Quantitative Analysis

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 \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 $(x_2, x_3, x_4...) \rightarrow$ integral ratio

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

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

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

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)

 $\begin{aligned} \mathbf{PV} &= \mathbf{nRT} & P = \text{Pressure in atm} \\ V &= \text{Volume in L} \\ n &= \text{Number of moles} \\ T &= \text{Temperature in }^\circ\text{K}; \, ^\circ\text{K} \text{ and }^\circ\text{C} \text{ are the same size, but } 0 \text{ K} = -273 \, ^\circ\text{C} \\ R &= \text{Gas Constant} \end{aligned}$

R is <u>0.082 L · atm.</u> mol . °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 $0^{\circ}C = 273 ^{\circ}K$; 1 mol of gas occupies 22.4 L at STP.

<u>Sample Question</u>: A certain amount of N₂ 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)?

$\frac{P_1 V_1}{P_2 V_2} = \frac{nRT_1}{nRT_2}$	divide equations to gi	divide equations to give		
D 7(0 II	T 272 0V	V O		

 $\begin{array}{ll} P_1 = 760 \mbox{ mmHg} & T_1 = 273 \mbox{ }^{\circ} K & V_1 = \ ? \\ P_2 = 750 \mbox{ mmHg} & T_2 = 298 \mbox{ }^{\circ} K & V_2 = 3 \mbox{ mL} \end{array}$

Solve for V₁

 $V_{1} = \frac{T_{1}P_{2}V_{2}}{T_{2}P_{1}} = \frac{(273 \text{ °K})(750 \text{ mmHg})(3 \text{ mL})}{(298 \text{ °K})(760 \text{ mmHg})} = 2.71 \text{ mL}$

Question: How many moles of N₂ is 2.71 mL at STP and what is its mass?

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

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

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

Atomic Theory:

- Niels Bohr (1913) – Won the Nobel prize for his atomic theory – <u>NOT fully correct</u>



- 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)

 $Particles \leftrightarrow Waves$

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

$$\psi$$
 = orbital

 ψ^2 = (orbital)² = electron density distribution

For the hydrogen (H) atom: >98% of electron density is found in a sphere with diameter of 1\AA (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 (+)	<u>Neutrons</u>	<u>1s electrons</u>	2s electrons	<u>2p electrons</u>
	<u>= Atomic #</u>				
Н	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





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 <u>ionic bonding</u> 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 Li^{+} + F^{-} Loss of 1e⁻ Gain of 1e⁻

Isoelectronic = Same electron configuration



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

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



1 Å 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 <u>share</u> 4e⁻ (covalent bonding)





- the other 8 e- are the outer shell electrons drawn as line bond

Energetics of Forming Bonds

As two hydrogen atoms come together, molecular hydrogen (H₂) is formed

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









LCAO

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