Chapter I. Reminders of some important definitions

I.1 Introduction

Since antiquity, measurement began with body-based units (like cubits and feet), then moved to local standards in trade and construction. The scientific revolution pushed for precision, and the **18th century** brought the metric system. Today, measurements rely on universal constants and advanced technology for global accuracy.

I.2 Mole and Avogadro number

In chemistry, a **mole** (mol) represented by the symbol "*n*" is simply a unit of measurement. It is one of the International System **SI** of unit (SI). it is invented when the existing units are inadequate to bridge the gap between exceptionally small and exceptionally large numbers.

The ***Avogadro's*** number "N_A", which is the number of atoms in 12 grams of carbon-12, is equal to **6.02214076 ×10²³** elementary entities (like atoms, molecules, or ions) of that substance. This number, bridges the enormous numbers of particles involved in chemical reactions with a usable amount of substance for lab work. A mole provides a direct link between the mass of a substance and the number of particles it contains.

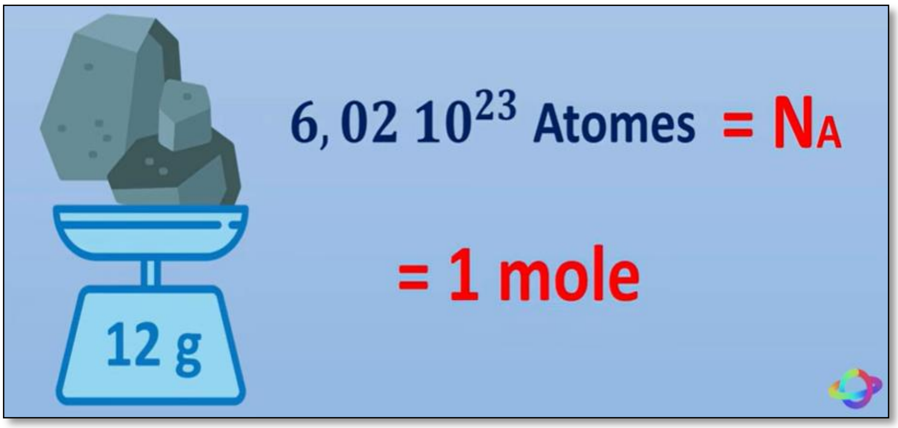

Figure I.1: The number of moles.

The amount of substance in a chemical sample is the number of moles present in that sample. It's given:

$$n = \frac{N}{N_A} \qquad I.1$$

Such as:
n: the amount of substance
N: the number of unites (atoms, ions, particles)
N_A: Avogadro number

Activity:

How many atoms of carbon are in 0.5 moles of carbon (C)?

Solution :

$N = N_A \times n$

$N = 0.5 \times 6.022 \times 10^{23}$

$N = 3.011 \times 10^{23}$ atoms. So, 0.5 moles of carbon contain 3.011×10^{23} atoms.

I.3 Molar mass

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Molar mass is defined as the mass in **grams** of **one mole** of a substance. It's symbolized by "**M**" and its unit is grams *per* mole, abbreviated as **g/mol**.
The molar mass is given by the equation:

$$m = N \times m_{unit}$$
$$m = n \times N_A \times m_{unit}$$
$$m = n \times M$$
$$M = \frac{m}{n} \qquad I.2$$

Activity:
Find the molar mass of each of the following compounds:
- Sand - silicon dioxide (SiO_2)
- Draino - sodium hydroxide (NaOH)

Solution:

$$M_{SiO2} = M_{si} + 2M_O$$

$$M_{Si} = 28{,}0\ g/mol$$
$$M_0 = 16\ g/mol$$
So : $$M_{SiO2} = 60\ g/mol$$

$$M_{NaOH} = M_{Na} + M_O + M_H$$
$$M_{Na} = 23\ g/mol$$
$$M_O = 16\ g/mol$$
$$M_H = 1\ g/mol$$
$$M_{NaOH} = 40\ g/mol$$

I.4 Molar volume

Molar volume is the volume occupied by one mole of a substance and is calculated by dividing the total volume by the number of moles (V/n). It depends on temperature and pressure, but for an ideal gas, the molar volume is approximately 22.4 L/mol at standard temperature and pressure (STP), i.e., 0 °C and 1 atm.

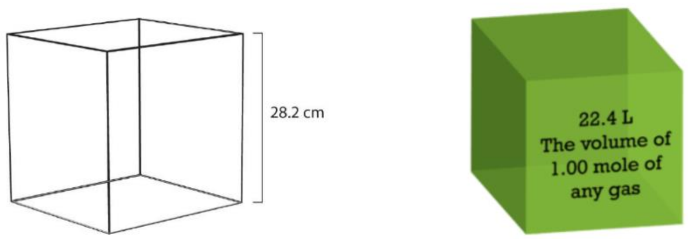

Figure I.2: Molar Volume. A mole of gas at STP occupies 22.4 L, the volume of a cube that is 28.2 cm on a side.

At the same temperature and pressure, equal volumes of all ideal gases contain the same number of molecules. This means, 1 mole of any ideal gas occupies the **same volume** under the same conditions, and at standard temperature and pressure (STP: 0 °C and 1 atm), 1 mole of any gas occupies 22.4 L.

$$V_m = \frac{V}{n} \qquad I.3$$

Such as:

V_m: *molar volume* (L/mol)

V: *gas volume*

n : *number of moles*

In 1811, ***Amadeo Avogadro*** explained that the volumes of all gases can be easily determined. Avogadro's hypothesis states that equal volumes of all gases at the same temperature and pressure contain equal numbers of particles. Since the total volume that a gas occupies is made up primarily of the empty space between the particles, the actual size of the particles themselves is nearly negligible. A given volume of a gas with small light particles, such as hydrogen (H_2), contains the same number of particles as the same volume of a heavy gas with large particles, such as sulfur hexafluoride, SF_6.

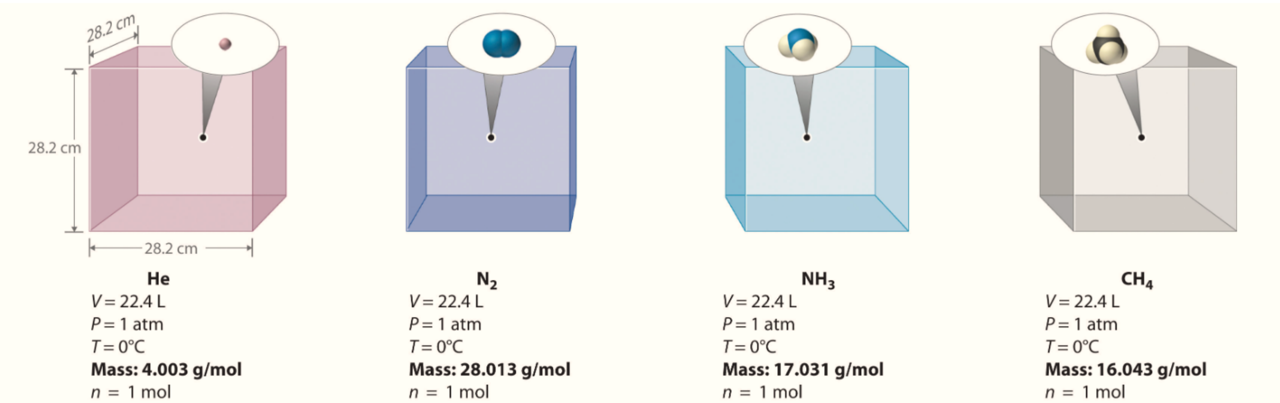

Figure I.3: Avogadro's Hypothesis: Equal volumes of four different gases at the same temperature and pressure contain the same number of gaseous particles.

Activity:

How many moles of *Ar* are present in 38.7 L at STP?

Solution:

We can use the molar volume, 22.4 L/mol, as a conversion factor, but we need to reverse the fraction so that the L units cancel and mol units are introduced. It is a one-step conversion :

$$\mathbf{38.7\,L \times \frac{1\,mol}{22,4\,L} = 1.73\,mol}$$

I.5 The fraction or percentage

The fraction or percentage is a value used in chemistry or metallurgy to express the composition of a compound or alloy. The sum of all the mole fractions in a mixture is always equal to one and this value is dimensionless, that is, it has no units.

I.5.1 Mole fraction

The mole fraction is a quantity that expresses the concentration of a component in a mixture. It is calculated by dividing the **number of moles** of a constituent by the total number of moles of all the constituents in the **mixture**. It is given by the following equation:

$$X_i = \frac{n_i}{n_{total}} \qquad I.4$$

$$X_i(\%) = \frac{n_i}{n_t} \times 100 \qquad I.5$$

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$$\sum Xi = 1 \qquad I.6$$

X_i: *mole fraction of component 'i'*
n_i: *number of moles of component 'i'*
n_{total}: *total number of moles of all components*

I.5.2 Mass fraction

Mass fraction is a way of expressing **the concentration** of a constituent in a **mixture** or compound. It is defined as the ratio of the mass of that constituent to the total mass of the mixture or compound. It is calculated using the formula:

$$P_i = \frac{m_i}{m_t} \qquad I.7$$

$$P_i(\%) = \frac{m_i}{m_t} \times 100 \qquad I.8$$

$$\sum P_i = 1 \qquad I.9$$

I.5.3 Volume fraction

Volume fraction is a dimensionless ratio that expresses **the volume** of a particular component in a **mixture** relative to the total volume of that mixture. It is calculated using the formula:

$$\emptyset_i = \frac{V_i}{V_{total}} \qquad I.10$$

$$\emptyset_i(\%) = \frac{V_i}{V_t} \times 100 \qquad I.11$$

$$\sum \emptyset_i = 1 \qquad I.12$$

Such as:
$\emptyset_i$: *Volume fraction of component i*
V_i: *Volume of component i*
V_{total}: *total volume of mixture*

Activity:

A gas mixture contains 4L of CO_2 and 6L of O_2 (at the same temperature and pressure). Calculate the volume fraction of each gas.

Solution:

The total volume is 4 + 6 =10L

- ⇨ The volume fraction of CO_2: $\emptyset_{CO2} = \frac{4}{10} = 0.4$
- ⇨ The volume fraction of O_2: $\emptyset_{O2} = \frac{6}{10} = 0.6$

So, the mixture is composed by 40% CO_2 and 60% O_2 by volume.

I.5.4 Relationship between mole fraction (Xi) and mass fraction (Pi)

The relationship between mole fraction and mass fraction depends on the molar mass of the components in a mixture, as mole fraction relates to the number of particles (moles) and mass fraction relates to the mass of each component. It is given by the following equation:

$$X_i = \frac{n_i}{\sum n_i} = \frac{m_i/M_i}{\sum m_i/M_i} = \frac{P_i/M_i}{\sum P_i/M_i} \qquad I.13$$

Activity:

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A gas mixture contains: $X_{H2} = 0.6$ and $X_{O2} = 0.4$. find the mass fraction of H_2 and O_2.

Solution:

$P_i = \frac{X_i M_i}{\sum X_t M_t}$, M_{H2} = 2 g/mol, M_{O2} = 32 g/mol

$$\sum X_t M_t = (0.6 \times 2) + (0.4 \times 32) = 1.2 + 12.8 = 14.0$$

$$P_{H2} = \frac{0.6 \times 2}{14.0} = \frac{1.2}{14} \approx 0.086$$

$$P_{O2} = \frac{0.4 \times 32}{14} = \frac{12.8}{14} \approx 0.914$$

So: the mass fraction of H_2 is 0.086 and for O_2 is 0.914.

I.6 Volumetric mass

Or Mass density or mass-to-volume ratio, is a physical property of a material, defined as **the mass** of a sample per **unit volume.** It represents the mass per unit volume occupied by the substance (at specific temperature and pressure). and expressed with units (e.g. kg/m^3). The rule to calculate it is:

$$\rho = \frac{m}{V} (kg/m^3, kg/L, ou\ g/cm^3) \qquad I.14$$

Such as:
m: is the mass of the sample
V: is the volume

Activity:

A material block has a mass of 540g and a volume of $200m^3$. Calculate its mass density "ρ" in g/cm^3 and in kg/m^3.

Solution :

$\rho = \frac{m}{V} = \frac{540}{200} = 2.7\ g/m^3$,

$1g/cm^3 = 1000kg/m^3$ ➔ $2.7 \times 1000 = 2700\ kg/m^3$

I.7 Density

Also called **specific gravity,** is a dimensionless ratio, calculated by dividing the **density of a substance** by **that of a reference material** (usually water), indicating whether the substance is more or less dense than that reference material. It compares the density of a substance to a reference, indicating whether the object floats or sinks in that reference.

- A density less than 1 means the object is lighter than water and will float.
- A density greater than 1 means the object is heavier than water and will sink.

We can determine two laws to calculate density:

a/ Density of solid and liquid materials with respect to water:

It is determined by comparing a certain mass of the substance with the mass of the same volume of water.

$$d = \frac{m_{sample}}{m_{water}} = \frac{\rho_{sample} \times V}{\rho_{water} \times V} = \frac{\rho_{sample}}{\rho_{water}} (no\ unit) \qquad I.15$$

$$\rho_{water} = 1kg/L$$

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b/ Density of gases with respect to air:
Air and gases are taken under the same conditions of temperature and pressure.

$$d = \frac{\rho_{gaz}}{\rho_{air}} (no\ unit) \qquad I.16$$

$$\rho_{air} = 1.293\ g/L$$

In normal conditions (T=0°C and P=101325 Pa)

$$\rho_{air} = \frac{m_{air}}{V_{air}} = \frac{m_{air}/n}{V_{air}/n} = \frac{M_{air}}{V_m}$$

$$M_{air} = \rho_{air} \times V_m = 1.293 \times 22.4 = 29 g/mol$$

$$M_{air} = 29 g/mol$$

$$d = \frac{\rho_{gas}}{\rho_{air}} = \frac{m_{gas}/V}{m_{air}/V} = \frac{m_{gas}}{m_{air}} = \frac{m_{gas}/n}{m_{air}/n} = \frac{M_{gas}}{M_{air}} = \frac{M_{gas}}{29}$$

Activity:

Calculate the volumetric mass of the given substances:

1. Kerosene (Liquid Fuel) with a specific gravity of 0.78
2. Concrete with a specific gravity of 2.5
3. Carbon Dioxide with a density of 1.53 at 0 degrees Celsius

Solution:

1. $d = \frac{\rho_{sample}}{\rho_{water}} = \rho_{kerosene} = d \times \rho_{water} = 0.78 \times 1 = 0.78 kg/L$
2. $\rho_{concrete} = d \times \rho_{water} = 2,5 \times 1 = 2.5 kg/L$
3. $\rho_{CO2} = d \times \rho_{air} = \frac{M_{co2}}{29} \times \rho_{air} = \frac{12+2.16}{29} \times 1.293 = 1.962 g/L$

I.8 Material balances

Material balances are nothing more than the application of the law of conservation of mass, which states that mass can neither be created nor destroyed.

A material balance is the accounting of all mass entering, leaving, and transforming inside a system, ensuring that mass is conserved.

Material balances are essential in various fields, including chemical engineering, environmental science, and analytical chemistry. They help in designing and optimizing chemical processes, understanding reaction kinetics, and assessing the efficiency of a given reaction or system.

$$aA + bB \leftrightarrow cC + dD \qquad I.17$$

$$\frac{|\Delta n_A|}{a} = \frac{|\Delta n_B|}{b} = \frac{\Delta n_C}{c} = \frac{\Delta n_D}{d} \qquad I.18$$

The change in each quantity of substance for reactant or even for product can be expressed in a quantity called **the reaction progress** "***x***" and expressed in moles.

$$n_i = n_{i0} \pm \nu_i x \qquad I.19$$

Knowing that, $\boldsymbol{\nu_i}$ is the stoichiometric coefficient of the substance i.
Generally, in chemistry when we want to study the molar balance, we must create a table that named "progress table" containing the progress of the consumed reactant quantities and the quantities of the products formed during three states: at t=0, at t and at least at T_{max}.

Chemical equation	***aA*** +	***bB*** ↔	***cC*** +	***dD***
t=0	n_{A0}	n_{B0}	0	0

t	$n_{A0} - ax$	$n_{B0} - bx$	cx	dx
T_{max}	$n_{A0} - ax_{max}$	$n_{B0} - bx_{max}$	cx_{max}	dx_{max}

For any reaction of transformation, there are three cases: complete, maximal and under stoichiometric conditions.

- ⇨ *Complete reaction*: in this case we are in presence of "**limiting reactant**". When this reactant disappears completely, the other reactants may still present to the final state and they are called "**excess reactant**".
- ⇨ *Maximal reaction*: in this case, the reaction is "**incomplete**", and the final progress is less than the maximum progress.
- ⇨ *Under stoichiometric condition*: in this case the reactants are added in respect to the stochiometric coefficient.

Note: most chemical reactions are not complete, this is referred as a state of equilibrium characterized by the **equilibrium constant** "K".

$$K = \frac{[A]^a[B]^b}{[C]^c[D]^d} \qquad I.20$$

If:
K < 10^{-4}: weak reaction
10^{-4} < K < 10^{4}: reaction in equilibrium state
K > 10^{4}: complete reaction

I.8.1 Material balances: The ratio progress

The final progress rate, donated by "τ", is equal to the ration of the final progress to the maximum progress:

$$\tau = \frac{x_{final}}{x_{maximal}} \qquad I.21$$

There are two cases:
$0 < \tau < 1$: *non complete reaction*
$\tau = 1$: *complete reaction*
The ratio progress is:

$$\tau\% = \frac{x_{final}}{x_{max}} \times 100 \qquad I.22$$

There are two cases:
$0 < \tau\% < 100$: *non complete reaction*
$\tau = 100$: *complete reaction*

- ⇨ In case of complete reaction:

$$x_{max} = \frac{n_{limiting\ reactant}}{coefficient\ of\ limitant\ reactant} = x_{final} \qquad I.23$$

- ⇨ In case of non-complete reaction:

Experimental parameters, such as pH, concentration, absorption, determine the final progress empirically.

I.8.2 Material balances: The conversion rate

The conversion rate of reactant A is equal to the ratio of the number of moles of A reacted during the chemical reaction to the initial number of moles of A (A_0) present. Therefore, we can write:

$$X_A = \frac{n_{i,0} - n_i}{n_{i,0}} \qquad I.24$$

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The conversion percentage:

$$X_A(\%) = \frac{n_{i,0} - n_i}{n_{i.0}} \times 100 \qquad I.25$$

I.8.3 Material balances: Reaction yield

The chemical reaction yield is the ratio of the actual amount of the obtained product to the maximum amount of that product if all reactant were converted to products.

$$R\,\% = \frac{\text{Actual quantity of the product}}{\text{Maximun quantity}} \times 100 \qquad I.26$$

Activity:

The combustion of methane is given by the following equation:

$$CH_4(g) + 2O_2(g) => CO_2(g) + 2H_2O\,(g)$$

The initial quantity of matter of methane is: $n_{0,CH4} = 2{,}0 \times 10^{-2} mol$, and for the oxygen is $n_{0,O2} = 4{,}5 \times 10^{-2} mol$. What is the material balance of this reaction? The percentage of progress as well as the yield knowing that the masse of CO_2 obtained after experimentation is m_{co2}=0.70g.

1/ The material balance:

	$CH_4(g)$ +	$2O_2(g)$ =>	$CO_2(g)$ +	$2H_2O\,(g)$
t=0	$2{,}0 \times 10^{-2}$	$4{,}5 \times 10^{-2}$	0	0
t	$2{,}0 \times 10^{-2} - x$	$4{,}5 \times 10^{-2} - 2x$	x	2x
t_{max}	$2{,}0 \times 10^{-2} - x_{max}$	$4{,}5 \times 10^{-2} - 2x_{max}$	x_{max}	$2x_{max}$

2/ The limiting reactant:

$$n_{CO2} = \frac{m_{co2}}{M_{co2}} = \frac{0.70}{44} = 0.0159 mol = x_{final}$$

$$0.0159 \times 2 = x_{final} = 0.0318 mol$$

So:

$2{,}0 \times 10^{-2} - 0.0159 = 0.0041\ mol$

$4{,}5 \times 10^{-2} - 0.0159 = 0.0291\ mol$

We can remark that the CH_4 is the limiting reactant.

3/ The percentage of progress:

$$\tau = \frac{x_{final}}{x_{max}} \times 100 = \frac{0.0159}{0.0291} \times 100 = 54{,}6\%$$

4/ The yield of the reaction

$$R\,\% = \frac{\text{Actual quantity of the product}}{\text{Maximun quantity}} \times 100$$