Quantitative Analysis

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

$$\begin{tikzcd}
 & & & & N_2 + H_2O \\
\text{Organic compound} \arrow[r, "O_2", "\Delta\text{ (heat)}"'] & CO_2 \arrow[r, phantom, "+"] & H_2O \arrow[r, phantom, "+"] & & NO_2 \arrow[u, "{[H] = \text{Reduction}}"']
\end{tikzcd}$$

MW (g/mol): 44 18

Compound (4.34 mg) $\longrightarrow$ 10.35 mg 3.42 mg 0 mg
contains C, H, O

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.

Percent Composition

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

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

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

Now one can calculate percentage composition:

% Composition:

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

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

% 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: $10 \times 12 = 120$ g/mol
H: $16 \times 1 = 16$ g/mol
O: $3 \times 16 = 48$ 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 = Moles
T = Temperature in °K; K and °C are the same size, but 0 K = - 273 °C

$$R \text{ is a constant } \frac{0.082\ L \cdot atm.}{mol\ .\ K}$$

Standard conditions for temperature and pressure (STP)
old definition of STP used in this course
Standard pressure is 1 atmosphere, or 760 mmHg; standard temperature is 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 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 $\quad T_1 = 273$ °K $\quad V_1 = ?$
$P_2 = 750$ mmHg $\quad T_2 = 298$ °K $\quad V_2 = 3$ mL

Solve for V_1

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

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

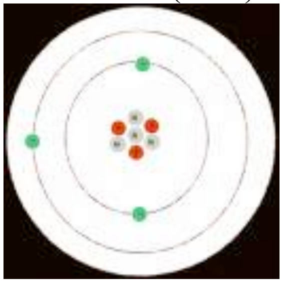
Note: 1 mole of an ideal gas occupies 22.4 L at STP.

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

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
- The electrons (negatively charged) orbit the nucleus much like planets orbiting the Sun

- 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)

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

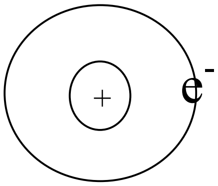
ψ = orbital

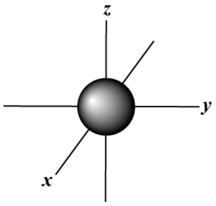
ψ^2 = $(\text{orbital})^2$ = electron density distribution

For the hydrogen (H) atom: >95% of electron density is found in a sphere with diameter of 1Å (10^{-8} cm)

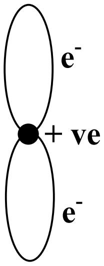
Orbitals:

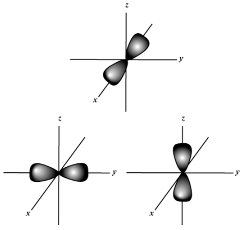
1. *s*-Orbital - Spherical shaped (electron density)





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





Basic Principles:

- Like charges repel each other; unlike charges attract each other
- Atoms want to have an inert gas electron configuration (isoelectronic with inert gas, such as He, Ne, Ar. Helium is the inert gas that hydrogen can be isoelectronic with)

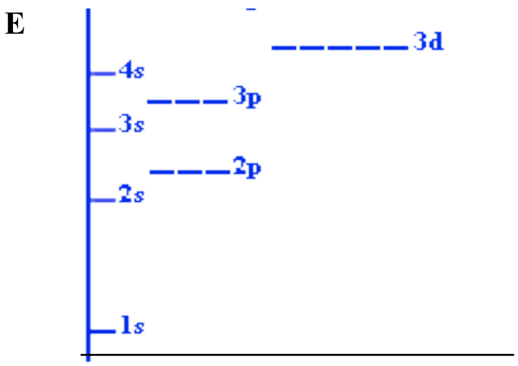
Atoms	**Protons (+) = Atomic #**	**Neutrons**	**1s electrons**	**2s electrons**	**2p electrons**
H	1	0	1		
He	2	2	2		
Li	3	3	2	1	

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

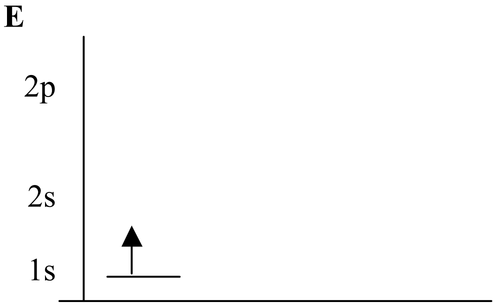
1) Add electron to the lowest energy orbital available
2) Maximum of two electron per orbital (each having opposite spin quantum number)
    - Pauli Exclusion Principle
3) Place one electron into each orbital of the same energy (degenerate orbitals), before adding a second electron
    - Hund's Rule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

Abbreviation of electron: $\mathbf{e}^-$
Mass Number = (Number of Protons) + (Number of Neutrons)
Atomic Number – Number of Protons

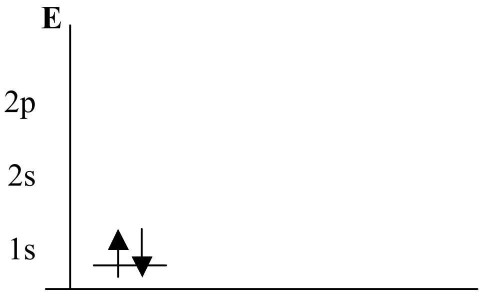
Energy (E) Level Diagram for an Atom:



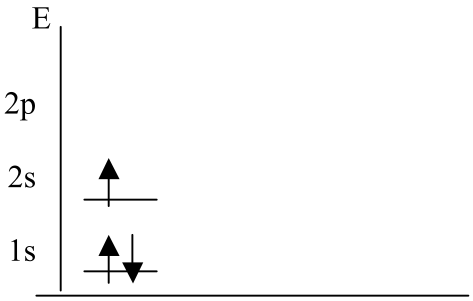
Hydrogen (H)



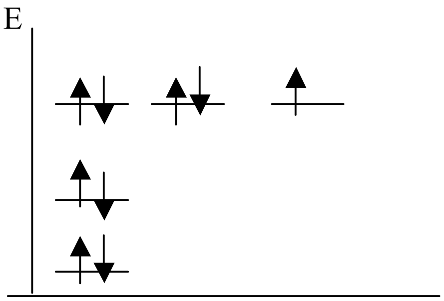
Helium (He)



Lithium (Li)



Fluorine (F)



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).

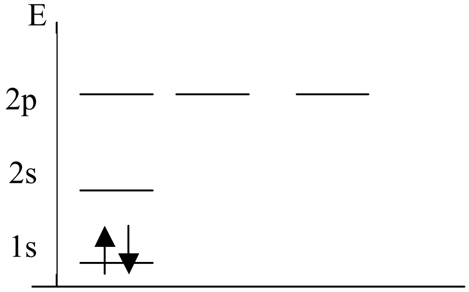
Ionic Bonding

Lithium fluoride 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$^-$).

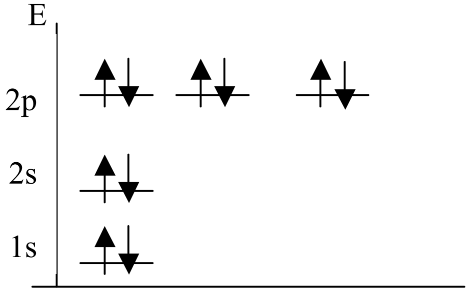
$$\mathrm{Li^o} \quad + \quad \mathrm{F^o} \quad \rightarrow \quad \mathrm{Li^+} \quad + \quad \mathrm{F^-}$$

Isoelectronic = Same electron configuration

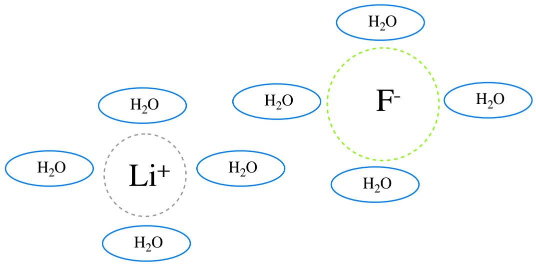
Li$^+$ (cation) Isoelectronic with He



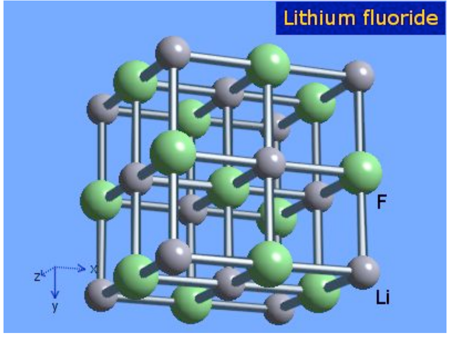
F$^-$ (anion) Isoelectronic with Ne



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)



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



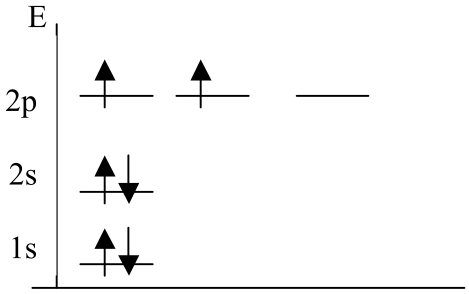
Covalent Bonding

- <u>Sharing</u> of electrons between the atoms
- More common in organic chemistry

Electronic configuration of carbon (C):

- Atomic number = 6
- Atomic weight = 12

<u>Carbon (C)</u>



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

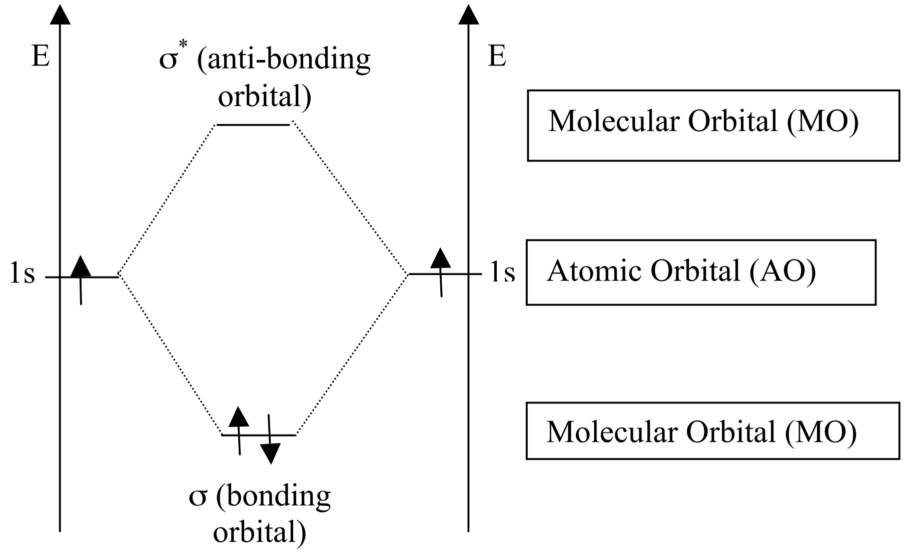
- C^{4+} is isoelectronic with He

- C^{4-} is isoelectronic with Ne

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

Energetics of Forming Bonds

e.g. H_2



As these two hydrogen atoms come together, molecular hydrogen (H_2) is formed

$$H^{\cdot} \longrightarrow H{:}H \longleftarrow {}^{\cdot}H$$
