CHEM 121 Lecture 2

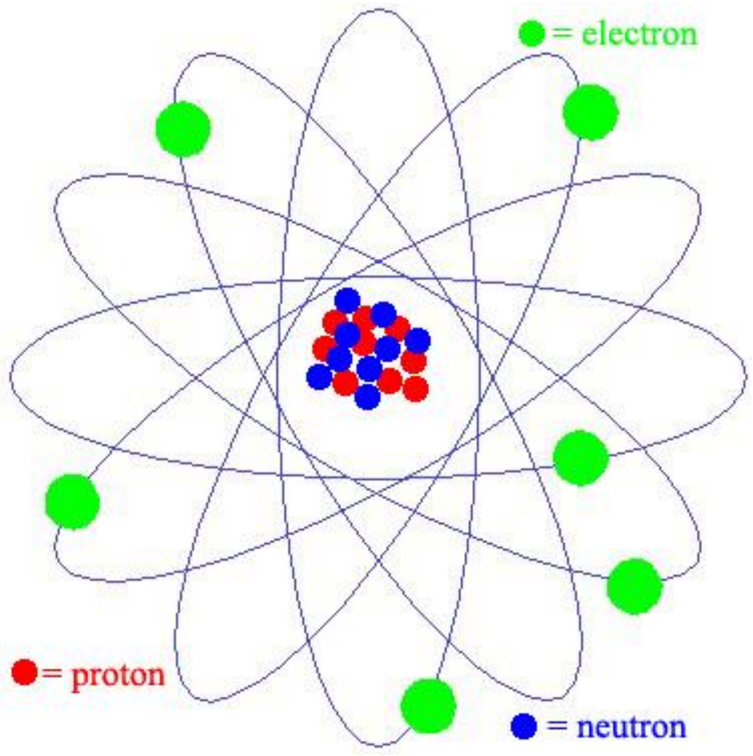
Fall 2019, Revised Spring 2020

The Atom: A Q&D Intro

- Atoms of the same element have the same average mass.
- Those of different elements have different average masses.
- Atom comes from "atomos" which means "not cuttable".
- Atoms consist of protons, neutrons and electrons:

<table>
<tr><th colspan="3">Atoms</th></tr>
<tr><th>Protons</th><th>Neutrons</th><th>Electrons</th></tr>
<tr><td>Positively charged; located in the nucleus of an atom; we write it as either p or p^+</td><td>Have no charge; found in the nucleus; written as n</td><td>Negatively charged; in the energy shells/orbitals around the nucleus; written as e^-</td></tr>
<tr><td>In an element, the number of protons = the number of electrons; the number of protons is also equal to the atomic number of that element.</td><td>Effects atomic mass.</td><td>Has no effect on atomic mass; in elements, the number of electrons equals the number of protons.</td></tr>
<tr><td colspan="2">The number of protons + the number of neutrons = the atomic mass</td><td></td></tr>
</table>

Electricity and The Atomic Nature of "Things"



- Electrostatics = study of fixed or stationary, electric charges.
- Static electricity is the most common form we encounter.
- Electric charges = ±
- Smallest units = electrons (-) and protons (+)
- Have equal magnitude with opposite signs

Remember

- Static electricity is an excess of electric charge trapped on the surface of an object. The charge remains until it is allowed to escape to an object with a weaker or opposite electrical charge, such as the ground, by means of an electric current or electrical discharge.
- Static electricity is named in contrast with current electricity, which flows through wires or other conductors and transmits energy.

Electrons

- May travel from atom to atom
- Protons don’t
- Discussions of electricity, then, with negative charges
- An object is electrified if it has excess or missing electrons
- How lose or gain electrons?
- Touch
- Sock feet on carpet
- Using a magnet to induce an electrical current.

Four Laws of Electrostatics

1) Law of Electrical Charges

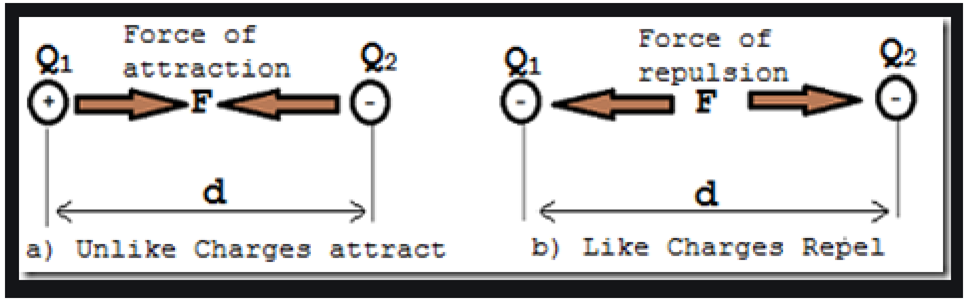
2) Law of Electrification

3) Law of Electric Charge Distribution

4) Law of Electric Charge Concentration

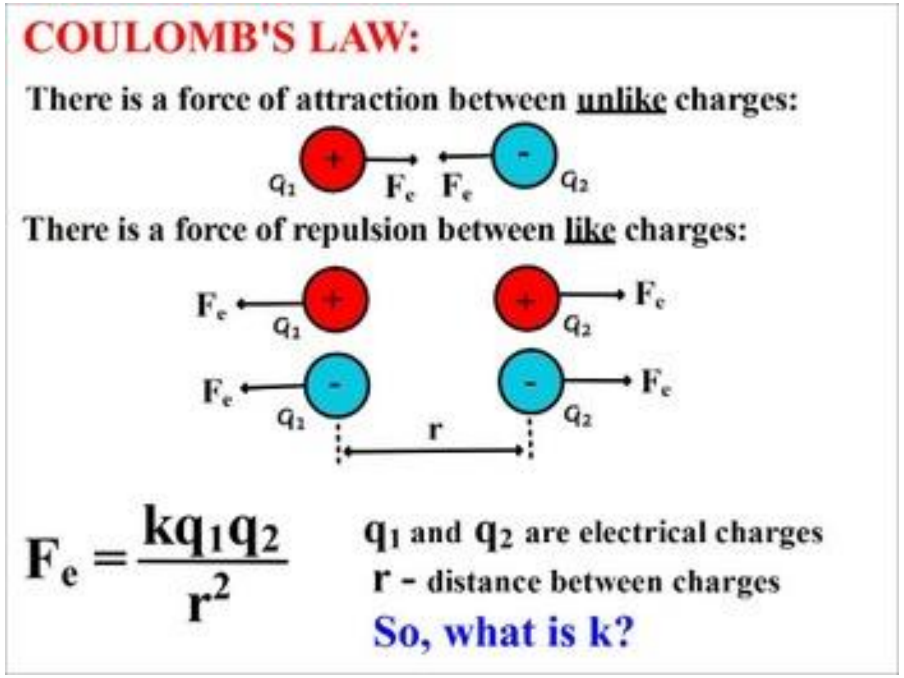
Law of Electrical Charges -- #1 – Repulsion: Attraction

- Unlike charges attract
- Like charges repel
- The force of attraction or repulsion is the electrostatic force



a) Unlike Charges attract

b) Like Charges Repel



COULOMB'S LAW:

There is a force of attraction between unlike charges:

There is a force of repulsion between like charges:

$$F_e = \frac{kq_1q_2}{r^2}$$

q_1 and q_2 are electrical charges

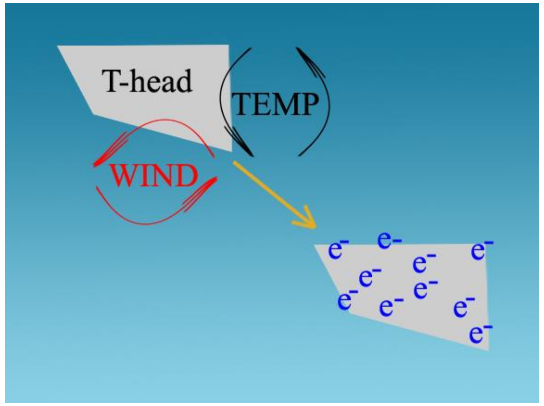
r - distance between charges

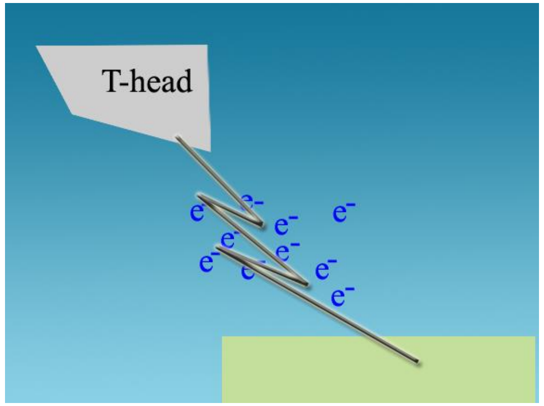
So, what is k?

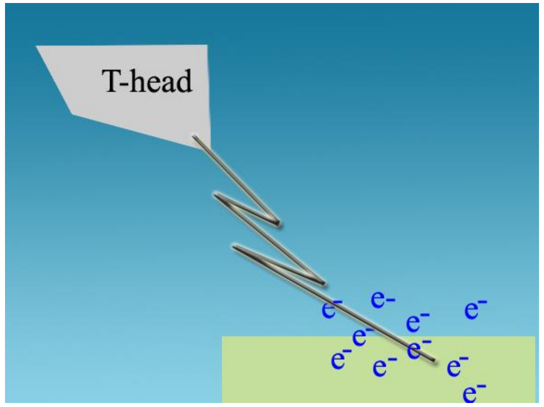
Law of Electrification -- #2

- Electrification occurs because of the movement of negative electric charges.
- When a negatively charged object is in contact with an electrically neutral object, charges are transferred to the neutral object.
- If the transfer is sufficiently violent, makes a spark – of interest is the strap in “booties” for OR – was to reduce sparking by grounding person so patient wouldn’t blow up on the table

Thundercloud Example



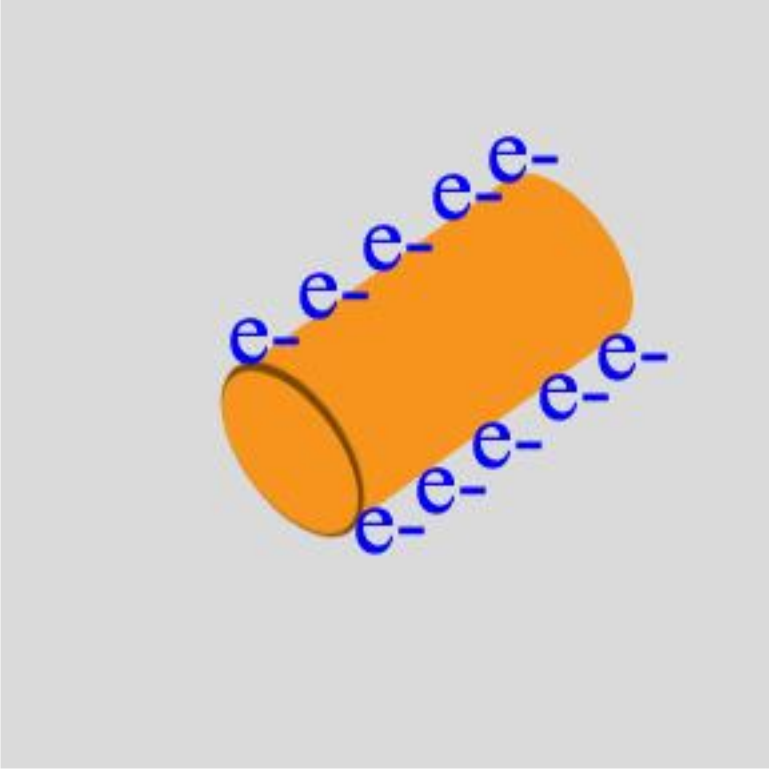




- Electron movement = lightning
  - CAN occur between clouds
- USUALLY between clouds and earth

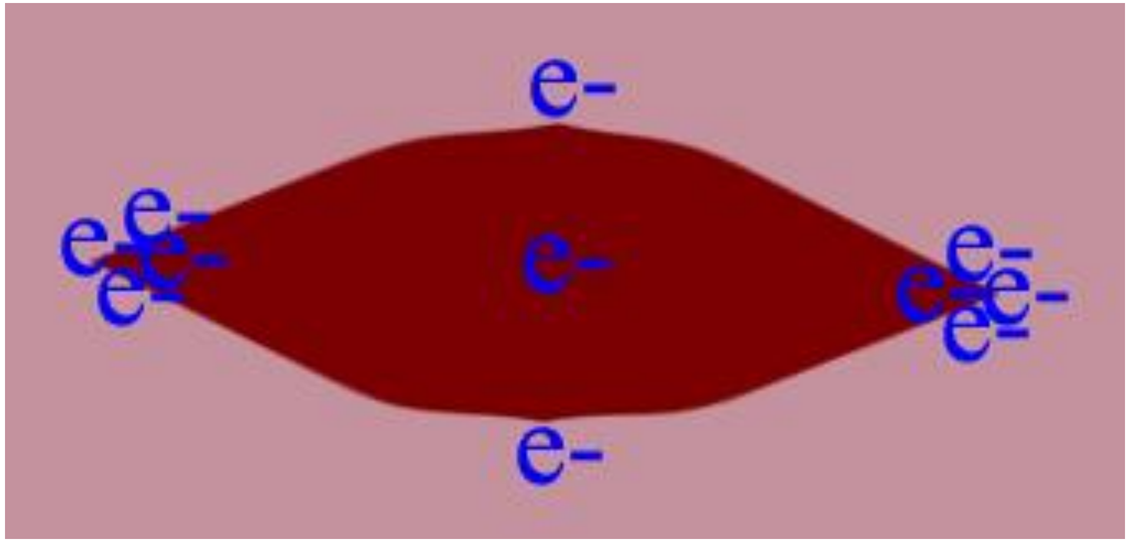
Law of Electric Charge Distribution -- #3

- A diffuse non-conductor object (cloud) has charges distributed throughout the object.
- A conductor (Cu wire) has excess electrons over its outer surface:



Law of Electric Charge Concentration -- #4

- Electric charges are concentrated along the sharpest curvature of a surface:

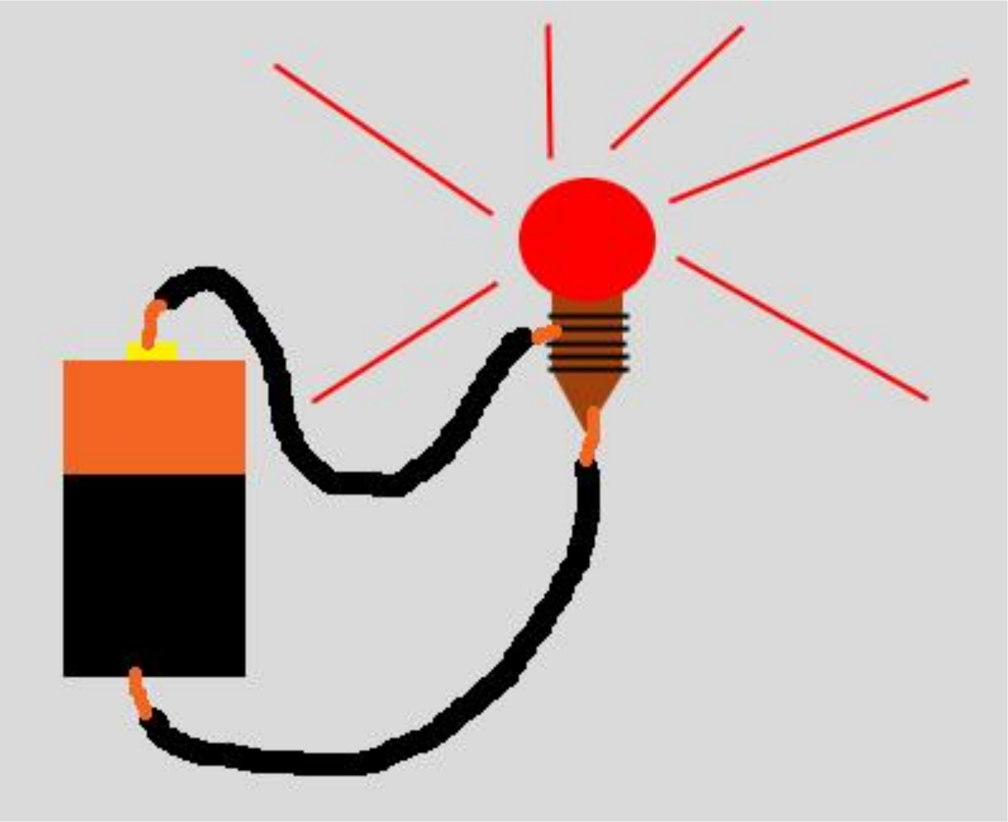


Electrodynamics

- We recognize electrodynamic phenomena as electricity.
- The flow of electrons along a wire is the electric current.
- a ***conductor*** is an object or type of material that allows the flow of charge (*electrical* current) in one or more directions.

Electric Circuits

- Electrons flow along the outer wire surface.
- The wire can be modified to resist the flow in certain regions.
- When resistance (Ω) is controlled and conductor is in a closed path, you've got an electric circuit.

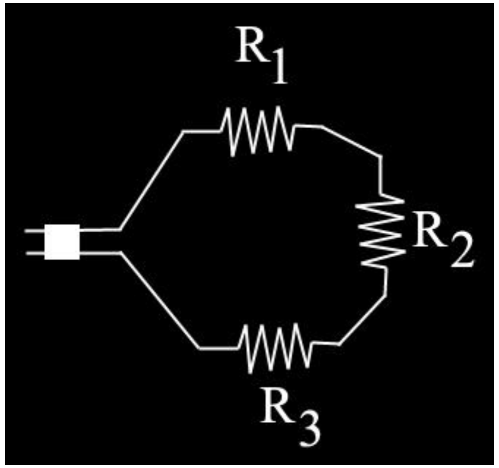


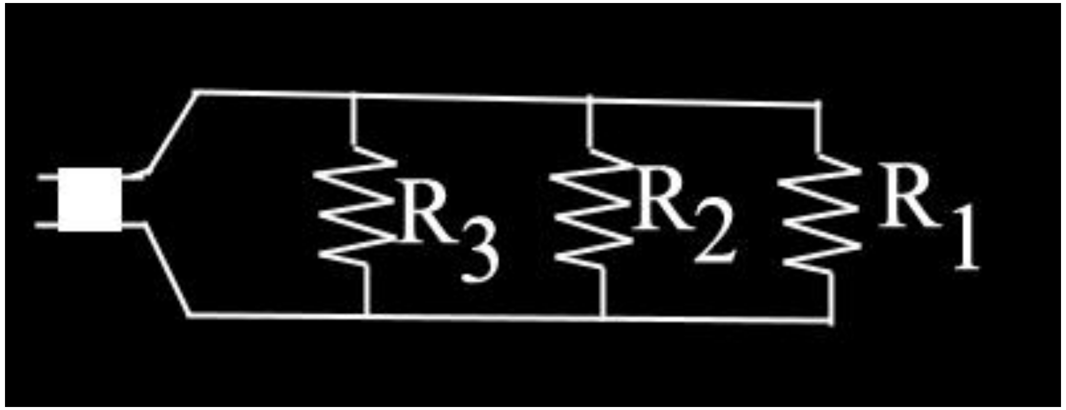
- Current is measured in amperes (amps; I in equations)
- The electrical potential is measured in volts (V)
- Resistance is measured in ohms (Ω; R in equations)
  - Ohm's Law
    - $V = I R$

Electric Power

- $P = I V = I^2 R$
- 1 kW = 1000 Watts
- 1kWh = 1000 watts used in one hour

Electrical Circuits





- Series (left) – set up like X-mas lights: one goes out, they all go out – Greatest Ω, least electron flow
  - Parallel (right) – one goes out, the rest stay on – Least Ω, greatest electron flow (conductance)

Blood Vessels

Is also why circulatory system is set up in parallel – most flow with least amount of resistance

Fundamentals of Chemistry

Elements	Compounds	Mixtures
Elements are pure substances made up of **HOMO**atomic molecules. Elements can not be chemically subdivided into simpler substances.	Compounds are those made up of **HETERO**atomic molecules. Compounds can be chemically subdivided into simpler substances. Compounds are products of chemical subdivisions and produce either elements or simpler compounds.	These occur by blending two or more compounds or elements in any relative amounts.

Element (HOMOatomic)	Compound (HETEROatomic)	Compound (HETEROatomic)
X-X O-O = O_2 = Oxygen	X-O-X H-O-H = H_2O = Water	X-O-Z-Q C-H-H-H-H-N-N-O = CH_4N_2O = Urea

Monoatomic molecules are molecules that contain only a single atom. Homoatomic molecules are molecules that contain only one kind of atom. Heteroatomic molecules are molecules that contain 2 or more kinds of atoms. Polyatomic molecules are molecules that contain 2 or more atoms. The table, below, graphically illustrates these new terms:

Monoatomic	Homoatomic	Heteroatomic
	Polyatomic, also	Polyatomic, also
X Ca = Calcium	X-X-X-X-X-X-X O-O-O = O_3 = Ozone	X-O-Q NH_4OH = ammonium hydroxide

All matter gives rise to the Law of Definite Proportion: the elements in specific compounds are combined in the same proportion by mass, e.g.:

Water (H_2O) at the simplest:	Methanol (CH_3OH) at the simplest:	Glucose ($C_6H_{12}O_6$) at the simplest:
1.0 g hydrogen and 8 g oxygen = 9.0 g water	3 g carbon, 1 g hydrogen and 4 g oxygen = 8 g methanol	6 g carbon, 1 g hydrogen and 8 g oxygen = 15 g glucose

Elemental symbols [is] are [a] symbols assigned to an element based on the name of the element.
These symbols are represented by either one capital letter or one capital letter followed by a lower case letter:

One capital letter		One capital letter and one lower case letter	
B = boron	O = oxygen	Ag = silver	He = helium
C = carbon	P = phosphorus	Au = gold	Ne = neon
F = fluorine	S = sulfur	Pt = platinum	Ar = argon
H = hydrogen	U = uranium	Hg = mercury	Tc = technetium
I = iodine	V = vanadium	Mg = magnesium	Fe = iron
K = potassium	W = tungsten	Ca = calcium	Co = cobalt
N = nitrogen	Y = yttrium	Be = beryllium	Mn = manganese

Compound formulas are symbols for the molecule of compounds, consisting of the symbols of the atoms found in the molecule. Atoms present in numbers greater than one have a number indicated by a subscript (number behind and below that atom):

HCl = hydrochloric acid	H_2SO_4 = sulfuric acid	HNO_3 = nitric acid	H_3PO_4 = phosphoric acid
$NaOH$ = sodium hydroxide	KOH = potassium hydroxide	$CaCO_3$ = calcium carbonate	Li_2CO_3 = lithium carbonate
$HC_2H_3O_2$ = acetic acid	$Al(OH)_3$ = aluminum hydroxide	$C_6H_{12}O_6$ = glucose	CH_4N_2O = urea
Na_3PO_4 = sodium phosphate	Al_2S_3 = aluminum sulfide		CaC_2O_4 = calcium oxalate

When mixtures are blended, this is a physical change.
A physical change is defined any change without a chemical reaction.
A chemical reaction is an event in which substances change into other substances:

Reactants	→	Products
$H_2O_2 + Fe^{3+}$	→	$H_2O + O_2$
$Na + H_2O$	→	$NaOH + H_2$
$C + S + KNO_3$	→	BOOM!
$H_2 + O_2$ + spark	→	H_2O*
Urea + H_2O	→	"ice pack"#

*This is an exothermic reaction (a reaction that generates and gives off heat).

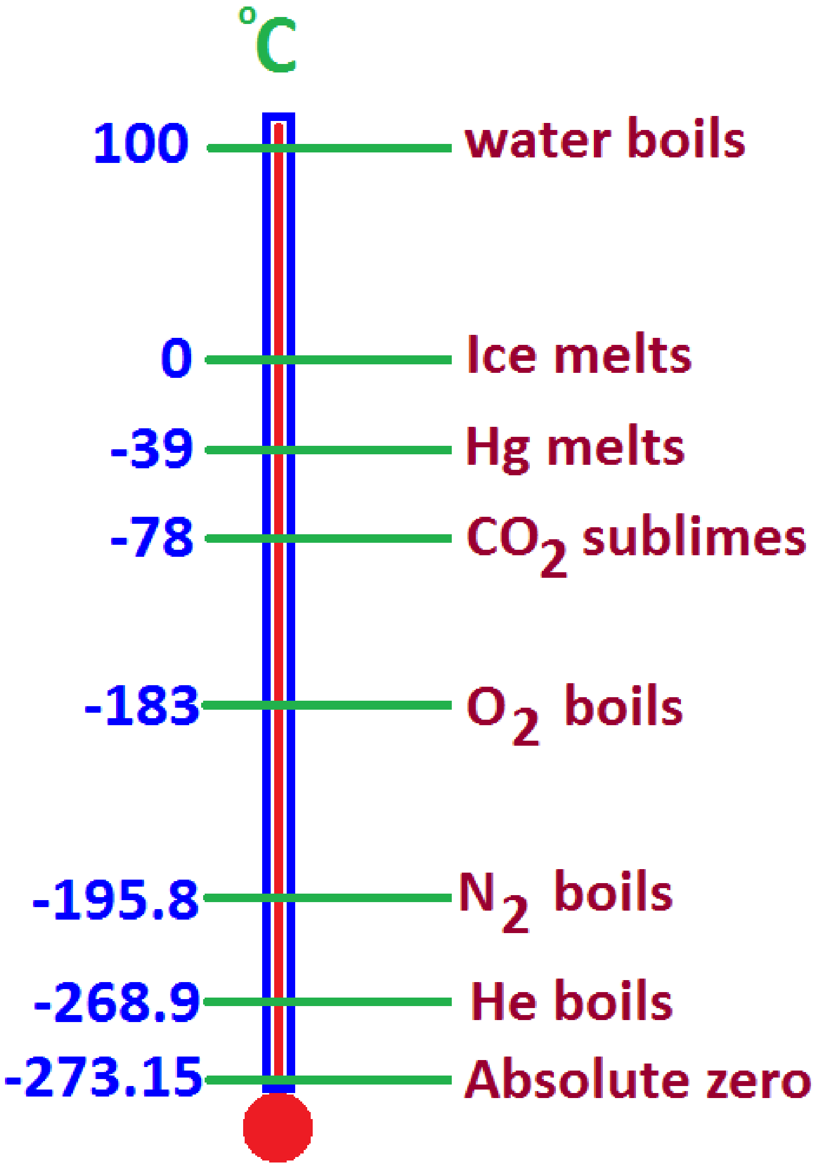
#This is an endothermic reaction (a reaction that absorbs heat and feels cold).

All chemical reactions follow the Law of Conservation of Mass. This Law says that mass is neither gained nor lost in a chemical reaction, i.e., mass is conserved.

Staying with our earlier examples from the Law of Definite Proportions:

Reactants	→	Products
1.01 g H + 8 g O	→	9.01 g H_2O
3 g C + 1 g H + 4 g O	→	8 g CH_3OH
6 g C + 1 g H + 8 g O	→	15 g $C_6H_{12}O_6$
6 g C + 1 g H + 8 g O	→	15 g $HC_2H_3O_2$ (HOAc is slang)

- Some of the more common temperatures in chemistry.

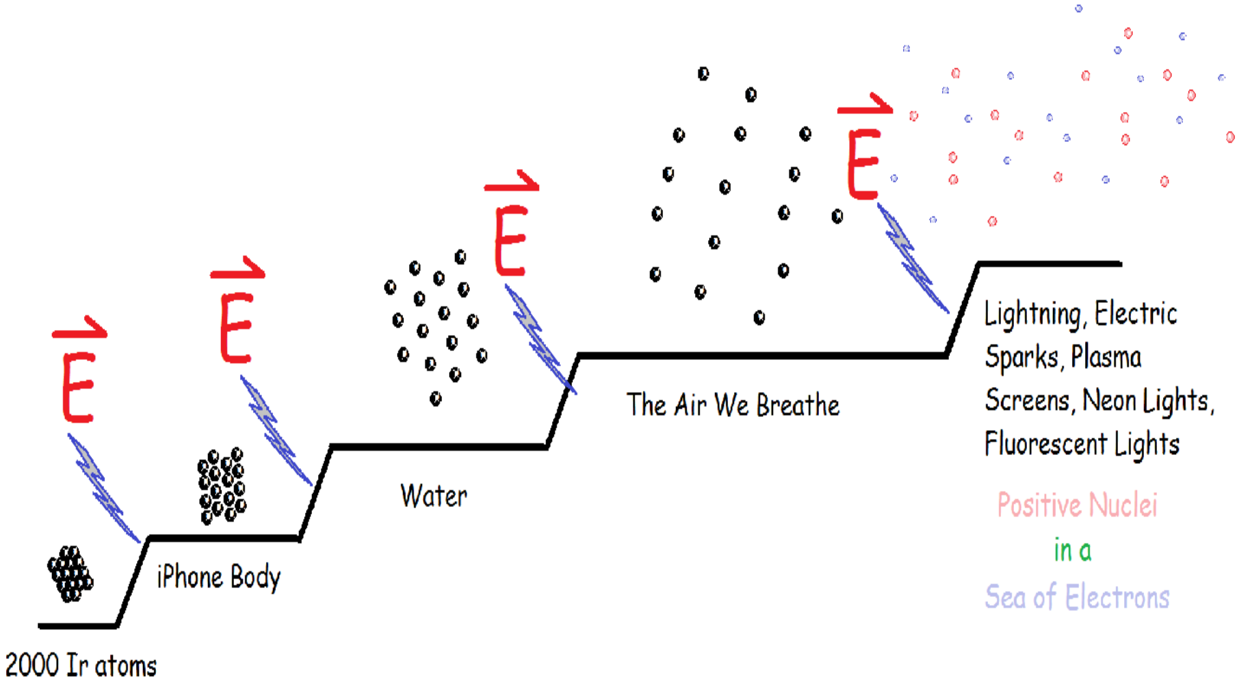


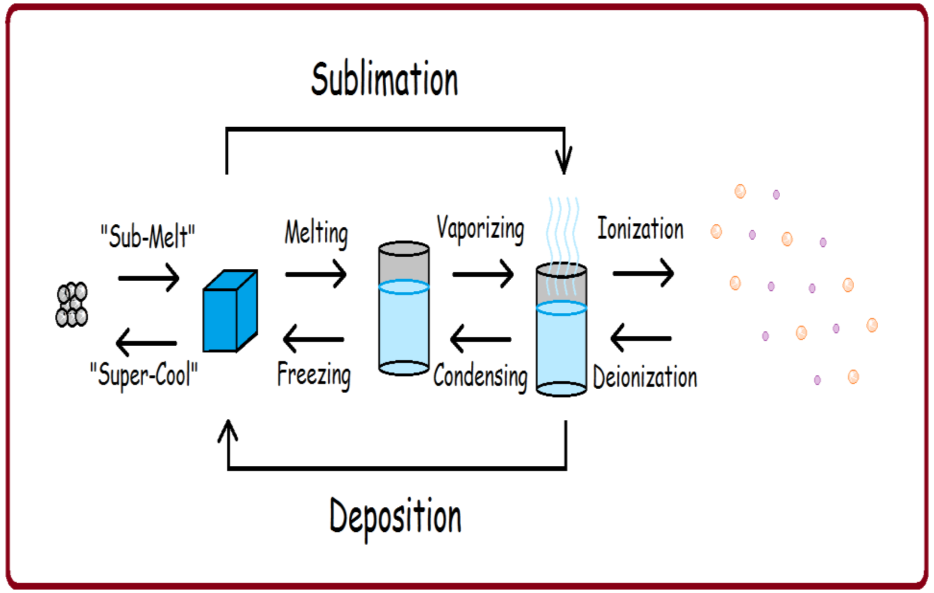
°C	
100	water boils
0	Ice melts
-39	Hg melts
-78	CO_2 sublimes
-183	O_2 boils
-195.8	N_2 boils
-268.9	He boils
-273.15	Absolute zero

Terms to Memorize

- **Freezing Point**: is the temperature at which a liquid becomes a solid at normal atmospheric pressure.
- **Melting Point**: is the temperature at which a solid becomes a liquid at normal atmospheric pressure.
- **Boiling Point**: the temperature at which a pure solvent’s or solution’s vapor pressure = atmospheric pressure
    - The properties of the elements are a periodic function of their atomic numbers. In general, across periods, boiling point increases from left to right with increasing atomic number. Boiling point decreases from top to bottom with increasing atomic number.
- **Flash Point**: is the lowest temperature at which a liquid can form an ignitable mixture in air near the surface of the liquid. The lower the flash point, the easier it is to ignite the material.
- **Critical Temperature**: is the temperature above which a substance can not be liquified REGARDLESS how much pressure is applied.
- **Critical Pressure**: is the pressure required to liquify a gas at its critical temperature.

Five Phases of Matter





- Matter is anything that occupies space and has mass. There are five states of matter we'll explore: Bose-Einstein Condensates, Solids, Liquids, Gases and Plasma.

- **Bose-Einstein condensate (BEC),** is a state of matter in which separate atoms or subatomic particles, cooled to near absolute zero (1995, Cornell and Wiemann (shared 2001 Nobel Prize in Physics), cooled a gas of rubidium atoms to 1.7 × 10^{-7} K above absolute zero), coalesce into a single quantum mechanical entity—that is, one that can be described by a wave function—on a near-macroscopic scale.

http://www.britannica.com/EBchecked/topic/74640/Bose-Einstein-condensate-BEC

- BEC theory traces back to 1924, when Bose considered how groups of photons behave.
- Photons belong to one of the two classes of elementary or submicroscopic particles defined by whether their quantum spin is a non-negative integer (0, 1, 2, …)
  - These are called bosons, includes photons, whose spin is 1
- or an odd half integer (1/2, 3/2, …).
  - These are called fermions, which includes electrons, whose spin is 1/2.

http://www.britannica.com/EBchecked/topic/74640/Bose-Einstein-condensate-BEC

- BECs are related to two remarkable low-temperature phenomena:
  - superfluidity, in which each of the helium isotopes ^{3}He and ^{4}He forms a liquid that flows with zero friction;
- and
  - superconductivity, in which electrons move through a material with zero electrical resistance.
- ^{4}He atoms are bosons, and although ^{3}He atoms and electrons are fermions, they can also undergo Bose condensation if they pair up with opposite spins to form boson-like states with zero net spin.
- He is an unusual noble gas.

http://www.britannica.com/EBchecked/topic/74640/Bose-Einstein-condensate-BEC

- The most intriguing property of BECs is that they can slow down light. In 1998 Lene Hau of Harvard University and her colleagues slowed light traveling through a BEC from its speed in vacuum of 3×10^8 meters per second to a mere 17 meters per second, or about 38 miles per hour.
- Since then, Hau and others have completely halted and stored a light pulse within a BEC, later releasing the light unchanged or sending it to a second BEC. These manipulations hold promise for new types of light-based telecommunications, optical storage of data, and quantum computing, though the low-temperature requirements of BECs offer practical difficulties.

http://www.britannica.com/EBchecked/topic/74640/Bose-Einstein-condensate-BEC

Bose Einstein Condensates – BEC's

Fermions	half-integral spin	only one per state	Examples: electrons, protons, neutrons, quarks, neutrinos
Bosons	integral spin	Many can occupy the same state	Examples: photons, ^{4}He atoms, gluons

Bosons have intrinsic angular momenta in integral units of $h/(2\pi)$. For instance the spin of a photon is either +1 or -1 and the spin of a ^{4}He atom is always zero. Many bosons can occupy a single quantum state. This allows them to behave collectively and is responsible for the behavior of lasers and superfluid helium.

Gluons: a subatomic particle of a class that is thought to bind quarks together

http://www.pa.msu.edu/courses/1997spring/phy232/lectures/atomic/bosons.html

- Only one fermion can exist in a given quantum state. This is known as the Pauli exclusion principle.
- Fermions tend to avoid each other, for which reason each electron in a group occupies a separate quantum state (indicated by different quantum numbers). In contrast, an unlimited number of bosons can have the same energy state and share a single quantum state.
- Any object which is comprised of an even number of fermions is a boson, while any particle which is comprised of an odd number of fermions is a fermion.
- For example, a proton is made of three quarks, hence it is a fermion.
- A ^{4}He atom is made of 2 protons, 2 neutrons and 2 electrons, hence it is a boson.

http://www.pa.msu.edu/courses/1997spring/phy232/lectures/atomic/bosons.html

http://www.britannica.com/EBchecked/topic/74640/Bose-Einstein-condensate-BEC

The Solid State and X-Ray Crystallography

- Solids have a definite, fixed shape and volume
- The atoms in a solid occupy fixed positions in a crystal lattice.

Why Use X-Rays to Study Solids?

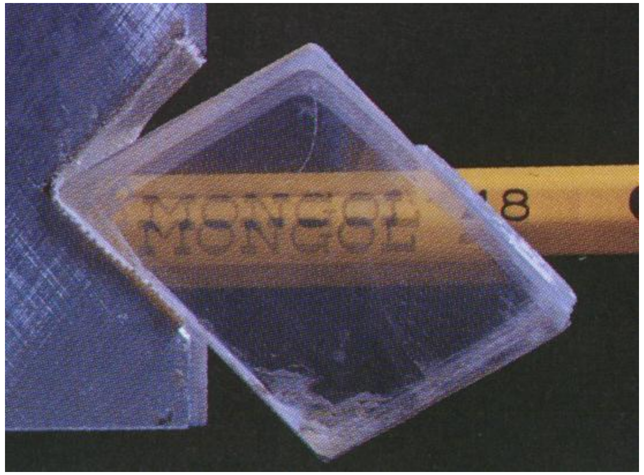
- X-rays typically have wavelengths around 0.1 nm.
- The spaces between the planes in solid crystals are about 0.1 nm.
- Hence, x-rays fit “perfectly”.

The Solid State and X-Ray Crystallography

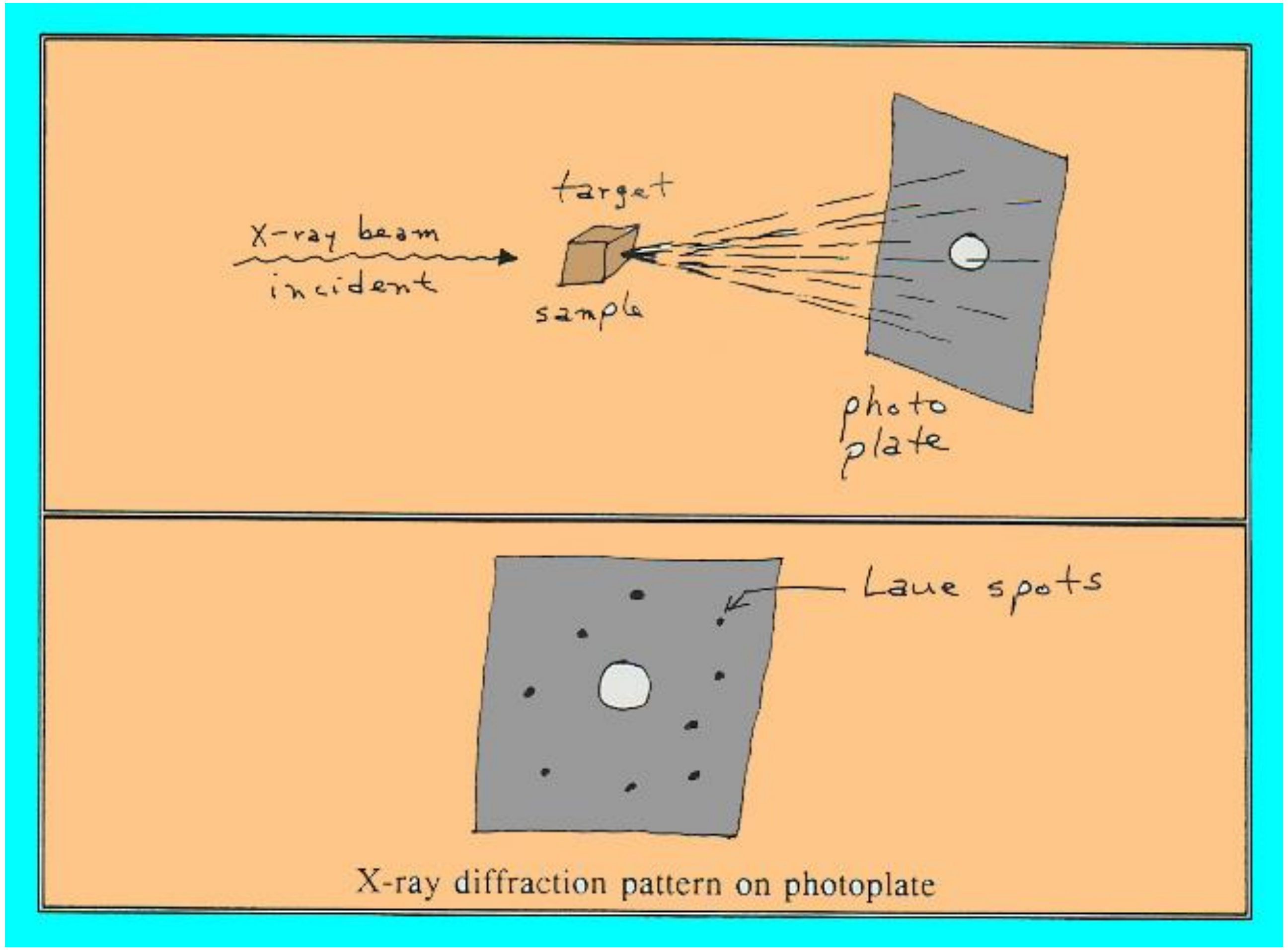
- Different compounds which crystallize in the same structure are called ISOMORPHOUS
- Examples
  - NaF, KCl, CaS all have the same crystalline structure as NaCl
  - $SrCl_2$, ZrO_2 and CdF_2 all have the same crystalline structure as CaF_2

- Compounds that have 2 or more crystalline structures under different conditions undergo POLYMORPHISM
- Examples
  - Low temperature $CaCO_3$ is rhombohedral and called calcite
  - High temperature $CaCO_3$ is orthorhombic and called aragonite
- Crystalline structure of the lattice is determined by X-Ray Diffraction

Calcite ($CaCO_3$) precipitates at temperatures less than 30° C. It has the property of optical birefringence (double refraction): when a beam of light enters calcite, it is split into two beams and two images are observed.



Photoplate? History.

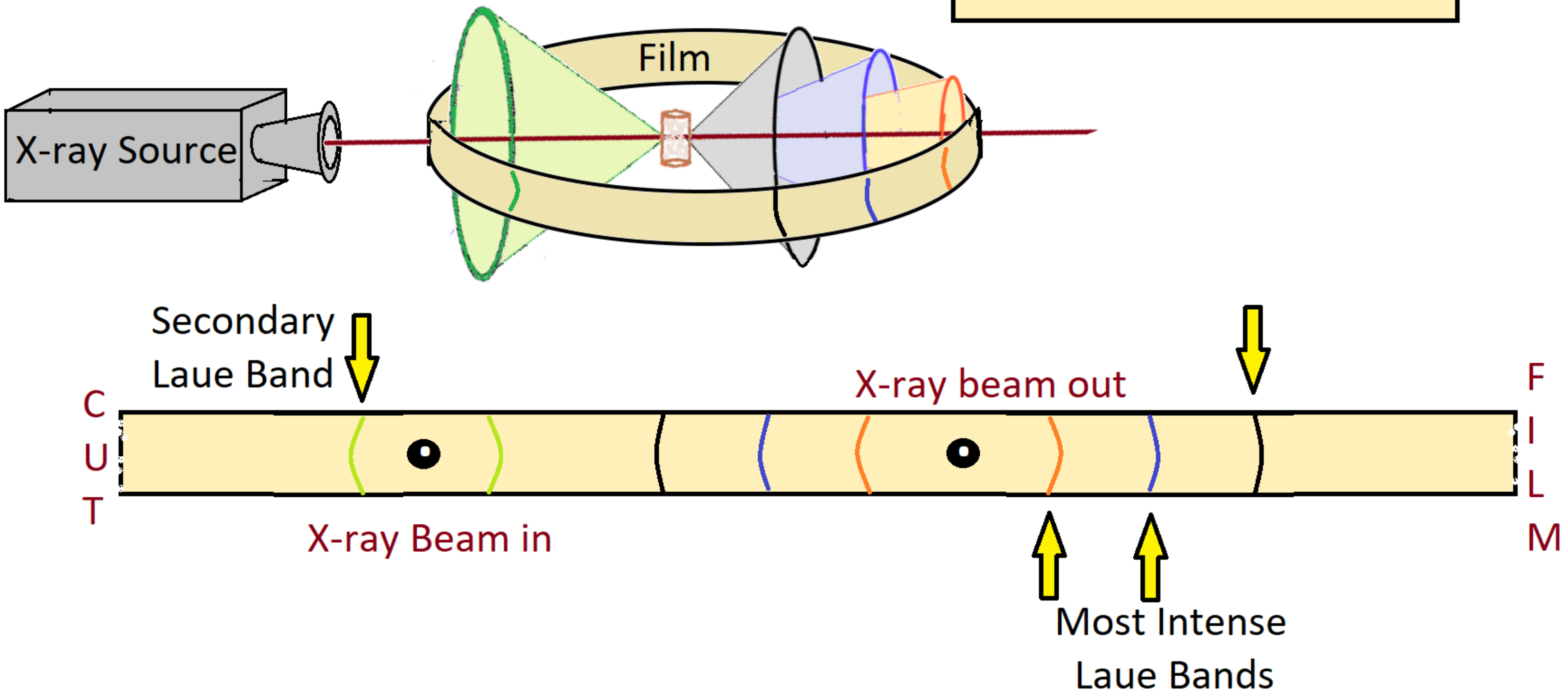


X-ray diffraction pattern on photoplate

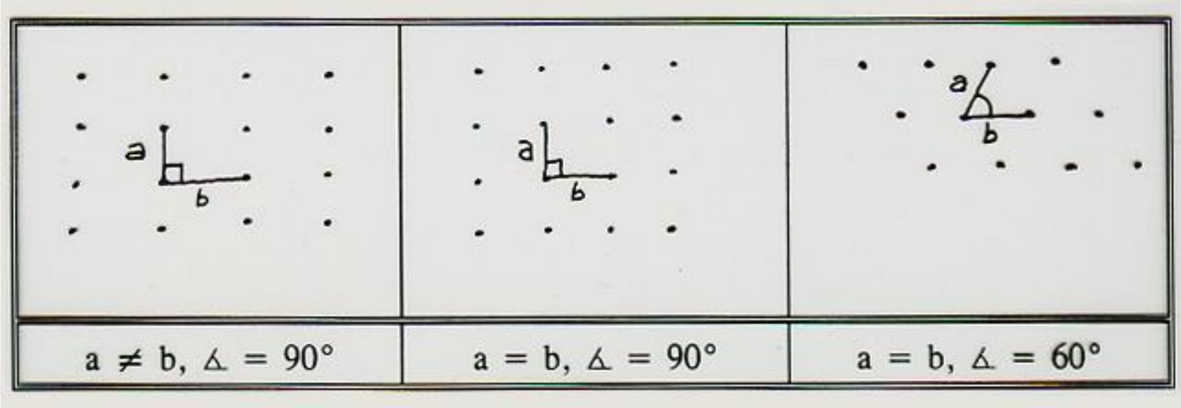
Different crystalline lattices give different x-ray diffraction patterns

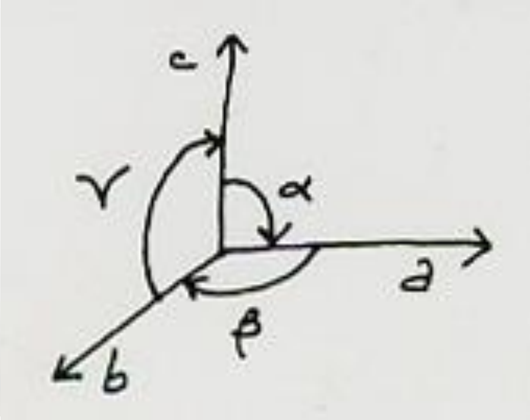
How Were Lattices Discovered? 1911 and 1913 – von Laue and Bragg's (Nobel Prize 1914 (L) and 1915 (B's))

Laue Diffraction Cones



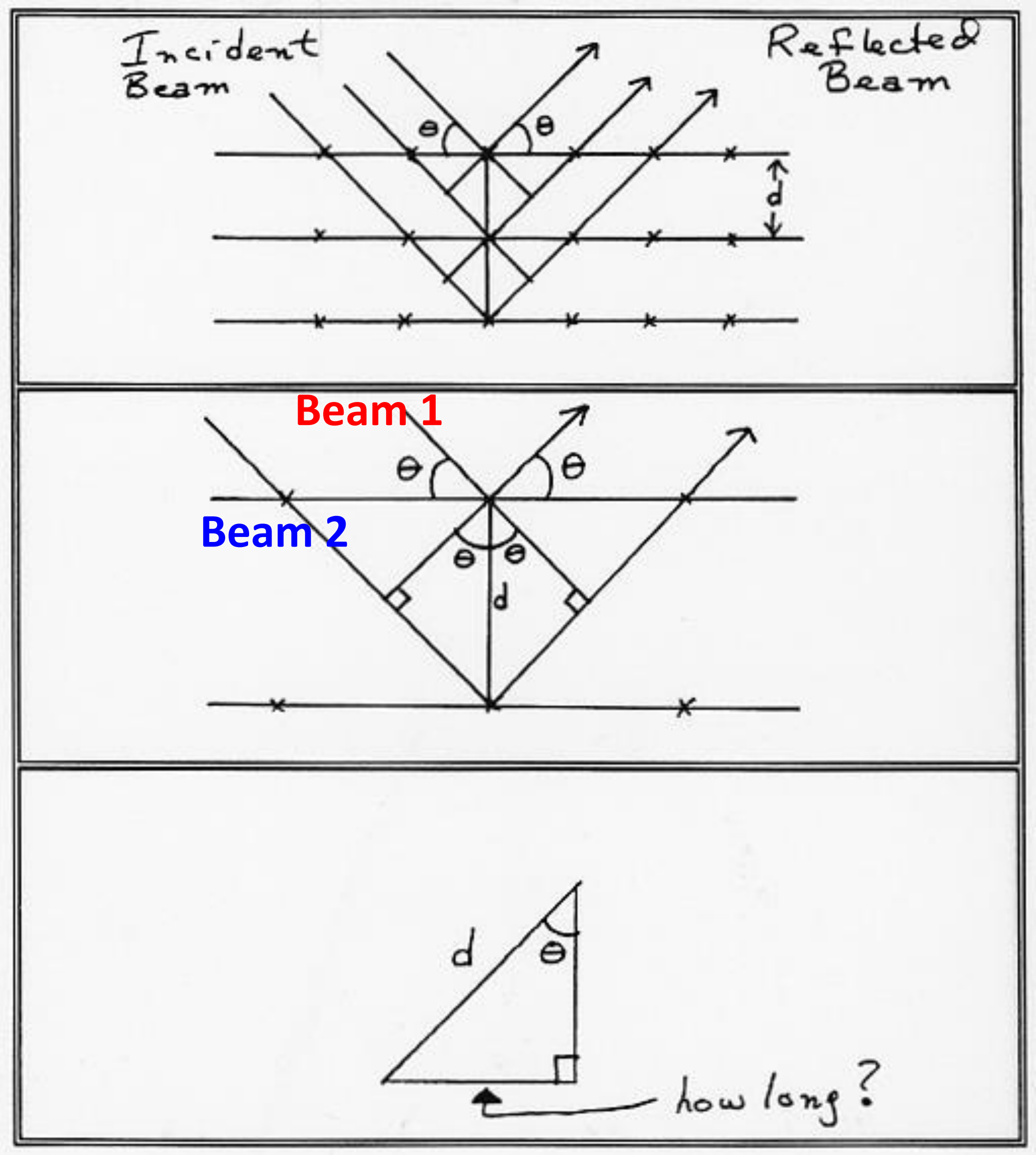
Crystal Lattices





- A lattice is a highly ordered structure in which the atoms are arranged periodically in 3-D
- The kinetic energy of these atoms is manifested by atomic/ionic vibrations in these fixed positions
- Left, above = 2-D; Right, above = 3-D

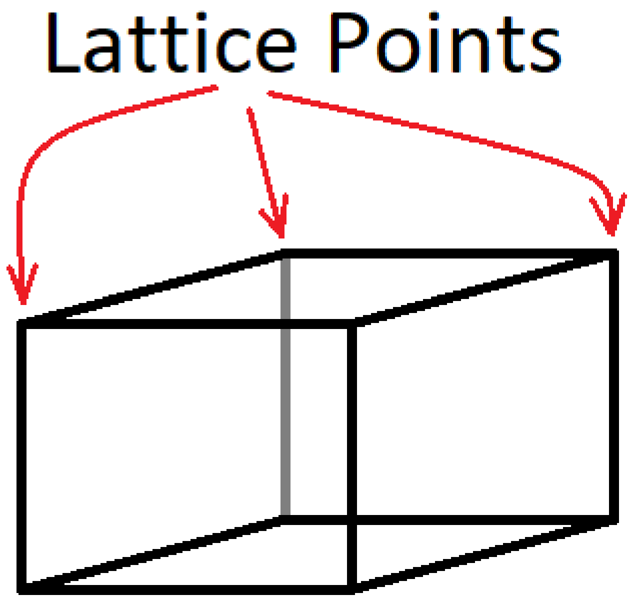
- d = distance (edge length) between lattice planes (“reflectors”) and
- θ = the angle of incidence and reflection of x-rays
- “x” = atoms/ions in planes of unit cells
- Length of side “how long” important because it tells us that beam 2 travels **2 d sin θ** than beam 1



Crystalline Solids: Structures

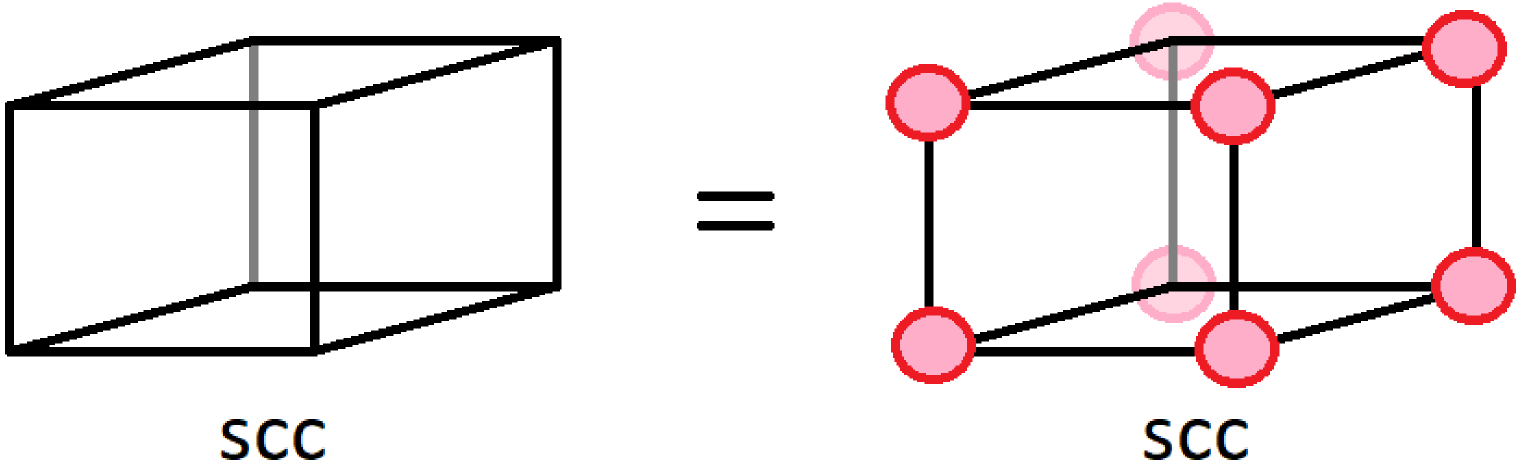
- The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit: its unit cell. The unit cell consists of lattice points that represent the locations of **atoms or ions**.

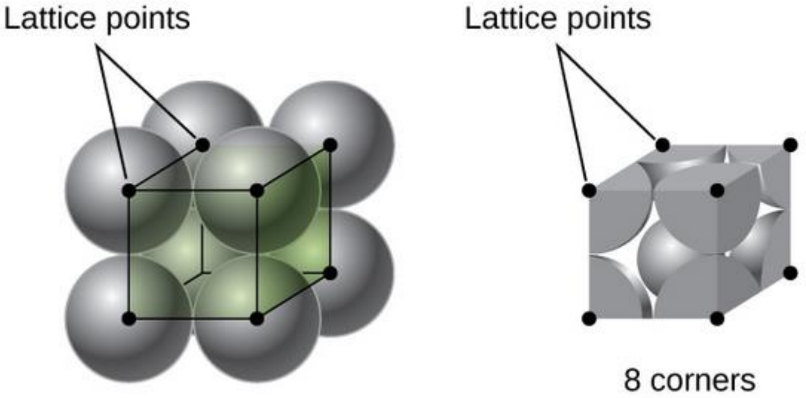
- Most solids are crystalline.



Crystalline Solids: Structures

- The simplest unit cell is the simple cubic cell (scc):
- Note that the atoms or ions are in contact with each other:
- Examples: CsCl, NaCl, ZnS

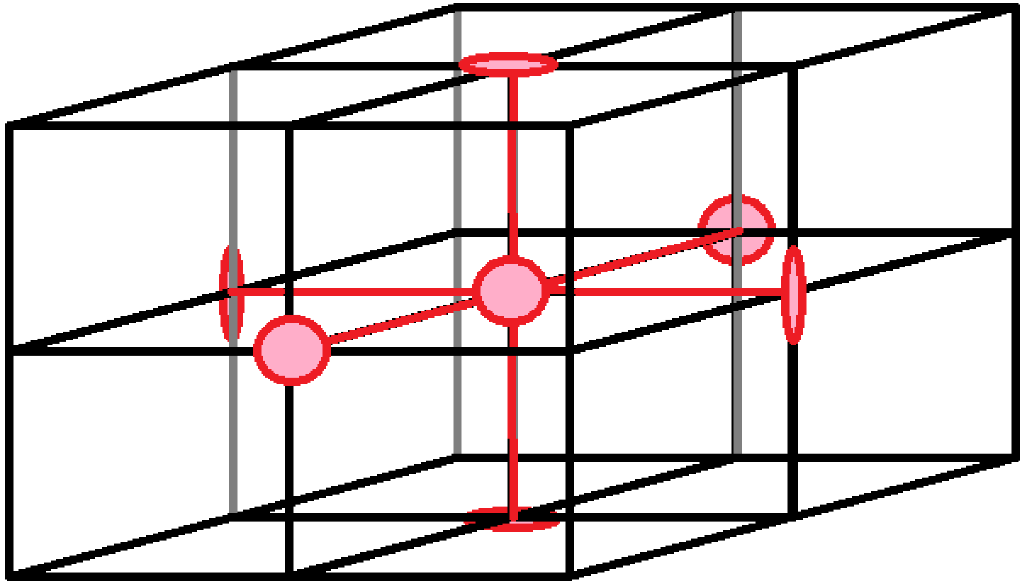


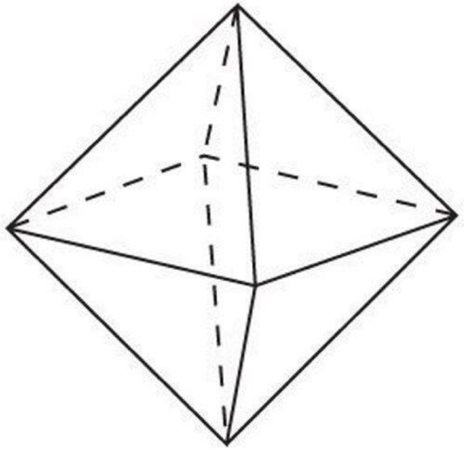


Simple cubic lattice cell

Crystalline Solids: Structures

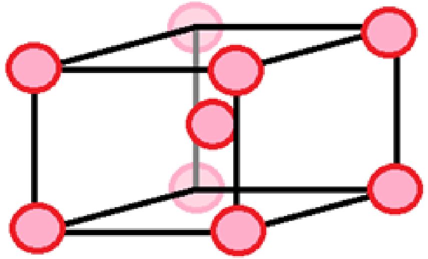
- The entire structure consists of this unit cell repeating in three dimensions:
- Note the central atom/ion has 6 “arms”. This central atom/ion is in contact with 6 other atoms/ions. This is called its **coordination number**.
- The **coordination number** is the number of atoms or ions immediately surrounding a central atom in a complex or crystal.
- If one draws triangle faces from top to middle and bottom to middle, this coordination number of 6 corresponds to an octahedron (8 faces around the central atom/ion)



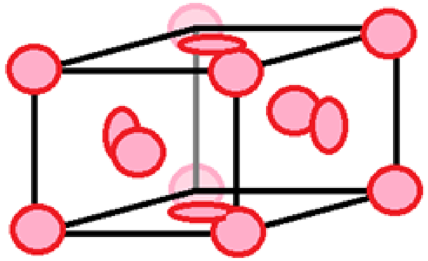


Crystalline Solids: Structures

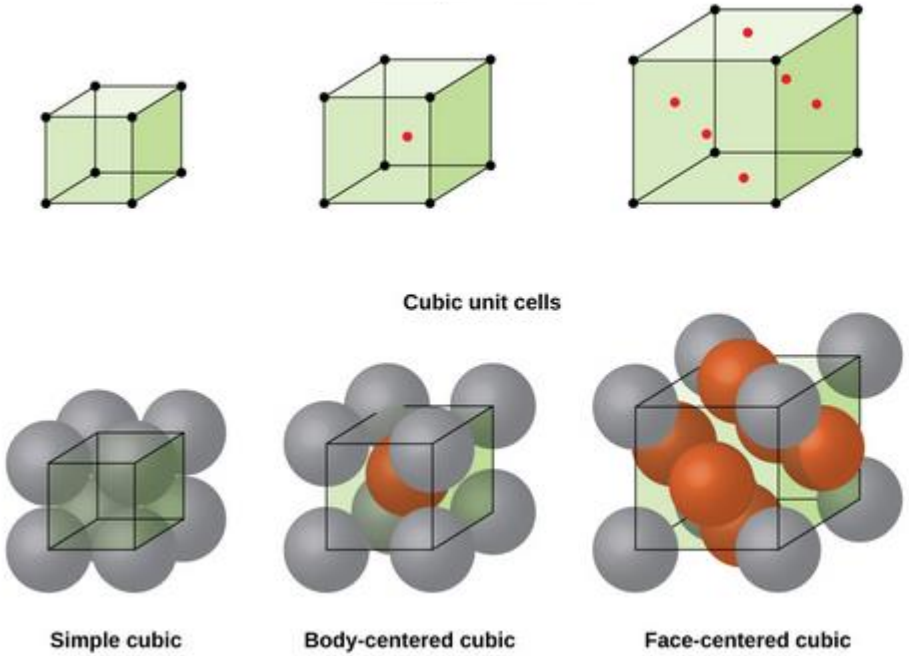
- Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic cells (scc; which we have already seen), body-centered cubic (bcc) unit cell, and face-centered cubic (fcc) unit cell:



bcc

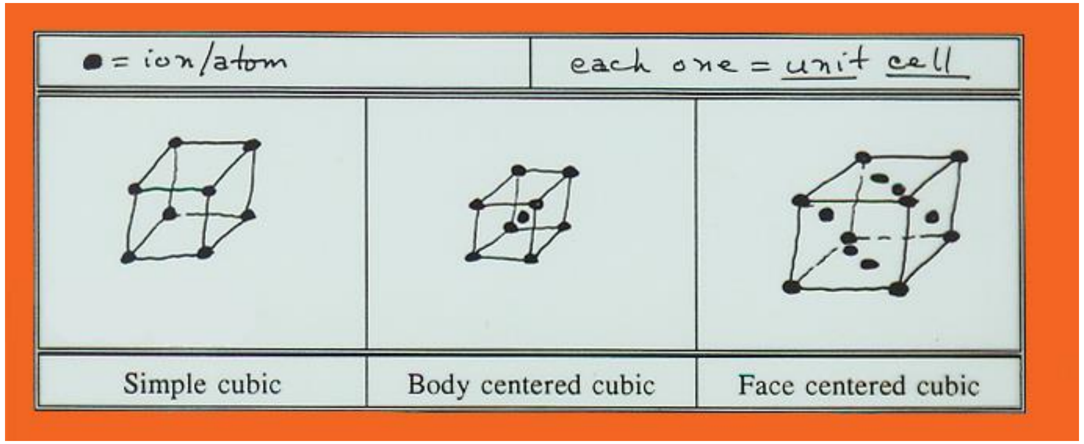


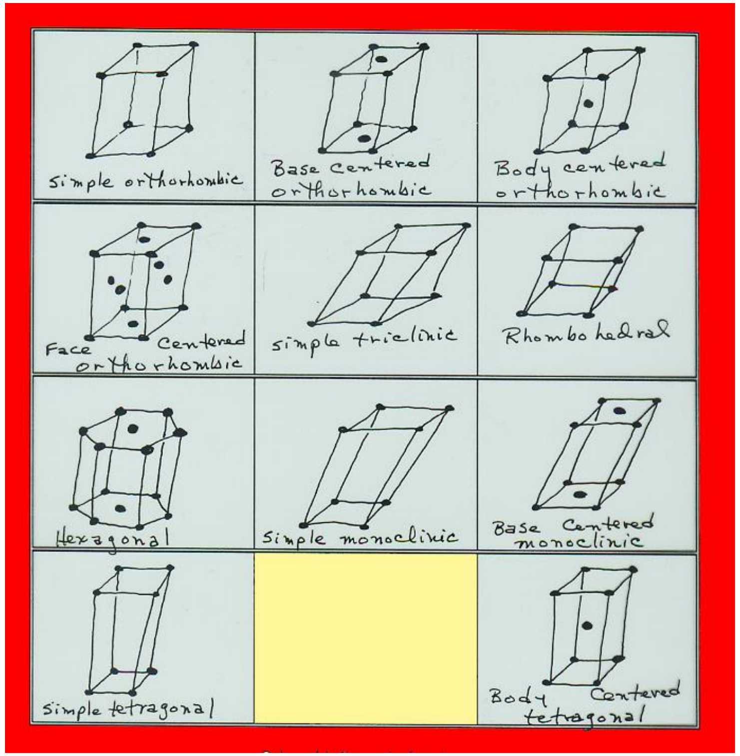
fcc



How Use with Lattices?

There are 14 Bravais Lattices and Rules for Using Them.





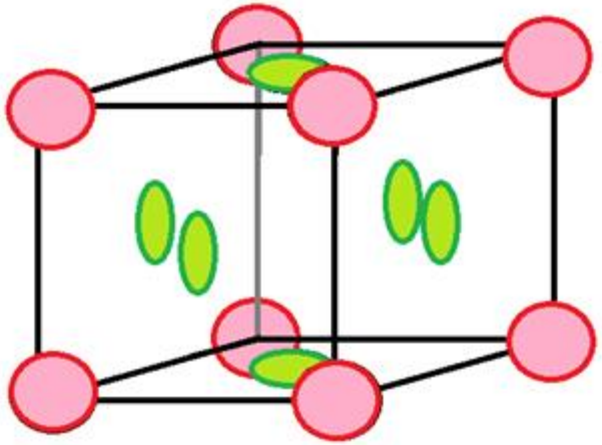
Three Examples, above.

Rules for Counting Atoms in Unit Cells:

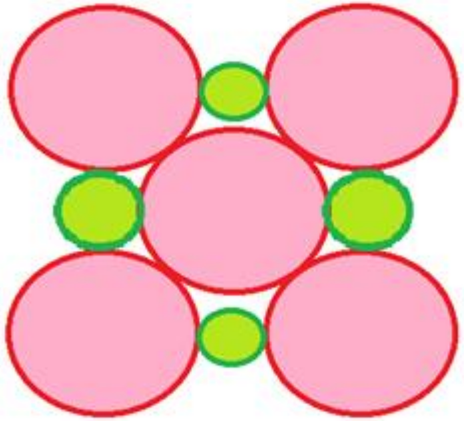
1. Corner atoms are shared with 8 unit cells, therefore, each corner is worth 1/8 of an atom at each corner **UNLESS in hexagon, then = 1/6**
2. Edge atoms are shared with 4 unit cells, therefore, each edge = ¼ of an atom at each edge
3. Face-centered atoms are shared with 2 unit cells, therefore, each face = ½ of each atom at each face
4. Body centered atoms are shared with 1 unit cell, therefore each body = 1 full portion of each atom in “body”

Crystallography: Application

Knowing the edge length of a unit cell, we may then calculate the ionic radii. E.g., Calculate the ionic radius for Li^+ if LiCl (face centered) edge length = 0.514 nm; assume anion-anion contact. An ion is an atom or molecule with a net electric charge due to the loss or gain of one or more electrons. A cation is positively charged and an anion is negatively charged.



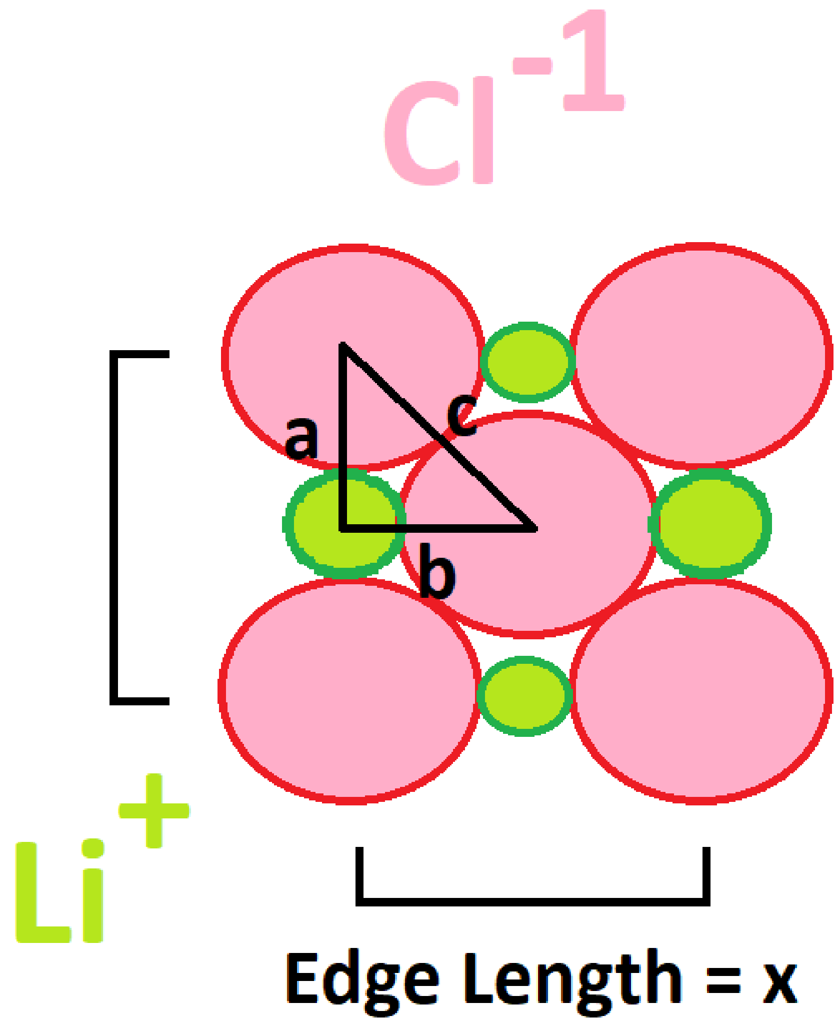
Face Centered Cubic Lattice



One Face of FCC Lattice Anion-to-Anion Contact

Crystallography: Application

Knowing the edge length of a unit cell, we may then calculate the ionic radii. E.g., Calculate the ionic radius for Li^+ if LiCl (face centered) edge length = 0.514 nm; assume anion-anion contact. An ion is an atom or molecule with a net electric charge due to the loss or gain of one or more electrons. A cation is positively charged and an anion is negatively charged.



Crystallography: Application

$$a=\frac{x}{2}=\frac{0.514}{2}=0.257\ \ nm\ \ (Li^{+}\rightarrow Cl^{-})$$

$$b=\frac{x}{2}=\frac{0.514}{2}=0.257\ \ nm\ \ (Li^{+}\rightarrow Cl^{-})$$

$$How\ \ get\ \ Cl^{-}\rightarrow Cl^{-}\ ???$$

$$c^{2}=a^{2}+b^{2}$$

$$c=\sqrt{(a^{2}+b^{2})}\ =\ \sqrt{(0.257\ )^{2}+(0.257\ )^{2}}$$

$$c\ =\ 0.363\ \ nm\ =\ ionic\ \ DIAMETER\quad (Cl^{-}\rightarrow Cl^{-})$$ ✓

$$ionic\ \ radius\ \ of\ \ Cl^{-}\ =\ \frac{0.363}{2}=0.182\ nm$$

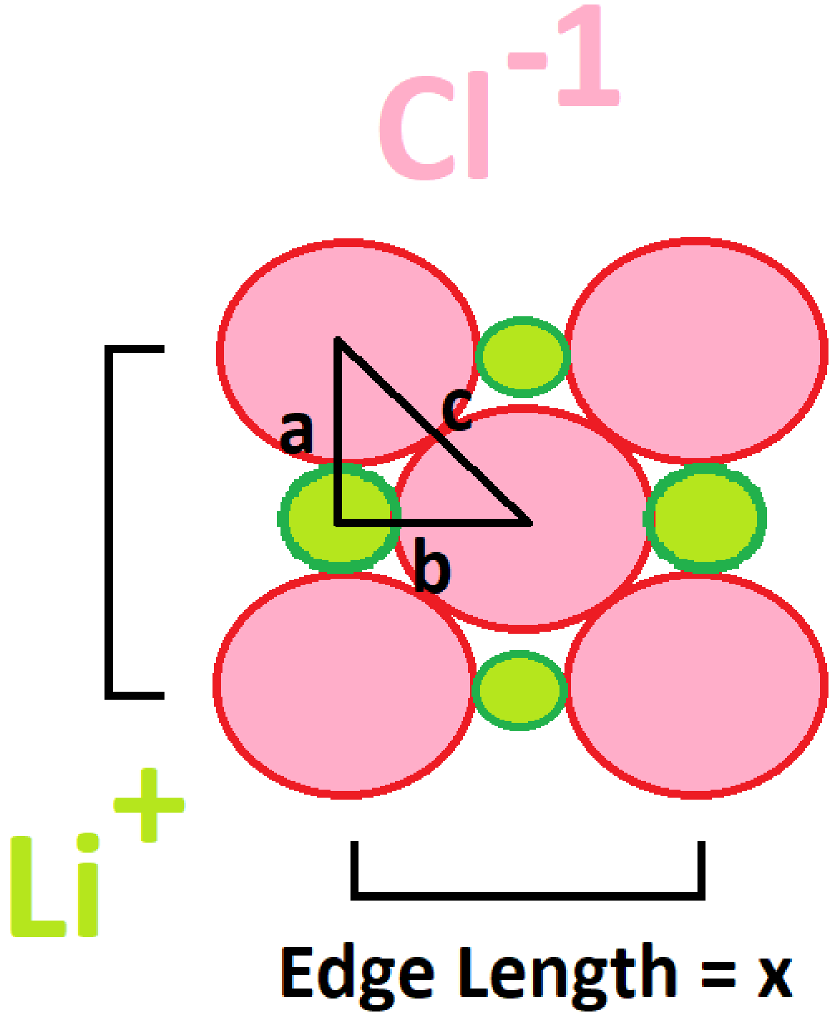
If center to center between Li^{+} and Cl^{-} is 0.257 nm, can calculate the Li^{+} ionic radius:

$$Li^{+}\ \rightarrow\ Cl^{-}\ =\ 0.257\ \ nm$$ ✓

$$Cl^{-}\ \ radius\ \ =\ 0.182$$

$$\therefore$$

$$0.257\ \ nm\ -\ 0.182\ \ nm\ =\ 0.075\ \ nm\ =\ Li^{+}\ \ radius$$ ✓

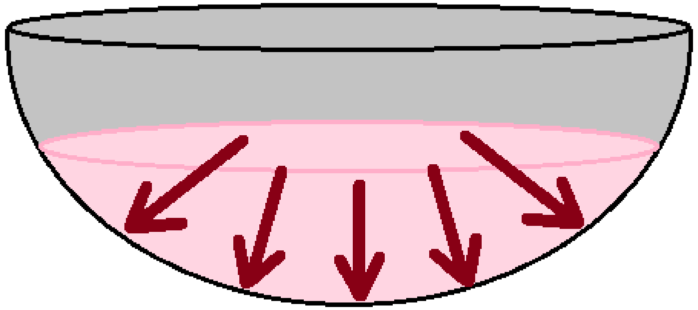


Liquids

Is the only state with a definite volume but no fixed shape


[redacted]

A liquid can flow, assume the shape of a container, and, if placed in a sealed container, will distribute applied pressure evenly to every surface in the container.



Hydrostatic Pressure

Liquids are covered in greater detail in a later chapter.

Gases

- A gas is a compressible fluid. Not only will a gas conform to the shape of its container but it will also expand to fill the container.
- A liquid may be converted to a gas (or vapor) by heating at constant pressure to the boiling point.

- Gases are covered in greater detail in a later chapter.

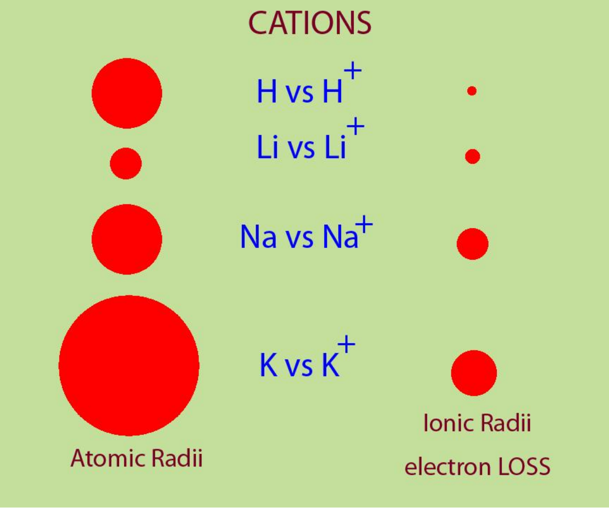
Plasma:

Plasma is the fifth state of matter. Simply stated, a plasma is an ionized gas, a gas into which sufficient energy is provided to free electrons from atoms or molecules and to allow both species, ions and electrons, to coexist. A gas is usually converted to a plasma in one of two ways, either from a huge voltage difference between two points, or by exposing it to extremely high temperatures.

Like a gas, plasma does not have a definite shape or volume. Unlike gases, plasmas are electrically conductive, produce magnetic fields and electric currents, and respond strongly to electromagnetic forces. Positively charged nuclei swim in a "sea" of freely-moving disassociated electrons, similar to the way such charges exist in conductive metal.

Plasma discussed in some more detail in Nuclear CHEM.

Atoms, Ions and Their Radii



CATIONS

H vs H^+

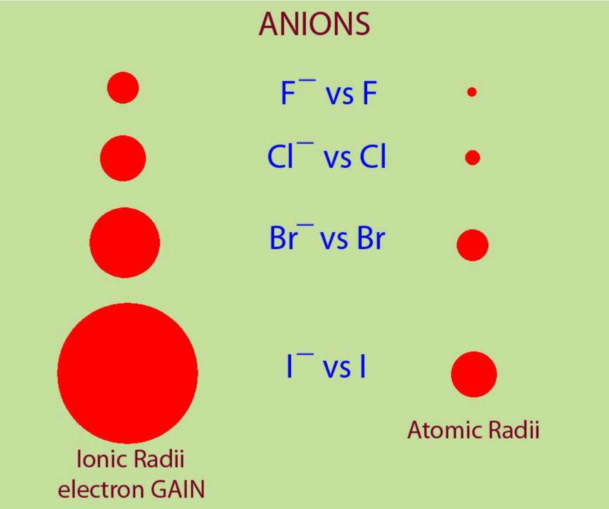
Li vs Li^+

Na vs Na^+

K vs K^+

Atomic Radii

Ionic Radii
electron LOSS



ANIONS

F^- vs F

Cl^- vs Cl

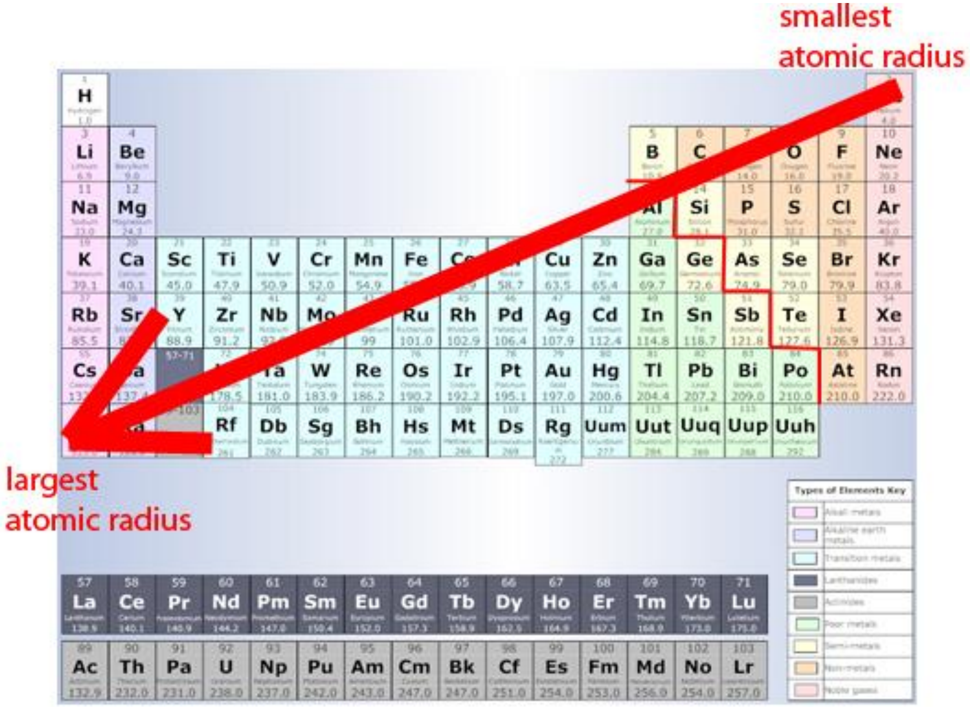
Br^- vs Br

I^- vs I

Ionic Radii
electron GAIN

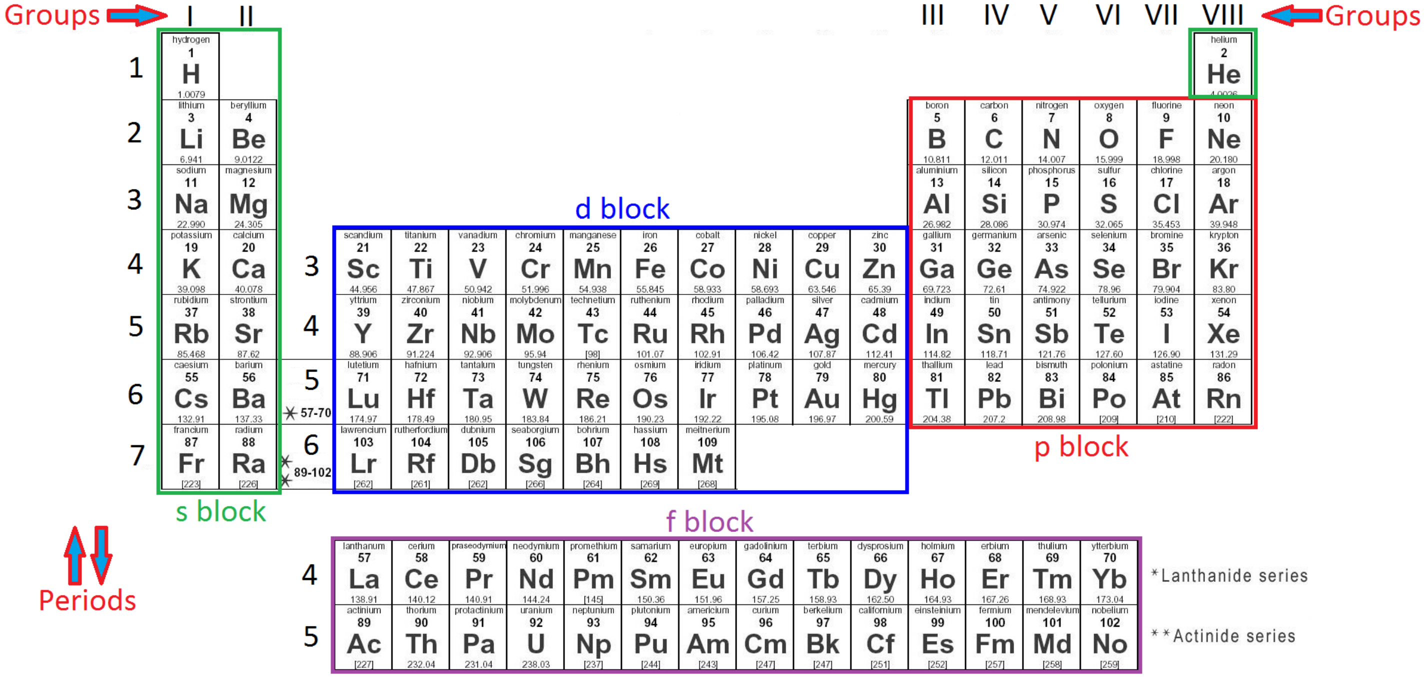
Atomic Radii

- The atomic radius increases from right to left and top to bottom of the periodic table with those elements in the lower left having the greatest atomic radius.
- Those elements in the upper right of the periodic table have the smallest atomic radii



Ions and Electrolytes

- 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**.



Ionization

- 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 and anions are collectively known as electrolytes: charged particles that conduct an electrical current in aqueous solution.
- Biological Application???

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

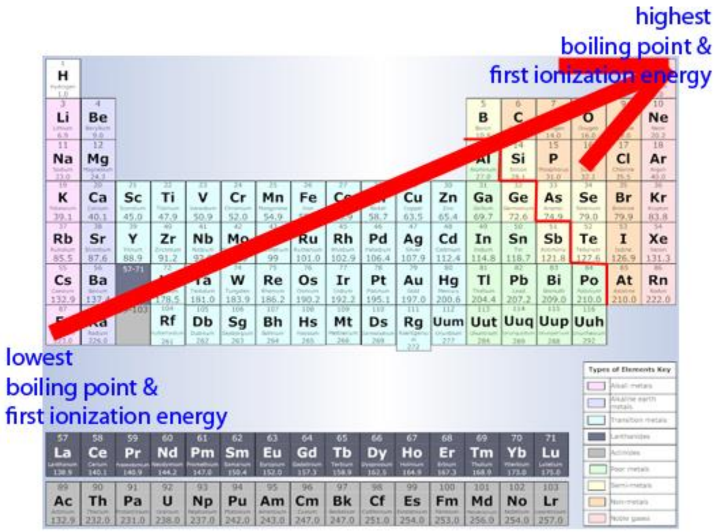
- Elements in Groups V, VI and VII have more than 4 electrons in their outer shells (specifically, the have 5, 6 and 7 electrons, respectively).
- In order for these elements to be most stable when they ionize, i.e., to attain the electronic configuration of the following noble gas, the must gain 3, 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.

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.

Electron Affinity: Ionization, Revisited

- Continuing with the theme of ionization, figure, right, illustrates the electron affinity of elements across the periodic table. Electron affinity is the measure of an atom's tendency to gain (or lose) an electron.
- In general, across periods, the first ionization energy increases from left to right with increasing atomic number.
- The first ionization energy decreases from top to bottom with increasing atomic number.
  - The first ionization energy is the amount of energy needed to remove the most loosely bound electron from the valence shell of the neutral atom
  - While there is a small increase in electron affinity from top to bottom of the periodic table, the biggest increase is from left to right.
  - Electron affinity follows first ionization energies: lower left has the lesser electron affinity while upper right has the higher electron affinity.



- Fr is the most electro-positive element on the periodic table and has the lowest electron affinity.
- F is the most electro-negative element on the periodic table and has the highest electron affinity.
- What this means is that Fr gives up its outer electron the easiest and F gains its last electron the easiest to attain stability, i.e., the electronic configuration of the previous and the following noble gases, respectively.
- For practical purposes, this means that elements in low left easily give up their electrons and elements in upper right hang on to their electrons.

Characteristics of Elements in

The Groups of The Periodic Table

Group I

Element	Configuration	Atomic radius	Ionic radius	Density	Melting point	Boiling point
Li	[He]2s^1	Smallest	Smallest	Least	Highest	Highest
Na	[Ne]3s^1		Ionic radii are smaller than their atomic radii.			
K	[Ar]4s^1					
Rb	[Kr]5s^1					
Cs	[Xe]6s^1					
Fr	[Rn]7s^1	Largest	Largest	Most	Lowest	Lowest

Hydrogen

- Note that I did not include hydrogen, here.
- It's a funny element that has numerous contradictory characteristics that make it in a class by itself.
- In fact, some of the older periodic tables put H in the middle above the periodic table because of that.

Group I elements are also known as the alkali metals.
They are known as that as they produce alkali when reacted with water.
The table below summarizes the types of reactions that alkali metals undergo with examples of each reaction.
Note: "M" represents any alkali metal. "X" represents any halogen, e.g., F, Cl, Br, I.

Reaction type	Example
With water (rapid! hot!) Forms hydroxides.	$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2$
With halogens (rapid! hot!) Forms halides.	$2M(s) + X_2 \rightarrow 2MX(s)$
With hydrogen. Forms hydrides.	$2M(s) + H_2(g) \rightarrow 2MH(s)$
With oxygen. Forms oxides.	$4Li(s) + O_2(g) \rightarrow 2Li_2O(s)$ $2Na(s) + O_2(g) \rightarrow Na_2O(s)$ $4K(s) + O_2(g) \rightarrow 2K_2O(s)$
With nitrogen. Forms nitrides.	$6Li(s) + N_2(g) + \text{heat} \rightarrow 2Li_3N(s)$

Elements in Group II are called the alkaline earth metals as they are found in earthy substances.

They also react with water to form alkalis.

The table, below, summarizes the properties of these elements:

Element	**Configuration**	**Atomic radius**	**Ionic radius**	**Density**	**Melting point**	**Boiling point**
Be	**$[He]2s^2$**	**Smallest**	**Smallest**	**Higher**	**Highest**	**Highest**
Mg	**$[Ne]3s^2$**					
Ca	**$[Ar]4s^2$**			**Smallest**	**Way lowest**	**Way lowest**
Sr	**$[Kr]5s^2$**			↓	↓	↓
Ba	**$[Xe]6s^2$**			↓	↓	↓
Ra	**$[Rn]7s^2$**	**Largest**	**Largest**	**Highest**	**Lowest**	**Lowest**

For some strange reason, Ca has really weird properties.

Otherwise it fits into Group II.

The table, below, summarizes the reaction types and example reactions for this group:

Reaction type	Example
With water (vigorous) **Forms hydroxides.**	**$M(s) + 2H_2O(l) \rightarrow 2M(OH)_2(aq) + H_2$** **When "M" = Mg, add heat for the reaction to go**
With halogens (rapid! hot!) **Forms halides.**	**$M(s) + X_2 \rightarrow MX_2(s)$**
With hydrogen. **Forms hydrides.**	**$M(s) + H_2(g) + \text{heat} \rightarrow MH_2(s)$**
With oxygen. **Forms oxides.**	**$2M(s) + O_2(g) \rightarrow 2MO(s)$** **When "M" = Be or Mg, add heat for the reaction to go** **$Ba(s) + O_2(g) + \text{heat} \rightarrow BaO_2(s)$**
With nitrogen. **Forms nitrides.**	**$3M(s) + N_2(g) + \text{heat} \rightarrow M_3N_2(s)$**

Alkaline earth compounds have numerous uses:

Compound	Formula	Common name and use
Magnesium hydroxide	$Mg(OH)_2$	Milk of magnesia; laxative
Magnesium oxide	MgO	Magnesia -- fire bricks
Magnesium sulfate	$MgSO_4$	Magnesium sulfate heptahydrate is Epsoms salts and used for laxative; magnesium sulfate is used to treat pre-term labor
Calcium carbonate	$CaCO_3$	Primary ingredient in limestone, marble, coral, shells, Tums
Calcium hydroxide	$Ca(OH)_2$	Slaked lime -- aqueous is white wash
Calcium chloride	$CaCl_2$	Desiccant (drying agent); melts ice, too
Calcium sulfate	$CaSO_4$	The dihydrate salt is called gypsum (sheet rock); hemihydrate is plaster of Paris
Barium sulfate	$BaSO_4$	Opaque to x-rays; x-rays of GI tract
Calcium oxide	CaO	Lime -- used in mortar, cement, plaster

Jumping across to the halogens (Group VII), their characteristics are summarized, below. Halogens react to form halides -- salts.

Element	Valence shell configuration	Atomic radius	Ionic radius	Density	Melting point	Boiling point	Reactivity
F	$2s^22p^5$	Smallest	Smallest	Lowest	Lowest	Lowest	Highest
Cl	$3s^23p^5$		Ionic radii are bigger than atomic radii				
Br	$4s^24p^5$						
I	$5s^25p^5$	Largest	Largest	Highest	Highest	Highest	Lowest

The noble gases' properties are summarized, below:

Element	**Valence shell configuration**	**Atomic radius**	**Density**	**Melting point**	**Boiling point**
He	$1s^2$	**Smallest**	**Least**	**Lowest**	**Lowest**
Ne	$2s^22p^6$	**Note that there are no ionic radii -- these elements are in their stablest configuration: full shells**			
Ar	$3s^23p^6$				
Kr	$4s^24p^6$				
Xe	$5s^25p^6$				
Rn	$6s^26p^6$	**Largest**	**Greatest**	**Highest**	**Highest**

Properties of the Noble Gases

Element→	He	Ne	Ar	Kr	Xe	Rn
# of electrons in outer shell	2	8	8	8	8	8
Atomic radius (Å)	0.93	1.12	1.54	1.69	1.90	2.20
Critical Temperature (°C)	-267.9	-228.7	-122.3	-63.8	-16.6	105
Boiling Point	Lowest	→ → → → → → → → → → → →				Highest
Melting Point	Lowest	→ → → → → → → → → → → →				Highest

Composition of the Atmosphere

- This topic, I believe is of importance as our atmosphere does contain noble gases.
- The table summarizes the composition of our atmosphere.
- Keep in mind that as altitude increases, the per cent composition does not vary - the PRESSURE does, e.g.,
  - at sea level, atmospheric pressure is 760 mm Hg;
  - at 15000 feet, 400 mm Hg;
  - at 10 miles, 40 mm Hg and
  - at 30 miles, 0.1 mm Hg.

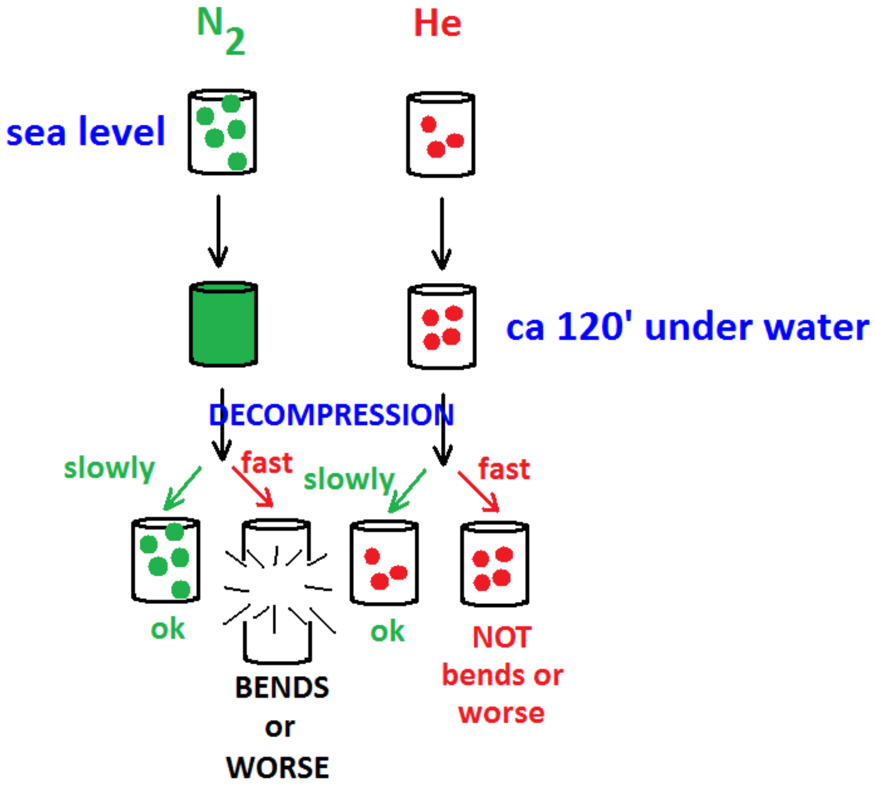
N_2	78%
O_2	20.99%
Ar ←	0.94%
CO_2	0.035-0.04%
H_2	0.01%
Ne ←	0.0012%
He ←	0.0005%
Kr ←	0.0001%
O_3	0.00006%
Xe ←	0.000009%

← All noble gases

General Comments Regarding Noble Gases

- He is an unusual noble gas.
- One form of $^4He_2$ has no electrical resistance.
- It has zero viscosity, i.e., it flows up and over the edges of the container until the levels of He inside and outside the container are level.
  - He coolant is contained in a thermally insulated container (dewar) called a cryostat. To keep the helium from boiling away, the cryostat is usually constructed with an outer jacket containing (significantly cheaper) liquid nitrogen at 77 K. Alternatively, a thermal shield made of conductive material and maintained in 40 K-60 K temperature range, cooled by conductive connections to the cryocooler cold head, is placed around the helium-filled vessel to keep the heat input to the latter at acceptable level.
- That it has no electrical resistance makes it useful as a super conductor.
- He, also has no triple point, unlike water.
- He is used in arc welding, to fill weather balloons, to fill blimps/dirigibles (it's non-flammable).

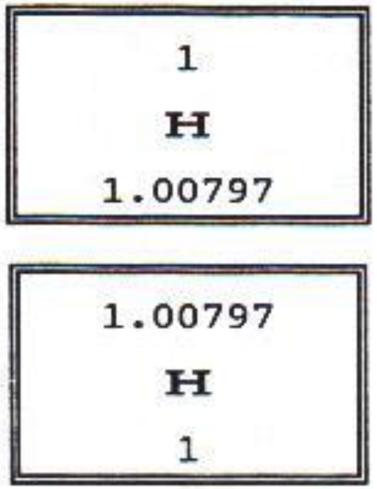
- He is also used in deep-sea diving:
- In general, He is much less soluble in water than are either oxygen or nitrogen.
- At the high pressures of deep sea diving, LOTS of nitrogen (N_2) dissolves in water, blood and cerebrospinal fluid.
- If decompression is attained appropriately, there is no problem.
- If, however, decompression is too rapid, the person develops the bends.
- In this part of the country, this is usually fatal as there is no decompression chamber at Tahoe, any more and the closest one is at Davis, I believe.
- OTOH, if He is substituted for the N_2, even rapid decompression is not as deadly as it is for nitrogen-containing gas mixtures.
- This means that for long term deep-sea diving, the likelihood of developing the bends is greatly reduced.



- Ar is cheaper than He.
- We use about $1.5*10^9$ pounds per year.
- It is used in incandescent bulbs to prevent bulb "burn out". Ne, Ar and Xe are often coupled with Kr in "neon lights".
- The color of the light is dependent upon the composition of the gases.
- Pure Ne gives an orange-red light; pure Xe gives a blue light.

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.



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

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.

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:

$$
\begin{array}{ll}
3 \times 35 & = 105 \ \mathit{for}\ 35Cl \\
1 \times 37 & = \ \ 37 \ \mathit{for} 37Cl \\
4 & = 142
\end{array}
$$

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

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:

$$
\begin{aligned}
&1\times 79 = 79\\
&1\times 81 = 81\\
&2 \quad\quad = 160\\
&Avgmass = \frac{160}{2} = 80
\end{aligned}
$$

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

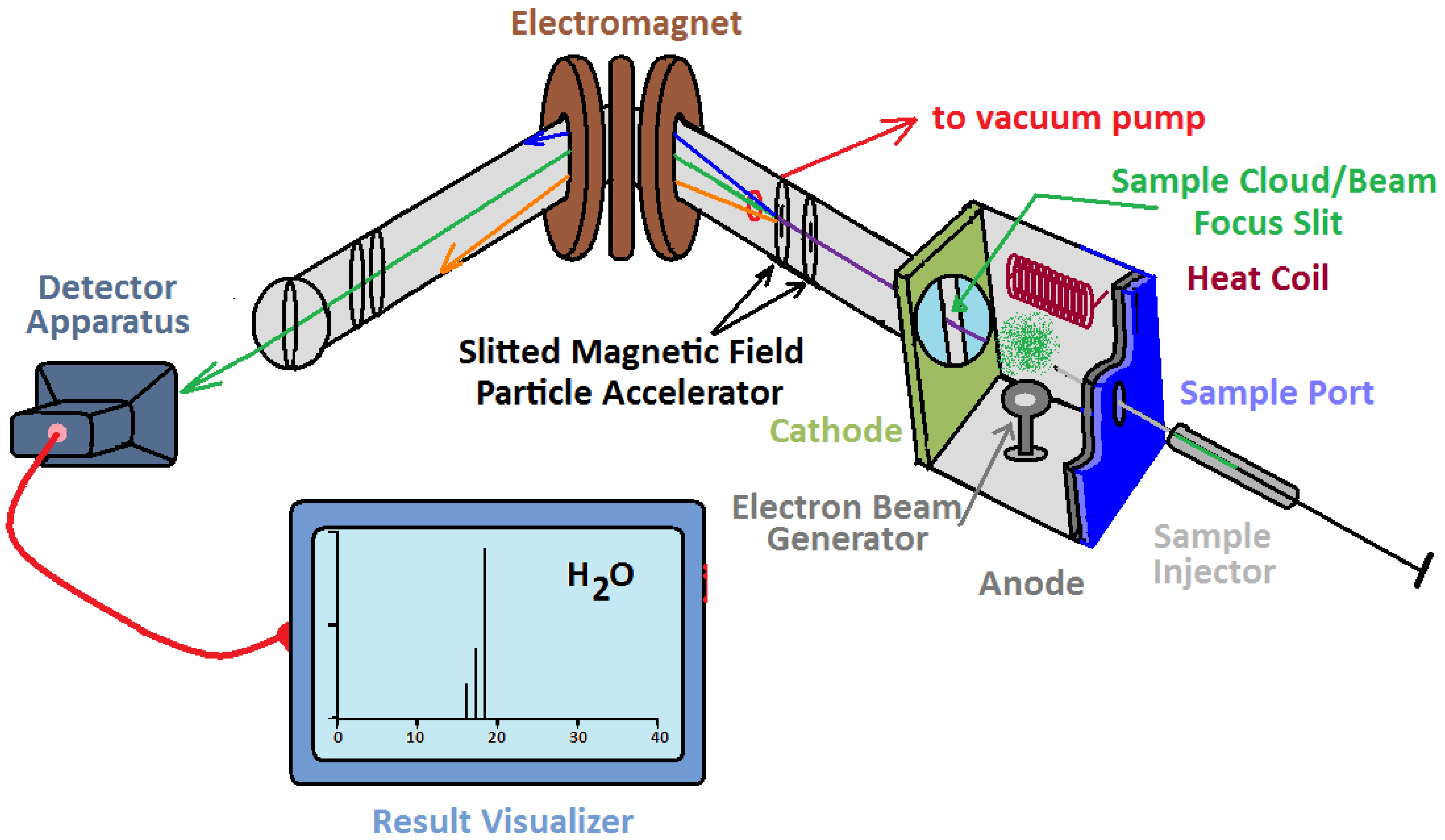
How Do We Know About (Or Measure) the Presence of Isotopes?

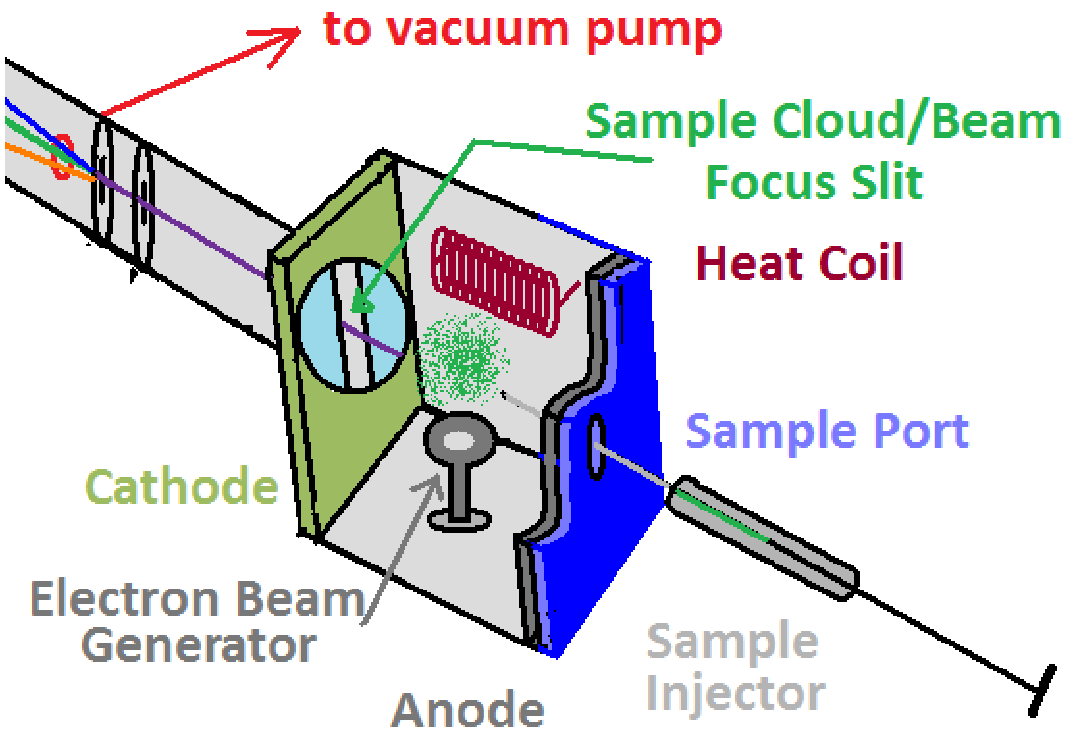
- Isotopes (be they radioactive or not) are relative new-comers to Chemistry and Physics.
- Isotopes were first studied following the initial development of the mass spectrometer by Wilhelm Wien in 1899, improved upon by J.J. Thomson ca 1912.
- Ca 1912, Thomson proved the presence of the first isotopes 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?

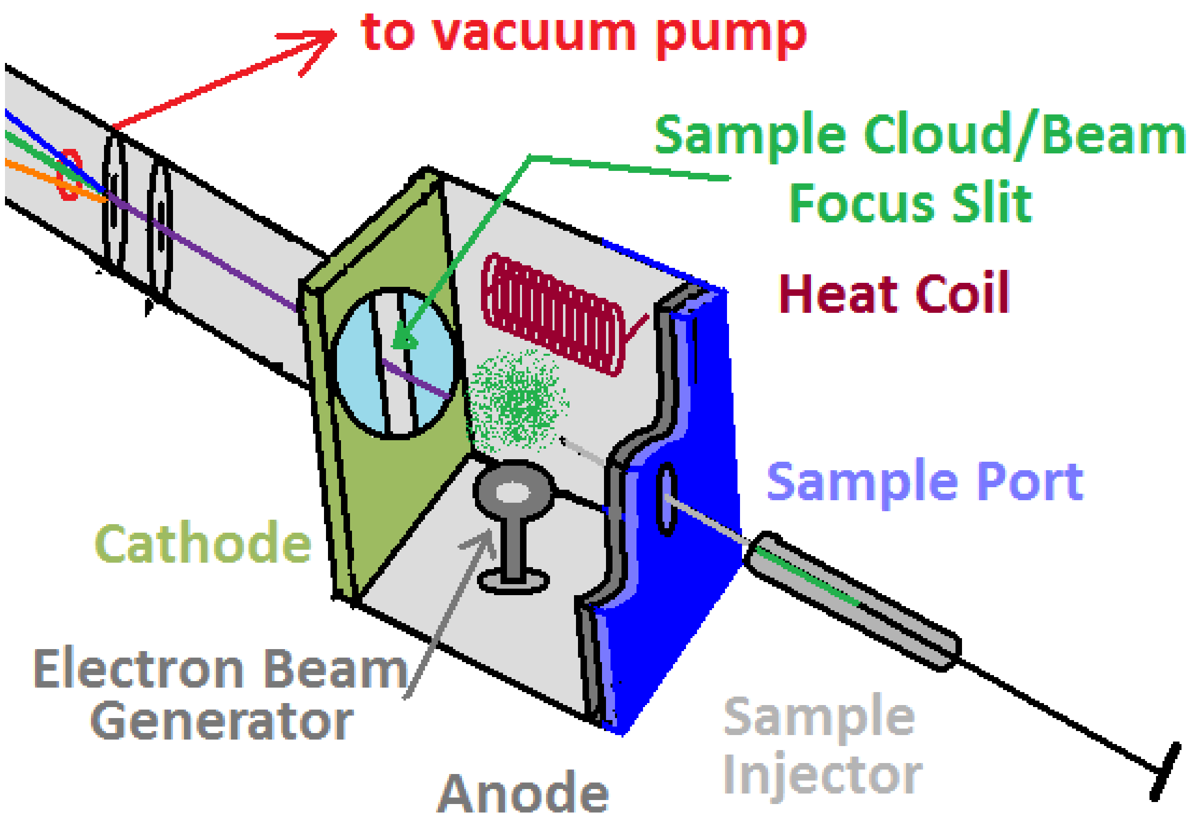
- Mass Spectrometry makes determining chemical formulas and structures fairly simple.
- Mass Spectrometry makes determining isotope presence and abundance fairly simple.

Mass Spectrometer Layout

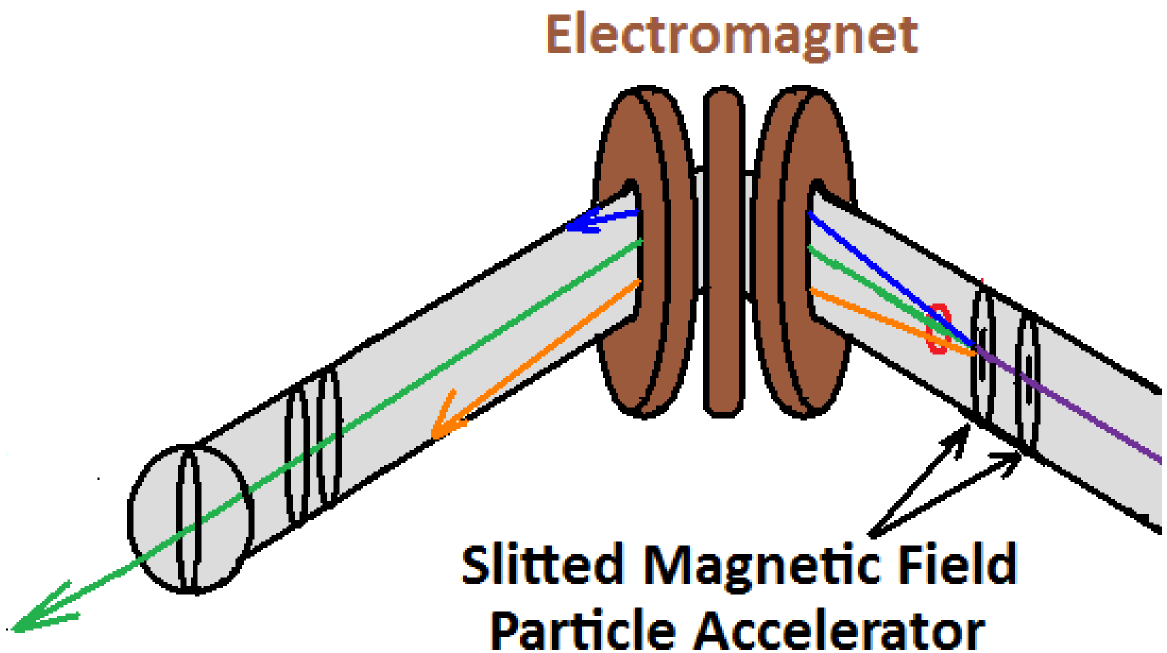




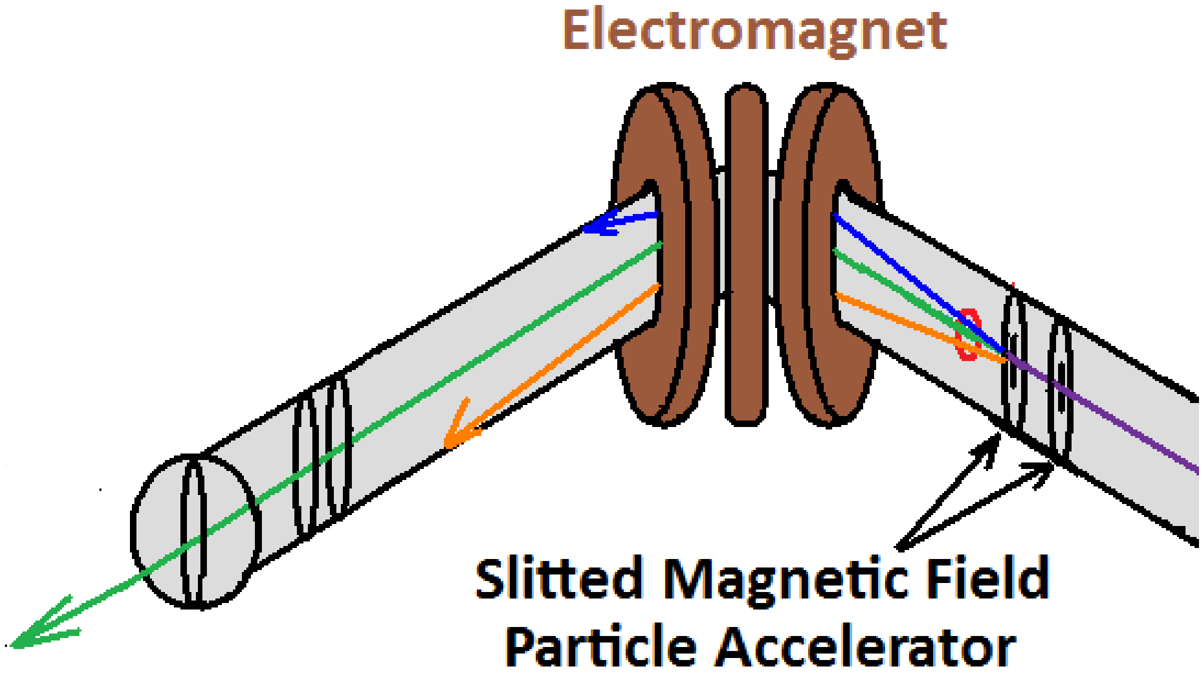
- Sample injected into sample holder/chamber
- Sample vaporized by heat coil
- Sample bombarded by electrons from electron beam generator (some folks call this an electron “gun”)
- Excess electrons boil off generator and are attracted to the Anode (positively charged)



- 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

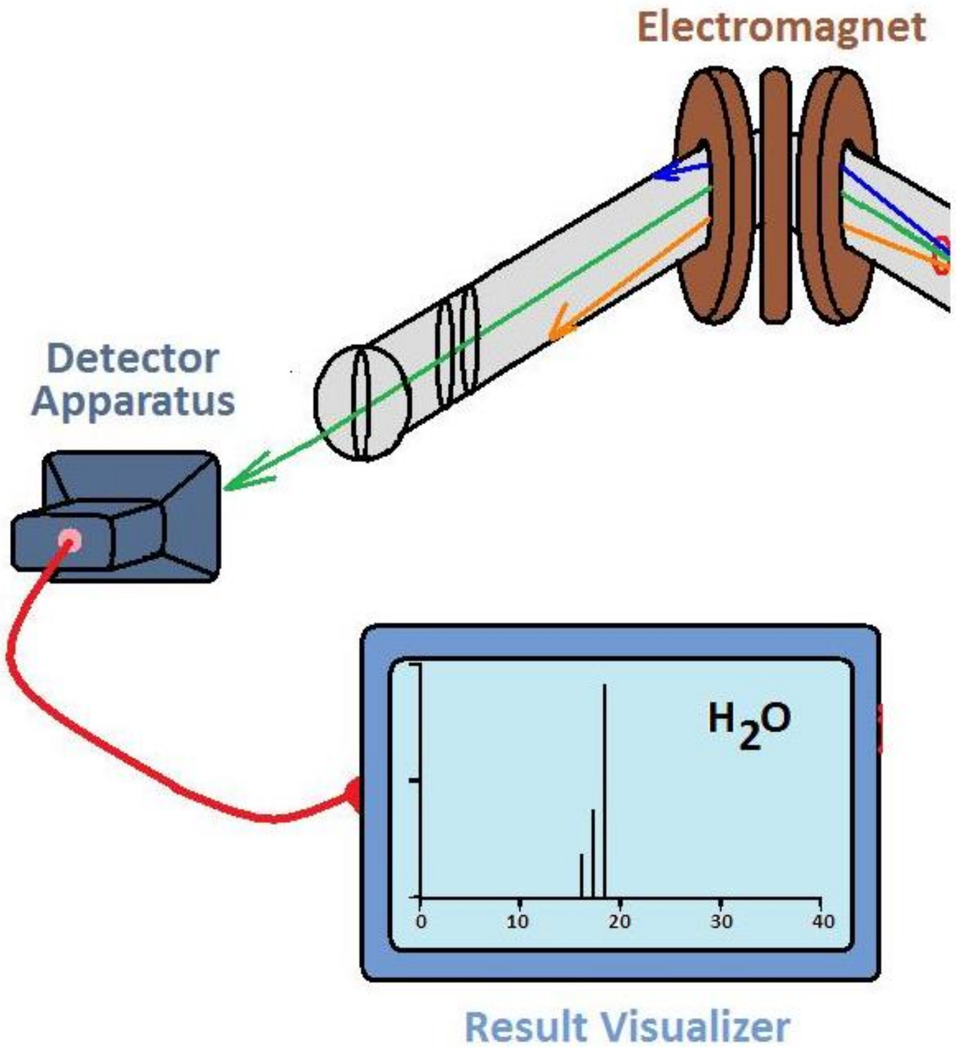


- Sample beam travels under vacuum to the slitted magnetic field particle accelerators – further focuses the beam of the sample cations and prepares the beam to “slingshot” around the tube bend.

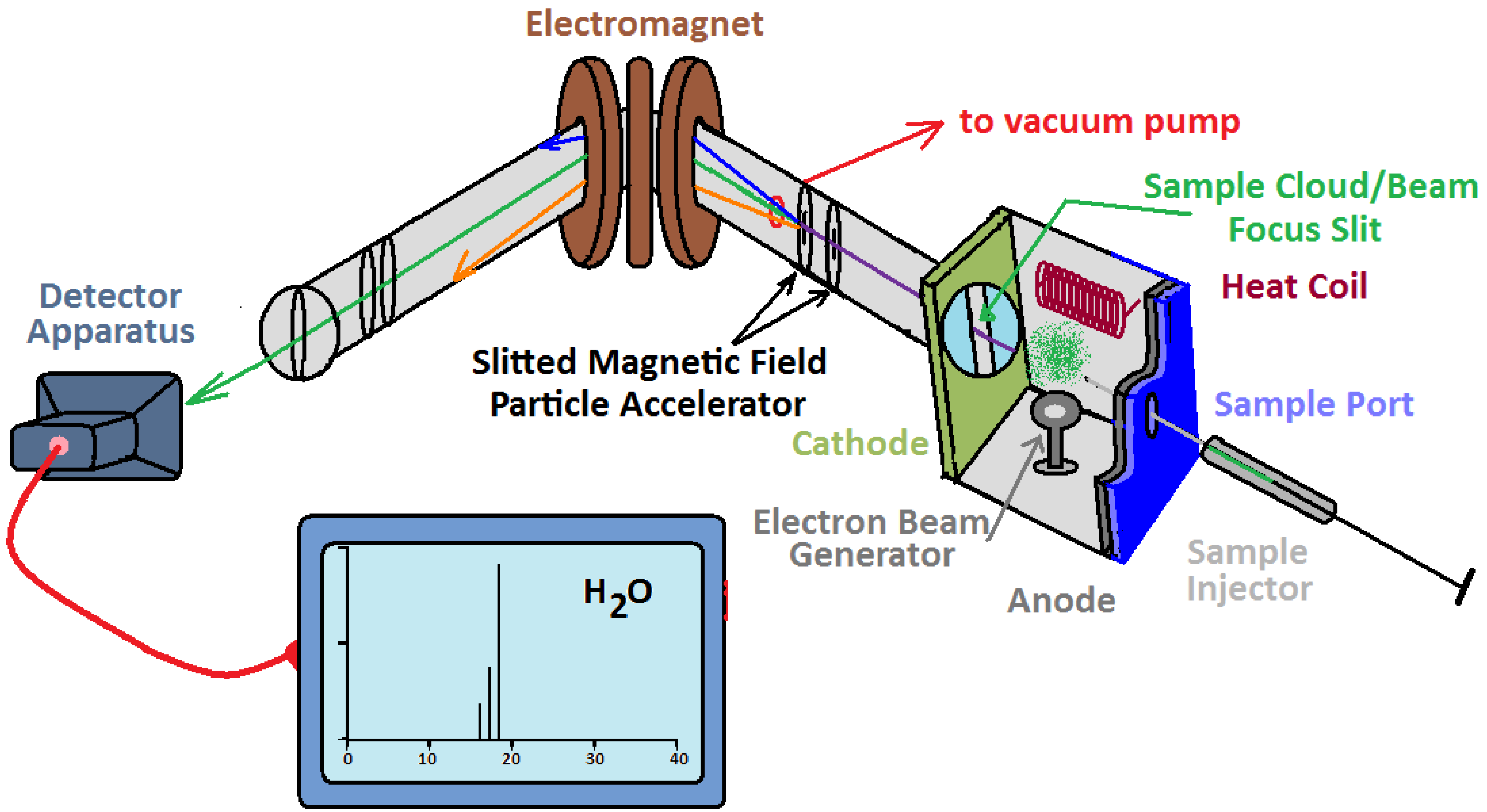


- As the beam approaches the electromagnet, the magnetic field causes the beam to split into “three” beams:
  - Heavy beam (**blue beam**)
  - “Correct beam” (**green beam**)
  - Light beam (**orange beam**)

- "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).

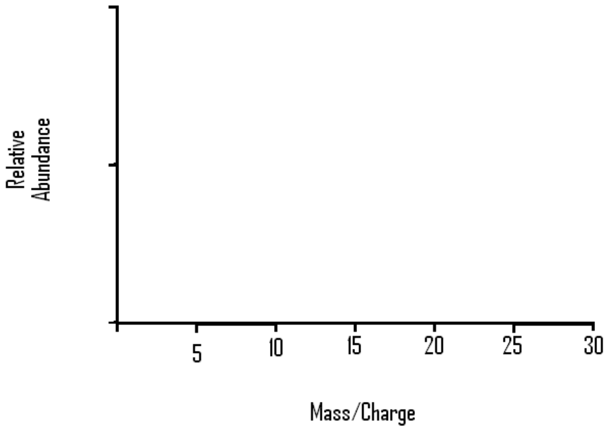


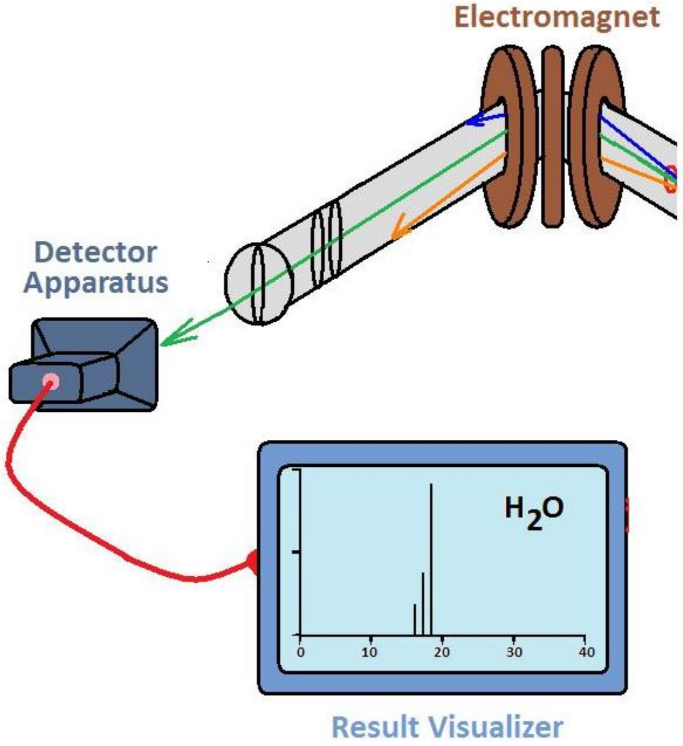
Mass Spectrometry: Some Examples



Result Visualizer

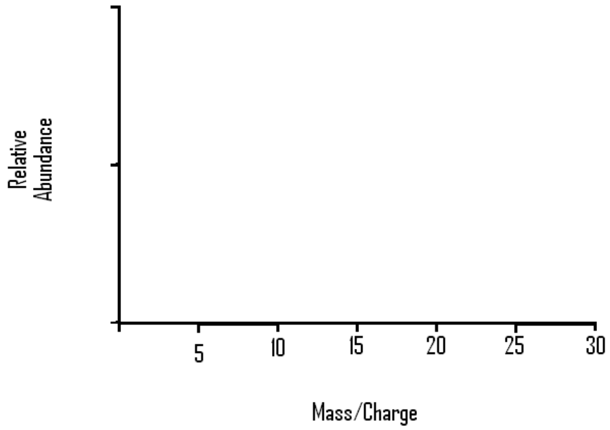
- The mass spectrum identifies molecular mass and molecular particle/fragment masses of a parent compound.
- When a mass spectrum is visualized, it is a “bar/line” graph set on a set of axes as at upper right.
- The mass spectrum for water, BTW, is lower right for an illustration of the “bar/line” graph.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

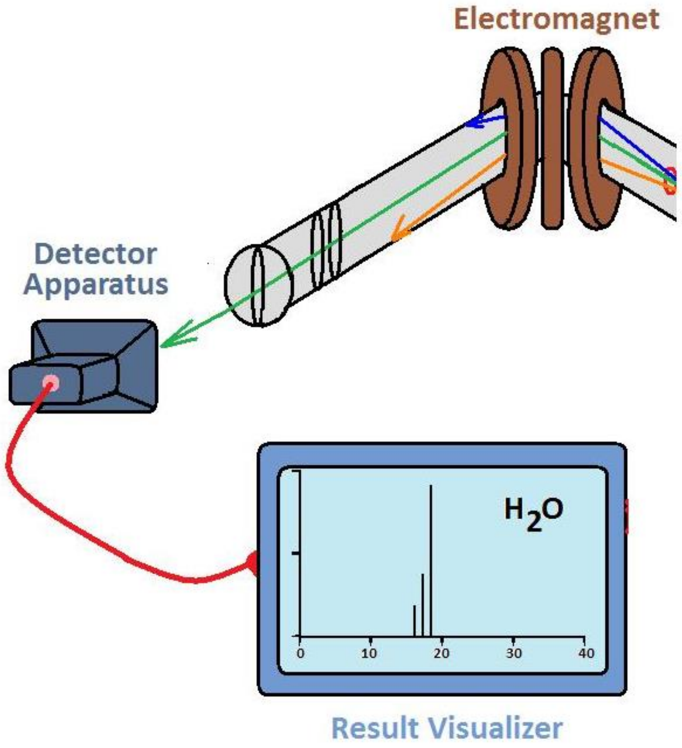




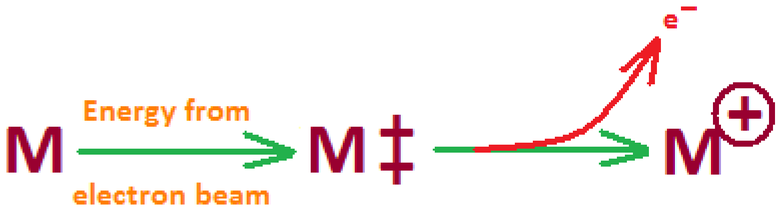
- The vertical axis is Relative Abundance – usually the highest peak is given the value of “100”.

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





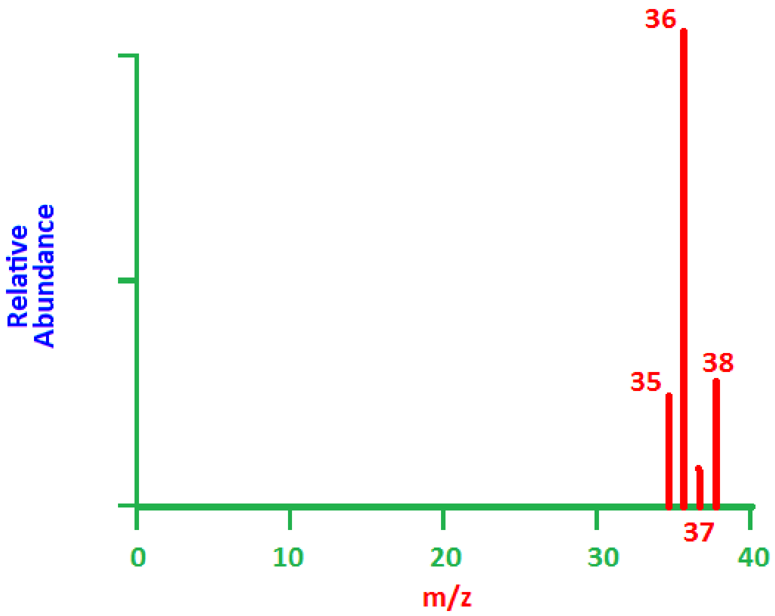
- How does one obtain the mass spectrum of a compound or a mixture of isotopes, barring the techno-mechanical portion of this activity?



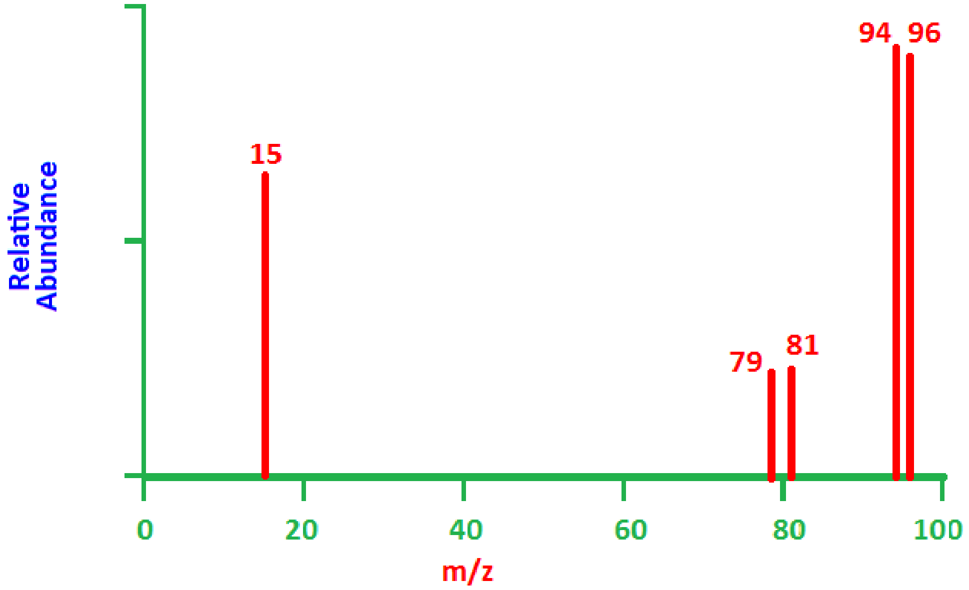
- “Circle +” = radical ion

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

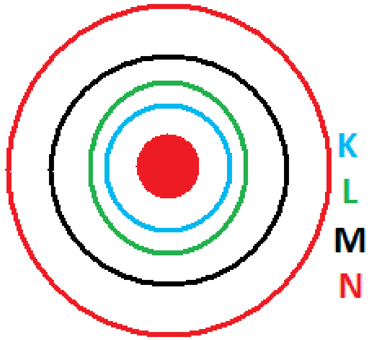


Mass Spectrometry Used to Determine Abundance of Isotopes in Nature



- 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.

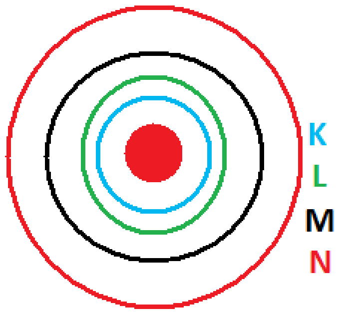
Electronic Configuration: Introduction



We start with the nucleus and work outward from there.

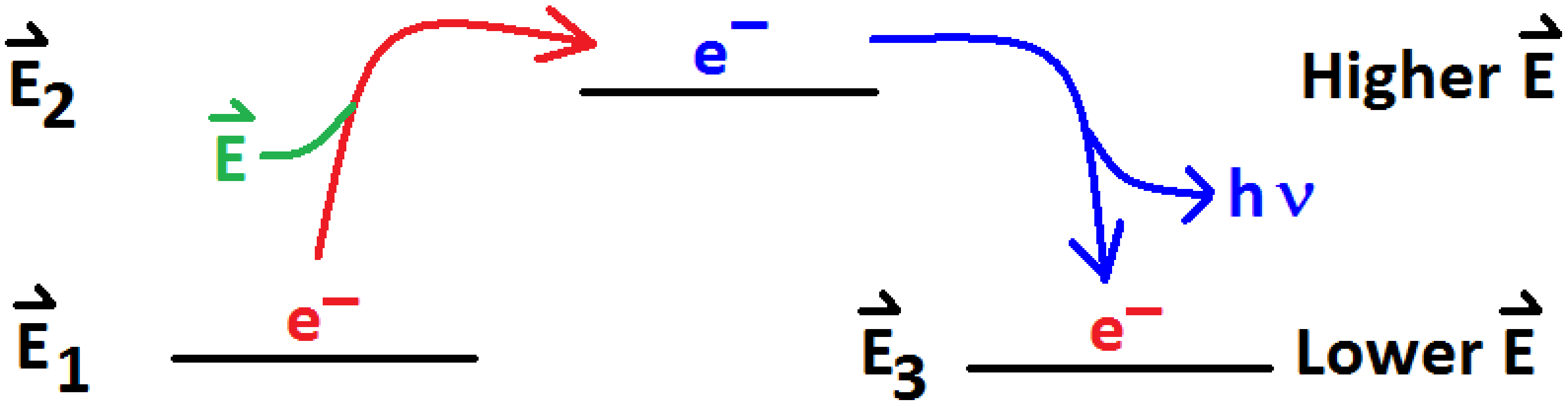
	Nucleus	K	L	M	N
H	1 p^+	1 e^-			
He	2 p^+ 2 n	2 e^-			
Li	3 p^+ 4 n	2 e^-	1 e^-		
Na	11 p^+ 12 n	2 e^-	8 e^-	1 e^-	
Sc	21 p^+ 24 n	2 e^-	8 e^-	9 e^-	2 e^-

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.



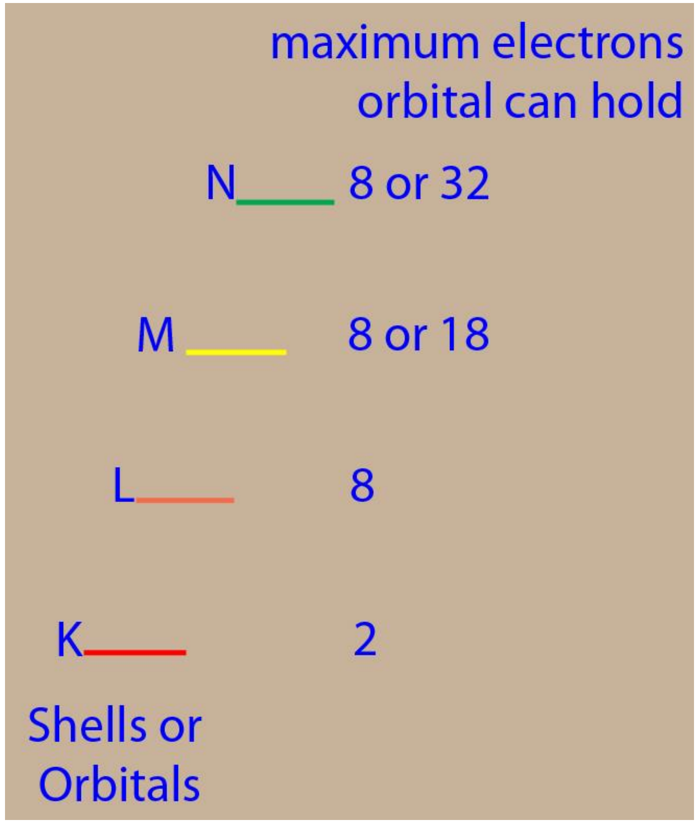
	Nucleus	K	L	M	N
H	$1p^+$	$1e^-$			
He	$2p^+$ $2n$	$2e^-$			
Li	$3p^+$ $4n$	$2e^-$	$1e^-$		
Na	$11p^+$ $12n$	$2e^-$	$8e^-$	$1e^-$	
Sc	$21p^+$ $24n$	$2e^-$	$8e^-$	$9e^-$	$2e^-$

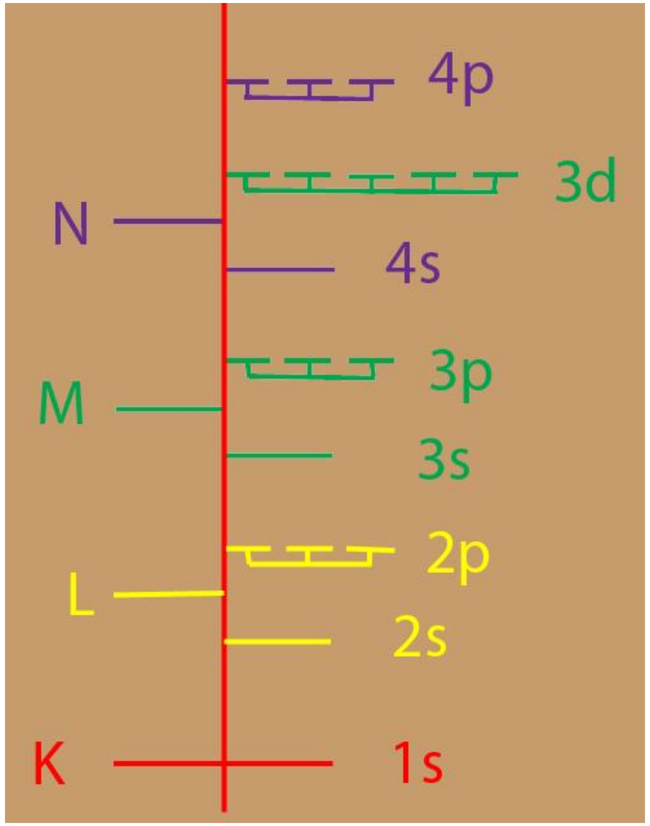
- These energy shells (I use orbitals interchangeably) do not explain, though, how electrons move between energy levels,



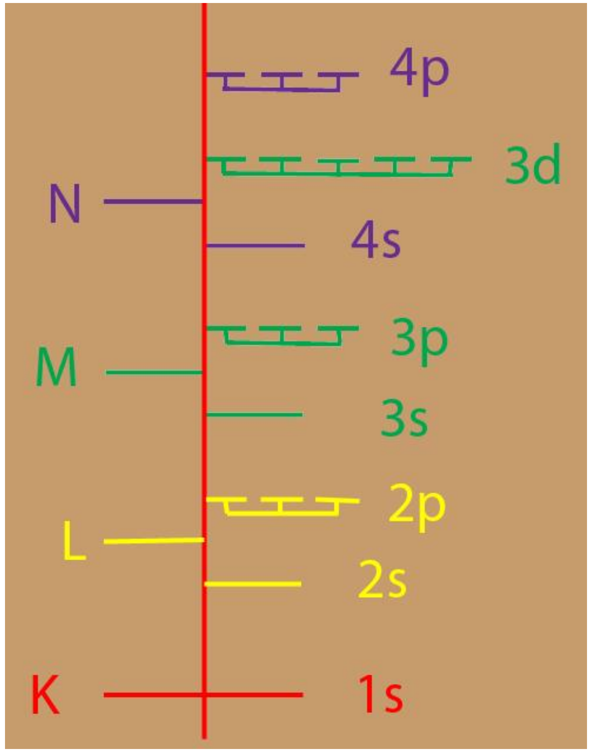
- When electrons become excited, they "jump" to a higher level.
- As they relax, they give off energy in the form of heat or light energy (hυ in the graphic).
- There must, therefore, be another way to examine this phenomenon.

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.

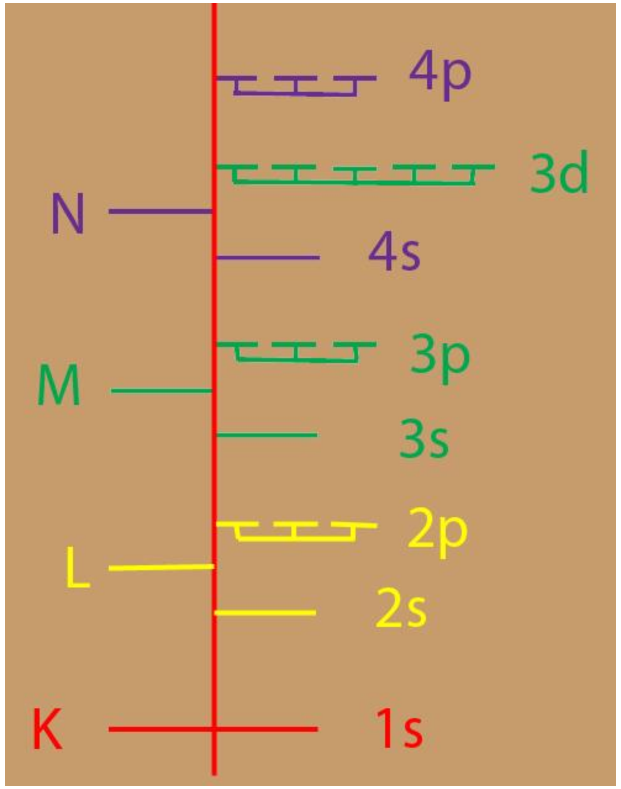




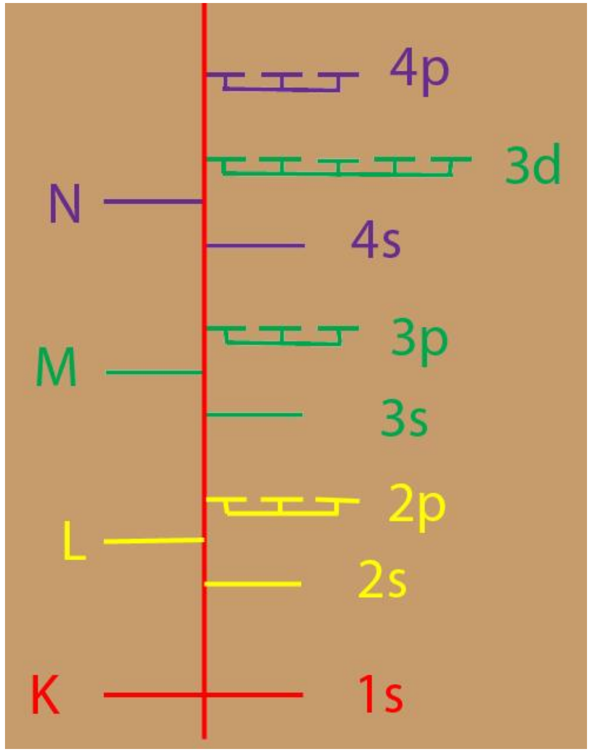
The L shell consists of 2 subshells: the 2s and the 2p subshells. The third electron goes into the 2s subshell. Once the 4th electron has filled the 2s subshell, the 5th electron has to go into the 2p subshell. Here's where it gets a bit messy. The 2p subshell consists of 3 sub-subshells. All subshells 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.

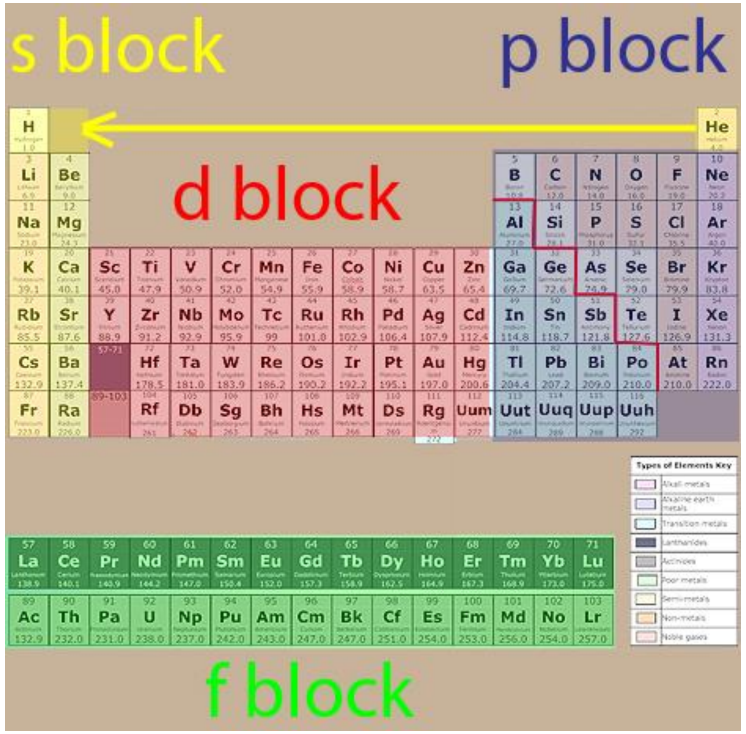


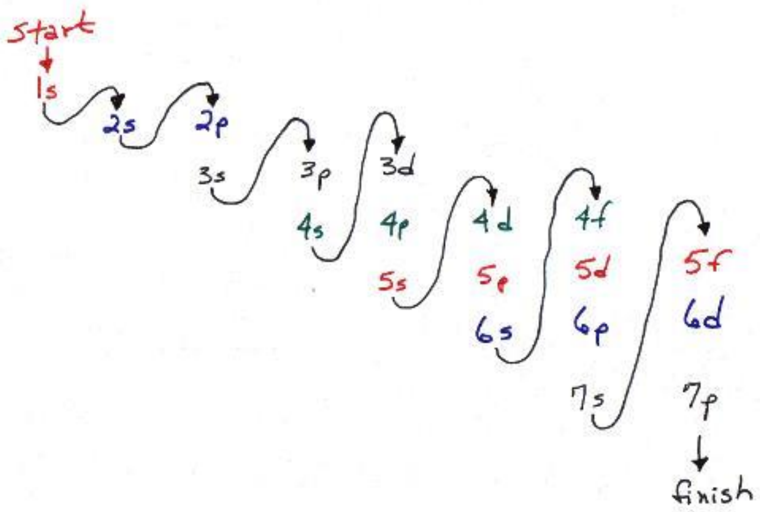
The N shell, remember, **may hold 8 or 32 electrons**, maximally. It may hold this many electrons because not only does it contain 4s, 4p and 4d subshells, it also contains a 4f subshell. The total number of electrons that an f subshell may hold is 14. Again, since electrons like to pair up, this says 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.

Electronic Configuration

- 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.

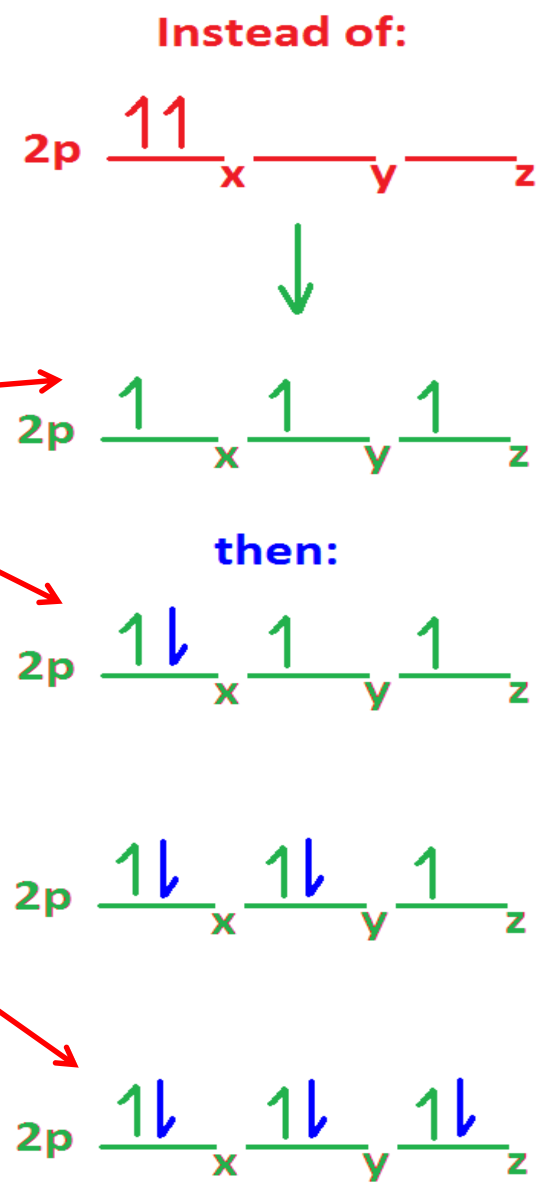
- Let's look at helium, now.
- He is in period 1.
- It is element number 2.
- It's electronic configuration is $1s^2$ -- period 1, s block and has 2 electrons.
- The 1s subshell is now full.
- Note: He is the exception to the p block elements -- it has no p electrons.

- 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 $1s^22s^2$.
- 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 $1s^22s^22p^1$.
- The 6th element is carbon (C).
- It has one more electron than B: $1s^22s^22p^2$.
- Nitrogen's (N) electronic configuration is $1s^22s^22p^3$.
- 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 $[Ne]3s^1$.
- For Mg, the electronic configuration is $[Ne]3s^2$.

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

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

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

Elemental states to their respective ionic states using electronic configuration:

- Let's first start examining atoms with some of their ions.
- Ions are electrically charged particles that result from the gain or loss of electrons.

- 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:

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

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

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

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

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

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

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

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

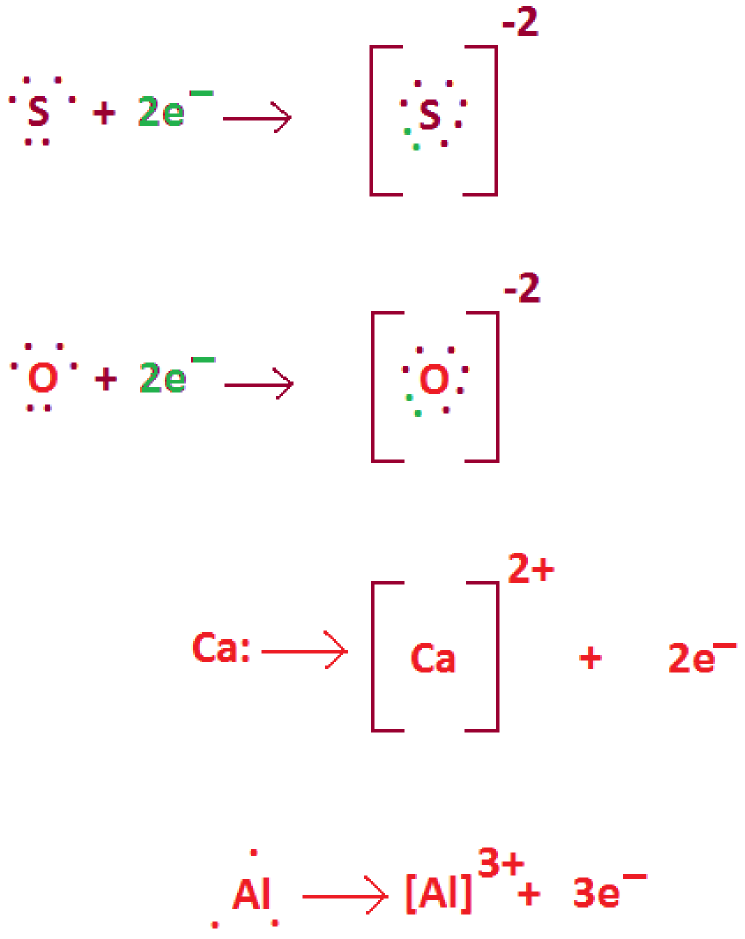
$$S^{-2} = S^{2-} = 1s^2 2s^2 2p^6 3s^2 3p^6$$

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

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

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.



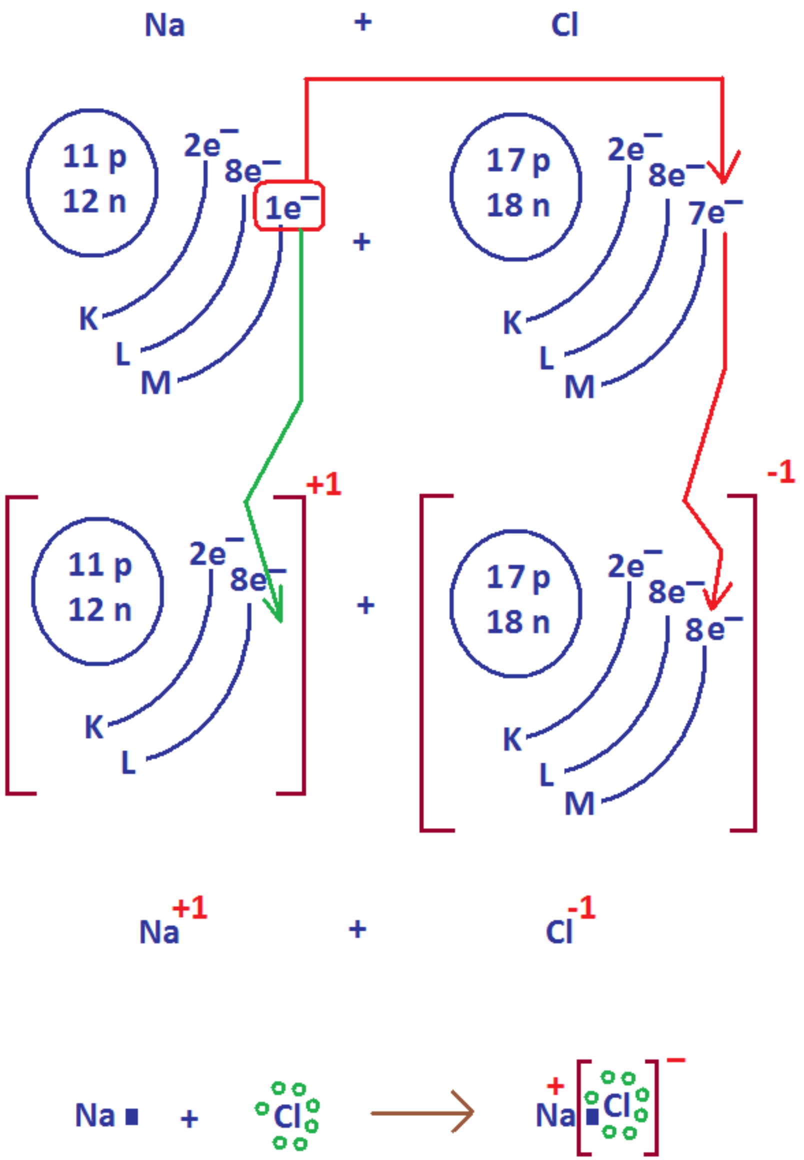
Ions and atoms with identical electronic configuration are called isoelectronic:

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

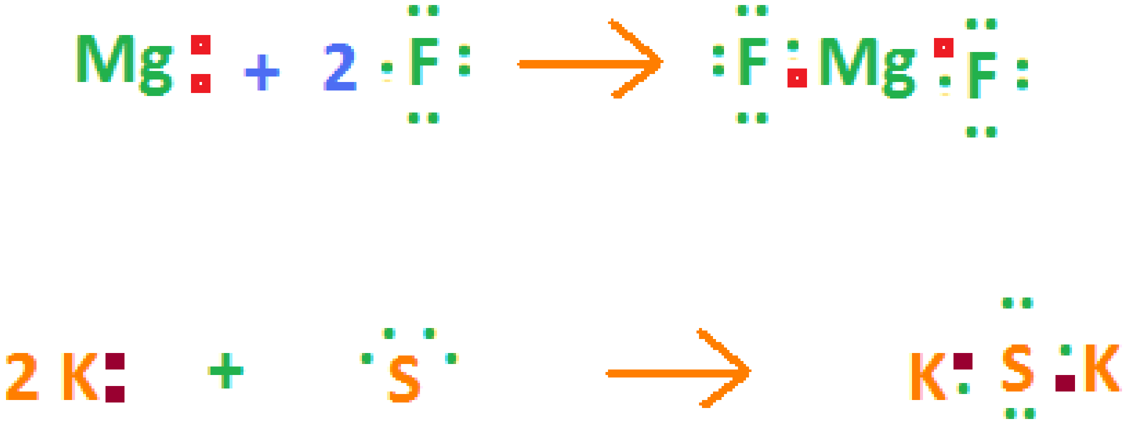
$$Ne = 1s^2 2s^2 2p^6$$

- 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).

- Ionic compounds form when electrons shift between atoms, Figure, right.
- In this example, elemental sodium reacts with elemental chlorine to form sodium chloride.
- The movement of electrons is that the sodium loses its single outer electron and chlorine gains it.
- Note the final Lewis Structure of sodium chloride.
- This occurs only when the sodium chloride is solid.
- Otherwise, when this is in water, table salt (sodium chloride) exists as two distinctly separate ions.
- Indeed, one does not actually taste NaCl, rather, when NaCl hits the mouth and mixes with the saliva, it dissolves and separates (dissociates) into its two ionic components.
- Each ion is detected by different portions of taste buds.
- The detected presence is converted into an electrical signal that is sent to our brains for interpretation.
- The message we receive following interpretation is that we have "tasted" salt.

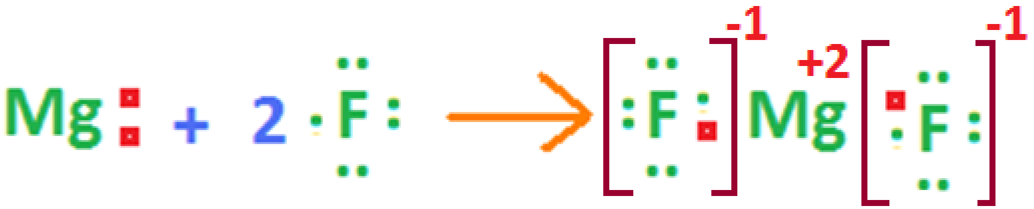


- The reactions between magnesium and fluorine and potassium and sulfur, below, respectively, form magnesium fluoride and potassium sulfide.
- To name these binary compounds (compounds which contain only two kinds of atoms), put the metal's name first, add the non-metal stem and add "ide".
- The non-metal stem for fluorine and sulfur are "fluor" and "sulf".
- These two examples also bring up something else we need to discuss: balancing chemical formulas.



- Balancing chemical formulas is not difficult.
- All of us can balance checkbooks, hence, we can all balance formulas.
- There are a number of methods by which to do this.
- Probably the simplest is to remember that for neutral compounds the sums of the charges for ALL of the ions involved must equal zero.

- Looking at magnesium fluoride, for example, below, note that it took 2 fluorides to balance the single magnesium.
- This is because the magnesium ionized to a +2 charge while the fluorine ionized to the -1 charged fluoride ion.
- Since +2 -1 is +1, it follows that there has to be 2 fluorides to give a total of -2 for the negative charges, i.e. +2-2 = 0 for a neutral compound.
- The same thing applies to the potassium in potassium sulfide.
- In this case, two potassiums are required to balance out the -2 charge on the sulfide ion.



Thus far, these two specific reactions are examples of what are called "redox" reactions.

Redox reactions are oxidation (a reactant loses electrons) and reduction (a reactant gains electrons) reactions.

If there is reduction, there MUST be oxidation -- i.e., ya can't have one without the other.

Each part of a redox reaction may be written separately as a half reaction.

When the oxidation half reaction and the reduction half reaction are added up and adjusted (balanced) for electron exchange, the complete redox reaction is obtained.

Note that when the electrons are not equal between each half reaction that they must be made equal -- this includes multiplying the whole half reaction by the exact same number you multiply the electrons by.

$$Fe \rightarrow Fe^{3+} + 3e^{-} \quad Oxidation$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu \quad \mathrm{Re}\, duction$$

$$3\,(Cu^{2+} + 2e^{-} \rightarrow Cu)$$

$$2\,(Fe \rightarrow Fe^{3+} + 3e^{-})$$

$$TOTAL\ :\ 3\,Cu^{2+} + 2\,Fe \rightarrow 3\,Cu + 2\,Fe^{3+}$$

- Whenever you work with redox reactions, there are 4 things to remember:
    - 1) the oxidizing agent is always reduced;
    - 2) the reducing agent is always oxidized;
    - 3) the oxidizing agent gains electrons;
    - 4) the reducing agent loses electrons.

Additional Redox Examples

$$Zn \rightarrow Zn^{2+} + 2e^-$$

$$Cu^{2+} + 2e^- \rightarrow Cu$$

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$

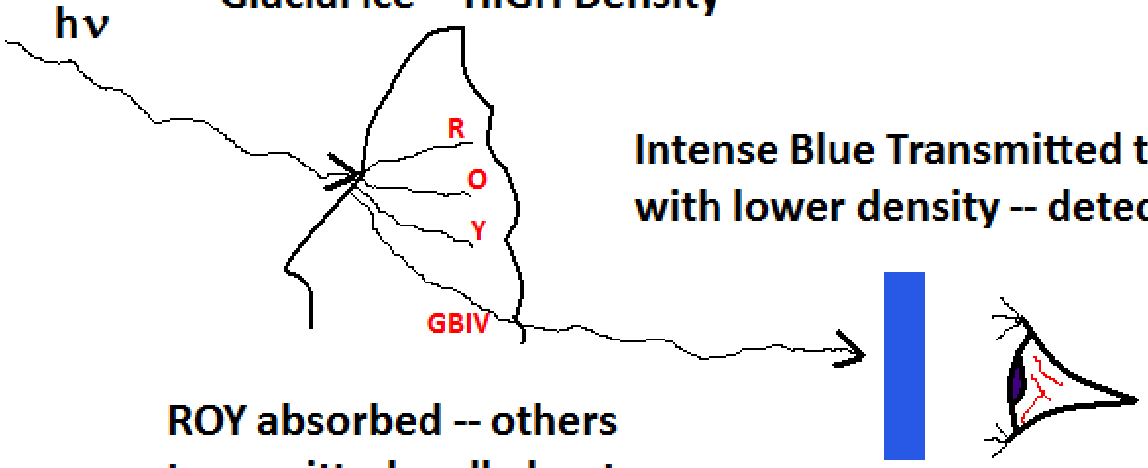
$$Mg^{2+} + 2e^- \rightarrow Mg$$

$$Ni \rightarrow Ni^{2+} + 2e^-$$

$$Mg^{2+} + Ni \rightarrow Ni^{2+} + Mg$$

Light, Atoms and Energy

Air low density



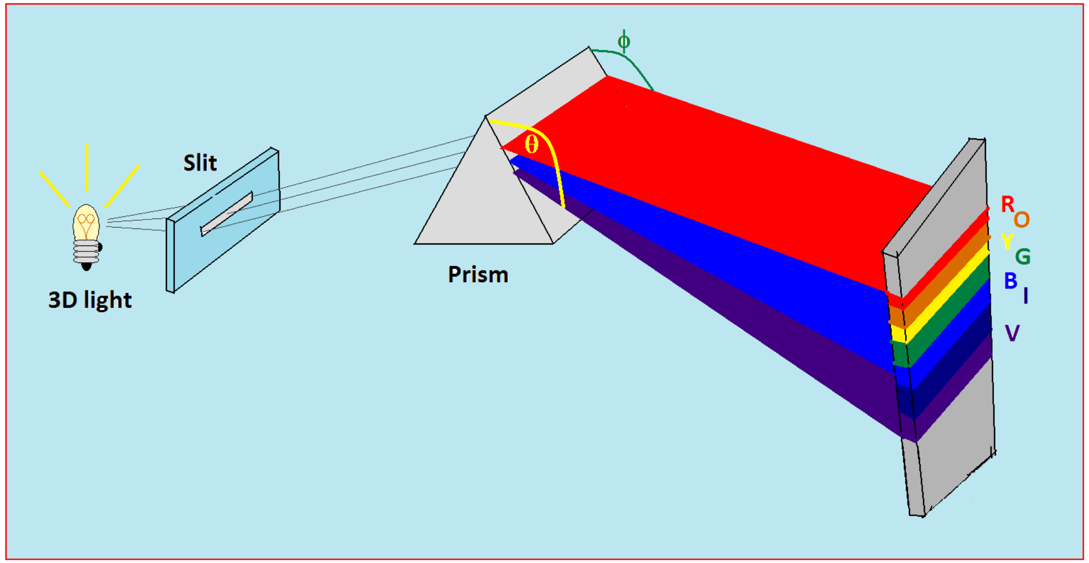
Glacial Ice -- HIGH Density

Intense Blue Transmitted through air with lower density -- detected by eyes

ROY absorbed -- others transmitted -- all about energy

- How is it that light does this, i.e., how is it possible that we may separate out individual colors from "white" light?
- Prisms or tiny slits or gratings "split", bend (refract) polychromic light into mono-chromic light.
- Another example of how this occurs is in the graphics, above and below:

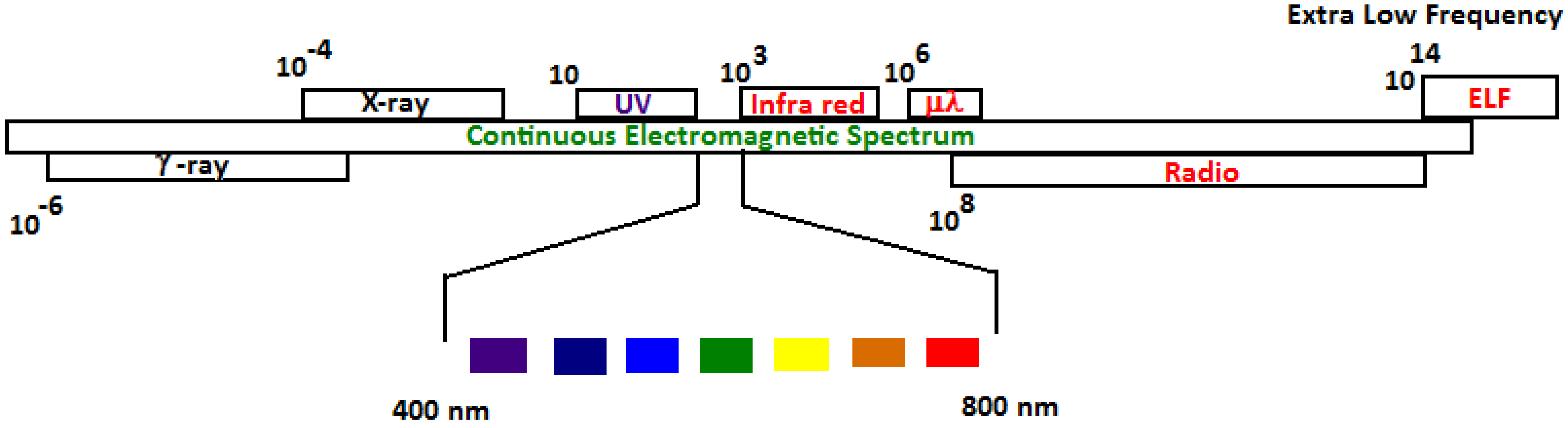
- The Light from the sun we see as "white" light.
- This light may be "split", though, into many colors, of which 7 are primary: Red, Orange, Yellow, Green, Blue, Indigo and Violet, or the colors of the rainbow.
- An easy way to split light color components from white light -- visible light -- is to pass it through a prism:
- This is from the visible portion of the electromagnetic spectrum.
- Note that the angle, ϕ, is less than the angle, θ.
- Red light is bent the least and blue light is bent the most.
- The blue light has the most energy.



Examples of "light" from the continuous electromagnetic spectrum are tabulated below:

Characteristic	"Color"
Warmth; night vision goggles	IR
Eyes, film	Visible light
Sun burned skin	UV
Radios	Radio waves

- The next graphic lays out an overview of the electromagnetic spectrum: below
- The center region of the graphic has been exploded so you may see how the visible spectrum fits into the scheme of things.
- Remember, too, that there are shades of varying colors between each specific primary color (from red-red-red to red-red-orange to red-orange to red-orange-orange to orange-orange-orange):
- 700 nm: RRR → RRO → RO → ROO → OOO: 600 nm



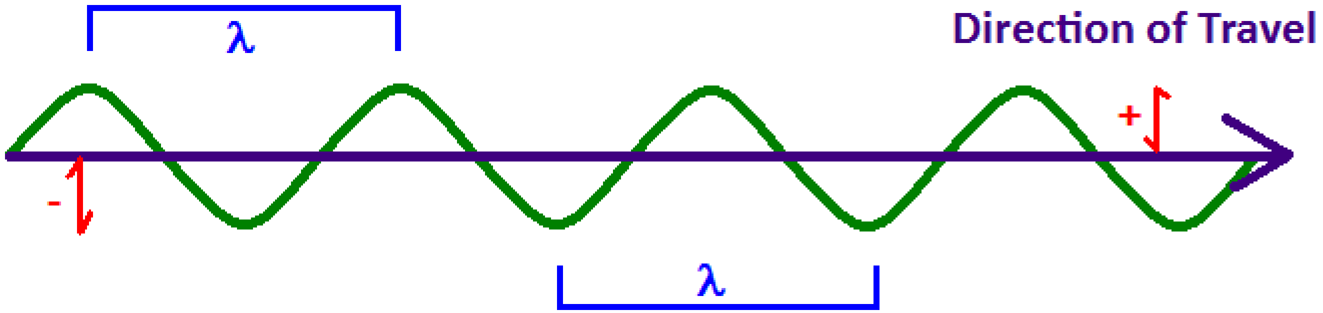
Polychrome Pass, AK, ca 1993

- 28 June 2008, Lake Angeline, Bighorn Mountains, Wyoming, 10,550 feet.
- Notice the green’s coming through; no red’s or orange’s.

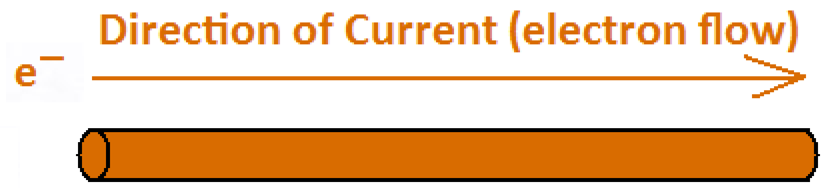
Photo Courtesy of Jason Reichelt.

- Note that different densities also effect the "splitting of light".
- (The visible spectrum, BTW, spans 400-800 nm, more or less.)
- These tools do this because light has dualistic properties.
- Planck and Einstein showed that in an elegant manner when they each developed their own equations to explain electromagnetic energy:
- $E = h \upsilon$ and $e = m c^2$
- The former equation is Planck's equation that describes the wavelike properties of electromagnetic energy/radiation and the latter is Einstein's equation that describes the particle like properties of electromagnetic energy/radiation.
- When the two equations are combined:
- $h \upsilon = m c^2$
- which says that electromagnetic energy/radiation has mass and acts like a wave.

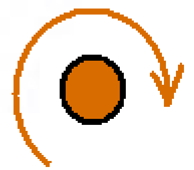
- A wave is described as a progressive, repetitive motion that moves from a point of origin to farther points.
- We've all seen what happens when a pebble is dropped in a pond: ripples form and spread out from the point of origin (where the pebble hit the water).
- The ripples are waves -- light -- Electromagnetic energy -- moves in the same way.
- If we look at electromagnetic energy (EME), the wave form looks like this:
- Where the distance between 2 peaks OR two valleys is the wavelength: λ.



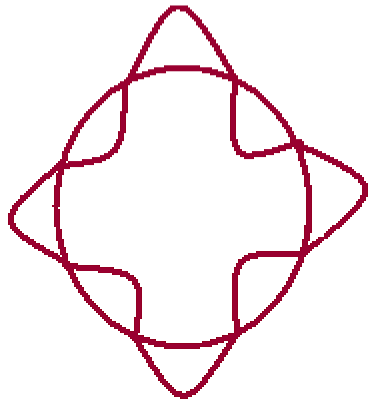
- The EME wave forms originate from the movement of electrons with respect to the atomic nucleus.
- The electron-ic movement produces oscillations in the electric/magnetic fields that are propagated over the electron's orbit:
- The circular orbit, overlapped by the wave-like oscillations is based on the hydrogen atom by Bohr in 1913. Keep in mind that as the electron is moving it is inducing a magnetic field perpendicular to the direction of its flow. (Remember the electromagnets you made as a kid with a battery, some wire and a nail.)



Direction of Current (electron flow)

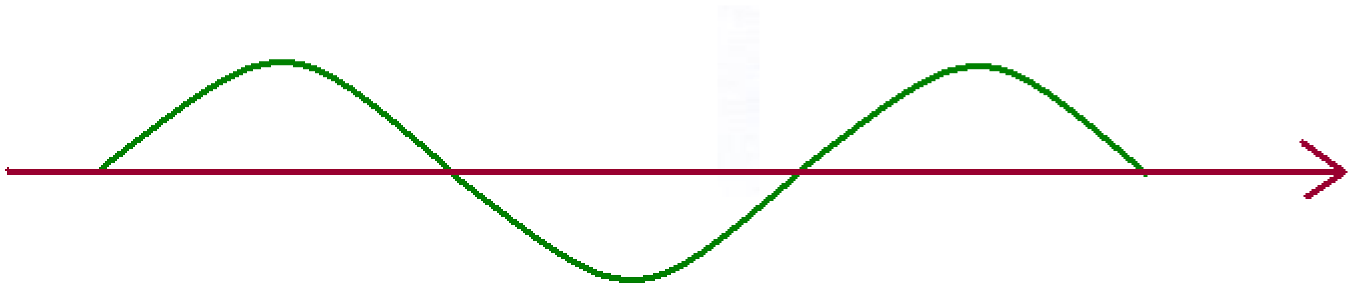


Induced Electromagnetic Field; Perpendicular to electron flow

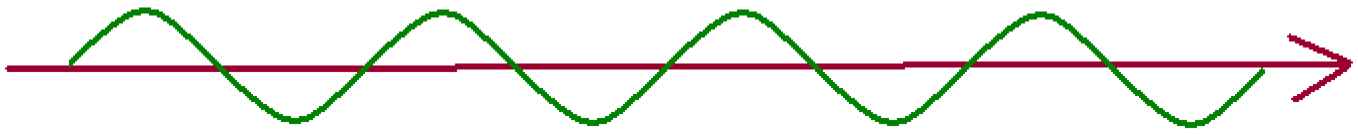


Electron-ic oscillations around orbit

- Wavelengths may be far apart:



- Wavelengths may be close together:



- The closer together, the greater the frequency (*f* or υ).
- The frequency is defined as the number of wavelengths that pass a point in time, e.g., if 4λ pass the same point in 0.25 seconds, then the frequency is equal to:

$$\nu = \frac{4\,\lambda}{0.25\,\mathrm{sec}} = 16\ Hz$$

- Hz = cps or is denoted as s^{-1}. The farther apart the less the frequency, e.g., if 4 λ pass a point in 2 seconds, then the frequency is equal to:

$$\nu = \frac{4\,\lambda}{2\,\mathrm{sec}} = 2\ Hz$$

- Since frequency is in units of reciprocal seconds (s^{-1}) and wavelength (λ) is in distance units (m in SI -- nm, for practical purposes), the product of the two is in units of m/s or velocity:
- $\lambda * f = c$ OR $\lambda * \upsilon = c$
- "c" is a special number: the speed of light in a vacuum, which is $3.0*10^8$ m/s.

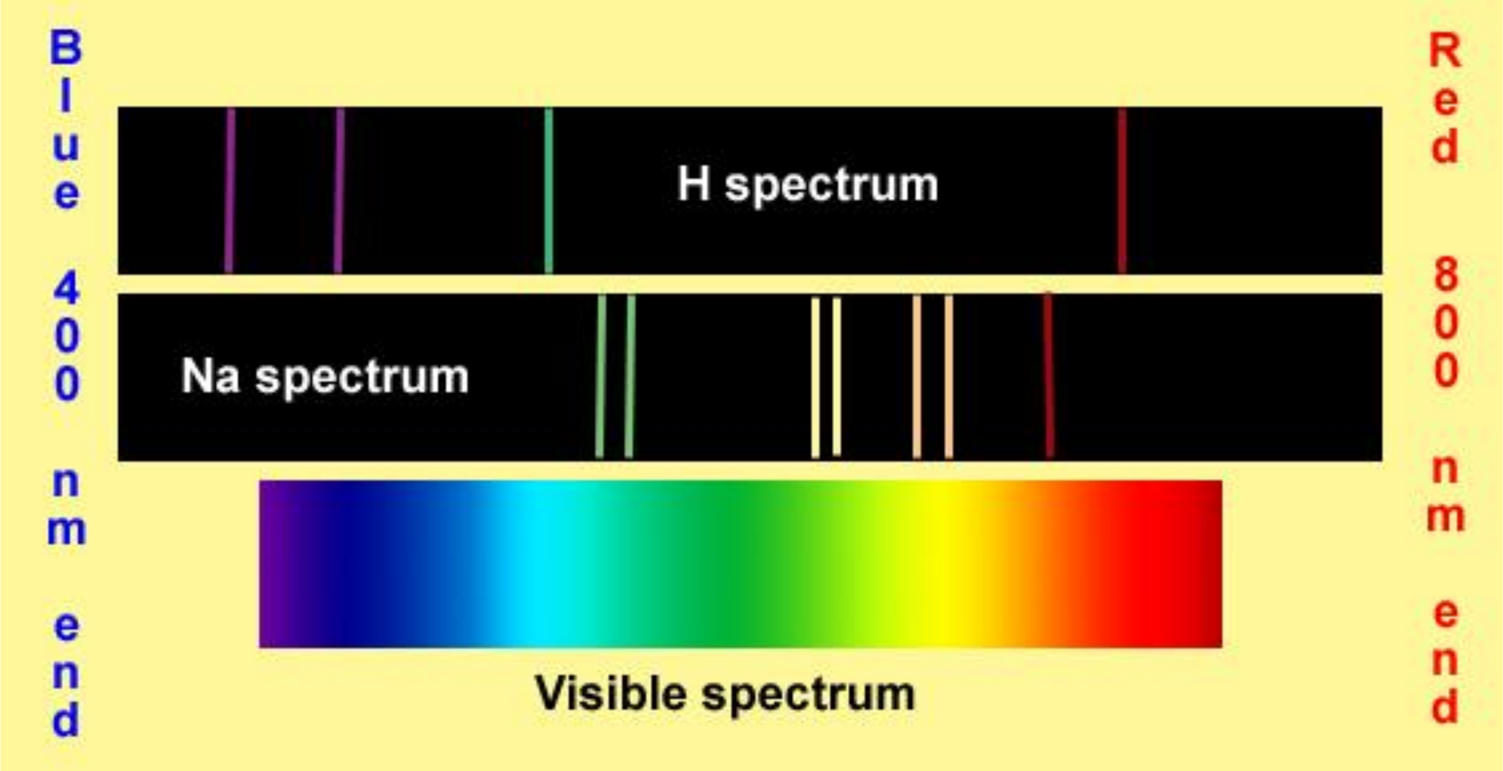
Notice that both f and ν are equal to the quotient of c/λ ,
where, again, f and ν are frequency in Hz, cps or s^{-1}.
Concepts to remember:

λ	f	color	energy
Long	Small	Red end	Low
Short	Large	Blue end	High

The red end may be likened to the bass end of the musical scale;
the blue end may be likened to the treble end of the musical scale.

- Why are atoms important in understanding colored light?
- Raindrops split visible sun light into a familiar continuous spectrum we know as a rainbow.
- 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		

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.

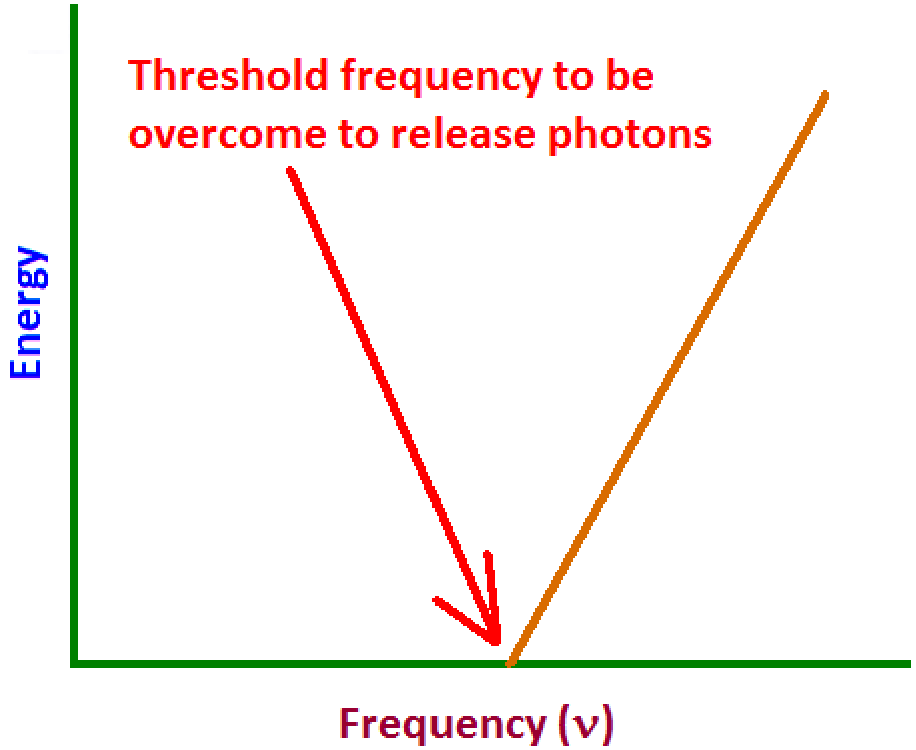
Black Body Radiation

- 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 ***solid's*** 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 $0.5 h \upsilon$, $2.4h \upsilon$, $3.7h \upsilon$, $7.65h \upsilon$.

- 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.

- 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:

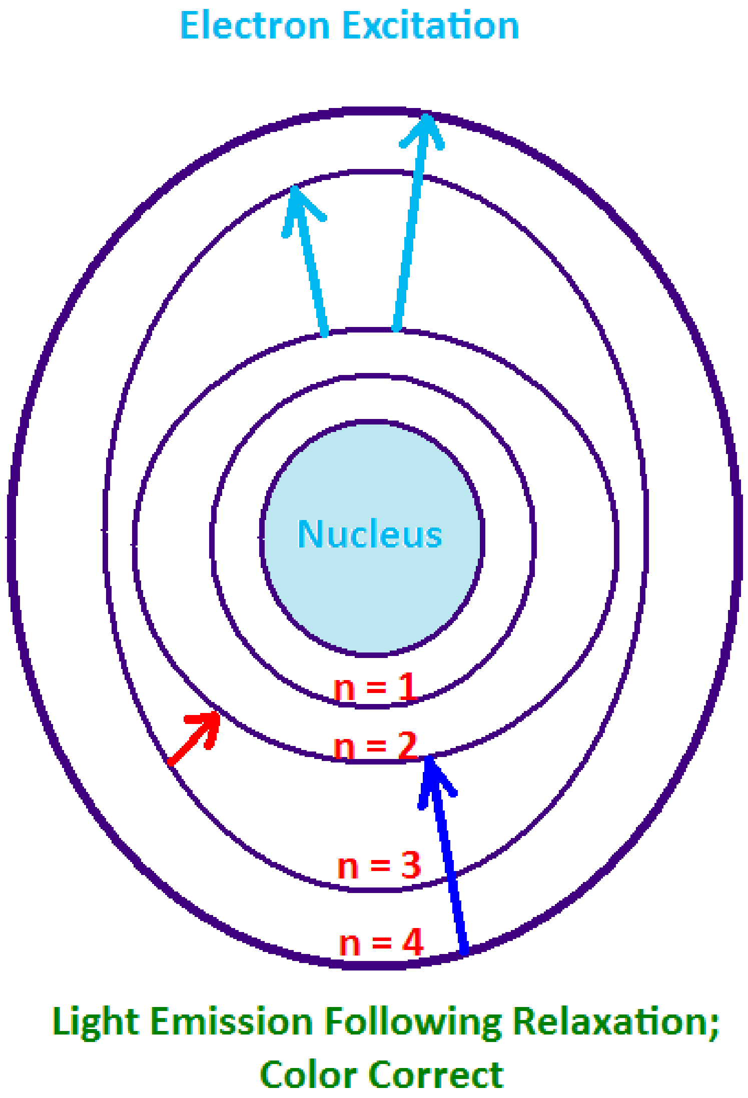


- When the photoelectric effect occurs, the release of light is quanta called photons.
- Analogy: VW stuck in mud: lot's of people can push one at a time to no avail -- a tractor can pull it out and give extra energy (kinetic energy) to it.
- Planck's equation allows us to also calculate the energy of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

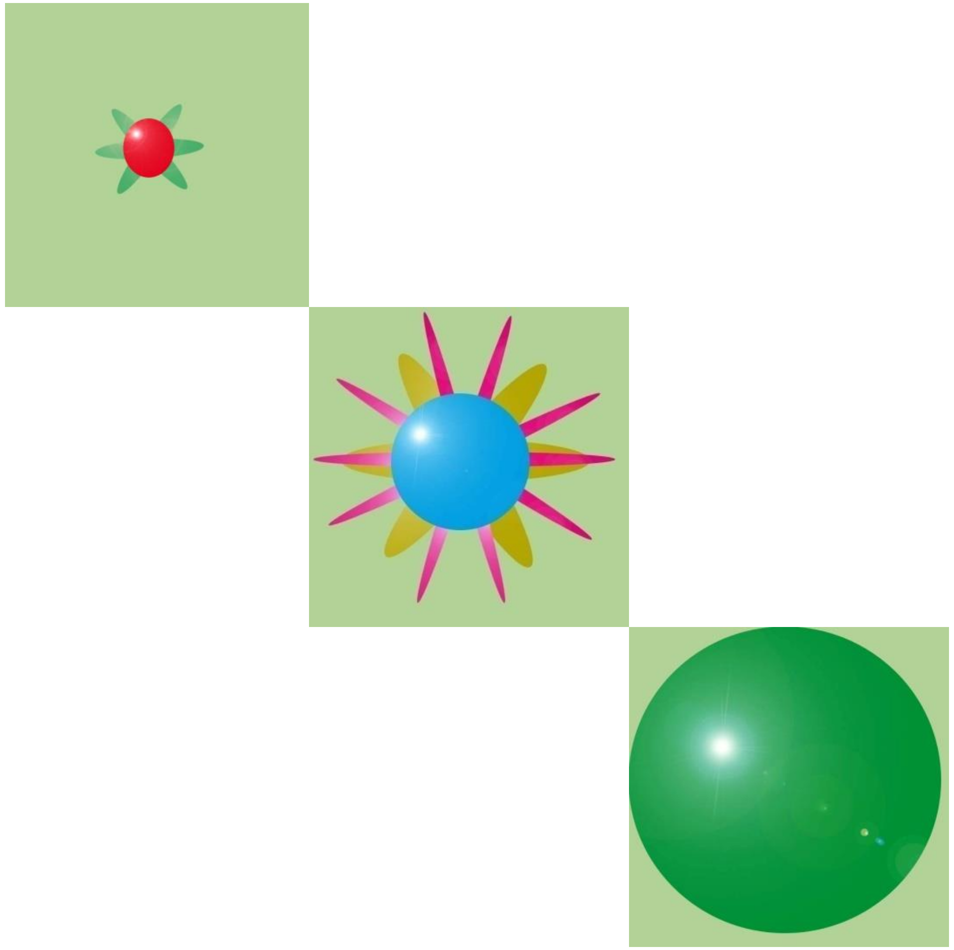
- **The importance of the structure of atoms as applied to line spectra became apparent in 1913 when Bohr discovered how to explain the line spectrum of hydrogen.**
- **He first derived an equation to explain the energy of electrons [E_n].**
- **Each energy value (E_1, E_2, E_3, E_4, E_5, E_6, ...) is called an energy level.**
- **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



- And the 2-D illustrations represent the layout of overlapping subshells from nucleus outwards to outer shells:
- Starting upper left: 1s, 2s, 2s2p, 3s, 3s3p, 3s3p3d, 4s
- Larger images: 2s2p, 3s3d3p, 4s



- In order to understand line spectra, we must look at <u>energy changes</u> or <u>differences</u> (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.,

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

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

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

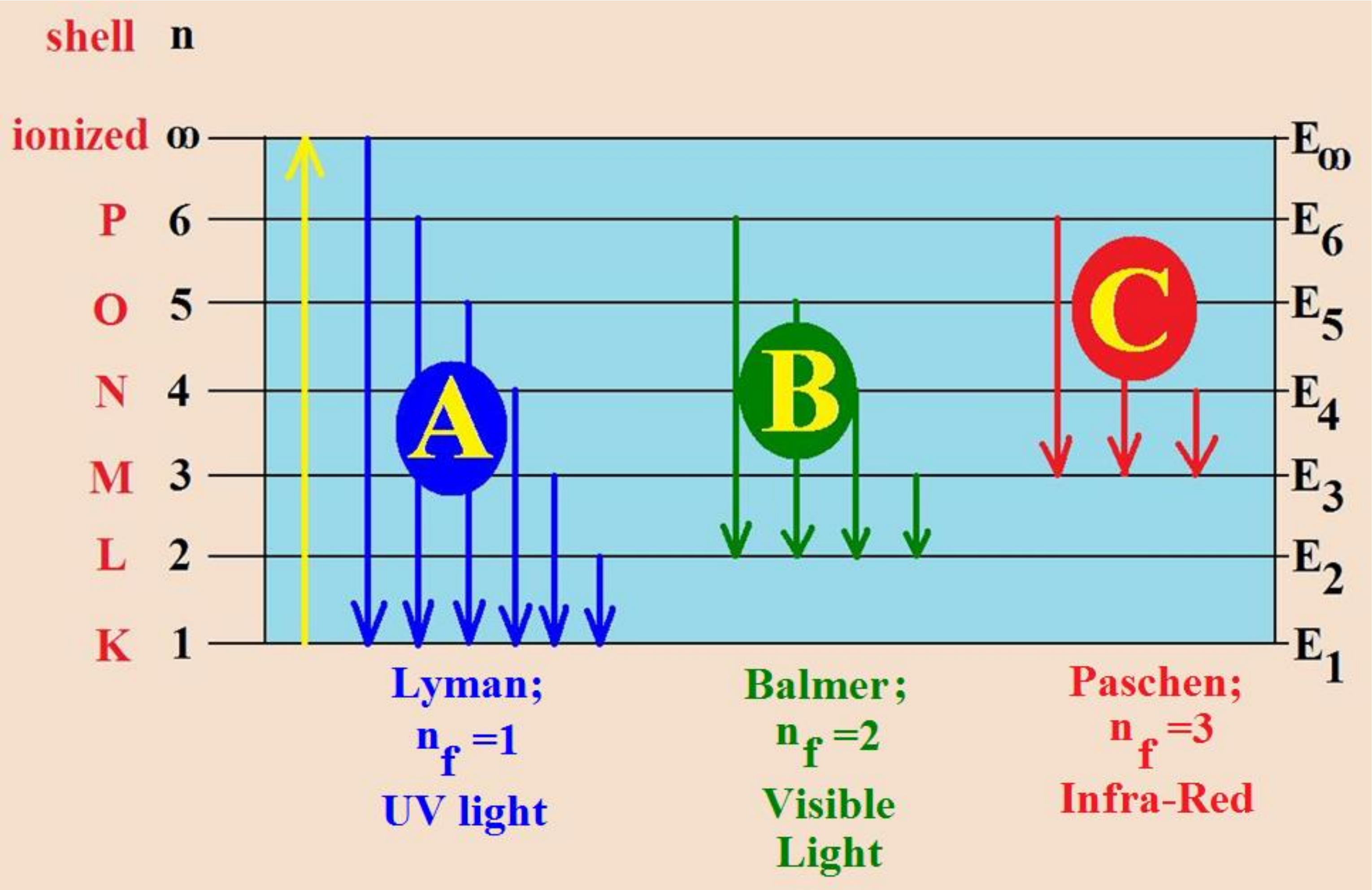
- Calculate the frequency in Hz of the EME released by the above electron energy-level change. Calculate the wavelength of this light, as well.
- First, lose the negative sign on the energy -- it's not useful, here
- E = h υ
- Now, solve for υ :

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

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

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

- 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.



- 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.

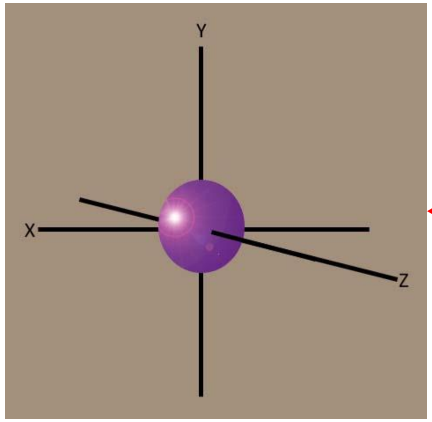
Wave Mechanics: An Introduction

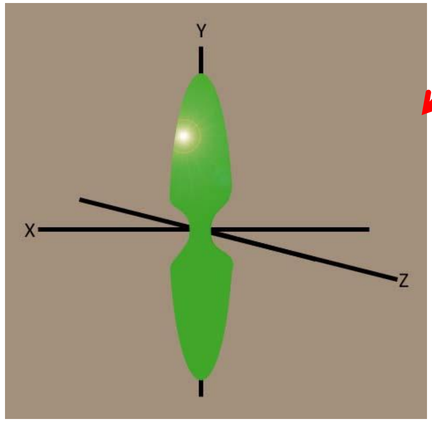
- Remember that light has dualistic properties.
- Louis DeBroglie looked at matter and wondered if matter had wave-form properties, i.e., does matter vibrate at its own unique frequency?
- DeBroglie's theory revolutionized the mathematical description of atoms and matter.
- DeBroglie's theory proposes 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.

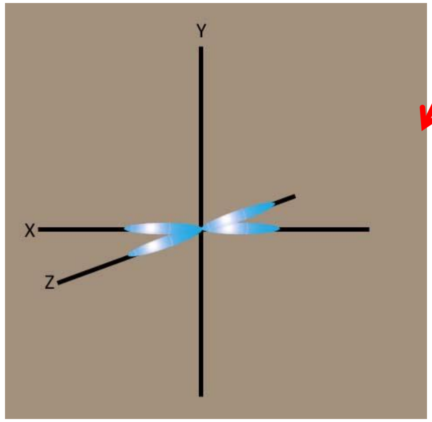
- Two other scientists took DeBroglie's work and applied to the wave-like properties of sub-atomic particles.
- Werner Heisenberg developed his uncertainty principle at the same time.
- His equation allows for the determination of the degree of uncertainty when measuring a particle's location and momentum 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.

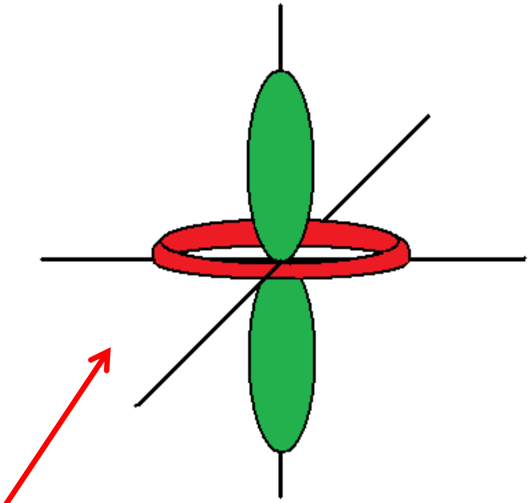
- Shown on the following slide are some representative orbital shapes -- the schematics are not inclusive, merely representative.
- These orbitals came about as a result of Schrödinger's Wave Equations.

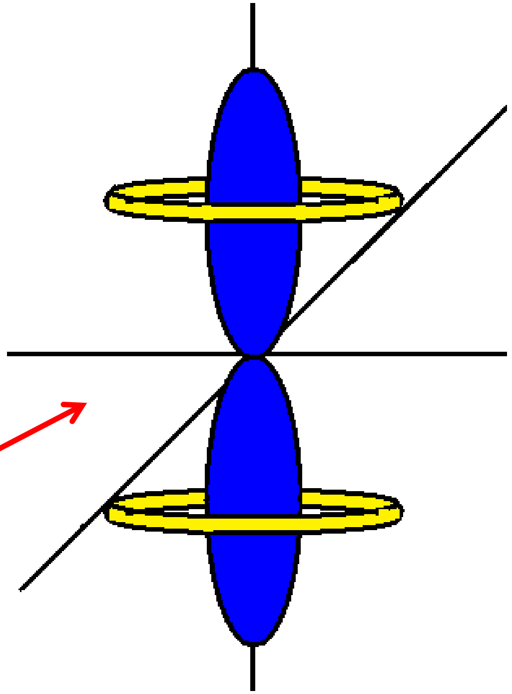






- s subshell: spherical
- p subshell: “dumb-bell” shaped
- d subshell: cloverleaf shaped
- d subshell: single-ringed dumb-bell
- f subshell: double ringed dumb-bell





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 $\pm\ell$) **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.

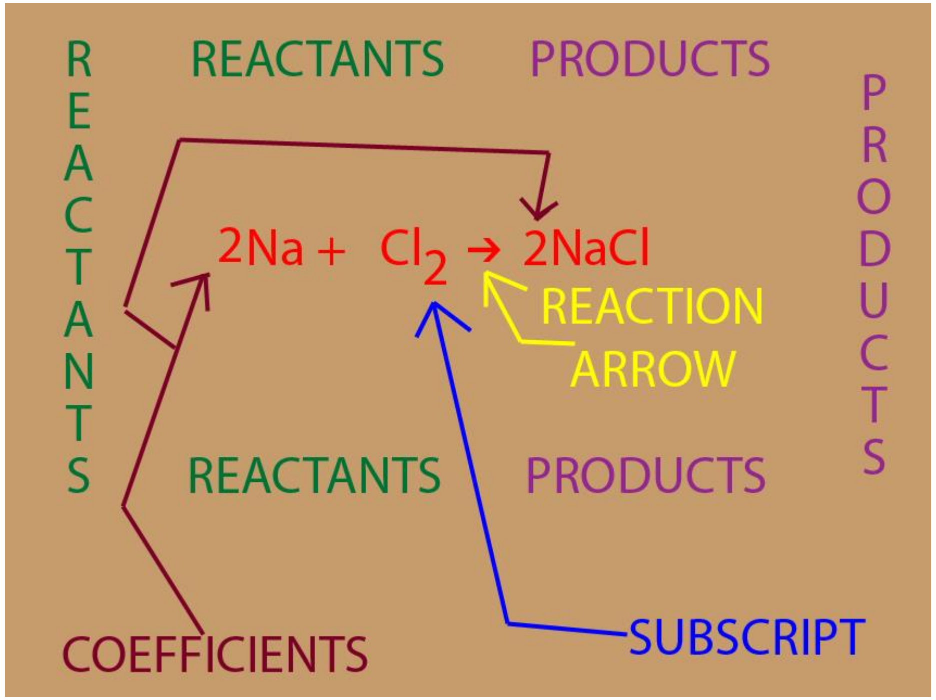
m = 0; this confirms that we're looking at an electron that is in a spherical subshell (orbital), which is an s subshell.

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.

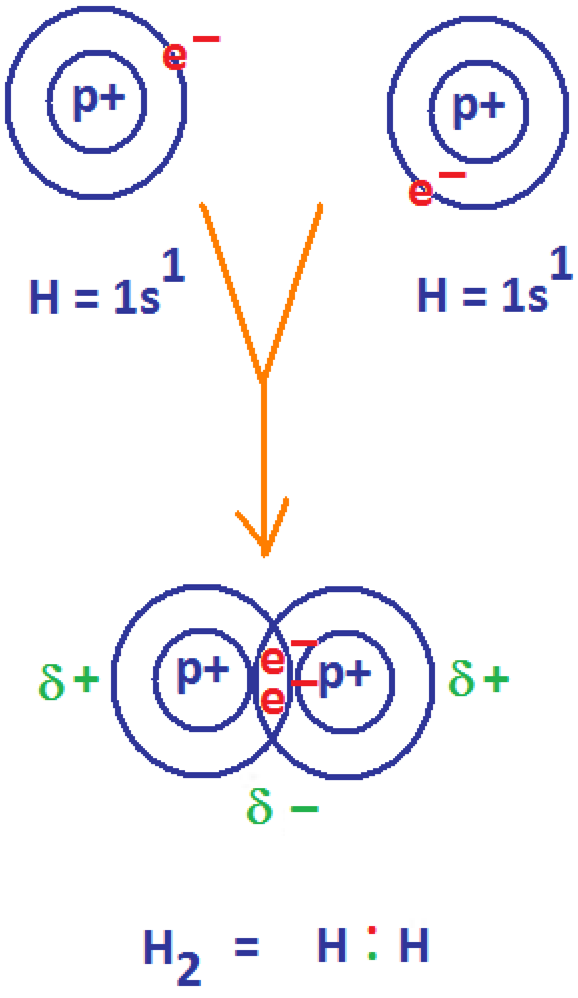
Molecular Geometry and Orbital Hybridization

Chemical Bonding & Reactions

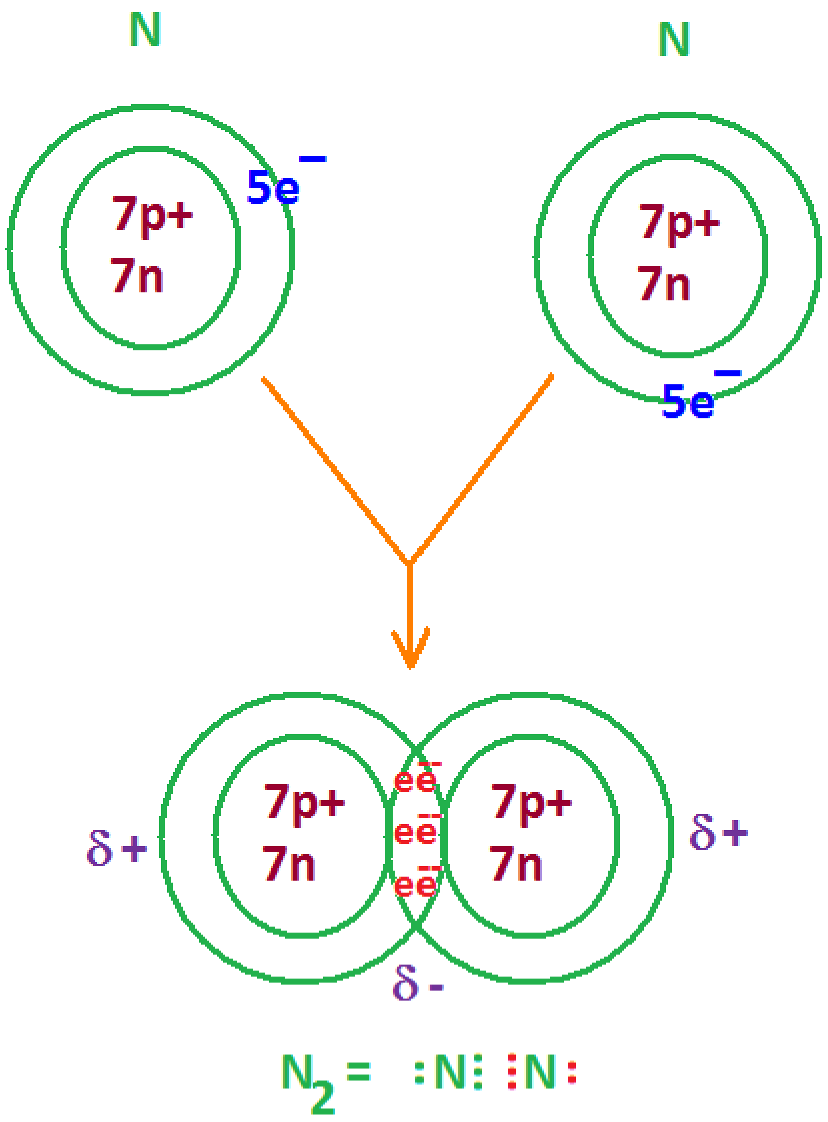


Covalent Compounds

- 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.

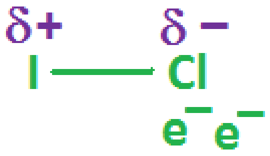
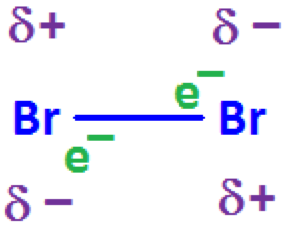
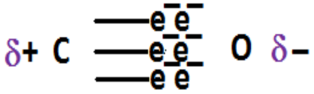
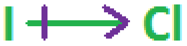
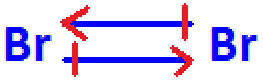
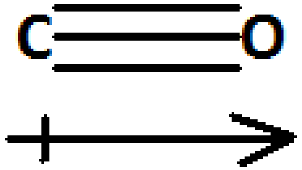


When discussing covalent molecules, there are several terms
one must know in order to fully appreciate the diversity of these molecules.
These terms are summarized in the table, below:

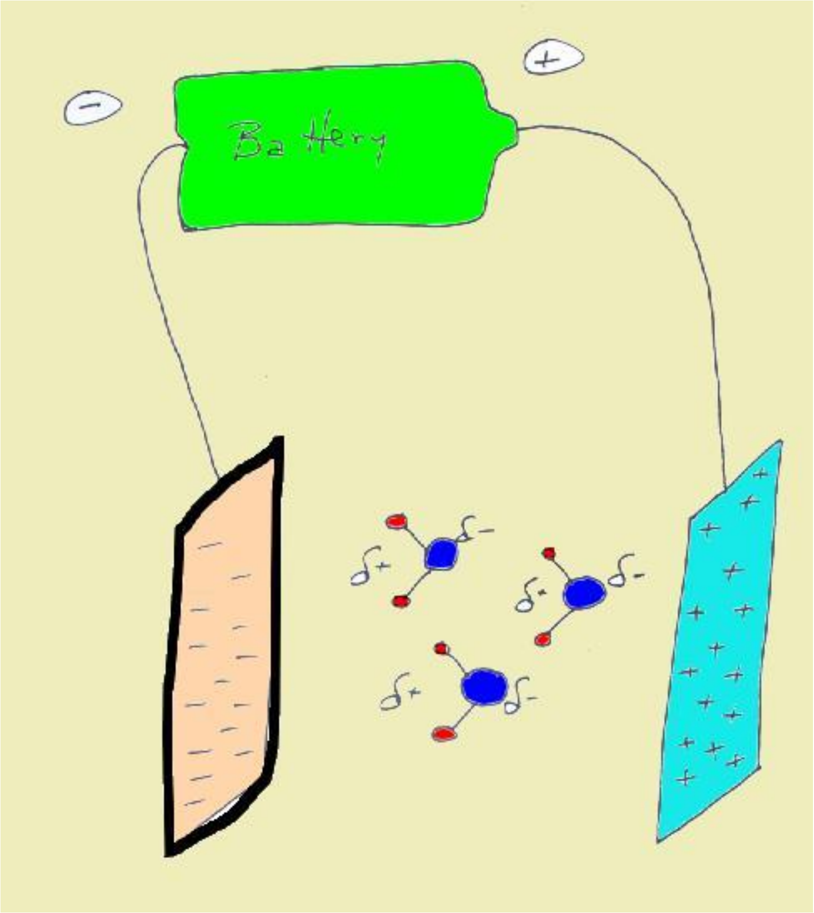
Nonpolar covalent bond	**A covalent bond in which the bonding pair of electrons is shared equally by the bonded atoms.**
Polar covalent bond	**A covalent bond that shows bond polarization (bonding electrons are not shared equally).**
Bond polarization	**The attraction of the shared electrons to the more 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:

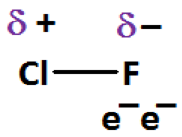
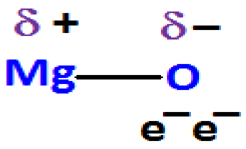
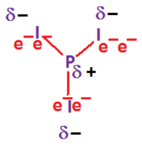
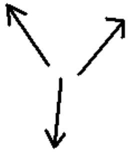
		H 2.1					
Li 1	Be 1.5		B 2	C 2.5	N 3	O 3.5	F 4
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.9	Ca 1.0		Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0		In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9						

- 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:

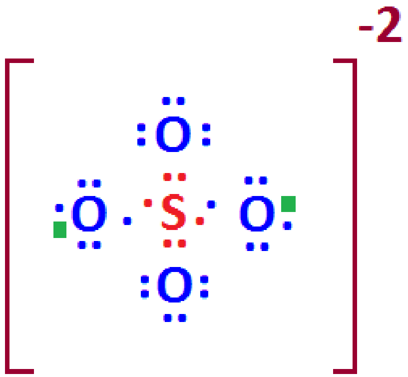
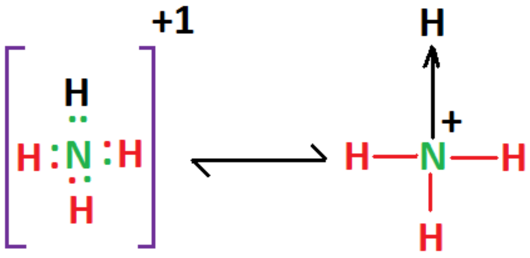
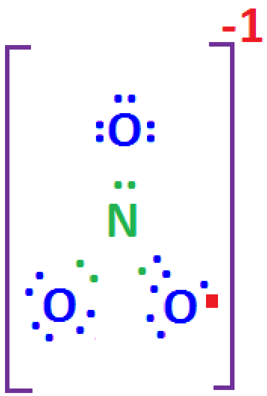
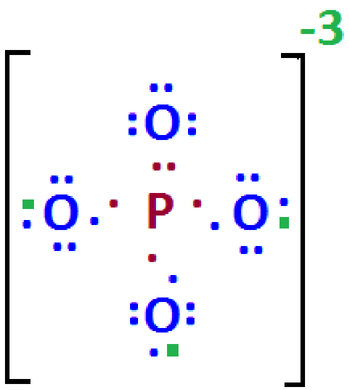
Range	Bond type
0	Non-polar covalent
0 - 2.0	Polar covalent
>2.0	Ionic

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-}	

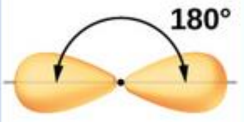
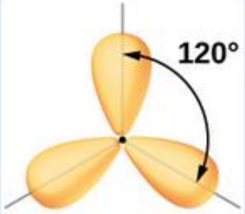
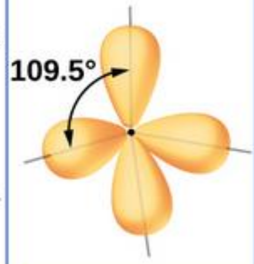
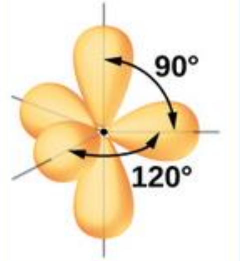
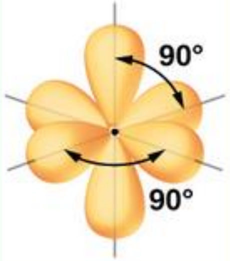
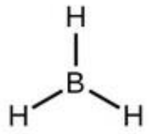
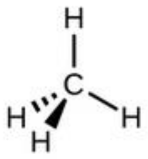
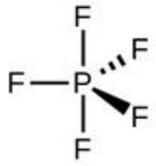
- The ammonium ion is a bit different from the other polyatomic ions -- besides being the only cation mentioned.
- It also contains a coordinate covalent bond.
- A coordinate covalent bond is a bond between 2 atoms in which one atom donates the 2 electrons (both electrons) to make the bond.
- In the 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.

VSEPR Theory

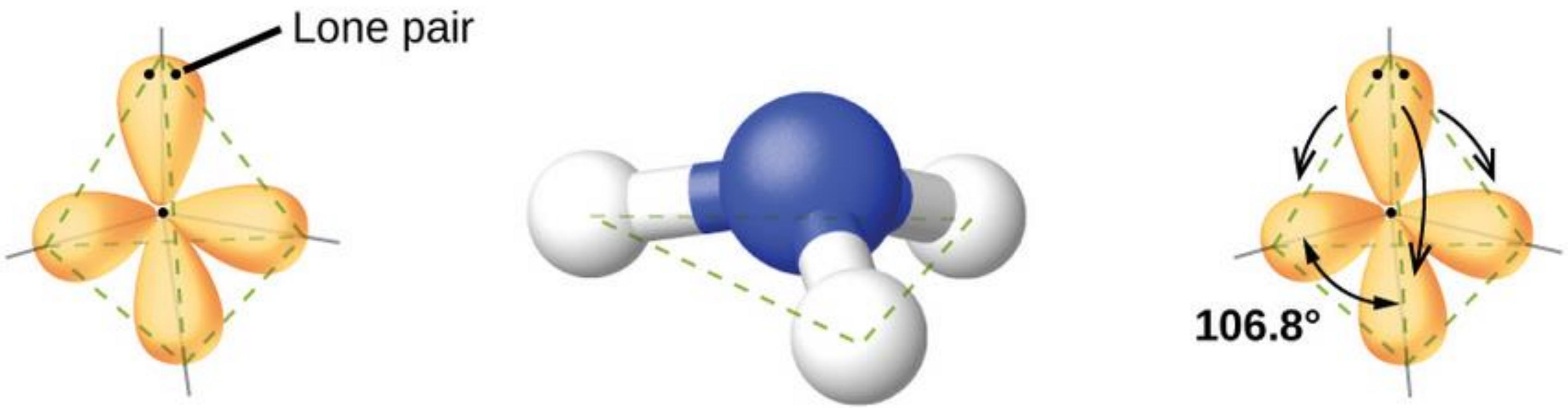
- Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure.
- The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them.
- The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs.
- The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

- VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule.
- Understand, however, that the theory only considers electron-pair repulsions.

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement					
Line-dash-wedge notation	H—Be—H				
Electron pair geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°

VSEPR Theory vs Electron Pair Geometry vs Molecular Structure

- It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure.
- The electron-pair geometries describe all regions where electrons are located, bonds as well as lone pairs.
- Molecular structure describes the location of the *atoms*, not the electrons.
- We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry.
- The structure that includes only the placement of the atoms in the molecule is called the molecular structure.
- The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.



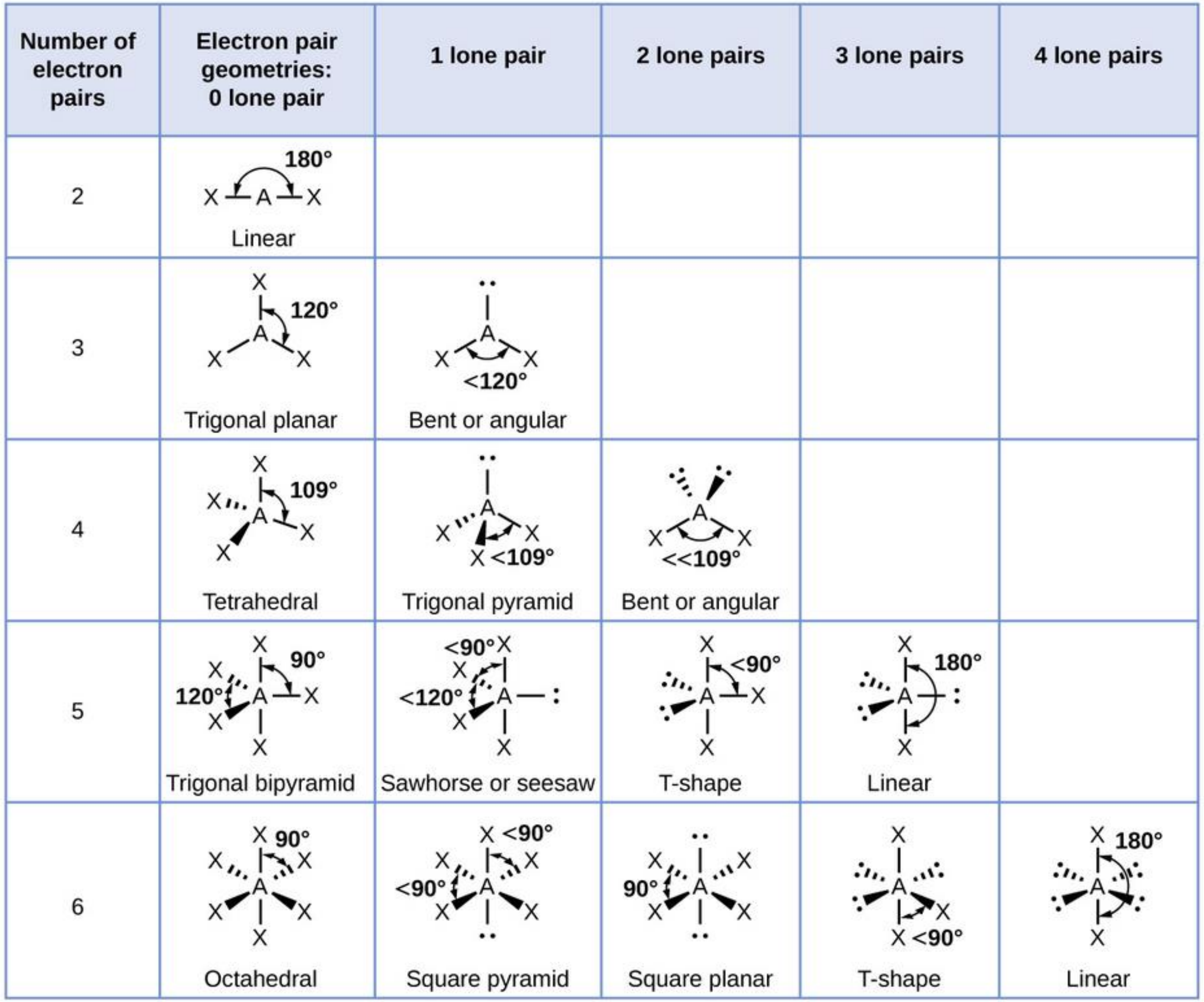
As seen in the image of ammonia, above, small distortions from the ideal angles can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. **The order of electron-pair repulsions from greatest to least repulsion** is:

lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. **The order of sizes from largest to smallest** is:

lone pair>triple bond>double bond>single bond

- The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

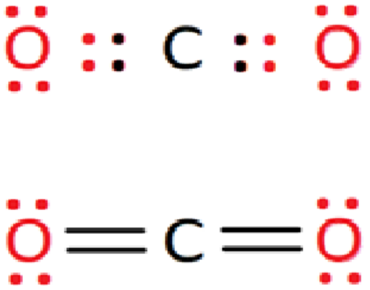


Number of electron pairs	Electron pair geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	Linear				
3	Trigonal planar	Bent or angular			
4	Tetrahedral	Trigonal pyramid	Bent or angular		
5	Trigonal bipyramid	Sawhorse or seesaw	T-shape	Linear	
6	Octahedral	Square pyramid	Square planar	T-shape	Linear

Predicting Electron Pair Geometry (EPG) and Molecular Structure (MS)

- The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:
  - Write the Lewis structure of the molecule or polyatomic ion.
  - Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
  - Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral.
  - Use the number of lone pairs to determine the molecular structure.
    - If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds.
    - In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position.
    - In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom (axial – opposite poles).

Predicting Electron-Pair Geometry (EPG) and Molecular Structure (MS)

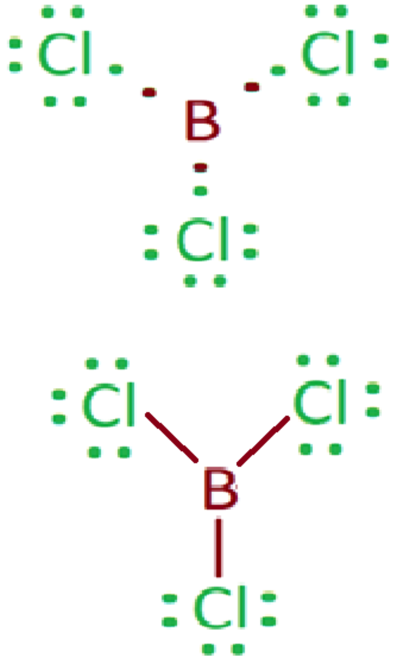


The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

The order of occupied space from largest to smallest is:

lone pair>triple bond>double bond>single bond



Carbon dioxide (CO_2) = EPG linear; MS linear

Boron trichloride (BCl_3) = EPG trigonal planer; MS trigonal planar (aka planar triangular)

Predicting Electron-Pair Geometry (EPG) and Molecular Structure (MS)

The order of electron-pair repulsions from greatest to least repulsion is:

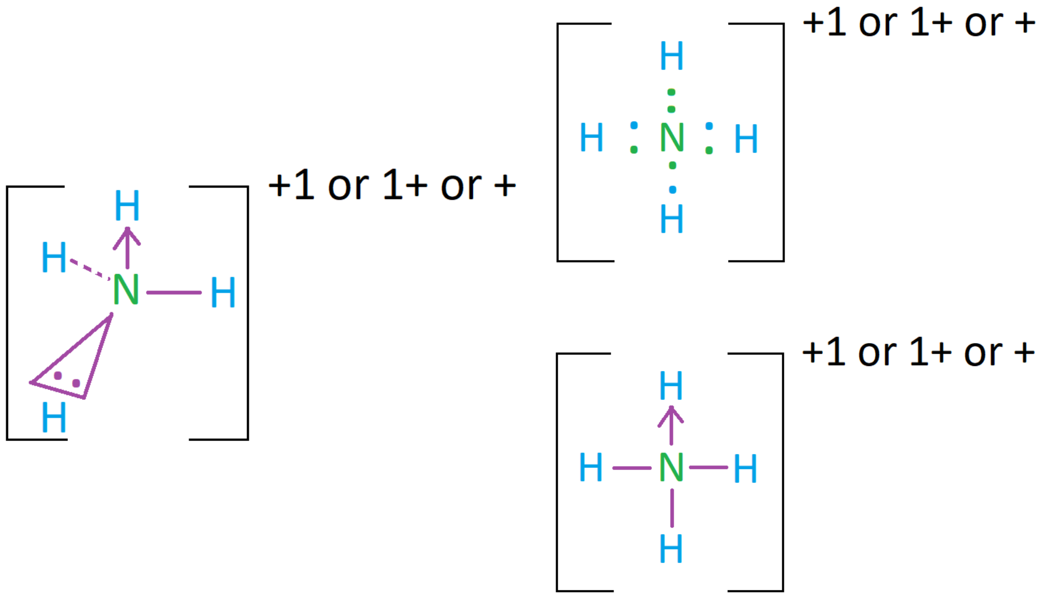
lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

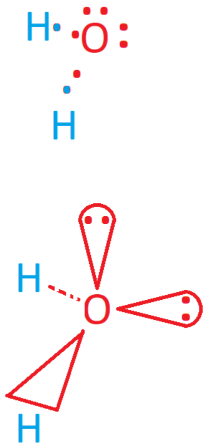
The order of occupied space from largest to smallest is:

lone pair>triple bond>double bond>single bond

Ammonium (NH_4^+) ion = EPG tetrahedral; MS tetrahedral

Water (H_2O) = EPG tetrahedral; MS bent





Predicting Electron-Pair Geometry (EPG) and Molecular Structure (MS)

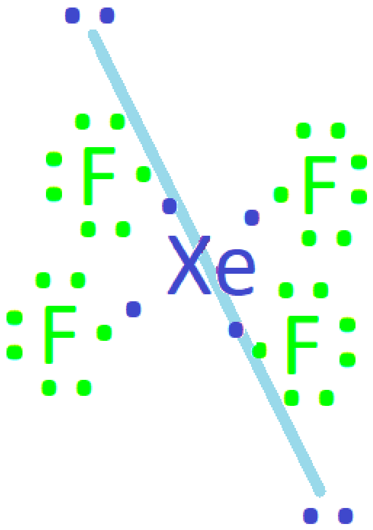
The order of electron-pair repulsions from greatest to least repulsion is:

lone pair-lone pair>lone pair-bonding pair>bonding pair-bonding pair

The order of occupied space from largest to smallest is:

lone pair>triple bond>double bond>single bond

Xenon tetrafluoride = EPG octahedral; MS square planar



- Xenon is water soluble and has found some use in compounds as an anesthetic.
- Xe is capable of attaining one of three hybridizations: sp, dsp^2 or d^2sp^3.
- The following reactions illustrate these hybridizations:

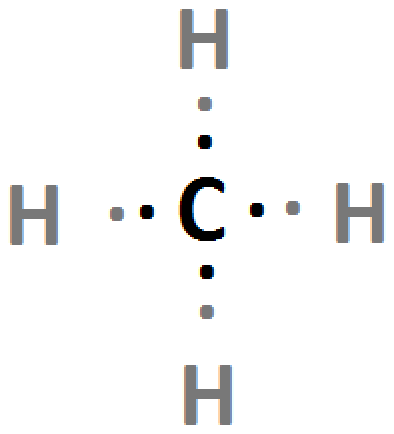
1. sp hybridization:
   - $Xe(xs\ g) + F_2(g) + >250° C + High Pressure \rightarrow XeF_2(s)$
2. dsp^2 hybridization:
   - $Xe(g) + 2F_2(g) + 400° C + 6\ atm \rightarrow XeF_4(s)$
3. d^2sp^3 hybridization:
   - $Xe(g) + 3F_2(g) + >250° C + >50\ atm \rightarrow XeF_6(s)$

Electron Pair Geometry vs Molecular Structure/Geometry Plus Orbital Hybridization

- 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

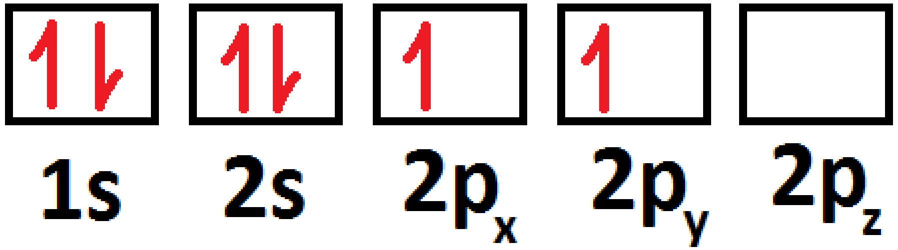
  bond consists of 2 electrons -- one electron from C (●) and

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

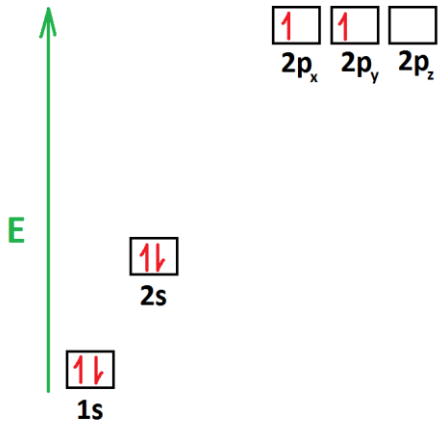


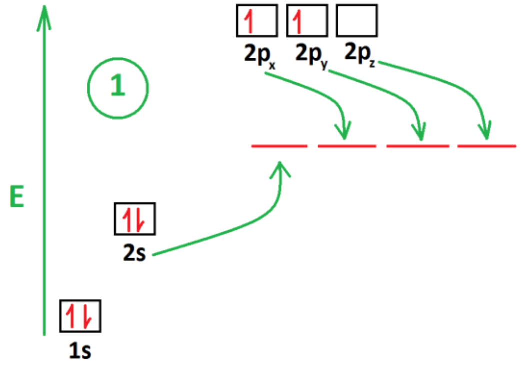
- The figure, below, illustrates the ground, or elemental, electronic configuration of carbon and of hydrogen.
- Note that, in carbon, that there are two sets of paired electrons and two sets of unpaired electrons.
- Remember that carbon is in Group IV on the periodic table and will make four bonds.
- 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.

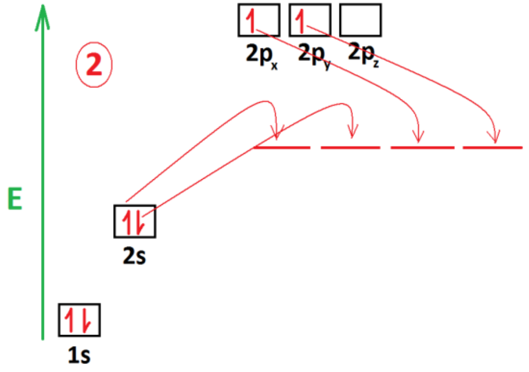
$$C = 1s^2 2s^2 2p^2$$

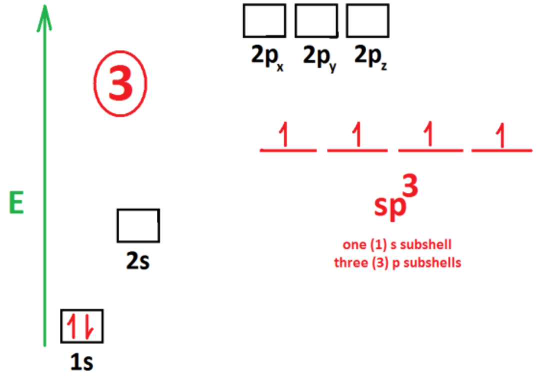


Figure, right, shows a representation of the ground state orbitals in terms of energy moving away from the nucleus (bottom of graphic) out (top of graphic).



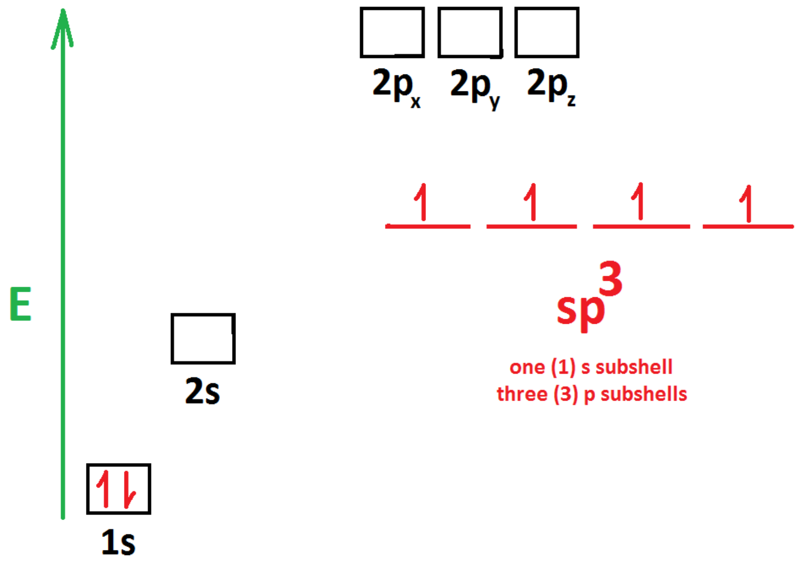




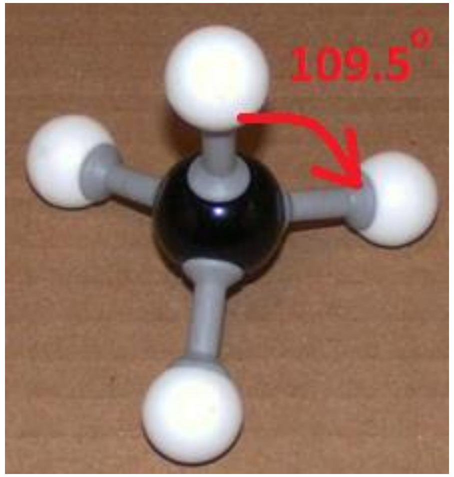


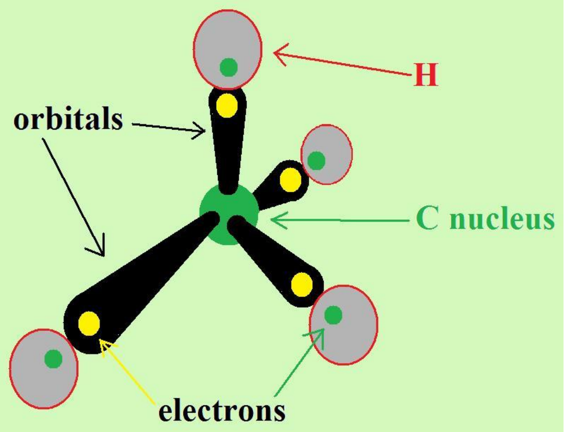
- Figures, below, shows what has to happen for the two 2s electrons to separate.
- In brief, the 2s and all three 2p sub-orbitals must gain and lose, respectively, energy **(1)** in order to force the separation of the two 2s electrons into unpaired electrons at the same energy as the two 2p electrons.
- 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)**.

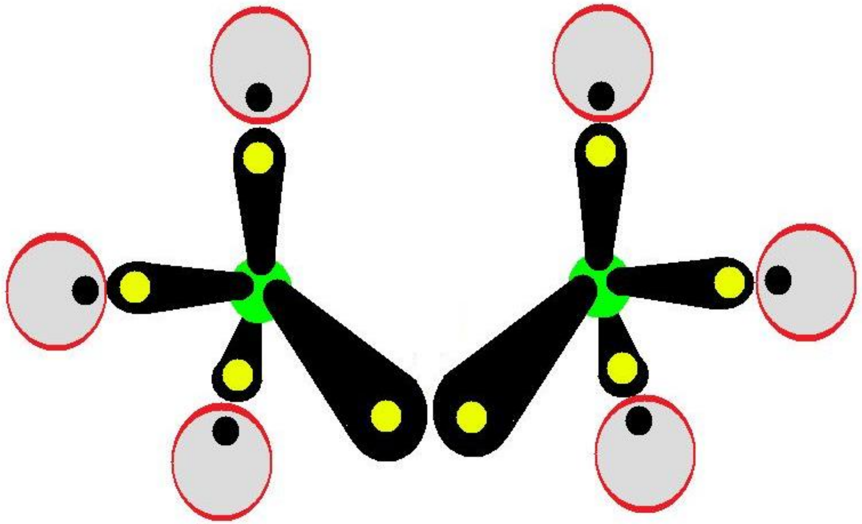
- **The result is seen at right**
- **While the 2s and 2p orbitals are shown as empty, the key is to remember that they are no longer "around" and that there is a new hybrid orbital.**
- **That new orbital contains all 4 electrons, unpaired, and is called an sp^3 hybridization.**
- **An sp^3 hybridized 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.**



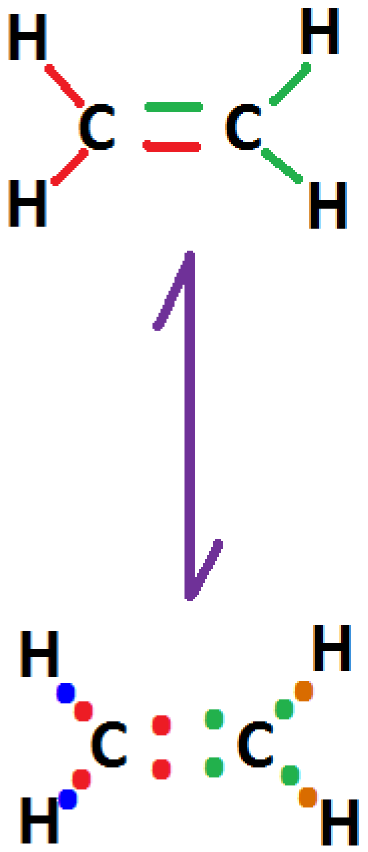
- Once we alter the orbitals, the shape (geometry) changes, as well.
- The shape of one sp^3 orbital is teardrop.
- Carbon has four of them.
- When they are arranged around the carbon nucleus, there are 109.5° between each orbital.
- What this means is that the actual shape of an sp^3 hybridized atom 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.





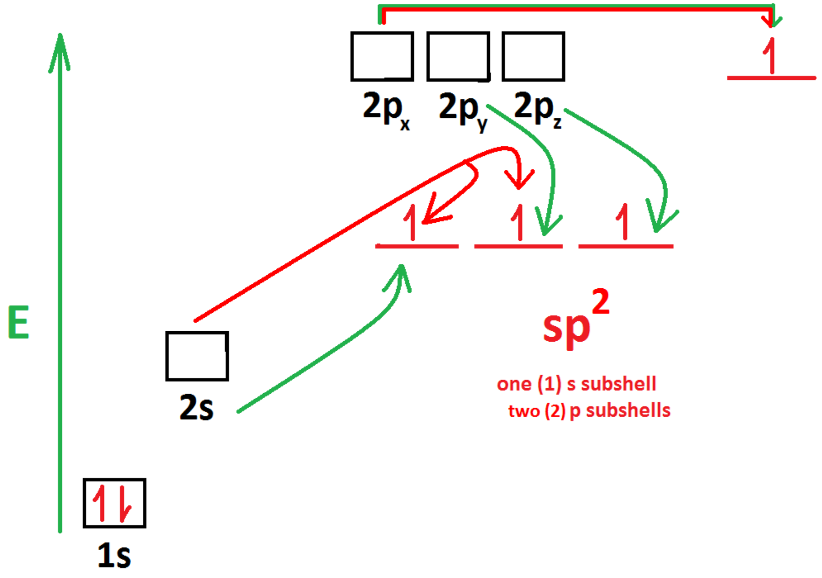


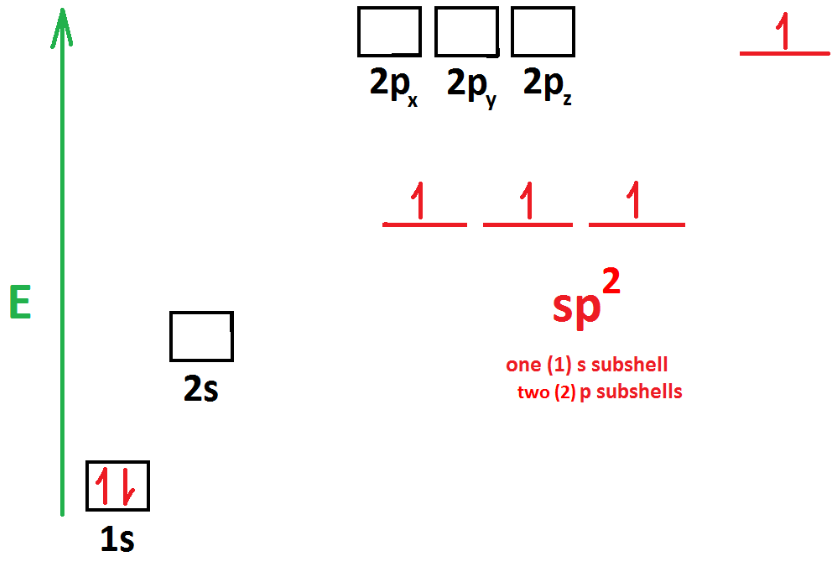
- Not all carbon compounds have all single bonds about the carbon atoms.
- Some have double bonds.
- If a single bond consists of 2 shared electrons, it follows that a double bond consists of 4 shared electrons, i.e., 2 electrons per bond still.
- The simplest carbon compound that contains a double bond 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.



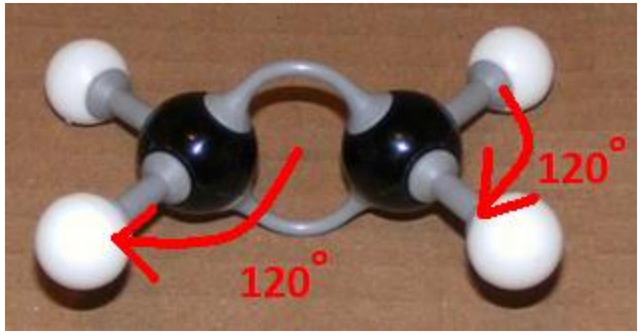
- The difference between hybridization to make four single bonds around carbon and to make a double bond and two single bonds around carbon is the rearrangement of the electrons:

- 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.

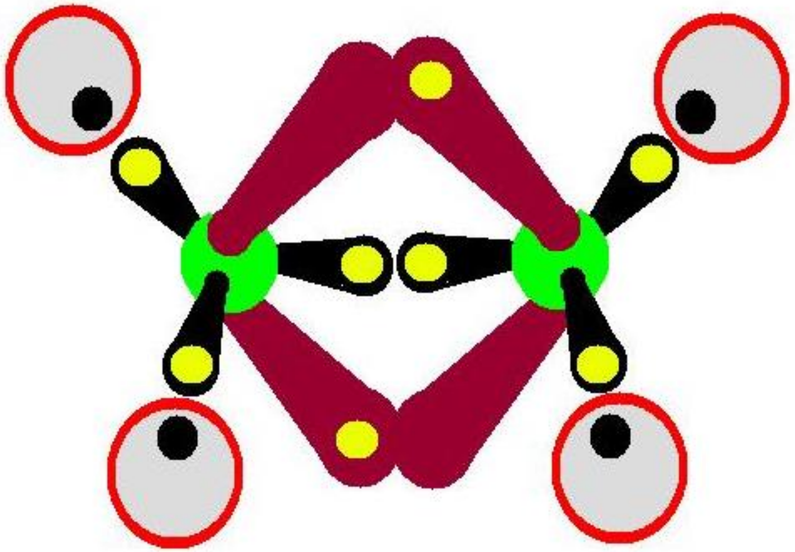




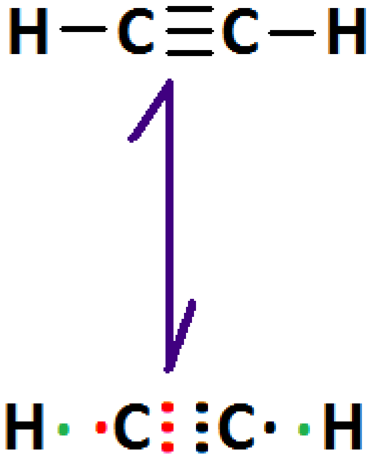
- When carbon has two single bonds and one double bond on it, it is in sp^2 hybridization.
- The shape about the carbon atoms in this hybridization, given 3 sp^2 orbitals, is triangular, planar triangular or trigonal planar, right.
- Each hybrid orbital is separated by 120° bond angles.
- As with the 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.



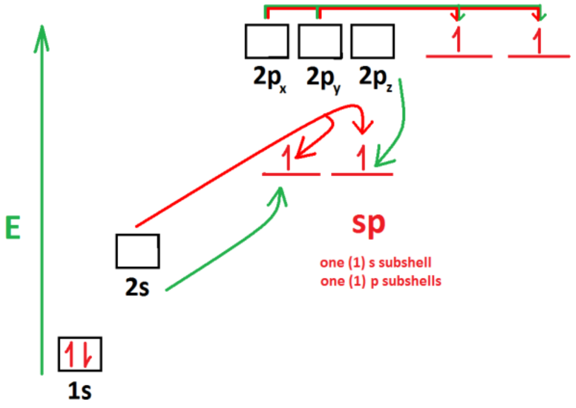
- sp^2 hybridization accounts for only one of the two bonds in the double bonds.
- The second bond in the double bond comes from the lone 2p electron.
- Here's how it works: the p orbital's geometry is dumb-bell shaped.
- When it is overlapped with the sp^2 hybrid orbitals, right, two kinds of bonds 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.



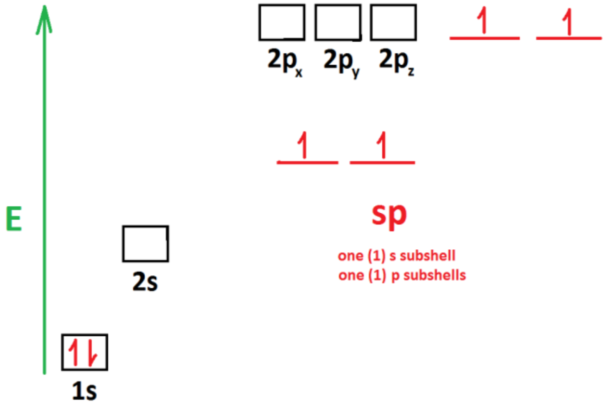
- The third, and last, carbon-based bond we'll examine is the triple bond. The simplest carbon-based compound that has a triple bond (three bonds; total of 6 electrons shared) is acetylene (common name), Figure, right.



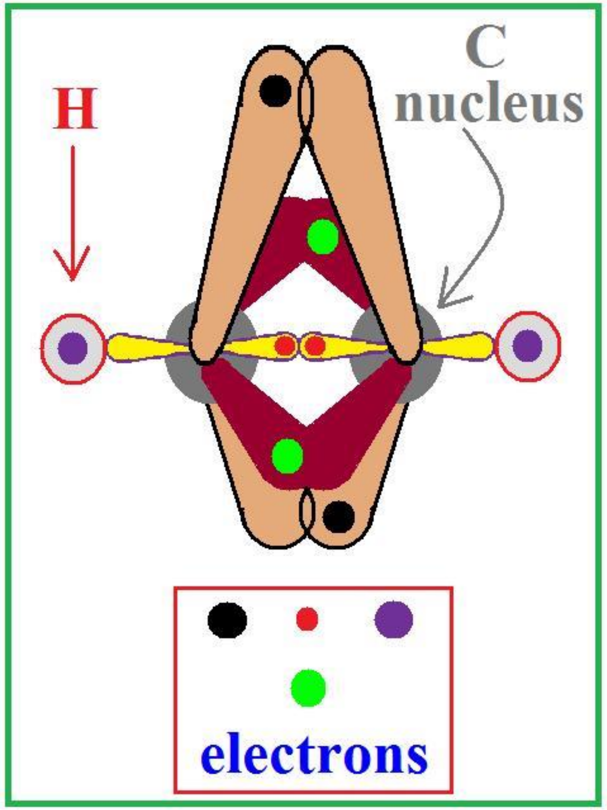
- While there are still four bonds on each carbon atom, three of those bonds are between the two carbon atoms. Figure, below, illustrates the mechanics that must occur in order for this new hybridization to actuate.



- 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.

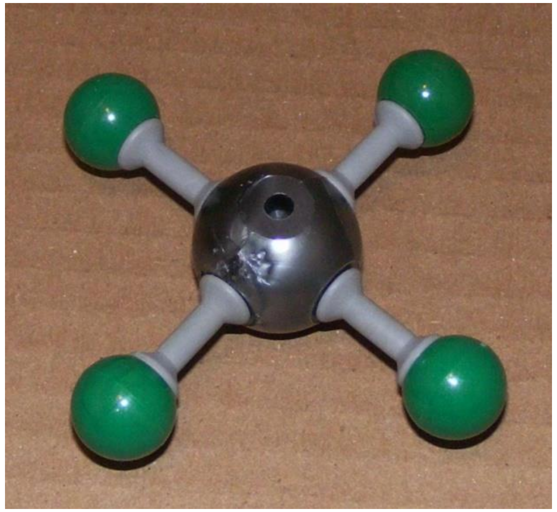


- sp hybridization accounts for only one o the three bonds about the two carbon atoms i the triple bonds.
- The actual sp hybridized orbital provides electrons for the end-to-end sigma bonds; the remaining two 2p orbitals provide the last two sets of electrons to form pi bonds to "seal it up", Figure,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

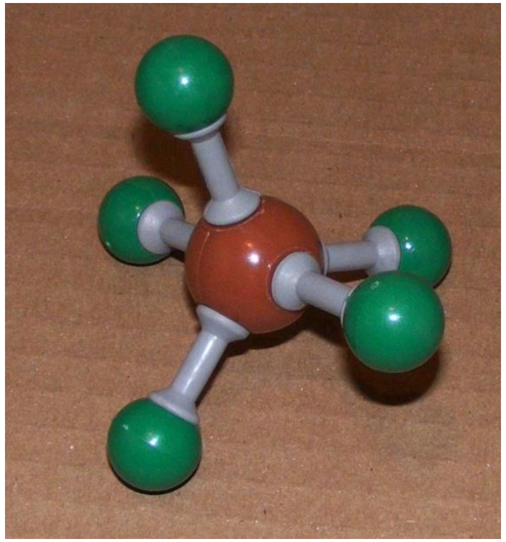


- Carbon is not the only atom to undergo orbital hybridization in order to make bonds.
- In many cases the hybridization pattern may be concluded by examining the periodic table and counting electrons in outer shells, e.g., Be is in Group II and undergoes sp hybridization yielding linear (aka digonal)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

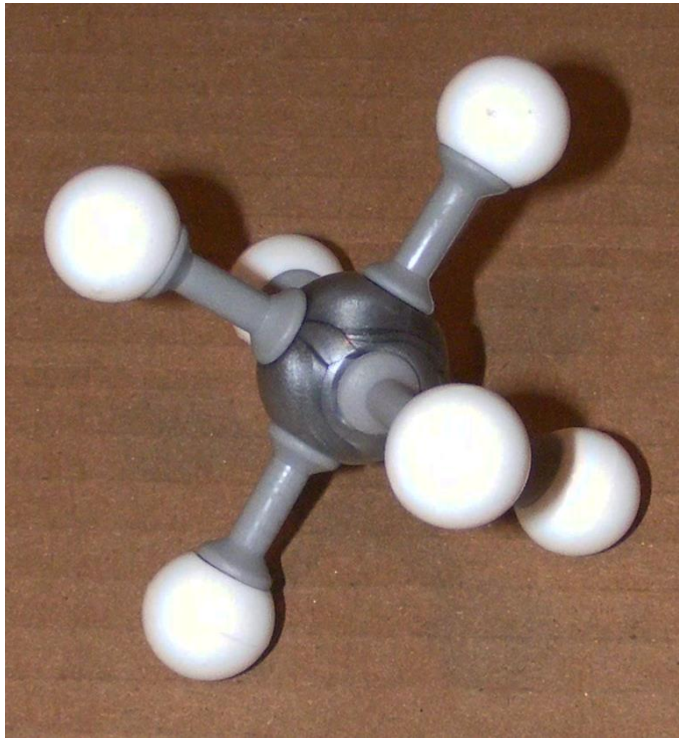
- Less obvious are Pt, Pd and Ni which undergo dsp^2 hybridization to give a square planar geometry -- note that sp^3 and dsp^2 hybrids are distinctly different hybridizations.



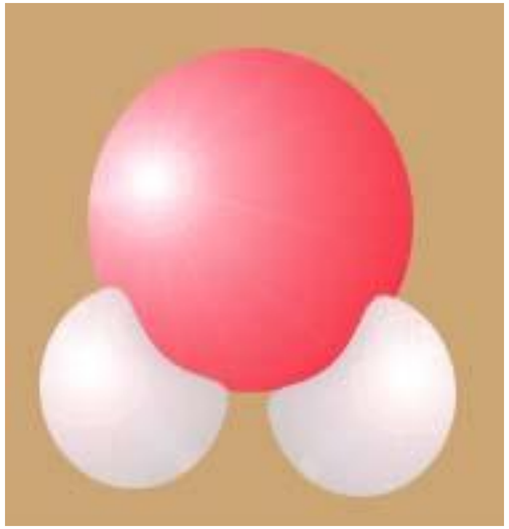
- Likewise, it's not always possible to determine that P (in a +5 state) undergoes dsp^3 hybridization to yield trigonal bipyramidal geometry, Figure, right .
- Do you see the 5 bonding sites?



- 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.