

Quantitative Analysis

Determining the empirical experimental formula: Done by burning organic compounds. If you have a pure unknown sample with a mass of 4.34 mg, how would you determine its empirical formula?

4.34 mg burned \rightarrow CO₂ + H₂O, 10.35 mg of CO₂ 3.42 mg of H₂O

12 g carbon / 44 g CO₂ (atomic weight of C/molecular weight of CO₂) x 10.35 mg = 2.82 mg C

2 g hydrogen / 18 g H₂O (atomic weight of H/molecular weight of H₂O) x 3.42 mg = 0.35 mg H

Oxygen by mass difference

Mass of C – Mass of H (2.82 mg – 0.35 mg) = Mass of O (1.17 mg)

%C = mass of C/mass of sample x 100% = 2.82 mg C / 4.34 mg sample = 65.1%

%H = mass of H/mass of sample x 100% = 8.83%

%O = mass of O/mass of sample x 100% = 26.1%

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 \rightarrow crude ratio
- 2) Divide each crude ratio by the smallest crude ratio \rightarrow refined ratio
- 3) Multiply the refined ratio by an integer value (x2, x3, x4...) \rightarrow integral ratio

<u>% Composition</u>	<u>Crude Ratio</u>	<u>Refined Ratio</u>	<u>Integral Ratio</u>
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 C₁₀H₁₆O₃. Using this formula an empirical weight can be calculated.

C: 10 x 12 = 120 g/mol

H: 16 x 1 = 16 g/mol

$$\text{O: } 3 \times 16 = 48 \text{ g/mol}$$

$$\text{C}_{10}\text{H}_{16}\text{O}_3 = 184 \text{ g/mol}$$

Note: Given a molecular weight of 368 g/mol, the molecular formula is obtained by multiplying the integral ratios by a factor of 2, resulting in $\text{C}_{20}\text{H}_{32}\text{O}_6$.

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

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

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.

Example: $\text{NH}_3(\text{l}) \rightarrow \text{NH}_3(\text{g})$. Ammonia molecular weight = 17 g/mol; 17 grams of ammonia = 22.4 liters

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 will it occupy at standard pressure and temperature (STP)?

$$\frac{P_1 V_1}{P_2 V_2} = \frac{nRT_1}{nRT_2} \quad \text{divide equations to give} \quad \frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$$

$$\begin{array}{lll} P_1 = 760 \text{ mmHg} & T_1 = 273 \text{ °K} & V_1 = ? \\ P_2 = 750 \text{ mmHg} & T_2 = 298 \text{ °K} & V_2 = 3 \text{ mL} \end{array}$$

Solve for V_1

$$V_1 = \frac{T_1 P_2 V_2}{T_2 P_1} = \frac{(273 \text{ °K})(750 \text{ mmHg})(3 \text{ mL})}{(298 \text{ °K})(760 \text{ mmHg})} = 2.71 \text{ mL}$$

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

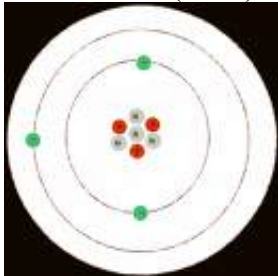
Note: 1 mole of an ideal gas occupies 22.4 L at STP.

$$2.71 \times 10^{-3} \text{ L} \times \frac{1 \text{ mole}}{22.4 \text{ L}} = 1.21 \times 10^{-4} \text{ moles of N}_2$$

$$1.21 \times 10^{-4} \text{ mol} \times 28 \text{ g/mol} = 3.4 \text{ mg of N}_2$$

Atomic Theory:

- Niels 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 ($p^+ + N$, both have a mass = 1 atomic unit)
- The electrons (negatively charged) orbit the nucleus much like planets orbiting the Sun
- The atom is mostly made up of empty

- 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 \leftrightarrow Waves

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

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

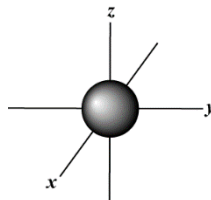
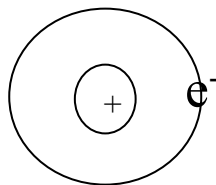
$$\psi = \text{Wave function}$$

$$\psi = \text{orbital}$$

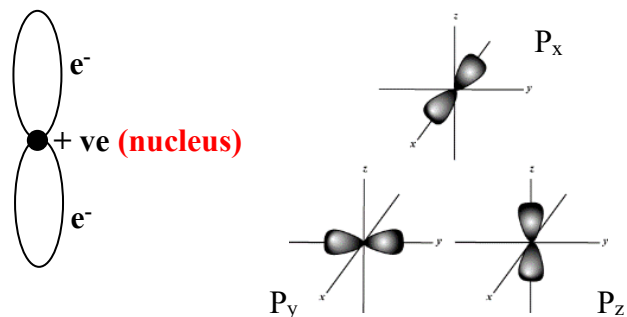
$$\psi^2 = (\text{orbital})^2 = \text{electron density distribution}$$

Orbitals:

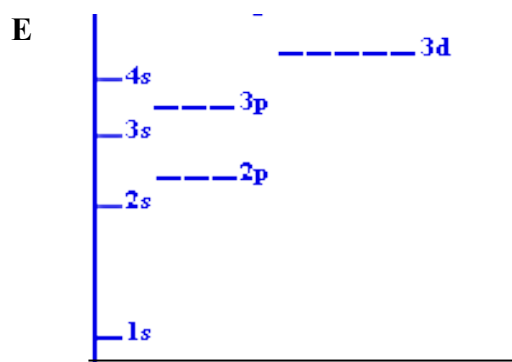
1. *s*-Orbital - Spherical shaped (electron density)



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



Energy (E) Level Diagram for an Atom:



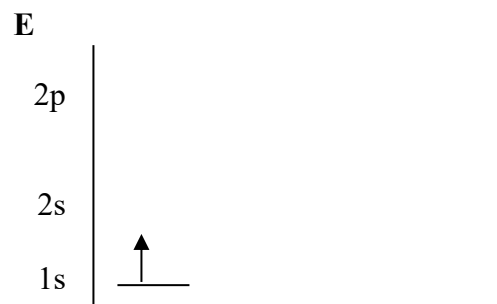
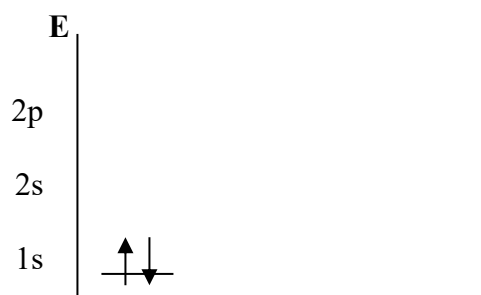
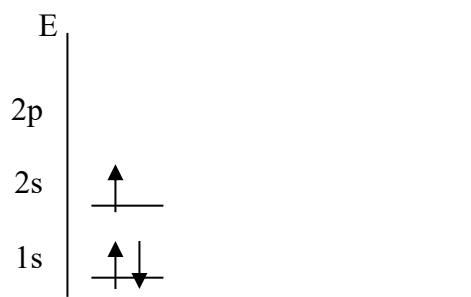
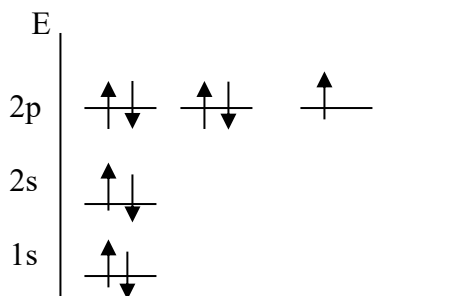
Degenerate orbitals have the same energy

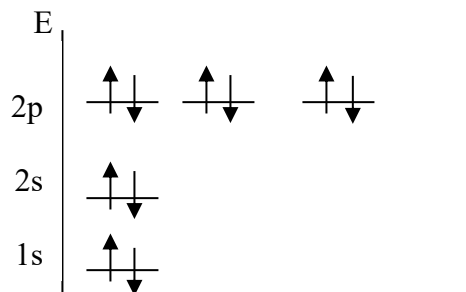
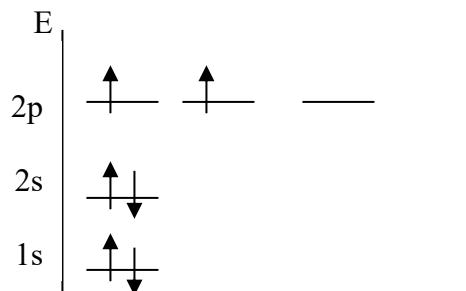
-e.g. all three 2p (p_x , p_y , p_z) orbitals have the same energy and are orthogonal to each other

<u>Atoms</u>	<u>Protons (+)</u> <u>= Atomic #</u>	<u>Neutrons</u>	<u>1s electrons</u>	<u>2s electrons</u>	<u>2p electrons</u>
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

Hydrogen (H) (*atomic no. 1*)Helium (He) (*atomic no. 2*)Lithium (Li) (*atomic no. 3*)Fluorine (F) (*atomic no. 9*)

Neon (Ne) (atomic no. 10)Carbon (C) (atomic no. 6)

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

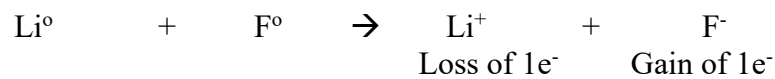
If Li loses an electron to become Li^+ and obtain inert gas configuration, it becomes isoelectronic with He

-Isoelectronic = same electronic structure

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

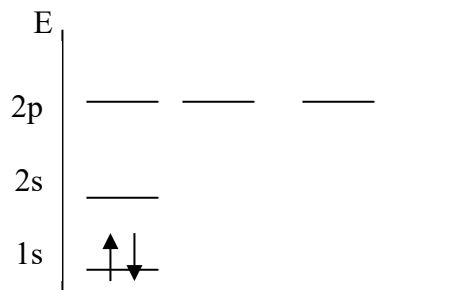
Ionic Bonding

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^-).

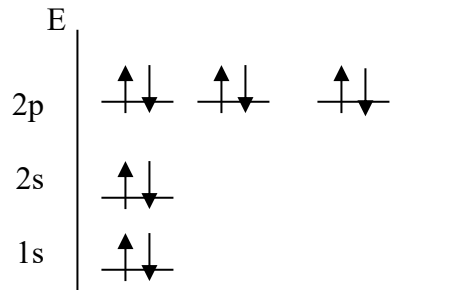


Isoelectronic = Same electron configuration

Li⁺ (cation) Isoelectronic with He



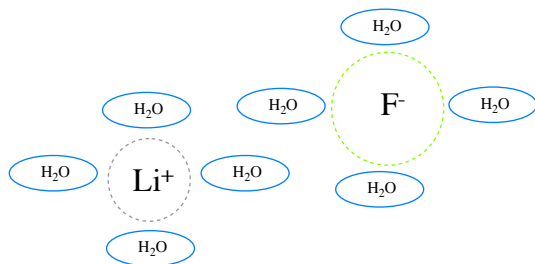
F⁻ (anion) Isoelectronic with Ne



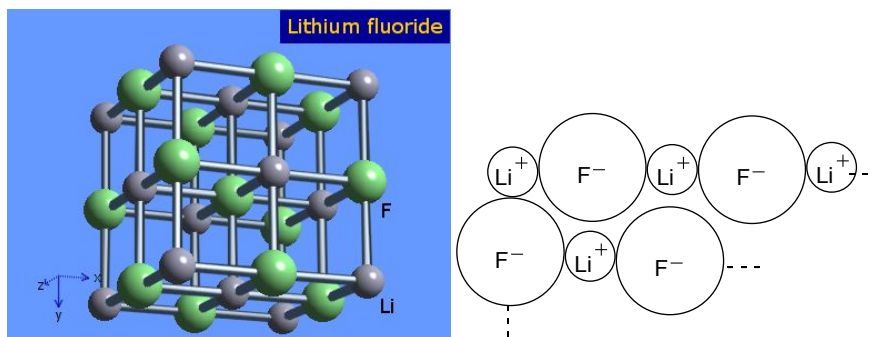
In space, Li⁺ and F⁻ would be attracted to each other

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

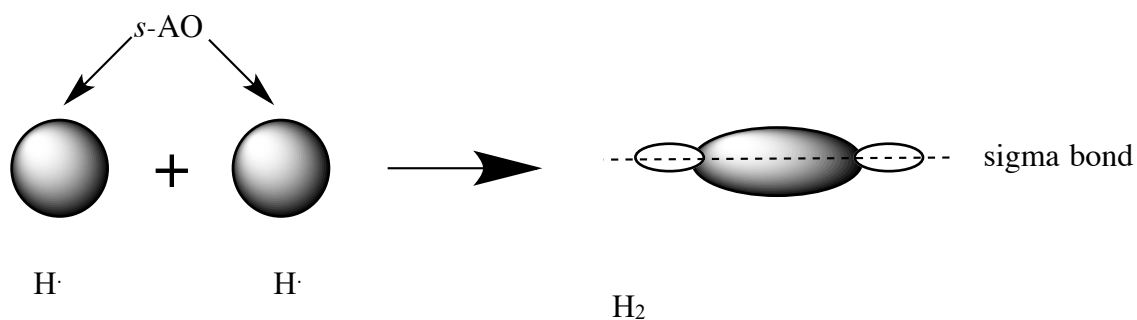
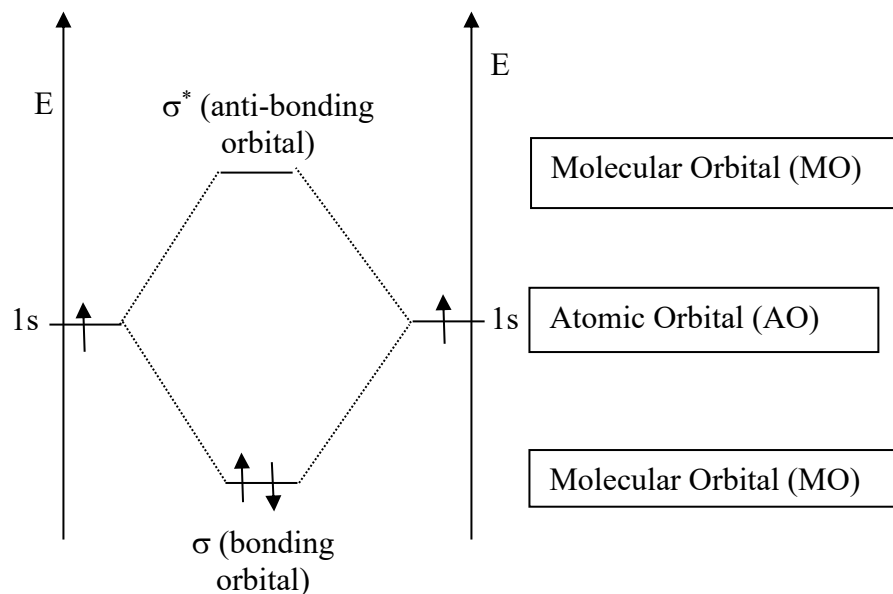
As two hydrogen atoms come together, molecular hydrogen (H_2) is formed to achieve inert gas configuration.



1Å is the average H-H bond distance

e.g. H_2

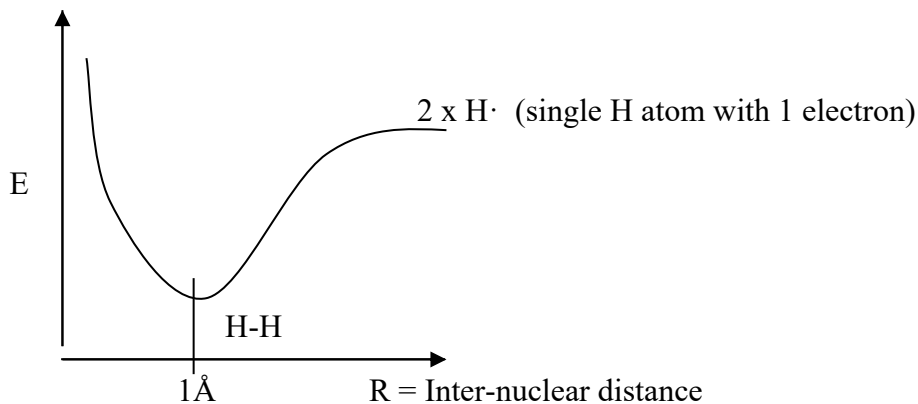
(σ = sigma)



LCAO

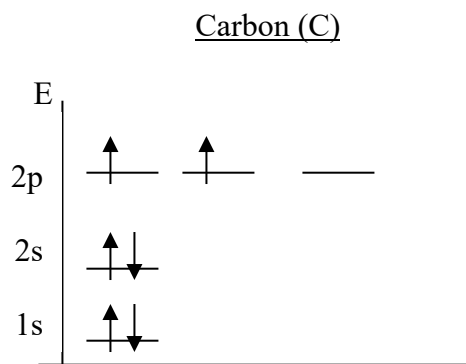
- Linear combination of atomic orbitals
- Combination of atomic orbitals of s- character gives molecular orbital called sigma molecular orbital (σ)

Energy diagram of two hydrogen atoms interacting to form a bond:



Electronic configuration of carbon (C):

- Atomic number = 6
- Atomic weight = 12



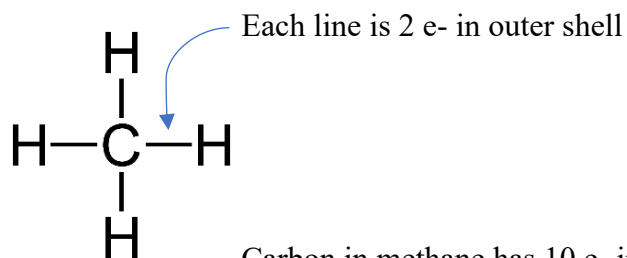
- Carbon needs to gain or lose 4e⁻ to get an inert gas configuration, but this would result in unfavourable charge buildup:

- C⁴⁺ is isoelectronic with He

- C⁴⁻ is isoelectronic with Ne

- So, carbon makes up to 4 bonds to share 4e⁻ (covalent bonding)

Methane (CH₄)



Carbon in methane has 10 e⁻ in total;

- the 2 e⁻ are in 1s and is not shown
- the other 8 e⁻ are the outer shell electrons drawn as line bond

Geometry of methane

- The orbitals in the second row undergo hybridization.
- Hybridization is the mixing of the 2s (s) orbital and the p_x , p_y , and p_z (p^3) to give sp^3 hybridization.

- Sp^3 = tetrahedron, bond angles are 109.5°