IV. Molality (m): It is number of moles of solute in kilogram of solvent.
Or no. of millimoles of solute in (g) of solvent.

$$m = \frac{W \times 1000}{M.wt. \times W\ solvent\ kg}$$

In dilute aqueous solution:

$$M = m$$

Weight of solution = Weight of solvent = Volume of solution

Molar Fraction (X):

It's the ratio between numbers of solute moles to number of moles of all solution contains.

$$Mole\ of\ Fraction\ of\ Solute(X) = \frac{no.moles\ of\ (solute)}{no.moles\ of\ (solution)}$$

no. of moles of solution = no. of solute moles + no. of solvent moles

$$Mole\ of\ Fraction\ of\ solvent(X) = \frac{no.moles\ of\ (solvent)}{no.moles\ of\ (solution)}$$

$$X\ solute + X\ solvent = 1$$

Ex.: Calculate the mole fraction of 5.8g acetone solution

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$ with 90g water? A.wt.: C = 12, O = 16, H = 1

$$\textit{Mole of Fraction of Solute}_{\text{Acetone}}(X) = \frac{no.moles\ of\ (solute)}{no.moles\ of\ (solution)}$$

$$\text{Moles (solute)} = \frac{Wt.}{M.wt.}$$

$$= \frac{5.8\ g}{(3\times12)+(1\times16)+(6\times1)=58g/mol}$$

$$\text{Mole}_{(solute)} = 0.1 \text{ mole}$$

$$\text{Mole}_{(solvent)} = \frac{90}{18} = 5 \text{ mole}$$

no.of solution moles = 5.0 +0.1 = 5.1 mole

$$\text{Mole Fraction of Solute} = \frac{no.moles\ of\ (solute)}{no.moles\ of\ (solution)}$$

$$X \text{ solute} = \frac{0.1}{5.1}$$

$$X = 0.0196$$

$$\text{Mole Fraction of Solvent} = \frac{5.0}{5.1}$$

$$X = 0.9804$$

Total Mole Fraction = 0.9804 + 0.0196

= 1.0

Aqueous Solution and Chemical Equilibria

Electrolysis: are solutes which are ionized in solution to produce an electrically conducting medium. There are two types of electrolytes.

Strong electrolytes: the compounds which are completely ionized or dissociate in solution.

$$HCl \longrightarrow H^{+} + Cl^{-}$$

Example of Strong electrolytes

1. Many inorganic acids: Hydrochloric acid HCl, nitric acid HNO_3, perchloric acid $HClO_4$, sulfuric acid H_2SO_4.
2. Alkali and alkaline-earth hydroxides: Sodium hydroxide NaOH , Potassium hydroxide KOH , Calcium hydroxide $Ca(OH)_2$, Barium hydroxide $Ba(OH)_2$.

$$Ba(OH)_2 \rightarrow Ba^{+2} + 2OH^{-}$$

3. Most salts:
 Sodium chloride NaCl, Sodium fluoride NaF , Potassium fluoride KF Sodium nitrate $NaNO_3$

$$NaCl \rightarrow Na^{+} + Cl^{-}$$
$$NaNO_3 \rightarrow Na^{+} + NO_3^{-}$$

Weak electrolytes: the compounds which are partially ionized or dissociate in solution to produce an electrically conducting medium.

$$CH_3COOH \rightleftharpoons CH_3COO^{-} + H^{+}$$

The dissociation of weak electrolyte undergoes in to two directions.

$$NH_4OH \rightleftharpoons NH_4^{+} + OH^{-}$$

Example of Weak electrolytes

1. Some inorganic acid: Carbonic acid H_2CO_3, Boric acid H_3BO_3, Phosphoric acid H_3PO_4, Hydrogen sulfide H_2S

$$H_2CO_3 \rightleftharpoons 2H^{+} + CO_3^{-2}$$
$$H_3PO_4 \rightleftharpoons 3H^{+} + PO_4^{-3}$$

2. Most organic acid :(Acetic acid CH_3COOH), Formic acid $HCOOH$).

$$HCOOH \rightleftharpoons HCOO^- + H^+$$

3. Many organic bases and ammonia, $H_2N\text{-}CH_2\text{-}CH_2\text{-}NH_2$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

4. Halides (chloride Cl^-, bromide Br^-, fluoride F^-, iodide I^-) , Cyanides (CN^-) and thiocyanate (SCN^-) of Hg , Zn and Cd.

$$ZnCl_2 \rightleftharpoons Zn^{+2} + 2Cl^-$$

$$HgCl_2 \rightleftharpoons Hg^{+2} + 2Cl^-$$

Conjugate Acids and Bases

$Acid_1 \rightleftharpoons Base_1 + H^+$ (Conjugate base of the parent acid)

$Base_2 + H^+ \rightleftharpoons Acid_2$ (Conjugate acid of the parent base)

The result in an acid /base or neutralization reaction:

$$Acid_1 + Base_2 \rightleftharpoons Base_1 + Acid_2$$

e.g.

A conjugate acid: is formed when a base accepts a proton H^+.

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

NH_4^+ is a conjugate acid of ammonia

A conjugate base: is formed when an acid loss a proton H^+.

e.g.

$$H_3O^+ \rightleftharpoons H_2O^+ H^+$$

H_2O is a conjugate base of H_3O^+

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

CH_3COO^- is a conjugate base of acetic acid

Neutralization Reaction:

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

$$HCl \longrightarrow H^+ + Cl^-$$

$$NaOH \longrightarrow Na^+ + OH^-$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Conjugated of NH_3 Conjugated base of H_2O

NH_3 , NH_4^+ are conjugate pair.

Amphiprotic compounds: -These compounds act as an acid in the presence of base and as base in the presence of an acid

$$CH_3OH + NH_3 \rightleftharpoons CH_3O^- + NH_4^+$$

$$CH_3OH + HNO_3 \rightleftharpoons CH_3OH_2^+ + NO_3^-$$

Amphiprotic Solvents :- Solvents act as an acid in the presence of base and as base in the presence of an acid.

$$H_2O + H^+ \rightleftharpoons H_3O^+$$

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

Acid Base Theories

1. *Arrhenius theory* (The theory of H^+ and OH^-)

Acid **:** is any compound which ionize (partially or completely) to give H^+

$$HCl \longrightarrow H^+ + Cl^-$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Base **:-** is any compound which ionize (partially or completely) to give OH-

$$NaOH \longrightarrow Na^+ + OH^-$$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

The disadvantage of Arrhenius theory

This theory applicable for aqueous media only and not applicable for organic media.

2. *Bronshted – Lowry Theory* (The theory of give and accept H^+)

Acid : is any compound which ionize (partially or completely) to give proton (H^+)

$$HCl \longrightarrow H^+ + Cl^-$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Base : is any compound which accept H^+

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$H_2O + H^+ \rightleftharpoons H_3O^+$$

Disadvantage / Advantage

The theory is applicable for aqueous and organic solvent. But isn't applicable for non-ionized solvent dioxane, hexane, CCl_4 carbon tetra chloride.

3. *Lewis Theory* (The theory of give and accept electron pair)

Acid : any compound which accept electron pair.
Base : any compound which give electron pair .

$$\underset{Base}{H_2O} + \underset{Acid}{H^+} \longrightarrow H_3O^+$$

$$\underset{Base}{NH_3} + \underset{Acid}{H_3O^+} \rightleftharpoons NH_4^+$$

$$\underset{Acid}{ALCl_3} + \underset{Base}{OR_2} \longrightarrow R_2OALCl_3$$

(Aluminum chloride) ether R-O-R

Lewis Theory give an explanation for organic compound and the effect of solvent.

Chemical Equilibrium

Many reactions used in analytical Chemistry never result in complete conversion of reactants to products.

Instead, they proceed to a state of chemical equilibrium that describe the concentrations of reactants existing among reactants product is constant.

Equilibrium constant expressions are algebraic equation that describe the concentration relationships existing among reactants and products at equilibrium.

Equilibrium- Constant Expressions:

A generalized equation for a chemical equilibrium is:

$$aA + bB \rightleftharpoons cC + dD$$

where the capital letters represent the formulas of participating chemical species and the lower case are the small whole numbers required to balance the equation.

a,b,c,d = mole of A,B,C,D.

The equilibrium –constant expression of the above reaction is :

$$K_{eq.} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Ex. 1. :

$$S_2O8 + 3I^- \rightleftharpoons 2SO_4^{-2} + I_3^-$$

H.W

Ex.2

Calculate the concentration of each of A,B of equilibrium state of 0.1 M AB solution (AB: weak electrolyte). $K_{eq} = 3\times10^{-6}$.

Solubility Product Constant

Solubility: is the amount of solute can be dissolved in a volume of solvent.

When one substance (solute) dissolves in any solvent, it is said to be ***soluble***. When one substance does not dissolve in another it is said to be ***insoluble***. Solubility depends on type of solvent, temperature and acidity (pH) of media.

The solubility can be determined by solubility product constant (K_{SP}).

In saturated solution of A_xB_y salt.

$$A_xB_y \rightleftharpoons xA^+ + yB^-$$

$$K = \frac{[A^+]^x[B^-]^y}{[A_x B_y]}$$ at equilibrium state

$\because$ Conc. of solid compound is constant

$\therefore K = [A^+]^x [B^-]^y$

For $AgCl_{(s)} \rightleftharpoons Ag^+ + Cl^-$

$\therefore Ksp = [Ag^+] [Cl^-]$

For $CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$

$\therefore Ksp = [Ca^{+2}] [F^-]^2$