

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 (b) weight / volume
(c) volume / weight (d) volume / volume.

m/m → NOT temp dependent.

v/m

m/v

v/v

} Temperature dependent

→ Molarity :- (M)

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

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 **molar solutions** we take
conc as amount of solute with
respect to **solvent**

Note

- Molarity is indirect expression of moles of the solutes to the moles of solvent.
- Molar 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.

Molar Mass of Acid

No of replaceable H^+

e.g. H_2SO_4

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

Equivalent wt = 49

Equivalent weight for base

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

eg NaOH

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

equivalent wt = 40

For species:-

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

eg 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.

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

eg 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

$$\text{Mole fraction} \times 100 = 100\%$$

Parts per million (ppm)

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

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

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

Ideal Solution

- obey Raoult's law
- $\Delta H(\text{mix}) = 0$
- $\Delta V(\text{mix}) = 0$
- No association & dissociation take place.
- NO chemical Rx b/w solute & solvent
- It does not form Azeotrope.

Here,

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

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

$$P_A = P_A^\circ \times X_A$$

$$P_B = P_B^\circ \times X_B$$

$$P_T = P_A + P_B$$

e.g

Benzene + toluene

Hexane + Heptane

Ethyl bromide + Ethyl Iodide

chlorobenzene + bromobenzene

all dilute solutions

$\text{CCl}_4 + \text{SiCl}_4$

Ethylene dichloride + Ethylene dibromide

Non-ideal solution

$$\rightarrow \Delta H(\text{mix}) \neq 0$$

$$\rightarrow \Delta V(\text{mix}) \neq 0$$

→ Don't obey Raoult's law

→ Association & dissociation

take place

→ It form Azeotrope.

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

Non-ideal solutions (Azeotropic mixtures)

zeotropic mixtures. Such liquid mixtures which distill with a change in composition

Example:- Methyl alcohol - water.

separation:-

separation 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

- (a) Non-ideal soln showing +ve deviation
- (b) " " " -ve deviation
- (c) " " showing +ve deviation

→ when $v_p >$ than expected according to Raoult's law.

→ It occurs 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

Acetone + CS_2

Acetone + C_6H_6

Acetone + C_2H_5OH

CCl_4 + Chloroform or Toluene

CH_3OH + H_2O

H_2O + C_2H_5OH

→ Here,

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

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

$$P_A > P_A^{\circ} \cdot X_A$$

$$P_B > P_B^{\circ} \cdot X_B$$

$$P_T > P_A^{\circ} X_A + P_B^{\circ} X_B$$

→ ΔS is more while ΔG has less -ve value

(b) Non-ideal solution showing Negative deviations.

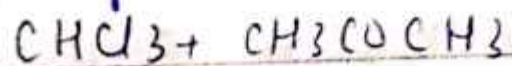
→ It is seen when total v_p for any mole fraction is $<$ than that expected from Raoult's law

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

It forms **Maximum B.P**

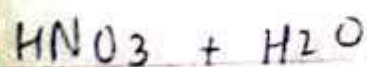
Azeotrope.

Examples.



chloroform + benzene

Acetone + Aniline



Acetic Acid + Pyridine

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

Does not obey Raoult's law.

Here,

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

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

$$P_A < P_A^\circ \cdot X_A$$

$$P_B < P_B^\circ \cdot X_B$$

$$P_T < P_A \cdot X_A + P_B^\circ \cdot X_B$$

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

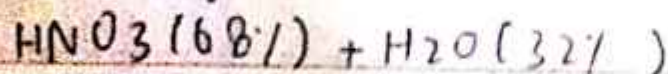
Types of Azeotropic Mixtures

- (a) Azeotropic mixture with maximum B.P
- (b) " " " minimum B.P

Azeotropic mixture with maximum B.P

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

Example:



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

V_p is maximum.

Example.

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

Note :-

Azeotropic mixtures
have same B.P.

Raoult's Law

Definitions from book

1st yr (pg # 260)

Expressions

$$\Delta P = P^0 \chi_2$$

$$\frac{\Delta P}{P^0} = \chi_2$$

$\frac{\Delta P}{P^0}$ = relative lowering of V_p

- \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.

$$P = (P_B^0 - P_A^0) X_B + P_A^0$$

composition of the vapour.

Mole fraction in vapour phase is high for volatile component.

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

$$X_n = \frac{P_A}{P_T} = \frac{P_A^0 X_n}{P_A^0 X_n + P_B^0 X_B}$$

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

According to Raoult's Law v.p can be study in term's of Henry's Law

$$P \propto X$$

$$P = K_H X$$

$K_H \rightarrow$ 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)

$$\frac{p^0 - p}{p^0} = \text{mole fraction of solute} = \frac{w_2}{w_1 + w_2}$$

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

$$\frac{\Delta p}{p^0} = \frac{n_2}{n_1} \quad n_1 = \frac{w_1}{M_1} \quad n_2 = \frac{w_2}{M_2}$$

$$\frac{\Delta p}{p^0} = \frac{\frac{w_2}{M_2}}{\frac{w_1}{M_1}}$$

$$\frac{\Delta p}{p^0} = \frac{w_2}{M_2} \times \frac{M_1}{w_1}$$

$$M_2 = \frac{p^0}{\Delta p} \times \frac{w_2 M_1}{w_1}$$

⇒ 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

$$\Delta T_b \propto m \text{ (molality)}$$

$$\Delta T_b = K_b m$$

K_b ↓ molal elevation constant /
ebullioscopic constant

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

units of K_b

$$K \text{ kg mol}^{-1}$$

R = gas constant

MA = molecular mass of solvent

T_0 = Normal B.P

l_v = latent heat of vaporization per gram of solvent

K_b of some common Solvents

Solvents	Value of K_b in $K \text{ kg mol}^{-1}$
Water	0.52
CH_3OH	0.80
Acetone	1.72
C_6H_6	2.53
CCl_4	5.03
CHCl_3	3.63
$\text{C}_2\text{H}_5\text{OH}$	1.20
ethyl ether	2.11

Determination of Molecular weight from K_b

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

⇒ 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

molar depression constant or
molar cryoscopic constant
"It is equal to depression
in F.P caused by one molar
solution"

$$K_f = \frac{RT_0^2}{1000 \lambda_f} = \frac{M_1 R T_0^2}{\Delta H_f \times 1000}$$

Units:-

$$K \text{ Kg mol}^{-1}$$

R = gas constant

T_0 = normal F.P

λ_f = heat of fusion

K_f = freezing constant

K_f of some common solvents

Solvent	K_f	Solvent	K_f
H ₂ O	1.86	Naphthalene	6.90
Acetic acid	3.90	Bromoforn	14.40
Phenol	7.27	Cyclohexane	20
C ₆ H 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 $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ is an artificially prepared semi-permeable membrane.

→ It is not suitable for non-aqueous solution
 $\text{CO}_3(\text{PO}_4)_2$ Another Artificial 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 v_p 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

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

Charles's - vant Hoff Law

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

$$\pi \propto T$$

vant Hoff equation for

Solutions- $\pi \propto CT \therefore \pi = SCT$

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 molecules have

same concentration

Relation b/w π and Lowering of v_p .

Relative lowering of vapour pressure
 $\propto \pi$

$$\frac{p^0 - p}{p^0} = \frac{\pi \times M}{dRT} \quad \therefore \frac{p^0 - p}{p^0} \times \pi \quad (\text{since } \frac{M}{dRT} \text{ const. ant})$$

Osmolarity:-

Osmotic behaviour of solutes undergoing association or dissociation is equal to molarity \times 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 H₂O is done by reverse osmosis.

Plasmolysis

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

plant cell undergoes shrinkage

Relation b/w Osmotic pressure & colligative properties

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

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

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

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 discrepancies b/w observed and calculated values of colligative properties. As,

colligative property $\propto \frac{1}{M}$, 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 = observed value of colligative property
calculated " " " " " "

i = No. of particles after association or dissociation
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.

$$\alpha = \frac{2 - i}{\frac{1}{m} - 1}$$

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

$$\frac{p^0 - p}{p^0} = \frac{m \times M}{1000} \quad \text{(Molarity)}$$

Relation b/w wt of two immiscible liquids

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

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 consolute 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 consolute 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 is 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 \rightleftharpoons gas in soln.

Statement

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

Mathematical form

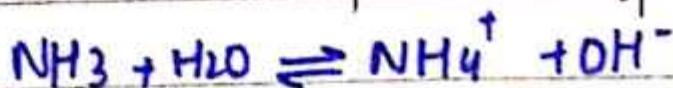
$$C \propto P$$

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

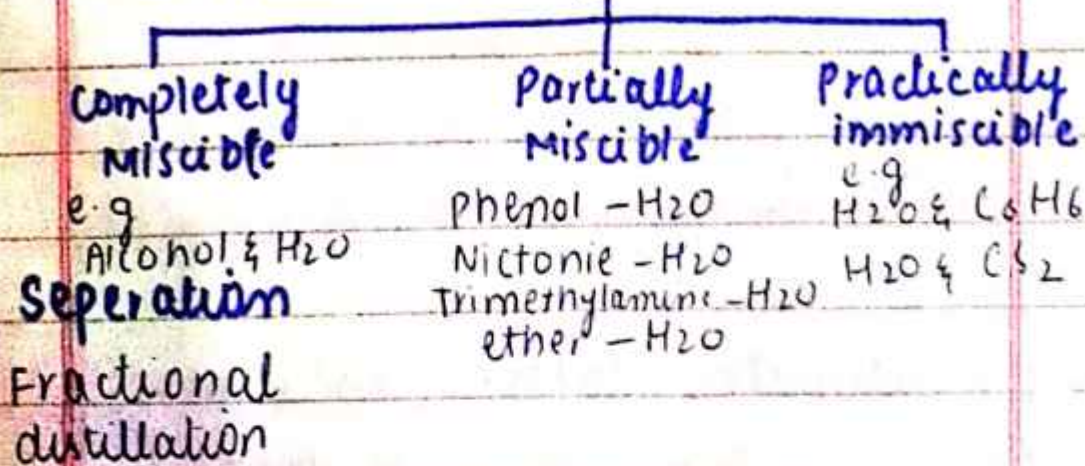
Dependence of K - Nature of gas, solvent & units of P & C .

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



Solutions of Liquids in Liquids



System	critical soln Temp	% age of 1st component given in bracket
Methanol - cyclonexane	49°C	29
Hexane - Aniline	59.6°C	52
CS_2 - methanol	49.5°C	80
Dimethylamine - H_2O	43°C	13
1-methyl piperidine - 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 equilibrium with the excess of solid at particular temp.

Solubility

concentration of solute in soln when it is in equilibrium 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 -Naphthol

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)

H₂ 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, H₂O in O₂, moisture
loaded air, gasoline-Air mixture
Chloroform mixed with N₂

Liquid in Liquid (emulsion)

Milk, Mayonnaise, C₂H₅OH in H₂O,
Antifreeze in H₂O, 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 H₂O),
sugar in H₂O, Jellies, paints
Syrup, I₂ in CCl₄,
amalgams, Aqueous NaCl

Solid in gas (Aerosol)

Dust particles in smoke
Butane lighter, I₂ vapours in air,
Naphthalene sublimed in air,
mothballs, Camphor in N₂
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
Brass (Cu in Ag)