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 (m*M)= 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:

$$M_{CH_2O} = \frac{1molC}{mol_{CH_2O}} \times \frac{12.0g}{molC} + \frac{2molH}{mol_{CH_2O}} \times \frac{1.0g}{molH} + \frac{1molO}{mol_{CH_2O}} \times \frac{16.0g}{molO}$$

$$M_{CH_2O} = 30.0g / molCH_2O$$

Molar mass of glucose $C_6H_{12}O_6$ is calculated as:

$$M_{C_6H_{12}O_6} = \frac{6molC}{mol_{C_6H_{12}O_6}} \times \frac{12.0g}{molC} + \frac{12molH}{mol_{C_6H_{12}O_6}} \times \frac{1.0g}{molH} + \frac{6molO}{mol_{C_6H_{12}O_6}} \times \frac{16.0g}{molO}$$

$$M_{C_6H_{12}O_6} = 180.0g / molC_2H_{12}O_6$$

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 g/mol)* that are contained in 2.00 g of the pure sodium carbonate.

$$Amount\ of\ Na_2CO_3(mol) = 2.00 g Na_2CO_3 \frac{1 mol Na_2CO_3}{106 g Na_2CO_3} = 0.01887 mol Na_2CO_3$$

$$Amount\ of\ Na_2CO_3(mmol) = 2.00 g Na_2CO_3 \frac{1 mmol Na_2CO_3}{0.106 g Na_2CO_3} = 18.87 mmol Na_2CO_3$$

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) *Cx* 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)

$$C_X = Molar\ concentration = \frac{no.moles\ of\ solute(n_X)}{volume\ in\ liters(V)}$$

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 → 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_{HNO3} *= 1.0 M totally dissolves in aqueous media, we can write:*

$[HNO_3]$ =0.00 M $[H^+]$ = 1.01 M $[NO_3^-]$ = 0.99 M

2. Percent Concentration

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

Weight percent (w/*w*)

=(mass of solute /mass of solution)×%100

Volume percent (*v/v*)

=(volume of solute/volume of solution)×%100

Weight/volume percent (*w/v*)

=(mass of solute,g /volume of solution,mL)×%100

Parts Per Million- Parts Per Billion

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

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

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

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

For dilute aqueous solutions, the density of solution is equalto 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 ^{0}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).

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

$$L_{conc.} \times \left(\frac{mol_{conc.}}{L_{conc.}} \right) = L_{dil.} \times \left(\frac{mol_{dil.}}{L_{dil.}} \right)$$

$$mL_{conc.} \times \left(\frac{mmol_{conc.}}{mL_{conc.}} \right) = mL_{dil.} \times \left(\frac{mmol_{dil.}}{mL_{dil.}} \right)$$

CHEMICAL STOICHIOMETRY

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

Reactants $\rightarrow$ 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.

$$2KI_{(aq)} + Hg(NO_3)_{2(aq)} \leftrightarrow HgI_{2(s)} + 2KNO_{3(aq)}$$

Mass	(1) $\longrightarrow$	Moles	(2) $\longrightarrow$	Moles	(3) $\longrightarrow$	Mass

(1) Divide by molar mass

(2) Multiply by stoichiometric ratio

(3) Multiply by molar mass

EXAMPLE : a) What mass of $Pb(NO_3)_2$ 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?