

CHAPTER 2

CALCULATIONS IN ANALYTICAL CHEMISTRY

In this chapter,

- ❖ atomic mass unit
 - ❖ mol
 - ❖ solutions and concentrations
 - ❖ chemical stoichiometry
 - ❖ calculations about above mentioned subjects
- will be considered.

SI BASED UNITS

Physical Property	Name of Unit	Symbol
Mass	kilogram	kg
Lenght	meter	m
Time	second	s
Temperature	kelvin	K
Amount of substance	mole	mol
Electric Current	ampere	A
Luminous intensity	candela	cd

Distinction between Mass and Weight

Mass (m), is an invariant measure of the quantity of matter.

Weight (w), *is* the force of gravitational attraction between that matter and Earth.

The relation between weight and mass is given as:

$$w = mg$$

$w \rightarrow$ weight of a substance

$g \rightarrow$ gravity force

$m \rightarrow$ mass of a substance

THE MOLE:

the SI unit for the amount of a chemical substance.

❖ It is always associated with specific microscopic entities such as atoms, molecules, ions, electrons, other particles, or specified groups of such particles as represented by a chemical formula.

1 mol of any species is equal to 6.022×10^{23} number of atoms, molecules, ions, electrons...

1 mol of Ca atom contains 6.022×10^{23} Ca atoms

1 mol of Ca^{+2} ion contains 6.022×10^{23} Ca^{+2} ions

1 mol of H_2O molecule contains 6.022×10^{23} 1 mol H_2O molecules

MILLIMOLE

The millimole is $1/1000$ of a mole.

The mass in grams of a millimole is the millimolar mass (mM)=
 $1/1000$ of the molar mass.

The **molar mass M** of a substance is the mass in grams
of **1 mole** of that substance.

Examples of calculating molar mass

Molar mass of formaldehyde CH_2O is calculated as:

$$M_{\text{CH}_2\text{O}} = \frac{1\text{molC}}{\text{molCH}_2\text{O}} \times \frac{12.0\text{g}}{\text{molC}} + \frac{2\text{molH}}{\text{molCH}_2\text{O}} \times \frac{1.0\text{g}}{\text{molH}} + \frac{1\text{molO}}{\text{molCH}_2\text{O}} \times \frac{16.0\text{g}}{\text{molO}}$$

$$M_{\text{CH}_2\text{O}} = 30.0\text{g} / \text{molCH}_2\text{O}$$

Molar mass of glucose $\text{C}_6\text{H}_{12}\text{O}_6$ is calculated as:

$$M_{\text{C}_6\text{H}_{12}\text{O}_6} = \frac{6\text{molC}}{\text{molC}_6\text{H}_{12}\text{O}_6} \times \frac{12.0\text{g}}{\text{molC}} + \frac{12\text{molH}}{\text{molC}_6\text{H}_{12}\text{O}_6} \times \frac{1.0\text{g}}{\text{molH}} + \frac{6\text{molO}}{\text{molC}_6\text{H}_{12}\text{O}_6} \times \frac{16.0\text{g}}{\text{molO}}$$

$$M_{\text{C}_6\text{H}_{12}\text{O}_6} = 180.0\text{g} / \text{molC}_6\text{H}_{12}\text{O}_6$$

Calculating the Amount of a Substance in Moles or Millimoles

EXAMPLE: Find the number of moles and millimoles of sodium carbonate, Na_2CO_3 ($M: 106.1 \text{ g/mol}$) that are contained in 2.00 g of the pure sodium carbonate.

$$\text{Amount of } \text{Na}_2\text{CO}_3(\text{mol}) = 2.00 \text{ g Na}_2\text{CO}_3 \frac{1 \text{ mol Na}_2\text{CO}_3}{106 \text{ g Na}_2\text{CO}_3} = 0.01887 \text{ mol Na}_2\text{CO}_3$$

$$\text{Amount of } \text{Na}_2\text{CO}_3(\text{mmol}) = 2.00 \text{ g Na}_2\text{CO}_3 \frac{1 \text{ mmol Na}_2\text{CO}_3}{0.106 \text{ g Na}_2\text{CO}_3} = 18.87 \text{ mmol Na}_2\text{CO}_3$$

Solutions and Concentrations

Four fundamental ways of expressing solution concentration:

1. molar concentration,
2. percent concentration,
3. solution-diluent volume ratio
4. 4. p-functions.

1. The molar concentration(M) C_x of a solution of a solute species X is the number of moles of that species that is contained in 1 liter of the solution.

1 M= (1 mol/liter – 1 millimol/milliliter)

$$C_x = \text{Molar concentration} = \frac{\text{no. moles of solute}(n_x)}{\text{volume in liters}(V)}$$

Analytical Concentration

Molar analytical concentration is the total number of moles of a solute, regardless of its chemical state, in 1 L of solution. The molar analytical concentration describes how a solution of a given concentration can be prepared.

To prepare 1 M CH_3COOH solution

1 mol \rightarrow 60 g CH_3COOH

is dissolved in 1 L.

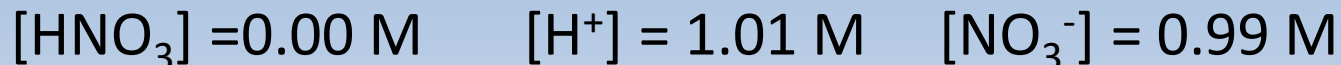
Equilibrium Concentration

Molar equilibrium concentration is the molar concentration of a particular species in a solution at equilibrium.

To specify the molar equilibrium concentration of a species, it is necessary to know how the solute behaves when it is dissolved in a solvent.

Equilibrium molar concentrations are usually symbolized by placing square brackets around the chemical formula for the species.

For example; HNO_3 with an analytical concentration of $C_{\text{HNO}_3} = 1.0 \text{ M}$ totally dissolves in aqueous media, we can write:



2. Percent Concentration

Chemists frequently express concentrations in terms of percent (parts per hundred, %):

Weight percent (w/w)

$$=(\text{mass of solute} / \text{mass of solution}) \times \%100$$

Volume percent (v/v)

$$=(\text{volume of solute} / \text{volume of solution}) \times \%100$$

Weight/volume percent (w/v)

$$=(\text{mass of solute, g} / \text{volume of solution, mL}) \times \%100$$

Parts Per Million- Parts Per Billion

$$C_{\text{ppm}} = \left(\frac{\text{mass of solute, g}}{\text{mass of solution, g}} \right) \times 10^6 \text{ ppm}$$

$$C_{\text{ppm}} = \frac{\text{mass of solute, mg}}{\text{mass of solution, L}} = \text{ppm}$$

$$C_{\text{ppb}} = \left(\frac{\text{mass of solute, g}}{\text{mass of solution, g}} \right) \times 10^9 \text{ ppb}$$

$$C_{\text{ppb}} = \frac{\text{mass of solute, } \mu\text{g}}{\text{mass of solution, L}} = \text{ppm}$$

For dilute aqueous solutions, the density of solution is equal to the density of water, 1.00 g/mL. Therefore, 1 ppm=1.00 mg/L is accepted.

3. Solution- diluent volume ratio

The composition of a dilute solution is sometimes specified in terms of the volume of a more concentrated solution and the volume of solvent used in diluting it.

1:4 nitric acid solution contains

four volumes of water for each volume of concentrated nitric acid .

4. p-function

Especially for very diluted solutions, instead of using exponential numbers, scientists frequently express the concentration of a species in terms of its **p-function**, or **p-value**.

The p-value is **the negative logarithm (to the base 10) of the molar concentration** of that species.

Thus, for the species X,

$$pX = -\log[X]$$

EXAMPLE : Calculate the p-value for each ion in a solution that is **0.013 M** aqueous KCl and **2.30×10^{-3} M** HCl.

Density and Specific Gravity of Solutions

- **Density** expresses the mass of a substance per unit volume. In SI units, density is expressed in units of **kg/L** or alternatively **g/mL**.
- **Specific gravity** is the ratio of the mass of a substance to the mass of an equal volume of water at a specified temperature (4 °C).(it has no unit)

Density and Specific Gravity of Some Commercially Available Solutions

Reagent	Concentration % (w/w)	Specific gravity
Acetic Acid CH_3COOH	99.7	1.05
Ammonia NH_3	29.0	0.90
Hydrochloric acid HCl	37.2	1.19
Hydrofluoric acid HF	49.5	1.15
Nitric acid HNO_3	70.5	1.42
Perchloric acid HClO_4	71.0	1.67
Phosphoric acid H_3PO_4	86.0	1.71
Sulfuric acid H_2SO_4	96.5	1.84

EXAMPLE : Describe the preparation of **100 mL 0.023 M** HNO_3 from a concentrated solution that has a specific gravity of 1.42 and is 70.5% (w/w) HNO_3 (63 g/mol).

$$V_{\text{conc.}} \times C_{\text{conc.}} = V_{\text{diluted}} \times C_{\text{diluted}}$$

$$L_{\text{conc.}} \times \left(\frac{\text{mol}_{\text{conc.}}}{L_{\text{conc.}}} \right) = L_{\text{dil.}} \times \left(\frac{\text{mol}_{\text{dil.}}}{L_{\text{dil.}}} \right)$$

$$\text{mL}_{\text{conc.}} \times \left(\frac{\text{mmol}_{\text{conc.}}}{\text{mL}_{\text{conc.}}} \right) = \text{mL}_{\text{dil.}} \times \left(\frac{\text{mmol}_{\text{dil.}}}{\text{mL}_{\text{dil.}}} \right)$$

CHEMICAL STOICHIOMETRY

Stoichiometry is the **quantitative relationship** among the amounts of reacting chemical species.

Reactants → Products

An **empirical formula** gives the simplest whole number ratio of atoms in a chemical compound.

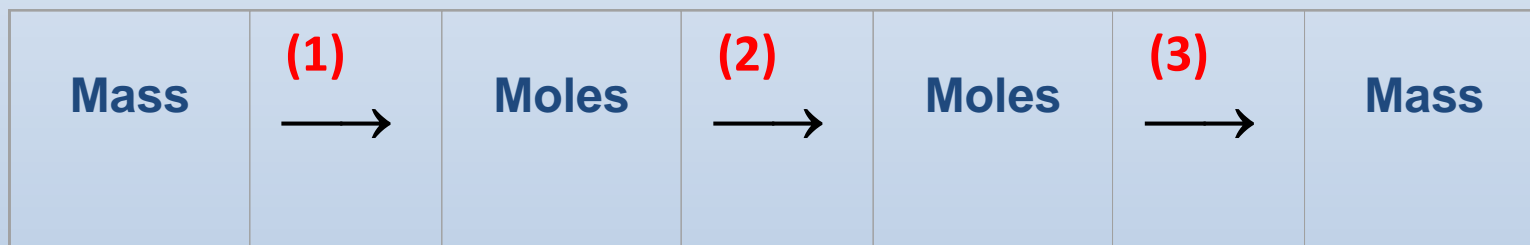
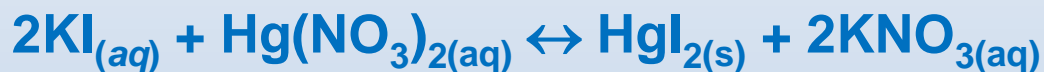
A **molecular formula** specifies the number of atoms in a molecule.

A **structural formula** reveal structural differences between compounds that are not shown in their common molecular formula.

We may calculate **the empirical formula** of a compound from its **percent composition**. To determine **the molecular formula**, we must know **the molar mass** of the compound.

STOICHIOMETRIC CALCULATIONS

A balanced chemical equation gives the combining ratios, or stoichiometry—in units of moles—of reacting substances and their products.



(1) Divide by
molar mass

(2) Multiply by
stoichiometric ratio

(3) Multiply by
molar mass

EXAMPLE : a) What mass of $\text{Pb}(\text{NO}_3)_2$ is needed to convert 2.33 g of Na_2CO_3 to PbCO_3 ? **b)** What mass of PbCO_3 (275.7 g/mol) will be formed?