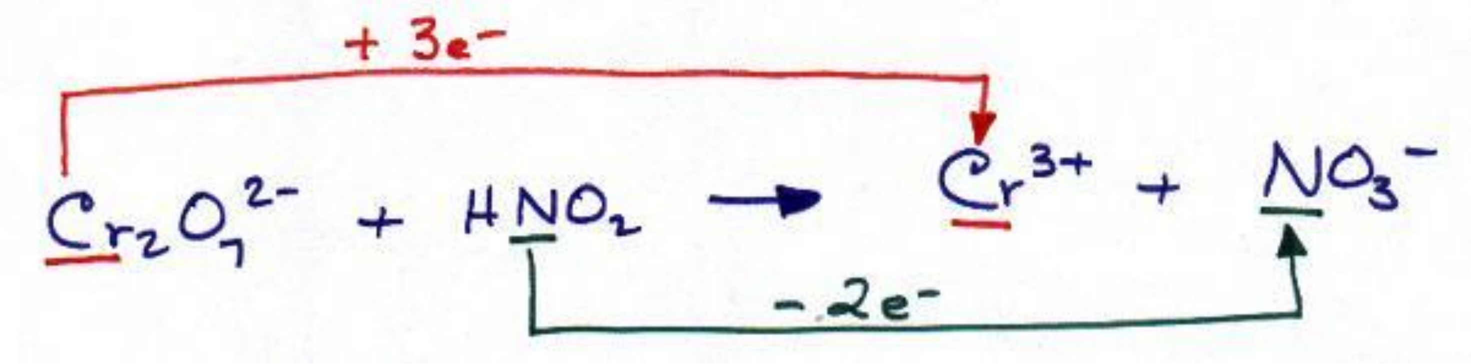
Method 2: Oxidation Number Method for Aqueous Solutions

- We'll still use the same example reaction, above. This method requires a slightly different approach.
- Step Number One: write the net ionic reaction. This means to write the reaction that is going to occur between the redox pair ONLY.
- Step Number Two: Assign oxidation numbers just as we did in the first method.

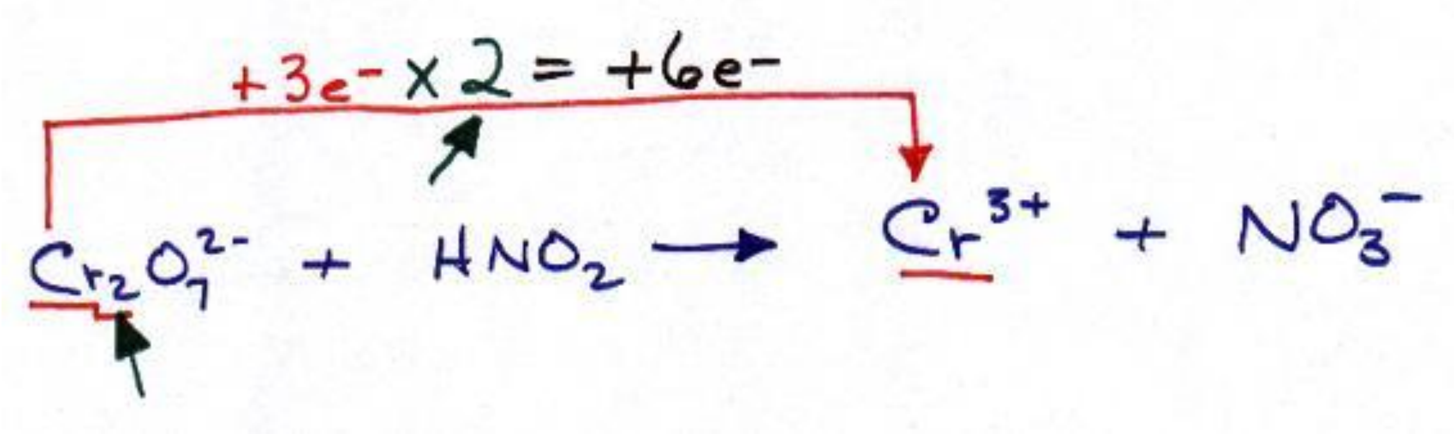


$$\overset{+6}{Cr_2}\overset{-2}{O_7^{2-}} + \overset{+1}{H}\overset{+3}{N}\overset{-2}{O_2} \longrightarrow Cr^{3+} + \overset{+5}{N}\overset{-2}{O_3^{-}}$$

- Step Number Three: Determine which reactant gains and loses electrons.



- Step Number Four: determine the loss and gain of electrons per formula unit -- this reaction is a great example: dichromate ion ($Cr_2O_7^{2-}$) has 2 Cr's.
- That means that EACH Cr (formula unit) gains 3 electrons as it's reduced for a total of 6 electrons gained (2 formula units times 3).



- Step Number Five: Balance the left side of the reaction based on electron gain/loss.

$$Cr_2O_7^{2-} + 3HNO_2 \longrightarrow Cr^{3+} + NO_3^-$$

- Step Number Six: balance the right side of the reaction.

$$Cr_2O_7^{2-} + 3HNO_2 \longrightarrow 2Cr^{3+} + 3NO_3^-$$

Step Number Seven: balance all but oxygen and hydrogen.

- Step Number Eight: Add up the charges on both sides of the reaction.

$$Cr_2O_7^{2-} + 3HNO_2 \longrightarrow 2Cr^{3+} + 3NO_3^{-}$$

$$-2 + 0 = -2 \qquad +3 = +6 - 3$$

- Step Number Nine: balance the charges by adding H^+ for positive charges and OH^- for negative charges.

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^{+} \longrightarrow$$
$$2Cr^{3+} + 3NO_3^{-}$$

- Step Number Ten: Balance the oxygens by putting water (H_2O) on the side opposite the hydroxide ions.
- Step Number Eleven: hydrogens ought to balance.
- Step Number Twelve: Write the balanced reaction.

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

Method 3: Half-Reactions for Aqueous Solutions Method

- Step Number One: write out the unbalanced reaction.
- Step Number Two: find the half reactions for each of the redox pair. This is done by looking them up in the appendix of traditional chemistry texts (Redox Potentials) or in the CRC Handbook of Chemistry and Physics.
- They will be given to you during the exams if they are needed and if they actually exist in the literature -- there are times there are no accessible half reactions for use; when that occurs, these problems are usually fairly simple.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-$$

- Step Number Three: Balance all but the oxygen and hydrogen in each half reaction.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3(HNO_2 + H_2O \longrightarrow NO_3^- + 3H^+ + 2e^-)$$

- Step Number Four: Balance oxygens with water added to the oxygen deficient side of the reaction.
- Step Number Five: Balance the hydrogens:
  - 1) in ACID with H^+;
  - 2) in BASE with 1 H_2O per needed hydrogen with an equal number of OH^- on the opposite side of the reaction.
- Step Number Six: Balance the charges with electrons on the side of each half reaction with the least negative charge.
- Step Number Seven: between the two half reactions, now balance electron gain and loss. In this step, it becomes necessary to turn one of the reactions around so that it will add to the other half-reaction, eventually. Note that two half reactions will make a whole reaction.
- Step Number Eight: Cancel out common elements, ions, and/or electrons between the 2 half reactions now balanced.

$$\mathrm{Cr_2O_7^{2-}} + \overset{5}{\cancel{14}}\mathrm{H^+} + \cancel{6e^-} \longrightarrow 2\mathrm{Cr^{3+}} + \overset{4}{\cancel{7}}\mathrm{H_2O}$$

$$3\,\mathrm{HNO_2} + \cancel{3\mathrm{H_2O}} \longrightarrow 3\mathrm{NO_3^-} + \cancel{9\mathrm{H^+}} + \cancel{6e^-}$$

- Step Number Nine: Add them up and write out the balanced reaction.

$$Cr_2O_7^{2-} + 3HNO_2 + 5H^+ \longrightarrow 2Cr^{3+} + 3NO_3^- + 4H_2O$$

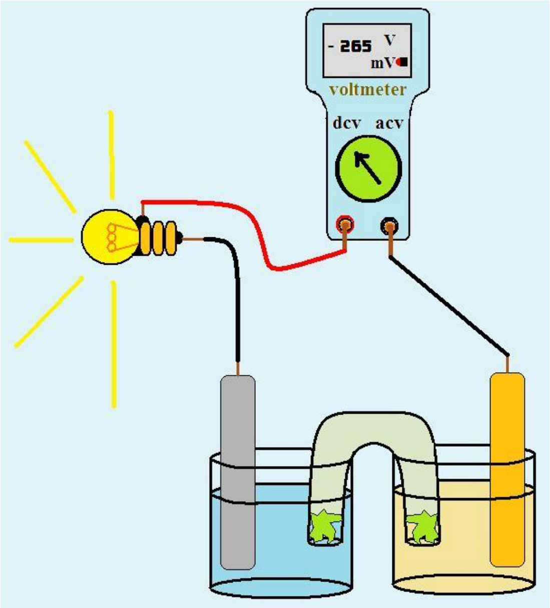
- One key concept to keep in mind is that if you've balanced the same reaction by each method above, and you don't get the same answer each time, then there is an error in the balancing.
- Go back and find it -- it usually jumps right out at you.

Batteries

Batteries are classic redox reactions, which is why the tables of redox potentials are called just that: tables of redox POTENTIALS.

A potential is, in common terms, volts.

Chemical changes can produce electricity.



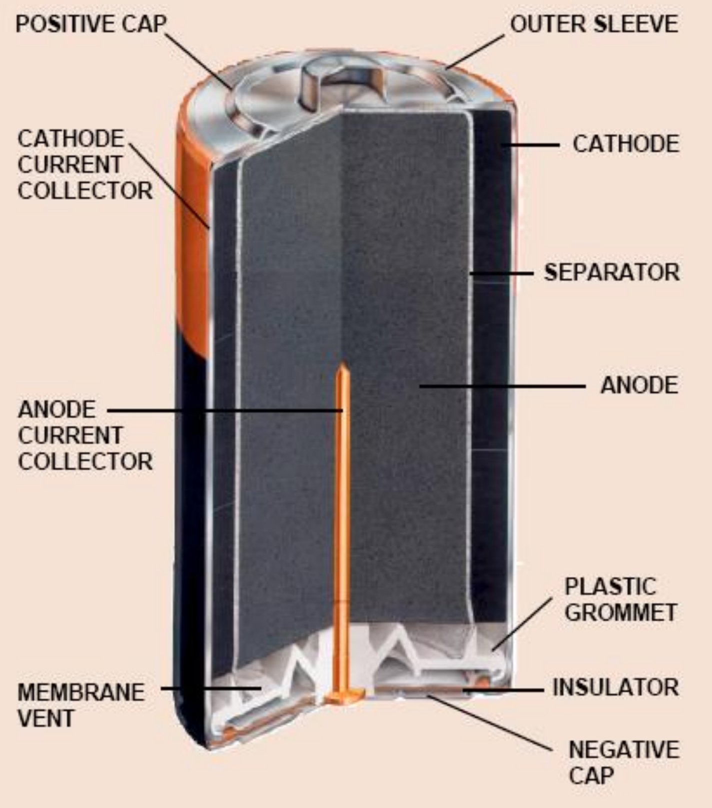
Used with permission from Duracell

Cathode = manganese dioxide (MnO_2)

Anode = Zn, brass or Cu

Electrolyte = potassium hydroxide (KOH)

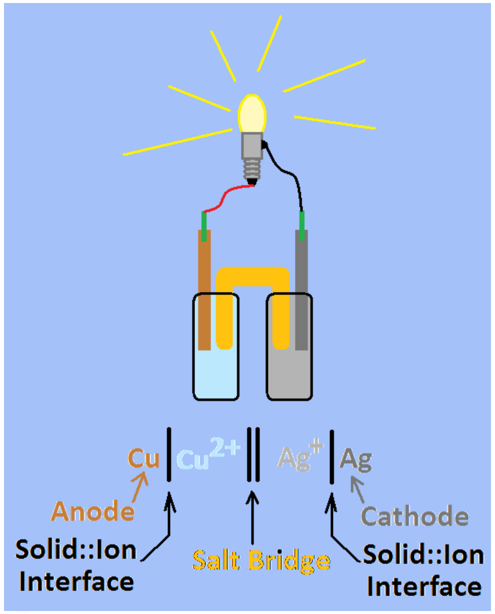
Figure 1

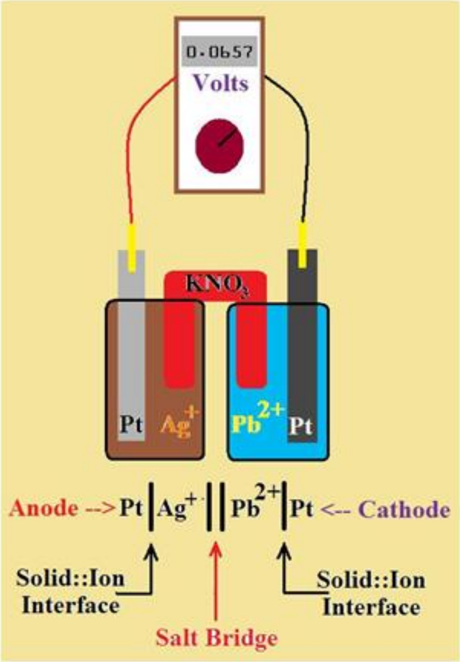


DURACELL® cylindrical alkaline cell.

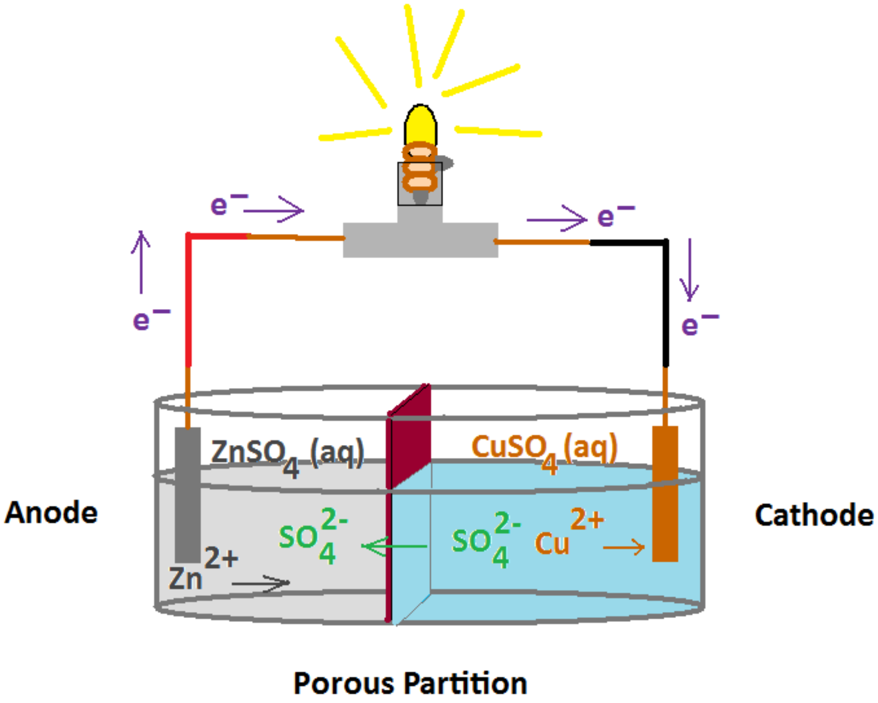
Battery Nomenclature

- In the graphics you can see a simple battery and one with inert electrodes.
- Beneath the battery is how batteries are illustrated without writing out the complete redox reaction (although you **can** derive the overall redox reaction and the flow of electrons using this format: Cu loses 2 e- and donates them to the Ag(I) ion to reduce it to Ag).
- The flow of electrons can be confirmed by using a voltmeter or by putting a light in the circuit and observing the light glowing.
- Inert electrodes can be used to electroplate cheaper metals with a thin layer of a more expensive (precious) metal.
- By convention, the anode is ALWAYS written on the left in this format.
  - 1 solid vertical line indicates the solid::Ion interface (where you dip the metal electrode in the corresponding ionic solution)
  - 2 solid vertical lines indicate the salt bridge (this maintains the flow of the anions to make sure that the circuit continues to flow and to ascertain that there is no increase in the anion concentration on the cathode side of the battery – vice versa on the anode side)



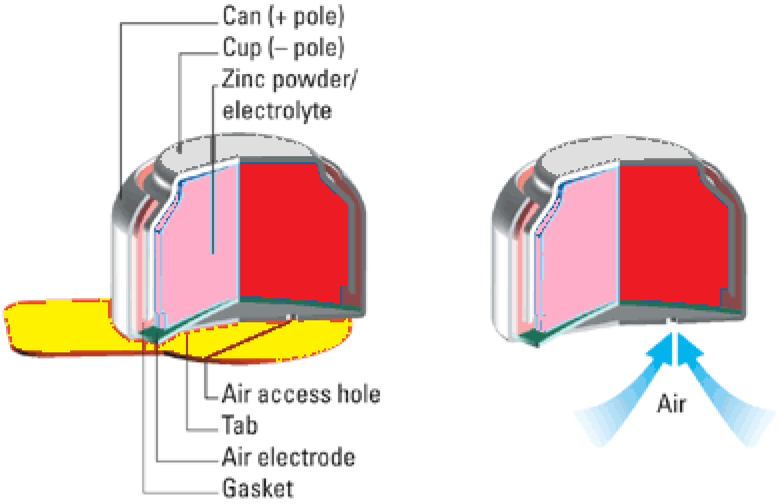


- The following graphic is an example of a fairly simple battery set up with a light in the circuit.
- Note the flow of electrons from the elemental zinc strip to the copper (II) side.
- The side of a battery that gives up electrons is the ANODE (I use the mnemonic "anoxia" -- "an" = anode and "ox" = oxidation), i.e., oxidation occurs on the anode of the battery.
- That means then, that the other side of the battery will be reduced.
- This side is the CATHODE, i.e., reduction occurs on the cathode side of the battery.
- The porous portion allows for anions to flow from one side of the battery to the other to maintain the negative charge balance lost and gained from the anode and cathode, respectively.
- The same net ionic reaction occurs in this simple battery as we saw with the Zn strip stuck in the aqueous copper (II) sulfate solution.
- The battery we have been describing (the one that lit the light) is called an electrochemical cell.



Zinc-Air Batteries

- Left: Inactivated (tab in place)
- Right: Activated (tab removed)
- Research is exploring battery development to run off of a person's blood sugar – ramifications: pacer's/defib's



Anode: $Zn + 4\,OH^- \rightarrow Zn(OH)_4^{2-} + 2\,e^-$

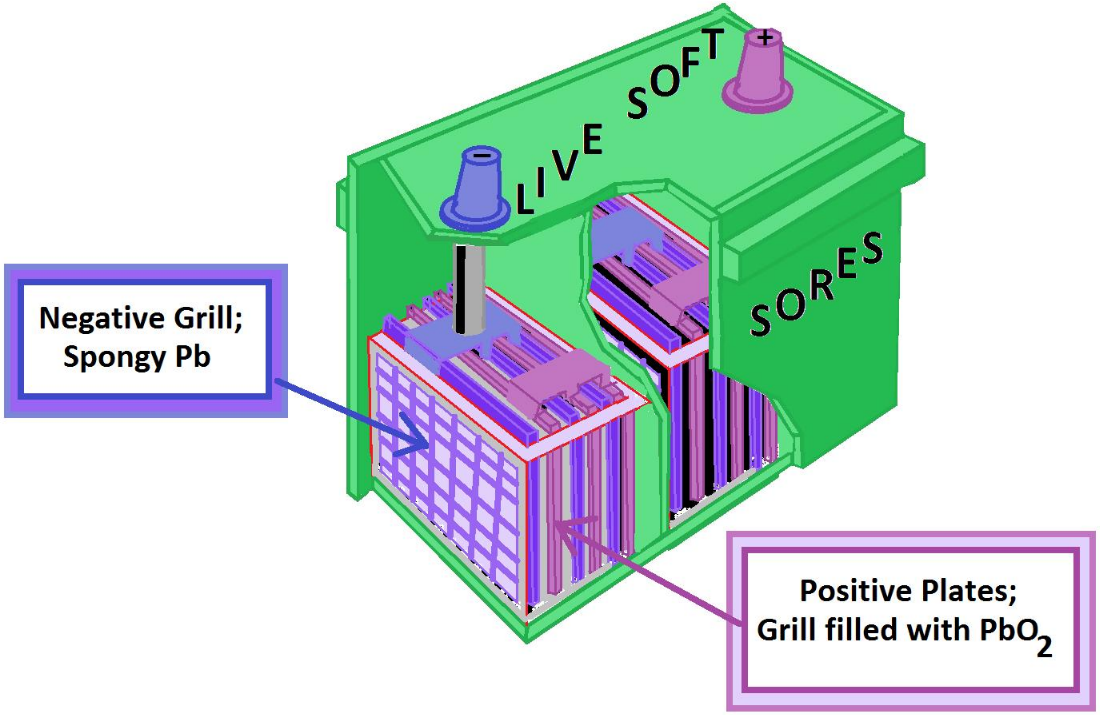
Fluid: $Zn(OH)_4^{2-} \rightarrow ZnO + H_2O + 2\,OH^-$

Cathode: $\tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \rightarrow 2\,OH^-$

Overall: $Zn + \tfrac{1}{2}\,O_2 \rightarrow 2\,ZnO$

ca 1.60 V produced theoretically

- A car battery is a series of 6 cells wired in series. On discharge (when you start the engine), the following reaction occurs:
- $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$
- And on recharge (when your car is running and the generator or alternator is recharging it), the following reaction occurs:
- $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

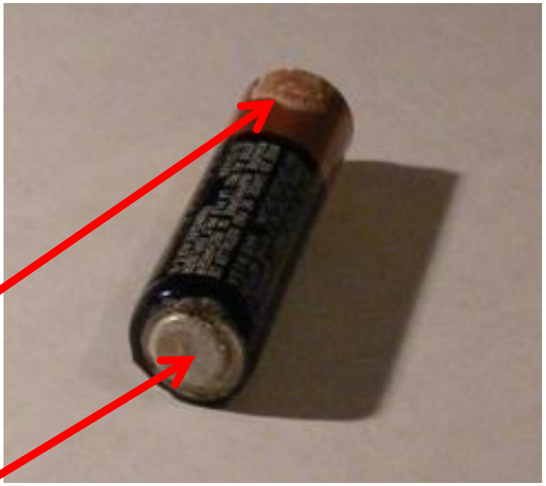


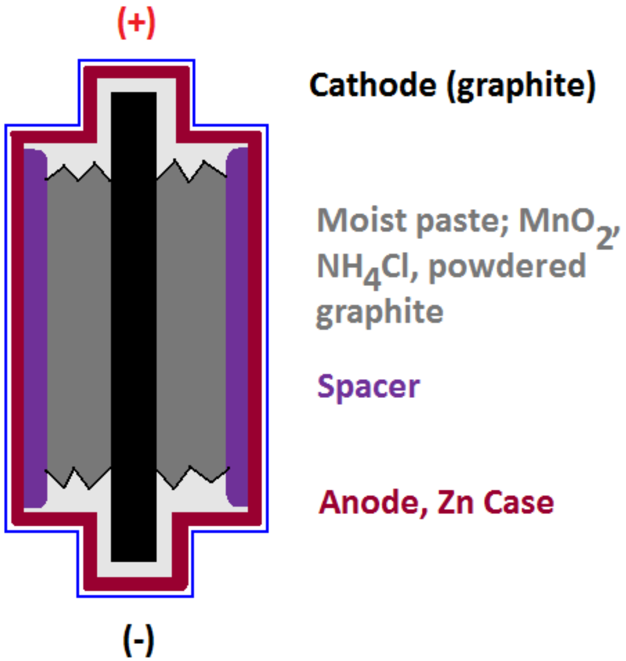
Negative Grill; Spongy Pb

Positive Plates; Grill filled with PbO_2

Corrosion

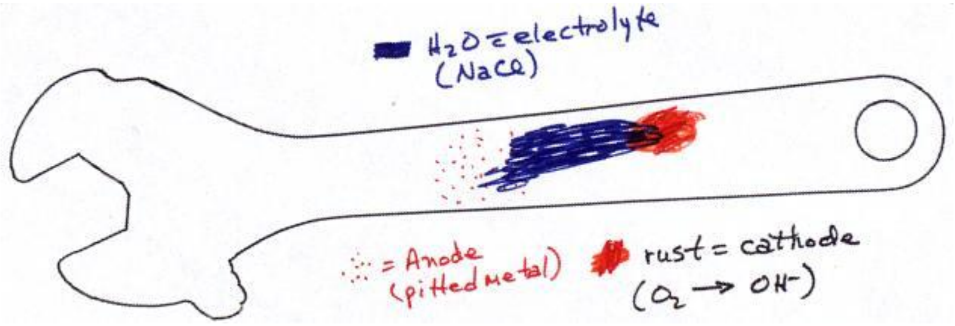
- Dry cells have been around quite a while, now.
- While each manufacturer has its own style, they all pretty much follow, in very general terms, the graphic of a generic dry cell.
- The cathode is a piece of graphite and the anode is the zinc case.
- It is the latter "disappearing" as the battery runs down that can cause corrosion inside your electronic whatever’s when the paste leaks out.
- The paste may be a combination of MnO_2, NH_4Cl and powdered graphite -- or something altogether different depending on the battery.
- For the battery I've described, the following chemical reaction occurs as it's used:
- $Zn + 2MnO_2 + 2H_2O \rightarrow Zn^{2+} + Mn_2O_3 + 2OH^-$





Corrosion

- Corrosion is another form of a battery -- tools are meant to be cared for, kept away from water of any form (including ice in freezers) and wrapped in greasy or lightly oiled cloths.
- If, for example, a prized flat-blade screwdriver is taken from its protected place in the toolbox and used to scrape ice out of a freezer or if a wrench is carelessly tossed out in the salted slush while one puts tire chains on, the tool will rust.
- How does this happen?
- Let's use the wrench as our example.



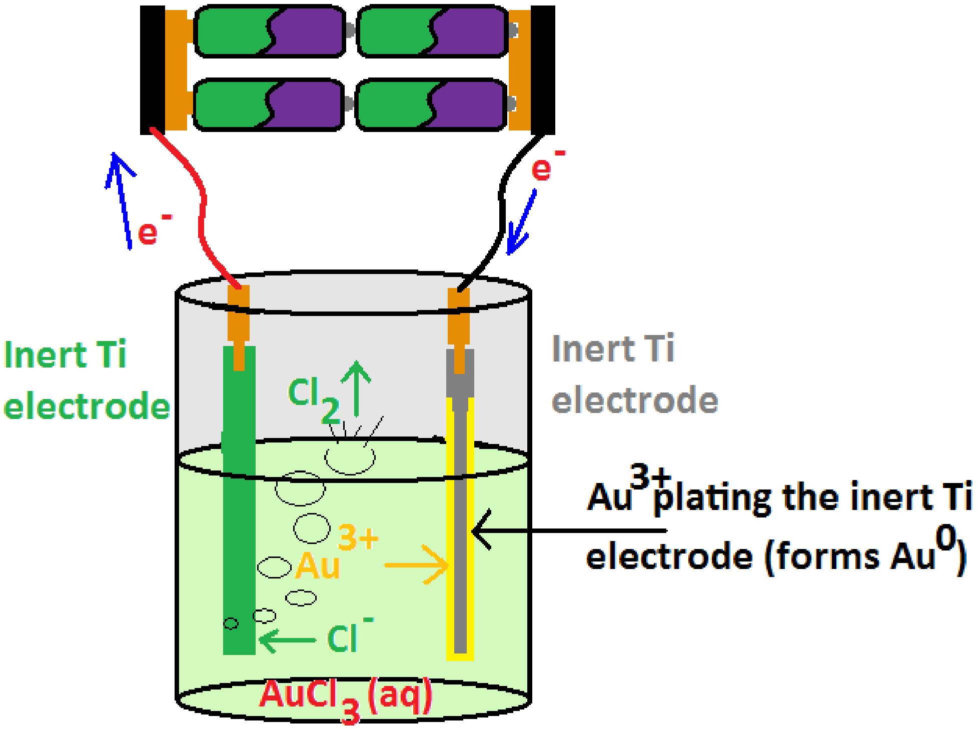
- The wrench is made out of metal.
- No matter how carefully the wrench is crafted, it will have lots of pits in its surface. These pits will act as the anode.
- If only pure water is exposed to these pits, it's more or less protected from oxygen by the water.
- If, however, the water has salt (NaCl) in it (an ionic compound), an electrolytic solution is made.
- If these pits in contact with the ionic compound "connect" with an area of rust (cathode) on the wrench, a battery is set up and more corrosion will occur on the wrench.

The reactions that occur on this wrench are as follow:

Location	Reaction
At anode	$Fe \rightarrow Fe^{2+} + 2e^-$
At cathode	$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$
Also at cathode	$Fe(OH)_2 + O_2 \rightarrow Fe(OH)_3$; $Fe(OH)_3 + O_2 \rightarrow Fe_2O_3$

The pitting makes the wrench more chemically reactive.

Electrolysis



Electrical energy is used to drive an otherwise "not runable" reaction to completion. This is done with an electrolytic cell.

In general, inert electrodes are used as both anode (which one is this?) and cathode (which one is this?).

They are "dipped" in a solution or solutions and an electrical current (out of the wall, a power source or batteries) is sent between them.

In the graphic example, the solution is gold (III) chloride.