Solutions / Surface chemistry.

Definition:-

1 "A solution is a homogeneous mixture of two or more substances existing in one or more states".

(Sana Ullah) Physical chemistry

2 "Solution is a homogeneous mixture of two or more chemically non-reacting substances whose components can be varied within certain limits" (B.S Bhal, Arun Bhal)

3 "A solution, on average, is a homogeneous mixture of two or more kinds of diff molecules or ionic substances". (F.Sc 1st year)

4 "A solution is a homogeneous mixture of two or more substances on molecular level" (Pearson guide)

Note:-

Solution of sugar in H_2O is Binary Solution

Binary solution :-

The solution which consist of two components

Note :-

Solvent has the same physical state as that of solution

Solute :- The substance which is present in Small quantity in a solution.

Solvent :- The substance which is present in large quantity in solution

concentration of solution :-

The amount of solute dissolved in a unit volume of solution (or a unit volume of solvent) is termed as the concentration ~~of~~ the solution

concentration units of solution.

1- %age of solution
2- Molarity
3- Molality
4- Normality
5- Mole Fraction
6- Parts per million

→ **%age of solution.**

The %age of solution can be
(a) weight / weight ⓑ weight / volume
ⓒ volume / weight ⓓ volume / volume.

m / m → **NOT temp dependent.**

$\left.\begin{matrix} v/m \\ m/V \\ v/V \end{matrix}\right]$ **Temperature dependent**

→ **Molarity :- (M)**

$$(M) = \frac{\text{Number of moles of solute}}{\text{Volume of solution } (dm^3)}$$

Temperature dependent.

units :- mol litre^{-1}

$$M \propto \frac{1}{T}$$

→ **Molality (m)**

$$(m) = \frac{\text{Number of moles of Solute}}{\text{Mass of solvent in Kg.}}$$

NOT temperature dependent

Note :-

In % age solution & in molar solutions we take concentration in terms of Amount of solute with respect to solution while in **molal solutions** we take conc as amount of solute with respect to solvent

Note

→ Moblity is indirect expression of moles of the solutes to the moles of solvent

→ Molal solutions are dilute as compared to molar

Normality :- (N)

$$(N) = \frac{\text{Equivalents of solute}}{\text{Volume of solution in litres}}$$

Temperature dependent.

Equivalent weight for Acid.

$$\frac{\text{Molar Mass Of Acid}}{\text{No of replacable } H^{\oplus}}$$

e.g **H_2SO_4**

$$\frac{98}{2}$$

Equivalent wt = 49

Equivalent weight for base

$$\frac{\text{Molo. Mass of base}}{\text{No of replacable } OH^{\ominus}}$$

e.g. NaOH

$$\frac{40}{1}$$

equivalent wt = 40

For species:-

$$\frac{\text{Mola. mass}}{\text{charge}}$$

e.g. Al^{+3}

$$\frac{27}{3} = 9$$

Mole Fraction:- (X)

→ This conc unit is for all type of solutions, i.e.. gas/gas, liq/liq, solid/liq etc.

→ It is also applicable to solution having more than two components.

$$X = \frac{\text{no of moles of component in mixture}}{\text{Total no of moles of all components}}$$

e.g. component A

$$X_A = \frac{n_A}{n_A + n_B + n_C}$$

→ Mole fraction of a component in a mixture is always **less than unity**.

→ Sum of mole fraction of all components is **equal to unity**

No units

Mole percent

Mole fraction $\leftarrow X \times 100 = 100\%$.

Parts per million (ppm)

$$ppm = \frac{\text{no of parts (w or V) of solute}}{\text{million parts (w or V) of solution}}$$

→ This is for very low conc. of solution **(to express impurity)**

$$ppm = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Ideal Solution	Non-ideal solution
→ obey Raoult's law	→ $\Delta H(mix) \neq 0$ → $\Delta V(mix) \neq 0$
→ $\Delta H(mix) = 0$	→ Don't obey Raoult's law
→ $\Delta V(mix) = 0$	
→ No association & dissociation take place.	→ Association & dissociation take place
→ NO chemical Rx b/w solute & solvent	
→ It does not form Azeotrope.	→ It form Azeotrope

→ Here,

$(V.P)_{obs} = (V.P)_{exp}$

$(B.P)_{obs} = (B.P)_{exp}$

$P_A = P^\circ_A x_A$

$P_B = P^\circ_B x_B$

$P_T = P_A + P_B$

e.g

Benzene + toulene

Hexane + Heptane

Ethyl bromide + Ethyl Iodide

chlorobenzene + bromobenzene

all dilute solutions

$CCl_4 + SiCl_4$

Ethylene dichloride + Ethylene dibromide

→ ideal solutions obey equation of osmotic pressure $\pi V = nRT$

Non-ideal Solutions (Azeotropic Mixtures)

V P - composition curve straight line

zeotropic Mixtures· such liquid mixtures which distill with a change in composition

Example:- Methyl alcohol - water.

Seperation:-

Seperation by distillation

Azeotropic mixtures:-

Such mixtures which boil at constant temperature and distil over without change in composition at any temperature like a pure chemical compound.

Types of non-ideal solutions

ⓐ Non-ideal soln showing +ve deviation

ⓑ " " " -ve deviation

" " Showing +ve deviation·

ⓐ

→ when vp > than expected according to Raoult's law

→ It occur when new interactions are weaker than in the pure.

→ $\Delta H = +ve$ $\Delta V = +ve$

→ It form minimum B.P Azeotropes

Examples

C_2H_5OH + cyclohexane

Acelone + CS_2

Acetone + C_6H_6

Acetone + C_2H_5OH

CCl_4 + Chlorform or Toulene

$CH_3OH + H_2O$

$H_2O + C_2H_5OH$

→ Here,

$(V \cdot P)_{obs} > (V \cdot P)_{exp}$

$(B \cdot P)_{obs} < (B \cdot P)_{exp}$

$P_A > P^o_A \cdot X_A$

$P_B > P_B^o \cdot X_B$

$P_T > P^o_A X_A + P^o_B X_B$

→ **ΔS** is more while **ΔG** has less -ve value

(b) Non-ideal solution showing Negative deviations.

→ It is seen when total vp for any mole fraction is < than that expected from Raoult's law

→ when new interactions are stronger than interactions in the pure components

It forms **Maximum B·P Azeotrope.**

Examples.

$CHCl_3 + CH_3COCH_3$

chloroform + benzene

Acetone + Aniline

$HNO_3 + H_2O$

Acetic Acid + Pydridine

$\Delta H = -ve$ $\Delta V = -ve$

Does not obey Raoult's law.

Here,

$(V.P)_{obs} < (V.P)_{exp}$

$(B \cdot P)_{obs} > (B \cdot P)_{exp.}$

$P_A < P^\circ_A X_A$

$P_B < P^\circ_B X_B$

$P_T < P_A X_A + P^\circ_B X_B$

→ ΔS has less value while ΔG has more -ve values

Types of Azeotropic Mixtures

ⓐ Azeotropic mixture with maximum B.P

ⓑ " " " minimum BP

Azeotropic Mixture with maxinum B·P

formed by that composition of non-ideal solution showing (-ve) deviation for which vp is minimum.

Example·

$HNO_3 (68\%) + H_2O (32\%)$

boils at 393.5 K

Azeotropic mixture with minimum B·P

formed by that composition of a non-ideal solution showing positive deviation for which the

Vp is maximum.

Example.

C_2H_5OH (95.5%) + H_2O (4.5%)
boils at 351.5K

Note:-

Azeotropic Mixtures have same B.P.

Raoult's Law

Definitions from book
1st yr (pg # 260)

Expressions

$$\Delta P = P^o \chi_2$$

$$\frac{\Delta P}{P^o} = \chi_2$$

$\frac{\Delta P}{P^o}$ = relative lowering of Vp
$\downarrow$

- → is independent of temp.
- → depends upon conc of solute
- → is constant when equimolar proportions of diff solutes are dissolved in same mass of same solvent

Raoult's law for volatile solutes.

$P = (P^o_B - P^o_A) X_B + P^o_A$

composition of the vapour.

Mole fraction in vapour phase is high for voltalile component.

Dalton's law can be applied to study v p & Mole fraction

$$X_A = \frac{P_A}{P_T} = \frac{P^o_A X_A}{P^o_A X_A + P^o_B X_B}$$

Raoult's Law as special case of Henry's Law.

According to Raoult's Law vp can be study in term's of Henry's Law

$P \propto X$

$P = K_H X$

K_H → Henry constant

Raoult's Law for non-volatile solutes.

$$\frac{p^0 - p_s}{p^0} = \frac{n_2}{n_1 + n_2} = X_2$$

X_2 = mole fraction of solute
n_1 = moles of solvent
n_2 = moles of solute
P_s = v.p of solution
p^0 = v.p of pure solvent.

Colligative Properties:-

colligative properties are properties of a soln which depend only on the no of particles like ions or molecules of solute in a definite amount of solvent

→ They do not depend upon nature of solute

→ They are mainly for dilute solutions (ideal)

→ non-volatile solute

→ No Association or dissociation

→ These are properties of solutions and not of pure substances

colligative properties $\propto$ No of species

$\propto \frac{1}{M}$ **(Molar mass)**

→ Relative lowering of v p

→ osmotic pressure

→ Elevation in B.P

→ Depression in F.P

⇒ **Relative lowering of v.p**

It is measured by

Ostwald and walker's Method

(gas saturation method) (Dynamic Method)

$$\frac{p^0 - p}{p^0} = \text{mole fraction of solute} = \frac{W_2}{W_1 + W_2}$$

$$\frac{\Delta P}{P^0} = \frac{n_2}{n_1 + n_2}$$

$$\frac{\Delta P}{P^0} = \frac{n_2}{n_1} \qquad n_1 = \frac{W_1}{M_1} \quad n_2 = \frac{W_2}{M_2}$$

$$\frac{\Delta P}{P^0} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\frac{\Delta P}{P^0} = \frac{W_2}{M_2} \times \frac{W_1}{M_1}$$

$$M_2 = \frac{P^0}{\Delta P} \times \frac{W_2 M_1}{W_1}$$

⇒ Elevation in B.P

"It is the temp of a liq at which its v.p equal to the atm pressure".

It is also termed as **Ebullioscopy**.

Measurement:-

. It is measured by

→ **Land's berger's Method**

→ **Koltrell's Method**

$\Delta T_b \propto m$ (molality)

$\Delta T_b = K_b\, m$

$\downarrow$ molal elevation constant / ebullioscopic constant

$$K_b = \frac{RT_0^2}{1000 l_v} = \frac{M_A \cdot RT_0^2}{\Delta H_{vap} \times 1000}$$

units of K_b

K kg mol^{-1}

R = gas constant M_A = Molecular mass of Solvent

T_0 = Normal B.P

l_v = latent heat of vaporization per gram of solvent

Kb of Some common Solvents

Solvents	value of Kb in K kg mol⁻¹
water	0.52
CH_3OH	0.80
Acetone	1.72
C_6H_6	2.53
CCl_4	5.03
$CHCl_3$	3.63
C_2H_5OH	1.20
ethy ether	2.11

Determination of Molecular weight from Kb

$$M = \frac{K_b \times w \times 1000}{\Delta T_b \times W}$$

⟹ Freezing point and Depression in Freezing point

"The temp at which the v.p of solvent in its liquid and solid phase becomes the same"

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f \times m = \frac{K_f \times w \times 1000}{M \times W}$$

K_f

molal depression constant or molal **cryoscopic** constant

"It is equal to depression in F.P caused by one molal Solution"

$$K_f = \frac{R T_0^2}{1000\, l_f} = \frac{M_A R T_0^2}{\Delta H_f \times 1000}$$

Units:-

K Kg mol^{-1}

R = gas constant

T_0 = normal F.P

l_f - heat of fusion

K_f - freezing constant

K_f Of some common solvents

Solvent	**K_f**	**Solvent**	**K_f**
H_2O	1.86	Naphthalene	6.90
Acetic acid	3 90	Bromoform	14.40
Phenol	7.27	Cyclohexane	20
C_6H_6	5.12	camphor	37 70

Determination of Molecular weight by Depression in F.P

$$M = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

Measurement

→ The Beckmann Method

→ The Rast Method.

⇒ Osmosis & Osmotic pressure.

Osmosis :- The spontaneous flow of solvent through semi-permeable membrane from pure solvent to soln or from dil soln to concentrated soln.

Natural semi-permeable membrane.

→ Pig's bladder

→ Skin round white of egg

→ Membrane round red blood corpuscles

→ cell of plant

→ Fish bladder

→ cellophane

cupric ferrocyanide $Cu_2[Fe(CN)_6]$ is an Artifically prepared semi-permeable membrane.

→ It is not suitable for **non-aqueous solution**

$Co_3(PO_4)_2$ Another Artifical semi-permeable membrane.

Osmotic pressure (π)

The hydrostatic pressure developed on soln which just prevents the Osmosis of pure solvent into soln through semi-permeable membrane.

Or

The minimum external pressure applied to soln to just stop the process of osmosis

Or

The minimum external P applied on soln to make its vp equal to that of solvent.

Measurement

→ Pfeffer's method.

→ Berkeley & Hartley's method (most common)
→ Morse & Frozer's "
→ Townsend's (-ve) pressure method
→ De vries method.

Isotonic solutions.

Solutions having same Osmotic pressure

e.g. 0.9% NaCl soln is isotonic to human RBC's

Hypotonic solution.

Solutions having lower Osmotic pressure

Hypertonic solution

Solutions having higher Osmotic pressure

Vant Hoff Theory of dilute Solutions.

Dilute solutions behave like gases and gas laws can be applied to them

Boyle's - Vant Hoff Law

Osmotic pressure of a soln is directly proportional to its conc at given temp

$$\pi \propto C \propto \frac{1}{V}$$

Charle's -vant Hoff Law

Osmotic pressure of soln is $\propto$ to its temp at fixed conc

$$\pi \propto T$$

vant Hoff equation for Solutions:-

$$\pi \propto CT \quad \therefore \pi = SCT$$

S = Solution constant   C = Molar conc

T = Absolute Temp π = Osmotic pressure

Avogadro-vant Hoff law

Equal volumes of solution having the same π and T contain equal no of moles i.e have same concentration

Relation b/w π and Lowering of vp.

Relative lowering of v p is $\propto$ to π

$$\frac{p^\circ - p}{p^\circ} = \frac{\pi \times M}{dRT} \quad \therefore \frac{p^\circ - p}{p^\circ} \propto \pi \left(\text{since } \frac{M}{dRT} \text{ constant}\right)$$

Osmolarity:-

Osmotic behaviour of solutes undergoing association or dissociation is equal to molarity × no of particles produced per formula unit of solute is known as Osmolarity.

Reverse Osmosis:-

When external P applied on soln is more than π, the solvent flows from soln to pure solvent

e.g

Desalination of sea H_2O is done by reverse Osmosis.

Plamolysis

The flow of fluid from plant cell when placed in hypertonic soln

plant cell undergoes shrinkage

EXO-OSMOSIS

Outword Osmotic flow of fluid from cell through semipermeable membrane e.g. grape in conc NaCl soln

Endo-osmosis

Inword Osmotic flow of fluid from cell through semipermeable membranes e.g grape in H_2O

KONOWALOFF'S Rule:-

The mole fraction of more volatile component is always greater in vapour phase than in solution phase

Relation b/w total pressure and mole fraction of volatile components in liquid phase

$$P = P^{\circ}_{A} x_{A} + P^{\circ}_{B} x_{B}$$

" " ''' ' ' '

in vapour phase.

$$\frac{1}{P} = \frac{y_A}{P^{\circ}_{A}} + \frac{y_B}{P^{\circ}_{B}}$$

Relation b/w Osmotic pressure & colligative properties

$$\pi = \left(\frac{P_A^0 - P_A}{P_A^0}\right) \times \frac{dRT}{M_B}$$ Relative lowering of VP

$$\pi = \Delta T_b \times \frac{dRT}{1000 K_b}$$ Elevation in B P

$$\pi = \Delta T_f \times \frac{dRT}{1000 K_f}$$ Depression in F P

Abnormal Molecular mass & colligative properties

When solutes undergo association or dissociation in soln, there is decrease or increase in no of particles and there are discrepencies b/w observed and calculated values of colligative properties As,

colligative property $\propto \frac{1}{\text{M.mass}}$, hence high values are obtained in case of association **Example:-** Acetic Acid in C_6H_6

Van't Hoff factor (i)

Its values obtained by any of following expression

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{\text{Observed value of colligative property}}{\text{calculated " " "}}$$

$$i = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before " " "}}$$

Degree of dissociation

Fraction of total no of molecules undergoing dissociation,

$$\alpha = \frac{i-1}{m-1}$$

Degree of Association

Fraction of total no of molecules undergoing association.

$$\alpha = \frac{i-1}{\frac{1}{m}-1}$$

Relation b/w Relative lowering of v_p & 'm'

$$\frac{p^\circ - p}{p^\circ} = \frac{m \times M_1}{1000}$$

$\underset{\text{(Molality)}}{\downarrow}$

Relation b/w wt of two immiscible liquids

$$\frac{W_A}{W_B} = \frac{P_A \times M_A}{P_B + P_B}$$

where, W = weight of liq

P = Partial pressure

M = Molecular wt

conjugate solutions.-

when 2 partially miscible liquids A & B are mixed with each other, 2 layers are formed. First, solution of A in B and second B in A. Such solutions co-existing together are called conjugate solns.

phenol and H2O.

Critical solution Temp/upper consulate Temp

On heating the conjugate soln the mutual solubility of A & B ↑ A temp is reached when two phases disappear & one homogeneous phase is left. This solution is known as critical " ""

upper consulate Temp.

water - phenol system.

Lower consolute Temp.

In some cases, it is also possible to have a lower temp of similar kind. For e.g

Trimethylamine - H2O

Type of Solutions.

There r 9 possible type of solns.

Solutions of gases in gases

→ **complete Miscibility:-** According to KMT, a gas consist of tiny molecules moving about in vacant space & thus when one gas in dissolved in another gas they form "**homogeneous Solutions**"

→ Such solutions strictly holds **Dalton's Law of partial pressure.**

Note:- Dalton's Law holds strictly one when the partial pressures are not too high.

Henry's Law:-

The solubility of gas in solvent depends on T & P

gas ⇌ gas in soln.

Statement

"For a gas in contact with a solvent at constant "T", concentration of gas that dissolves in solvent ∝ to P of gas."

Mathematical form

$$C \propto P$$

$$C = KP \quad K = \text{Henry constant}$$

Dependence of K - Nature of gas, solvent & units of P & C.

Limitations of Henry's Law.

① at moderate T & P

② solubility of gas in solvent is low.

③ gas do not associate or dissociate in solvent.

④ gas don't react to form new species

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

Solutions of Liquids in Liquids

Completely miscible	Partially miscible	Practically immiscible
e.g Alcohol & H_2O	Phenol $-H_2O$	e.g H_2O & C_6H_6
	Nictonie $-H_2O$	H_2O & CS_2
	Trimethylamine $-H_2O$	
	ether $-H_2O$	

Seperation

Fractional distillation

System	critical soln Temp	%age of 1st component given in bracket
Methanol - cyclohexane	49°C	29
Hexane - Aniline	59.6°C	52
CS_2 - methanol	49.5°C	80
Dimethylamine - H_2O	43°C	13
1-methylpiperdine - H_2O	48°C	5

Solutions of Solids in liquids

Solubility principle

Like dissolve like

Recrystallization /precipitation

The process by which solute particles from soln are redeposited or recrystallized is called recrystallization or precipitation

Soln in contact with solid solute 2 opposing processes operate

Dissolution the particles of solute leaving solid & passing into soln.

Recrystallization the particles of solute returning from soln & depositing (or precipitating) on solid.

Saturated soln· soln which is in equilibirium with the excess of solid at particular temp

Solubility

concentration of solute in soln when it is in equilibirium with Solid substance at particular temp.

Solubility curves & Types

From F.Sc book Pg # 265, 266

Solids in Solids

Solution of Solid in another solid can be prepared by melting them together & cooling of mixture

examples

gold and silver
Naphthalene & β-Naphtol

Examples of Solutions

Gas in gas

Air, Scuba diver tank, Natural gas, oxygen acetylene mixture used in welding, Mixture of gases

Gas in liquid (Foam)

Humidity, O_2 in H_2O, CO_2 in H_2O (seltzer H_2O) Aerated drinks/H_2O, Froth, Whipped cream, carbonated H_2O Shaving cream, water in rivers & lakes containing oxygen

Gas in solid (solid foam)

H_2 adsorbed by Pd, Pt, Ni etc, Marshmallow, Air bubbles in ice cubes, gas stove lighter

Liquid in gas (Aerosol)

Mist, fog, clouds, liquid air pollutants, moist air, H_2O in O_2, moisture loaded air, gasoline-Air mixture Chloroform mixed with N_2

Liquid in Liquid (emulsion)

Milk, Mayonnaise, C_2H_5OH in H_2O, Antifreeze in H_2O, gasoline, vinegar, benzene in toluene

Liquid in solid (Solid emulsion)/gel

Butter, cheese, Hg in silver Gelatin, Amalgams, Mineral oil in paraffin, Hg in Na, Tooth fillings

Solid in liquid (Sol)

Tea, Salt water/sea H_2O,
Sugar in H_2O, Jellies, paints
Syrup, I_2 in CCl_4,
amalgum, Aqueous NaCl

Solid in gas (Aerosol)

Dust particles in smoke
Butane lighter, I_2 vapours in Air,
Naphthalene sublimed in air,
mothballs, Camphor in N_2
gas

Solid in solid (Solid sol)

Metal alloys pearls, Opals,
C in iron (steel), Ruby glass
Cranberry glass, stones,
Gold - Silver mixture, mixture
of alums, Bronze (Tin in Cu),
Cu dissolved in gold, sterling silver
(Cu in Ag)
Brass