Quantitative Analysis

Quantitative: How much of the compound of interest (quantity)
Amounts of atoms in a compound

$$\text{Organic compound} \xrightarrow[\Delta\ (\text{heat})]{} CO_2 + H_2O + NO_2 \xrightarrow{[H] = \text{Reduction}} N_2 + H_2O$$

MW (g/mol): 44 (CO_2), 18 (H_2O)

		CO_2	H_2O	NO_2
Compound (4.34 mg) Contains C, H, O	$\xrightarrow{O_2}$	10.35 mg	3.42 mg	0 mg

Note: Matter cannot be created or destroyed in a chemical reaction; therefore the amount of carbon in the CO_2 is equal to the amount of carbon in the starting sample.

<u>Percent Composition</u> – how much of each atom is present in the sample

$$\text{Weight of carbon (in sample)} = \frac{12\ \text{g/mol of C}}{44\ \text{g/mol } CO_2} \times 10.35\ \text{mg of } CO_2 = 2.82\ \text{mg of C}$$

Molecular Weight (MW) of CO_2 = 12 (C) + 2×16 (O) = 44 g/mol

$$\text{Weight of hydrogen} = \frac{2(1\ \text{g/mol of H})}{18\ \text{g/mol of } H_2O} \times 3.42\ \text{mg of } H_2O = 0.383\ \text{mg of H}$$

NB: H_2O contains two hydrogen. MW of $H_2O = \underbrace{(2\times1)}_{H_2} + \underbrace{16}_{O}$

Weight of oxygen = 4.34 mg sample – (2.82 mg of C + 0.383 mg of H) = 1.14 mg of O

Now one can calculate percentage composition:

<u>% Composition:</u>

$$\%\ C = \frac{\text{Mass of carbon}}{\text{Mass of sample}} \times 100\% = \frac{2.82\ \text{mg of C}}{4.34\ \text{mg}} \times 100\% = 65.1\%$$

$$\%\ H = \frac{0.383\ \text{mg of H}}{4.34\text{mg}} = 8.83\%$$

% O = 100% - 65.1% - 8.83% = 26.1%

The empirical (and with additional data, molecular formula) can be determined from % composition

Determining the empirical experimental formula:

Definition: Empirical formula is the ratio of atoms to each other in a molecular formula

There are three steps to calculate the empirical formula:

1) Divide each percentage (%) by the atomic weight of the element → crude ratio
2) Divide each crude ratio by the smallest crude ratio → refined ratio
3) Multiply the refined ratio by an integer value (x2, x3, x4…) → integral ratio

% Composition	Crude Ratio	Refined Ratio	Integral Ratio
65.1 % C	65.1 / 12.0 = 5.42 (% C / At Wt C)	5.42 / 1.63 = 3.34	3.34 x 3 = 10
8.83 % H	8.83 / 1.01 = 8.76	8.76 / 1.63 = 5.39	5.39 x 3 = 16
26.1 % O	26.1 / 16.0 = 1.63	1.63 / 1.63 = 1.00	1.00 x 3 = 3

From the integral ratio, the empirical formula is $C_{10}H_{16}O_3$. Using this formula an empirical weight can be calculated.

C: 10 × 12 = 120 g/mol
H: 16 × 1 = 16 g/mol
O: 3 × 16 = 48 g/mol

$C_{10}H_{16}O_3$ = 184 g/mol

Note: Suppose the molecular weight is given as 368 g/mol, then the molecular formula is obtained by multiplying the integral ratios by a factor of 2 and it would be $C_{20}H_{32}O_6$.

The molecular weight can be independently determined via mass spectrometry.

Gas Law: (Different kinds of units for pressure and volume can be used provided the value of the gas constant is adjusted to those units)

PV = nRT P = Pressure in atm
V = Volume in L
n = Number of moles
T = Temperature in °K; °K and °C are the same size, but 0 K = - 273 °C
R = Gas Constant

$$R \text{ is } \frac{0.082 \text{ L} \cdot \text{atm.}}{\text{mol} \cdot {}^\circ\text{K}}$$

Standard conditions for temperature and pressure (STP)
Old definition of STP used in this course
Standard pressure is 1 atmosphere = 760 mmHg; standard temperature is 0°C = 273 °K;
1 mol of gas occupies 22.4 L at STP.

Sample Question: A certain amount of N_2 gas occupies a volume of 3.0 mL at 750 mmHg and room temperature (298 °K). What volume it will occupy at standard pressure and temperature (STP)?

$$\frac{P_1V_1}{P_2V_2} = \frac{nRT_1}{nRT_2} \qquad \text{divide equations to give} \qquad \frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$$

P_1 = 760 mmHg T_1 = 273 °K V_1 = ?
P_2 = 750 mmHg T_2 = 298 °K V_2 = 3 mL

Solve for V_1

$$V_1 = \frac{T_1P_2V_2}{T_2P_1} = \frac{(273\ {}^\circ\text{K})(750 \text{ mmHg})(3 \text{ mL})}{(298\ {}^\circ\text{K})(760 \text{ mmHg})} = 2.71 \text{ mL}$$

Question: How many moles of N_2 is 2.71 mL at STP and what is its mass?

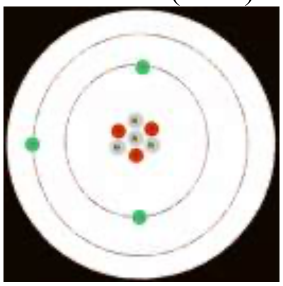
Note: 1 mole of an ideal gas occupies 22.4 L at STP.

$$2.71 \times 10^{-3} \text{ L} \times \frac{1 \text{ mole}}{22.4 \text{ L}} = 1.21 \times 10^{-4} \text{ moles of } N_2$$

1.21×10^{-4} mol × 28 g/mol = 3.4 mg of N_2

Atomic Theory:

- Neils Bohr (1913) – Won the Nobel prize for his atomic theory – NOT fully correct



- The neutrons (no charge) and protons (positively charged) occupy a dense central region called the nucleus (p^+ +N)
- The electrons (negatively charged) orbit the nucleus much like planets orbiting the Sun
- The atom is mostly made up of empty space

- de Broglie (1924) – His 12 page PhD thesis won him the Nobel Prize
  - He proposed that ordinary "particles" such as electrons and protons could behave as both particles and waves (wave - particle duality of matter)

Particles ↔ Waves

Often the electron density distribution is called an "orbital" by chemists
- The orbitals of an atom are described by wave functions (mathematical equations)
- These have no direct physical meaning, but when squared describe electron density

ψ = Wave function

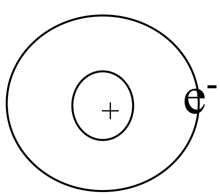
ψ = orbital

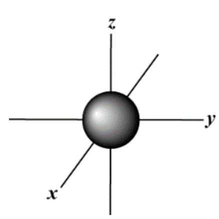
ψ^2 = $(\text{orbital})^2$ = electron density distribution

For the hydrogen (H) atom: >98% of electron density is found in a sphere with diameter of **1Å (10^{-8} cm)**

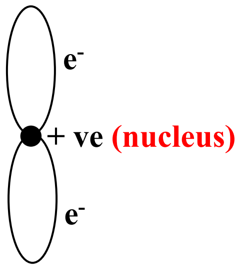
Orbitals:

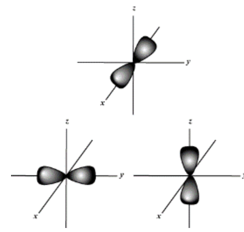
1. *s*-Orbital - Spherical shaped (electron density)



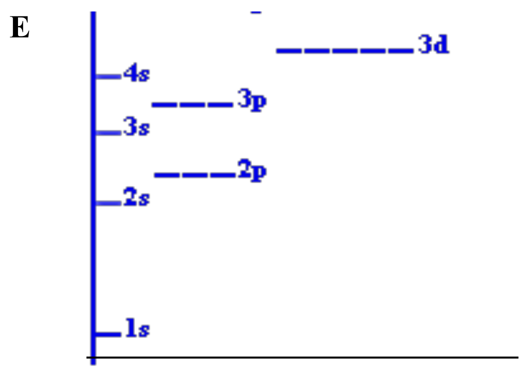


2. *p*-Orbital - Dumbbell-shaped (Three orientations: placed on the x, y and z-axis)





Energy (E) Level Diagram for an Atom:



Degenerate orbitals have the same energy

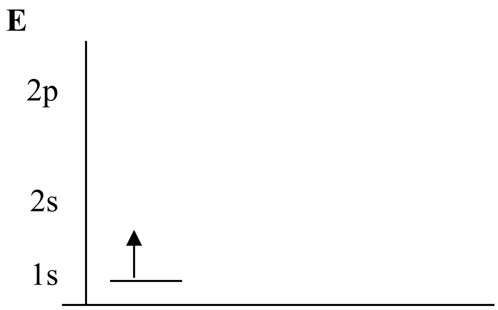
-e.g. all three 2p orbitals have the same energy

Atoms	Protons (+) = Atomic #	Neutrons	1s electrons	2s electrons	2p electrons
H	1	0	1		
He	2	2	2		
Li	3	3	2	1	

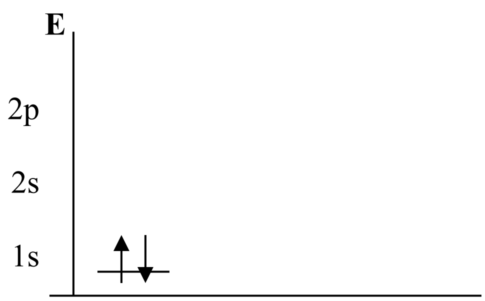
Rules for Filling Electron Orbitals – AUFBAU Rule (Building-Up Principle):

1) Add electron to the lowest energy orbital available
2) Maximum of two electron per orbital (each having opposite spin quantum number)
    - Pauli Exclusion Principle
3) Place one electron into each orbital of the same energy (degenerate orbitals), before adding a second electron
    - Hund's Rule of Maximum Multiplicity

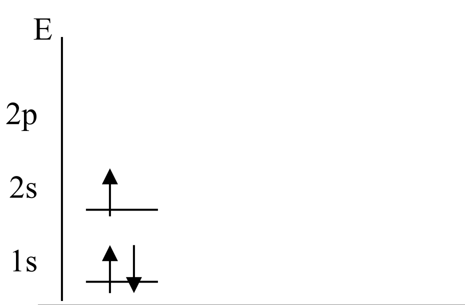
<u>Hydrogen (H)</u>



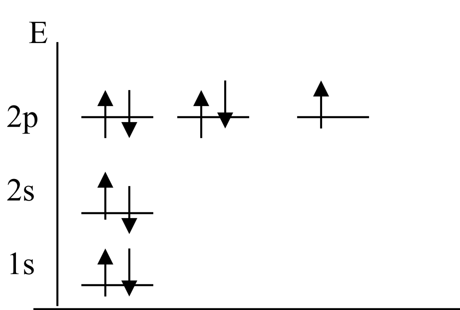
<u>Helium (He)</u>



<u>Lithium (Li)</u>



<u>Fluorine (F)</u>



All elements want an inert gas configuration (e.g. Ne) and from the diagrams above, both Li and F are unhappy with unfilled orbitals (not in an inert gas configuration).

If Li loses an electron to become Li^+ and obtain inert gas configuration, it becomes isoelectronic with He

-Isoelectronic = same electronic structure

If F gains an electron to become F^- and obtain inert gas configuration, it becomes isoelectronic with Ne

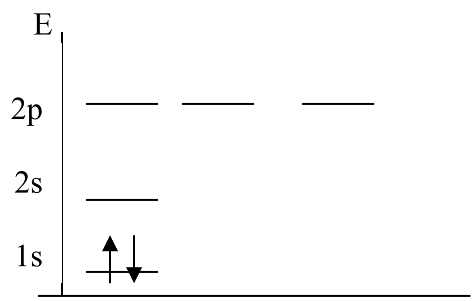
Ionic Bonding

Lithium fluoride (LiF) is an example of ionic bonding in which positive and negative species are bonded to each other. Li could lose 1e$^-$ from 2s orbital to become isoelectronic to He (as Li^+) and F could gain 1e$^-$ to become isoelectronic to Ne (as F^-).

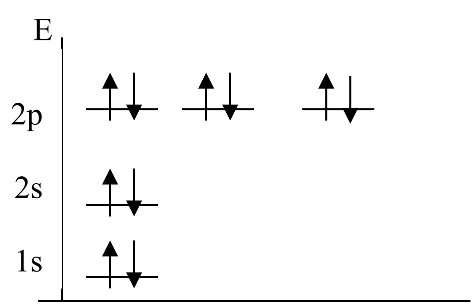
$$Li^o + F^o \rightarrow \underset{\text{Loss of 1e}^-}{Li^+} + \underset{\text{Gain of 1e}^-}{F^-}$$

Isoelectronic = Same electron configuration

Li^+ (cation) Isoelectronic with He

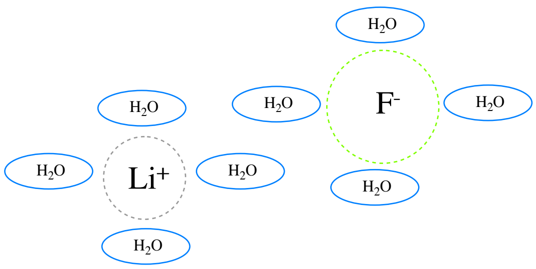


F^- (anion) Isoelectronic with Ne

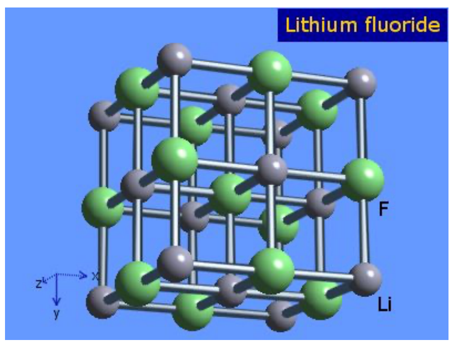


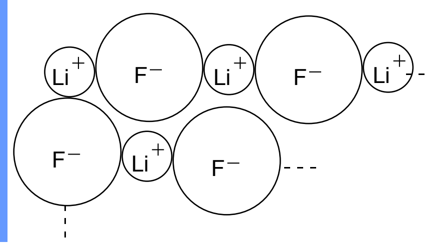
In space, Li^+ and F^- would be attracted to each other

In solution, Li^+ and F^- might be separated due to solvation (e.g. water would surround). Larger ions would have a higher degree of solvation than smaller ions (more water molecules would surround the larger molecule).



In a solid, Li^+ and F^- would form a cubic crystalline solid



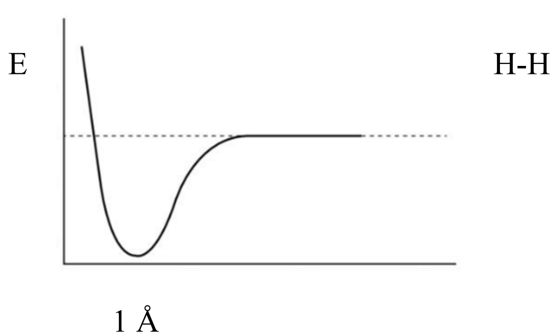


Electronegativity

- Desire of atoms for electrons
- Electronegativity increases from left to right across the period in the periodic table (atoms get stronger attraction as the nuclear charge increases
- Electronegativity increases from bottom to top in the group (Distance between nucleus and valence shell decreases)

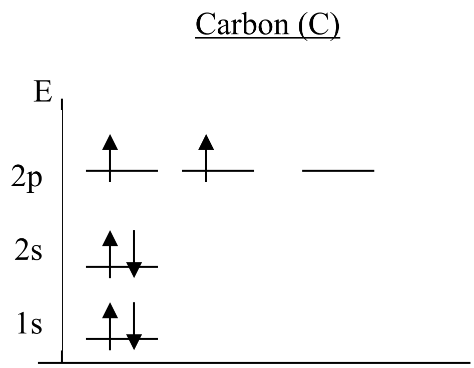
Covalent Bonding

- Sharing of electrons between the atoms
- More common in organic chemistry
- One bond represents 2 electrons



Electronic configuration of carbon (C):

- Atomic number = 6
- Atomic weight = 12



- Carbon needs to gain or lose 4e$^-$ to get an inert gas configuration, but this would result in unfavourable charge buildup:

- C^{4+} is isoelectronic with He

- C^{4-} is isoelectronic with Ne

- So, carbon makes up to 4 bonds to <u>share</u> 4e$^-$ (covalent bonding)