SOLUTION AND COLLIGATIVE PROPERTIES

Definition of Solution

When two or more chemically non-reacting substances are mixed and form homogeneous mixture is called **solution**.

When the solution is composed of only two chemical substances, it is termed a binary solution, similarly, it is called ternary and quaternary if it is composed of three and four components respectively.

Solution = solute + solvent

Solute : Generally the component present in lesser amount than other component in solution is called solute.

Solvent : Generally, the component present in greater amount than any or all other components is called the solvent.

* Physical state of solvent and solution is same.

Ex. In a syrup (liquid solution) containing 60% sugar (a solid) and 40% water (a liquid - same aggregation as solution), water is termed as the solvent.

Dilute Solution : A solution in which relatively a small amount of solute is dissolved in large amount of solvent is called a dilute solution.

Concentrated solution : A solution in which relatively a large amount of the solute is present is called a concentrated solution.

Saturated solution : The maximum amount of solute in grams, that can be dissolved in 100 g of a solvent at a particular temperature is called solubility of the solute and such a solution is called saturated solution.

Super saturated solution : A solution containing more amount of solute than that required for saturation of a given amount of solvent at a particular temperature, is called a supersaturated solution.

* It is unstable system.

Types of Solutions

S.No.	Solute	Solvent	Types of Solutions	Examples
Solid Solutions				
1	Solid	Solid	Solid in solid	All alloys like brass, bronze, an alloy of copper and gold, etc.
2	Liquid	Solid	Liquid in solid	Amalgam of mercury with Na, $CuSO_4.5H_2O$. $FeSO_4.7H_2O$
3	Gas	Solid	Gas in solid	Solution of H_2 in Pd, dissolved gases in minerals.
Liquid Solutions				
4	Solid	Liquid	Solid in liquid	Sugar solution, salt solution, I_2 in CCl_4
5	Liquid	Liquid	Liquid in liquid	Benzene in toluene, alcohol in water.
6	Gas	Liquid	Gas in liquid	CO_2 in water, NH_3 in water etc.
Gaseous Solutions				
7	Solid	Gas	Solid in gas	Iodine vapours in air, camphor vapours in N_2.
8	Liquid	Gas	Liquid in gas	Water vapours in air, $CHCl_3$ vapours in N_2.
9	Gas	Gas	Gas in gas	Air ($O_2 + N_2$)

Sp. Note : The solution of liquid in gas or solid in gas is not possible because the constituents can not form a homogeneous mixture.

Properties of a solution

(i) A solution consists of a single phase i.e. it is a monophasic system.
(ii) A solution is uniform throughout, so it has uniform properties such as density refractive index, etc.
(iii) Size of solute particles in a solution is of the order $10^{-7} - 10^{-8}$ cm.
(iv) The components of a solution can not be easily separated by physical methods.
(v) The properties of a solution are the properties of its components. i.e. the components do not lose their properties when they form a solution.
(vi) The composition of a solution is not definite but can vary within certain limits.
(vii) Certain properties of solution such as density, viscosity, surface tension, boiling point, freezing point etc. vary with the composition of the solution.

Percentage by weight

The number of grams of solute is dissolved in one gram of solution is called weight fraction of the solute. Thus,

$$\text{weight fraction} = \frac{w}{w+W}$$

Where 'w' grams of solute is dissolved in W grams of solvent.

$$\text{weight percent} = \frac{\text{weight of solute in grams} \times 100}{\text{weight of solution in grams.}}$$

$$w = \frac{w \times 100}{w+W}$$

Percent by volume (Volume fraction)

This method is used for solutions of liquid in a liquid. The volume of liquid (solute) in mL dissolved in one mL of solution is called volume fraction.

$$\text{Volume fraction} = \frac{\text{Volume of liquid solute in mL}}{\text{volume of solution in mL}}$$

$$\text{Volume percent} = \frac{\text{Volume of solute} \times 100}{\text{Volume of solution}}$$

Ex. If we have 6% w/w urea solution with density 1.060 g/mL, then calculate its strength in g/L ?

Sol. 6 g urea is present in 100 gm solution.

$$6 \text{ g in } \frac{100}{1.060} \text{ mL}$$

$$\frac{100}{1.060} \text{ mL} \longrightarrow 6 \text{ gm.}$$

$$\therefore 1000 \text{ mL} = \frac{6}{100} \times 1.060 \times 1000 = 10.6 \times 6 = 63.6$$

MOLE FRACTION

The ratio of the number of moles of one component to the total number of all the components present in the solution, is called the mole fraction of that component.

Mole fraction of solute X_A is given by $X_A = \dfrac{n_A}{n_A + n_B}$

Mole fraction of solvent X_B is given by $X_B = \dfrac{n_B}{n_A + n_B}$

Where n_A is moles of solute of A & n_B is moles of solvent of B.

MOLARITY (MOLAR CONCENTRATION)

It is defined as the number of moles of the solute dissolved in per litre or per dm^3 of the solution, i.e.,

$$\text{Molarity (M)} = \frac{\text{Number of moles of solute}}{\text{Number of litres of solution}}$$

or Molarity × Number of litres of solution = Number of moles of solute

Let w_A g of the solute of molecular mass m_A be dissolved in V litre of solution.

$$\text{Molarity of solution} = \frac{w_A}{m_A \times V}$$

or $\text{Molarity} \times m_A = \frac{w_A}{V}$ = Strength of the solution

If V is taken in mL (cm^3), then

$$\text{Molarity of the solution} = \frac{w_A}{m_A \times V} \times 1000$$

The unit of molarity is mol L^{-1} or mol dm^{-3}.

MOLARITY (SECOND METHOD)

Let d = density of solution in g/mL and let it contains x% solute by mass.

Then, mass of 1 litre solution = (1000 × d)g

$$\text{Mass of solute in 1 litre} = \frac{x}{100} \times (1000 \times d)\text{g}$$
$$= (x \times d \times 10)\text{g}$$

Number of moles of solute in 1 litre

$$= \frac{\text{Mass of solute in gram}}{\text{Gram molecular mass of solute}} = \frac{x \times d \times 10}{m_A}$$

where m_A = molecular mass of solute

$$\therefore \quad M = \frac{x \times d \times 10}{m_A}$$

Molarity of dilute solution

Before dilution		After dilution
M_1V_1	=	M_2V_2

MOLARITY OF MIXING

Let there be three samples of solution (containing same solvent and solute) with their molarity M_1, M_2, M_3 and volumes V_1, V_2, V_3 respectively. These solutions are mixed; molarity of mixed solution may be given as :

$$M_1V_1 + M_2V_2 + M_3V_3 = M_R(V_1 + V_2 + V_3)$$

where, M_R = Resultant molarity

$V_1 + V_2 + V_3$ = Resultant volume after mixing

[Note : Molarity is dependent on volume, therefore, it depends on temperature.]

1M	Molar solution, i.e., molarity is 1
0.5 M or M/2	Semimolar
0.1 M or M/10	Decimolar
0.01 M or M/100	Centimolar
0.001 M or M/1000	Millimolar

Relation between molarity 'M' and mole fraction

Let M be the molarity of solution, and x_A, x_B be mole fractions of solvent and solute, respectively.

Suppose n_A and n_B moles of solvent and solute are mixed to form solution.

Mass of solution $= n_A m_A + n_B m_B$ ......(i)

where m_A and m_B are molar masses of solvent and solute, respectively.

$$\text{Volume of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{(n_A m_A + n_B m_B)}{d}$$

$$\text{Molarity} = \text{Number of moles of solute} \times \frac{1000}{\text{Volume of solution}}$$

$$M = n_B \times \frac{1000 \times d}{(n_A m_A + n_B m_B)}$$

Dividing both numerator and denominator by $(n_A + n_B)$,

$$M = \left\{\frac{n_B}{n_A + n_B}\right\} \times \frac{1000 \times d}{\frac{n_A}{n_A + n_B} \times m_A + \frac{n_B}{n_A + n_B} \times m_B}$$

$$M = \frac{x_B \times 1000 \times d}{x_A m_A + x_B m_B}$$

Ex. If 20 ml of 0.5 M Na_2SO_4 is mixed with 50 ml of 0.2 M H_2SO_4 & 30 ml of 0.4 M $Al_2(SO_4)_3$ solution. Calculate $[Na^+]$, $[H^+]$, $[SO_4^{2-}]$, $[Al^{3+}]$. [Assuming 100% dissociation]

Sol. $\text{Molarity} = \frac{\text{moles}}{\text{volume}}$ = 10 m. moles of Na_2SO_4

$\Rightarrow$ 20 m. moles of Na^+

(i) $\therefore [Na^+] = \frac{20}{100} = 0.2$ M

(ii) $[H^+] = ?$

10 m. moles H_2SO_4

20 m. moles H^+

$[H^+] = \frac{20}{100} = 0.2$ M

(iii) $[SO_4^{2-}] = \frac{10+10+36}{100} = \frac{56}{100} = 0.56$ M

(iv) $[Al^{3+}] = \frac{24}{100} = 0.24$ M

Derive a relationship between molality & molarity of a solution in which w gm of solute of molar mass M g/mol is dissolved in W g solvent & density of resulting solution = 'd' g/ml.

say 1 L solution taken,

mass of 1 lit solution = (1000 d) g

moles of solute = (molarity)

mass of solute = (molarity) x m

mass of solvent = W

= 1000 d – (molarity) × m

$$\therefore \text{molality} = \frac{(\text{molarity}) \times 1000}{1000\,d - \text{molarity} \times \text{M.Wt}}$$ [Where no.of moles of solute = molarity]

Ex. Calculate molality of 1.2 M H_2SO_4 solution ? If its $\rho = 1.4$ g/mL

Sol. $$\text{Molality} = \frac{1.2 \times 1000}{1000 \times 1.4 - 1.2 \times 98} \qquad \mathbf{= 0.936}$$

NORMALITY (N)

The number of equivalents or gram equivalents of solute dissolved in one litre of the solution is known as normality (N) of the solution.

$$\text{Normality(N)} = \frac{\text{Number of gram equivalents of solute}}{\text{volume of solution in litre}}$$

$$= \frac{\text{weight of solute in gram}}{\text{equivalent weight} \times \text{volume of solution (litre)}}$$

$$= \frac{\text{strength of solution in gram / litre}}{\text{Equivalent weight of solute}}$$

Equivalent weight of a substance is that weight which reacts with or displaces one gram of hydrogen, 8 grams of oxygen or 35.5 grams of chlorine.

ஐ Solutions are expressed as : 1N, $\frac{N}{2}, \frac{N}{10}, \frac{N}{100}, \frac{N}{1000}$, etc.

1N = Normal
= One gram equivalent of the solute per litre of solution
= Normality is 1

$\frac{N}{2}$ = Seminormal
= 0.5 g equivalent of the solute per litre of solution
= Normality is 0.5

$\frac{N}{10}$ = Decinormal
= 0.1g equivalent of the solute per litre of solution
= Normality is 0.1

$\frac{N}{100}$ = Centinormal
= 0.01g equivalent of the solute per litre of solution
= Normality is 0.01

$\frac{N}{1000}$ = Millinormal
= 0.001g equivalent of the solute per litre of solution
= Normality is 0.001

MOLALITY (M)

The number of moles or gram molecules of solute dissolve in 1000 gram of the solvent is called molality of the solution.

$$\text{Molality of a solution} = \frac{\text{Number of moles of solute}}{\text{Amount of solvent in kg.}}$$

$$= \frac{\text{Number of moles of solute} \times 1000}{\text{Amount of solvent in grams.}}$$

* It is independent of temperature.

FORMALITY : It is the number of formula mass in grams present per litre of solution.

$$\text{formality} = \frac{\text{weight of solute in gram}}{\text{formula mass of solute in grams} \times \text{volume of solution in litre}}$$

- In case formula mass is equal to molecular mass, formality is equal to molarity.
- Depends on temperature.

Concentration or strength of a solution (S) :

The numbers of grams of solute dissolved in one litre solution is known as its strength in grams per litre.

* Strength in grams per litre

$$S = \frac{\text{wt. of solute in grams} \times 1000}{\text{volume of solution in mL}}$$

S = Molarity of solution × molecular wt. of solute.

S = Normality of solution × equivalent weight of solute.

Parts per million (ppm) : This method is used for expressing the concentration of very dilute solutions such as hardness of water, air pollution etc.

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

$$= \frac{\text{Volume of solute} \times 10^6}{\text{volume of solution}}$$

Relation between molarity and normality

$$S = \text{Molarity} \times \text{molecular weight of solute}$$

$$\text{and } S = \text{Normality} \times \text{equivalent weight of solute}$$

So we can write

Molarity × Molecular weight of solute = Normality × equivalent weight of solute.

$$\text{Normality} = \frac{\text{molarity} \times \text{molecular weight of solute}}{\text{equivalent weight of solute}}$$

$$= \frac{\text{molarity} \times \text{molecular weight of solute}}{(\text{molecular weight of solute / valency factor})}$$

$$\text{Normality} = \text{molarity} \times \text{valency factor}$$

$$N = M \times n \qquad N \geq M$$

Relation between molality and molarity

$$\frac{\text{Molarity}}{\text{Molality}} = \frac{\text{Moles of solute}}{\text{volume of solution}} \times \frac{\text{mass of solvent}}{\text{moles of solute}}$$

$$= \frac{\text{mass of solvent(kg)}}{\text{volume of solution (in litre)}}$$

$$= \frac{\text{mass of solvent(in grams)}}{\text{volume of solution (in mL)}} = \frac{W}{V}$$

Let the density of the solution be d g. mL^{-1}

Mass of solution = V × d

Mass of solute $= \text{number of moles} \times \text{molecular mass of solute}$

$= n \times m_A$

Mass of solvent(W) $=$ mass of solution – Mass of solute

$= (V \times d) - (n \times m_A)$

Thus
$$\frac{\text{Molarity}}{\text{Molality}} = \frac{(V \times d) - (n \times m_A)}{V}$$

$$\text{Molality (m)} = \frac{\text{molarity} \times V}{(V \times d) - (n \times m_A)}$$

$$m = \frac{\text{molarity}}{d - \left(\frac{n}{V} \times m_A\right)}$$

$$m = \frac{\text{molarity}}{d - (\text{molarity} \times m_A)}$$

Sp. Note

If the density of solution is approximately 1. then

Molality $>$ Molarity

DEMAL (D)

Demal (D) is another unit for expressing the concentration of a solution. It is equal to molar concentration at 0°C i.e., 1D represents one mole of the solute present in one litre of the solution at 0°C.

Ex. If we have 10 molal urea solution, Calculate mole fraction of urea in this solution & also calculate % w/w of urea (MW = 60).

Sol. 10 moles urea in 1000 g of water

$$X_{\text{urea}} = \frac{10}{10 + \frac{1000}{18}} = \frac{10}{65.55} = 0.1526$$

$$\text{\% w/w weight of urea} = \frac{10 \times 60}{10 \times 60 + 1000} \text{ x } 100 = 37.5\%$$

*** Note :** For dil. aq. solution molality $\approx$ molarity

$$\text{molality} = \frac{\text{molarity} \times 1000}{1000 \times d - \text{molarity} \times m} \approx (1 \text{ g/ml})$$

Ex. Calculate molarity of $CaCO_3$(aq.) solution which has concentration of $CaCO_3 = 200$ ppm.

Sol. 200 g of $CaCO_3$ in 10^6 g of water.

$\frac{200}{100} = 2$ moles of $CaCO_3$ in 10^3 liters of water. (density =1g/mL)

$$\text{So molarity} = \frac{2}{10^3} = 2 \times 10^{-3} \text{ M.}$$

Ex. If 0.4 gm of NaOH is present in 40 ml of solution. What is the molarity and normality [M.wt. of NaOH = 40]

Sol. We know that

$$\text{Molarity} = \frac{\text{wt. of solute} \times 1000}{\text{M.Wt. of solute} \times \text{volume of solution (mL)}} = \frac{0.4}{40 \times 40} \times 1000 \qquad = 0.25\ \text{M}$$

$$\text{and normality} = \frac{\text{wt.of solute}}{\text{Eq.wt. of solute} \times \text{volume of solution(mL)}} \times 1000$$

eq. wt. of NaOH = 40

so $$N = \frac{0.4}{40 \times 40} \times 1000 = 0.25\text{N}$$

Second method $N = m \times n$

here $n = 1$, $N = M, N = 0.25$

Ex. The normality of 1.5M H_3PO_4 is –

Sol. Basicity of H_3PO_4 is 3

We know that $N = M \times n$

$N = 1.5 \times 3 = 4.5$

Ex. How much volume of 10M HCl should be diluted with water to prepare 2.00 L of 5M HCl ?

Sol. In dilution the following equation is applicable :

$$M_1V_1 = M_2V_2$$

$$10\text{M HCl} = 5\text{M HCl}$$

$$10 \times V_1 = 5 \times 2.00$$

$$V_1 = \frac{5 \times 2.00}{10} = 1.00\ \text{L}$$

Ex. Find out the weight of H_2SO_4 in 150 mL, $\frac{N}{7}$ H_2SO_4.

Sol. $$N = \frac{\text{Weight in gram}}{\text{equivalent weight} \times \text{volume}}$$

wt. in gram = eq. wt × N × volume

$$= 49 \times \frac{1}{7} \times \frac{150}{1000} = \frac{21}{20} = 1.05\ \text{g}$$

Ex. Find out the molarity of 1 litre of 93% H_2SO_4 and its density is 1.84.

Sol. $$\text{Molarity} = \frac{\text{Wt. in g} \times \text{density} \times 1000}{\text{molecular wt.} \times 100} = \frac{93 \times 1.84 \times 1000}{98 \times 100} = 78.68\ \text{M}$$

Ex. A 100 cm^3 solution is prepared by dissolving 2g of NaOH in water. Calculate the normality of the solution.

Sol. $$2\text{ g NaOH} = \frac{2}{40}\text{ g. eq.} = \frac{1}{20}\text{ g eq.}$$

$$N = \frac{\frac{1}{20}}{100} \times 1000 = \frac{1}{2}$$

Normality of solution = $\frac{N}{2}$

Ex. Find the percentage by weight and weight fraction of aspirin in the solution prepared by dissolving 3.65 g of aspirin in 25.08 g of water.

Sol. weight of solution $= 3.65 + 25.08 = 28.73$ g

weight fraction $= \dfrac{3.65}{28.73} = 0.127$

weight percent $= 0.127 \times 100 = 12.7\%$

Ex. A solution was prepared by adding 125 cm^3 of isopropyl alcohol to water until the volume of the solution was 175 cm^3. Find the volume fraction and volume percent of isopropyl alcohol in the solution.

Sol. volume of solute $= 125\ cm^3$

volume of solution $= 175\ cm^3$

$\therefore$ volume fraction$= \dfrac{125}{175} = 0.714$

and volume percent $= \dfrac{125}{175} \times 100 = 71.4\%$

Ex. The density of a solution containing 13% by mass of sulphuric acid is 1.09 g/mL. Calculate the molarity and normality of the solution.

Sol. Volume of 100 g of the solution

$$= \frac{100}{d} = \frac{100}{1.09}\ \text{mL}$$

$$= \frac{100}{1.09 \times 1000}\ \text{litre}$$

$$= \frac{1}{1.09 \times 10}\ \text{litre}$$

Number of moles of H_2SO_4 in 100 g of the solution $= \dfrac{13}{98}$

$$\text{Molarity} = \frac{\text{No. of moles of } H_2SO_4}{\text{Volume of solution. in litre}} = \frac{13}{98} \times \frac{1.09 \times 10}{1} = 1.445\ \text{M}$$

Note: In solving such numericals, the following formula can be applied :

$$\text{Molarity} = \frac{\%\ \text{strength of solution} \times \text{density of solution} \times 10}{\text{Mol. mass}}$$

Similarly,

$$\text{Normality} = \frac{\%\ \text{strength of solution} \times \text{density of solution} \times 10}{\text{Eq. mass}}$$

We know that,

Normality $=$ Molarity $\times$ n

$$= 1.445 \times 2 \qquad \left[n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2 \right]$$

$$= 2.89\ \text{N}$$

VAPOUR PRESSURE

At a constant temperature, the pressure exerted by the vapours of a liquid on its surface when they (liquid and its vapours) are in equilibrium, is know as vapour pressure.

RAOULT'S LAW :

According to this law, the partial pressure of any volatile constituents of a solution at a constant temperature is equal to the vapour pressure of pure constituents multiplied by the mole fraction of that constituent in the solution.

(i) For liquid – liquid solution

Let a mixture (solution) be prepared by mixing n_A moles of liquid A and n_B moles of liquid B. Let P_A' and P_B' be the partial pressures of two constituents A and B in solution and P_A^0 and P_B^0 the vapour pressures in pure state respectivity.

Thus, according Raoult's law

$$P_A' = \frac{n_A}{n_A + n_B} PA^0 \qquad ....(1)$$

Partial pressure of A = mole fraction of A × $P_A^0 = X_A P_A^0$

$$\text{and } \; P_B' = \frac{n_B}{n_A + n_B} P_B^0 \qquad ....(2)$$

Partial pressure of B = mole fraction of B × $P_B^0 = X_A P_B^0$

If total pressure be P_S, then

$$P_S = P_A' + P_B'$$

$$= \frac{n_A}{n_A + n_B} P_A^0 + \frac{n_B}{n_A + n_B} P_B^0$$

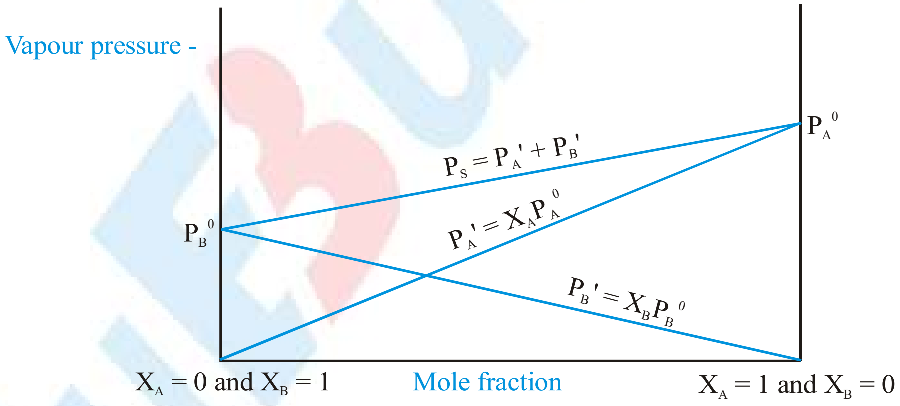
$$= X_A P_A^0 + X_B P_B^0 \qquad ....(3)$$

$$P_S = X_A P_A^0 + (1 - X_A) P_B^0 \qquad [\because \; X_A + X_B = 1]$$

$$P_S = X_A P_A^0 - X_A P_B^0 + P_B^0$$

$$P_S = X_A [P_A^0 - P_B^0] + P_B^0 \qquad .....(4)$$

Equation 1, 2 and 3 are the straight line equation so we can draw it as follows.



Ex. 1 mole heptane (V.P. = 92 mm of Hg) is mixed with 4 mol. Octane (V.P. = 31 mm of Hg), form an ideal solution. Find out the vapour pressure of solution.

Sol. total mole = 1 + 4 = 5

Mole fraction of heptane = X_A = 1/5

Mole fraction of octane = X_B = 4/5

$$P_S = X_A P_A^0 + X_B P_B^0$$

$$= \frac{1}{5} \times 92 + \frac{4}{5} \times 31$$

= 43.2 mm of Hg.

Ex. At 88°C benzene has a vapour pressure of 900 torr and toluene has a vapour pressure of 360 torr. What is the mole fraction of benzene in the mixture with toluene that will be boil at 88°C at 1 atm pressure, benzene – toluene form an ideal solution.

Sol. P_S = 760 torr, because solution boils at 88°C

Now $760 = 900 \times$ mole fraction of C_6H_6 $+ 360 \times [1 -$ mole fraction of $C_6H_6]$

$\therefore \quad 760 = 900\,a + 360 - 360\,a$

$a = 0.74$ where 'a' is mole fraction C_6H_6.

(ii) **For Solid – liquid solution**

A = non volatile solids

B = volatile liquid

According to Raoult's law –

✈ $P_m = X_A P_A^0 + X_B P_B^0$

for A, $P_A^0 = 0$

$\therefore \quad P_m = X_B P_B^0$ ....(5)

Let $P_B^0 = P^0$ = Vapour pressure of pure state of solvent.

here X_B is mole fraction of solvent

$$P_S = \frac{n_B}{n_A + n_B} P^0 \qquad \text{....(6)}$$

$$P_S \propto \frac{n_B}{n_A + n_B}$$

i.e. vapour pressure of solution ∝ mole fraction of solvent

$\Rightarrow P_S = X_B P_B^0$

$\Rightarrow P_S = (1 - X_A) P_B^0$

$\Rightarrow P_S = P_B^0 - X_A P_B^0$

$$\frac{P_B^0 - P_S}{P_B^0} = X_A$$

$$\text{or} \quad \frac{P^0 - P_S}{P^0} = X_A \qquad \text{....(7)}$$

$$\text{or} \quad \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B} \qquad \text{....(8)}$$

$$\text{or} \quad \frac{P^0}{P^0 - P_S} = \frac{n_A + n_B}{n_A}$$

$$\text{or} \quad \frac{P^0}{P^0 - P_S} = 1 + \frac{n_B}{n_A}$$

$$\text{or} \quad \frac{P^0}{P^0 - P_S} - 1 = \frac{n_B}{n_A}$$

$$\text{or} \quad \frac{P_S}{P^0 - P_S} = \frac{n_B}{n_A}$$

$$\frac{P^0 - P_S}{P_S} = \frac{n_A}{n_B} \qquad ....(9)$$

or $$\frac{P^0 - P_S}{P_S} = \frac{w_A.m_B}{m_A.w_B}$$

or $$\frac{w\ M}{m\ W} \qquad ....(10)$$

Ex. The vapour pressure of benzene at 90°C is 1020 torr. A solution of 5 g of a solute in 58.5 g benzene has vapour pressure 990 torr. The molecular weight of the solute is?

Sol. $$\frac{P^0 - P_S}{P_S} = \frac{w \times M}{m \times W}$$

$$\frac{1020 - 990}{990} = \frac{5 \times 78}{m \times 58.5}$$

$m = 220$

Ex. The vapor pressure of water at 80º C is 355 torr. A 100 ml vessel contained water–saturated oxygen at 80º C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 ml, vessel at the same temperature. What were the partial pressures of oxygen and of water vapor, what was the total pressure in the final equilibrated state ? Neglect the volume of any water which might condense.

Ans. $P_{O_2} = 810\text{mm Hg}$, $P_{H_2O} = 355\text{ mm Hg}$, $P_{total} = 1165\text{ mm Hg}$

Sol. In 100 ml vessel which contained water - saturated oxygen, the pressure of O_2 gas = 760 – 355 = 405 torr when the contents of this vessel were pumped into 50 ml vessel, at the same temperature, the pressure of oxygen gets doubled i.e. $P_{O_2} = 810$ torr.

But pressure of water vapour will remain constant, as some vapour in this 50 ml vessel, gets condensed.

So $P_{H_2O} = 355$ torr & Total pressure $= 810 + 355 = 1165$ torr.

APPLICATION OF RAOULT'S LAW

(1) Phase Diagrams of Two-Component Ideal Solutions: Bubble And Dew Points

The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This can be easily derived from Raoult's Law.

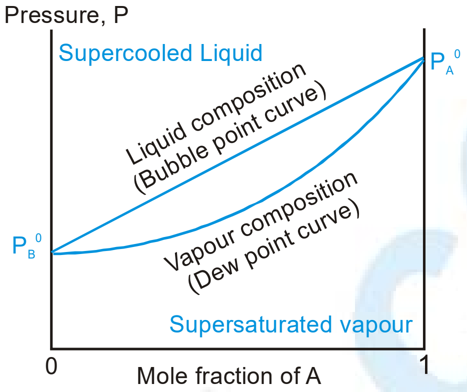
$$\frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0} = \frac{y_A}{P_A^0} + \frac{1 - y_A}{P_B^0}$$

$$P_T = \frac{P_A^0 P_B^0}{P_A^0 + (P_B^0 - P_A^0)y_A}$$

From the above equation, the plot of P_T with respect to y is a curve instead of a straight line. We can superimpose this curve on the diagram for graphical representation of Raoult's Law to get following phase diagrams.

(A) Pressure versus Composition Phase Diagram (At constant T): P vs. x and y

In this kind of phase diagram the temperature has a fixed value. The mole fraction of one component is plotted on the horizontal axis and the pressure is plotted on the vertical axis. If A is more volatile than B, then we get following diagram.



Explaination:

(i) On horizontal-axis we have plotted both x and y that is both liquid composition and vapour composition.

(ii) The lower curve (Dew Point Curve) represents the total pressure as a function of the composition i.e. mole fraction in the vapor phase at equilibrium with the liquid phase. It is plotted using P_T vs. y_A equation:

$$P_T = \frac{P_A^0 P_B^0}{P_A^0 + (P_B^0 - P_A^0)y_A}$$

(iii) The upper curve i.e. Bubble Point Curve (a straight line in the case of an ideal solution) represents the total pressure as a function of composition i.e. mole fraction in the liquid. It is plotted using P_T vs. x_A equation:
$P_T = (P_A^o - P_B^o)\,x_A + P_B^0$

(iv) The area between these two curves is vapour-liquid equilibrium region. Vapours cannot exist above the bubble point curve and liquid can not exist below the dew point curve.

(v) Suppose, initially the pressure over the solution is very high so that no vapour exist above the liquid. As we gradually decrease the pressure, a point (Bubble point) comes when we cross the Bubble-Point curve and first bubble of vapour starts forming. Hence, the name bubble point curve. Now we have entered the vapour-liquid equilibrium region. On further decreasing the pressure, a point (Dew Point) comes when we cross the Dew-Point curve when almost all the liquid has evaporated into vapour i.e. only the last drop of liquid (Dew) remains. Beyond this point no liquid exists in the system.

Ex. (a) A liquid mixture of benzene and toluene is composed of 1 mol of benzene and 1 mol of toluene. If the pressure over the mixture at 300K is reduced, at what pressure does the first bubble form?

(b) What is the composition of the first bubble formed.

(c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?

(d) What is the composition of the last drop of liquid?

(e) What will be the pressure, composition of the liquid and the composition of vapour, when 1 mol of the mixture has been vaporized? Given $P_T^0 = 40$mmHg, $P_B^0 = 100$mmHg

Ans. **(a)** 70 mmHg, **(b)** $x_b = 5/7$ **(c)** $P = 400/7 = 57.14$ mm

Sol. (a) $P = X_A P_A^0 + X_B P_B^0 = 0.5 \times 40 + 0.5 \times 100 = 70$

(b) $Y_A = \frac{0.5 \times 40}{70} = \frac{2}{7}$ $\qquad Y_B = \frac{5}{7}$

(c) at last trace of liquid $\qquad Y_A = 0.5 \qquad Y_B = 0.5$

$$\frac{1}{P} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} = \frac{0.5}{40} + \frac{0.5}{100}$$

$$P = \frac{400}{7}$$

(d) $Y_A = \frac{Y_A P_A^0}{P} \Rightarrow 0.5 = \frac{X_A 40}{400/7} \qquad X_A = \frac{5}{7} \qquad X_B = \frac{2}{7}$

(e) Let x mole of B be present in liquid phase.

	Mole of A	Mole of B
Liquid	1 - x	x
Vapour	x	1 - x

$P = 40(1 - x) + 100x$

$$\frac{1}{P} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0} \Rightarrow \frac{1}{P} = \frac{x}{40} + \frac{1-x}{100} = \frac{100x + (1-x)40}{40 \times 100}$$

So $\qquad P^2 = 40 \times 100$

$$P = 20\sqrt{10}$$

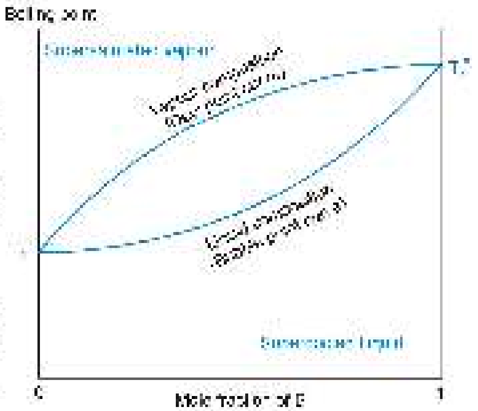
$$20\sqrt{10} = 40(1-x) + 100x = 40 + 60x$$

$$x = \frac{20\sqrt{10} - 40}{60} = \frac{\sqrt{10} - 2}{3}$$

(B) Temperature v/s Composition Phase Diagrams i.e. T vs x and y diagram

(i) In this type of phase diagram the pressure is held fixed. The mole fraction of one component is plotted on the horizontal axis and the boiling temperature is plotted on the vertical axis.

(ii) The upper curve (Dew-Point curve) gives the boiling temperature at the given pressure as a function of the mole fraction in the vapor phase, and the lower curve (Bubble-Point curve) gives the boiling temperature at the given pressure as a function of the mole fraction in the liquid phase.



Note: If a liquid has a high vapour pressure at a particular temperature, it means that its molecules can escape easily from the surface. The liquid with the higher vapour pressure at a particular temperature is the one with the lower boiling point. If A is more volatile than B, then we get following diagram.

(2) Distillation

(i) The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component.

(ii) In a simple distillation, the vapour over a boiling mixture is withdrawn and condensed in a separate container. The liquid collected in the new container is called condensate and the liquid remaining in the original container is called distillate. The condensate has higher mole fraction of the more volatile component than the original mixture. The distillate has higher mole fraction of the less volatile component than the original mixture. This is the principle of distillation and is used to separate a more volatile liquid from a less volatile liquid.

(iii) In fractional distillation, the boiling and condensation cycle is repeated successively to get a condensate which gets richer in the more volatile component after each cycle.

Ex. An equimolar mix of benzene & toluene is prepared the total V.P. of this mix as a fraction of mole fraction of benzene is found to be $P_T = 200 + 400\ X_{ben}$.

(a) Calculate composition of vapours of this mix. [Assume that the no. of moles going into vapour phase is negligible in comparison to no. of moles present in liq. phase].

(b) If the vapour above liq in part A are collected & are condensed into a new liquid calculate composition of vapours of this new liq.

Sol. (a) $P^0_{Beazene} = 600$ mm of Hg

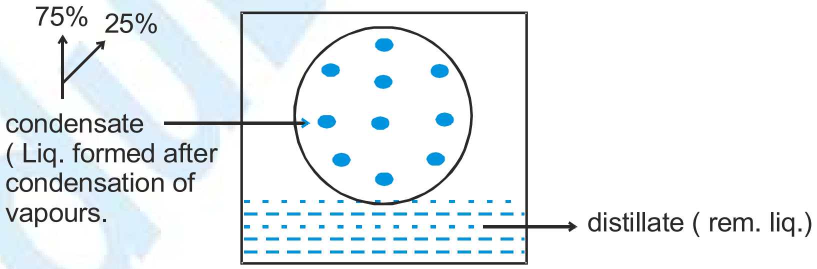
$P^0_{Toloune} = 200$ mm of Hg

$$P_T = \frac{1}{2} \times 600 + \frac{1}{2} \times 200 = 400 \text{ mm of Hg}$$

$$P_{benz} = x_{ben}{}' P^o_{ben} = y_{ben} P_{T.}$$

$$y_{benzene} = \frac{1/2 \times 600}{400} = \frac{3}{4} = 75\% \quad ; \quad y_{Toloune} = \frac{1}{4} = 25\%$$

(b)



$$P_T = \frac{3}{4} \times 600 + \frac{1}{4} \times 200 = 500 \Rightarrow \quad y_{ben} = \frac{3/4 \times 600}{500} = 0.9 = 90\%$$

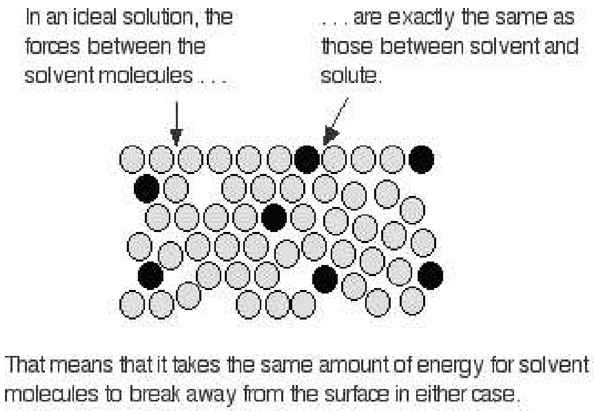
$y_{Toluene} = 0.1 = 10\%$

LIMITAIONS OF RAOULT'S LAW

Raoult's Law only works for ideal solutions. Very dilute solutions obey Raoult's Law to a reasonable approximation.

(1) Ideal Solutions

Those solutions which obey Raoult's law are called ideal solutions. When the forces of attraction between A — A, B — B is similar to A — B, then A and B will form ideal solution.



In an ideal solution, the forces between the solvent molecules . . .

. . . are exactly the same as those between solvent and solute.

That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Properties of ideal solution :

(i) Raoult's law is obeyed

(ii) $\Delta H_{mix} = 0$, i.e., there should not be enthalpy change when components of ideal solutions are mixed.

(iii) $\Delta V_{mix} = 0$, (1L + 1L = 2L) i.e., there should not be change in volume on mixing. e.g.; n-hexane and n-heptane; ethyl bromide and ethyl iodide; benzene and toluene; chlorobenzene and bromobenzene form ideal solutions.

(2) Non - Ideal Solutions

Those solutions which do not obey Raoult's law are called non-ideal solutions.

When the forces of attraction between A — A, B — B is different from A — B then 'A' and 'B' form non-ideal solutions. For these solutions :

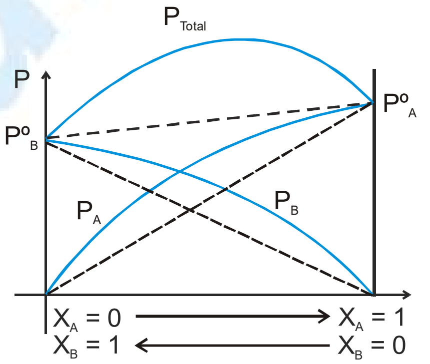
(i) Raoult's law is not obeyed. (ii) $\Delta H_{mix} \neq 0$; (iii) $\Delta V_{mix} \neq 0$.

Types of Non-Ideal Solutions

(A) Non-Ideal Solutions Showing Positive Deviation From Raoult's Law

(i) In this case, partial pressure of each component A and B is higher than that calculated from Raoult's law, and hence total pressure over the solution is also higher than if the solution were ideal, as shown in figure.

(ii) Boiling point of such a solution is relatively lower than the boiling points of both A and B.



$P^0_A > P^0_B$

Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution

Ex. : Water and ethanol, chloroform and water, ethanol and CCl_4, methanol and chloroform, benzene and methanol, acetic acid and toluene, acetone and ethanol, methanol and H_2O, C_2H_5OH + cyclohexane.

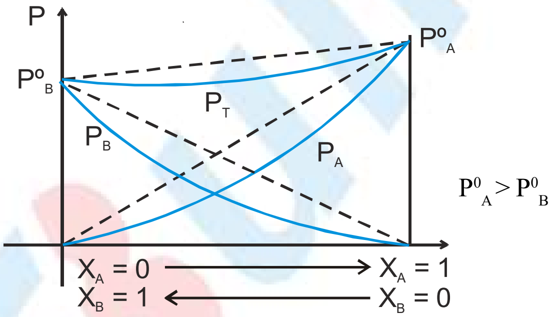
Explaination: The fact that the vapour pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids. That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

You can see this when you mix the liquids. Less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic.

(B) Non-Ideal Solutions Showing Negative Deviation From Raoult's Law

(i) In this case, partial pressure of each component A and B is lower than that calculated from Raoult's law, and hence total pressure over the solution is also lower than if the solution were ideal, as shown in figure.

(ii) Boiling point of such a solution is relatively higher than the boiling points of both A and B.

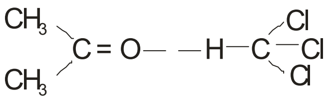


Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution

Ex. : chloroform and acetone, chloroform and methyl acetate, H_2O and HCl, H_2O and HNO_3, acetic acid and pyridine, chloroform and benzene.

Explaination: These are cases where the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

You can recognise this happening because heat is evolved when you mix the liquids - more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones.

Ideal Solution	Non - Ideal solutions :	
	+ ve deviation from Raoults law	+ ve deviation from Raoults law
1. Which follow Raoult's law and at all compositions $P_T = x_A P_A^{\ o} + x_a P_a^{\ o}$	Which do not follow Raoult's law (i) $P_{T,\ exp} > (x_A P_A^{\ o} + x_B P_B^{\ o})$	Which do not obey Rault's law (i) $P_{T,\ exp} < (x_A P^o + x_B P^o{}_B)$
2. Process of attraction between A-B are exactly same as A-A & B-B A———A = A ——— B = B ———B	(ii) $\begin{matrix} A\text{------}A \\ B\text{------}B \end{matrix} > A\text{---}B$ Weaker force of attraction between A-B than in pure A-A & B-B.	(ii) $\begin{matrix} A\text{------}A \\ B\text{------}B \end{matrix} > A\text{---}B$ Stronger force of attraction between A-B thanin pure A-A & B-B
3. $\Delta H_{mtc} = 0$	(iii) $\Delta H_{mtc} = +ve$ energy absorbed	(iii) $\Delta H_{mtc} = -ve$
4. $\Delta V_{mtc} = 0$	(iv) $\Delta V_{mtc} = +ve\ (1L + 1L > 2L)$	(iv) $\Delta V_{mtc} = -ve\ (1L + 1L > 2L)$
5. $\Delta S_{mtc} = +$ ve as for process to Proceed.	(v) $\Delta S_{mtc} = +$ ve	(v) $\Delta S_{mtc} = +$ ve
6. $\Delta G_{mtc} = -ve$	(vi) $\Delta G_{mtc} = -ve$	(vi) $\Delta G_{mtc} = -ve$
eg. (1) Benzene + Toluene (2) Hexane + heptane (3) $C_2H_5Br + C_2H_5I$	eg. $H_2O + CH_3OH$ $H_2O + C_2H_5OH$ C_2H_5OH + cyclohexane $CHCl_3 + CCl_4 \rightarrow$ dipole dipole interaction becomes weak	eg. $H_2O + HCOOH$ $H_2O + CH_3COOH$ $H_2O + HNO_3$ $CHCl_3CH_3OCH_3$ 

Azeotropic Mixtures : Very large deviations from ideality lead to a special class of mixtures known as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

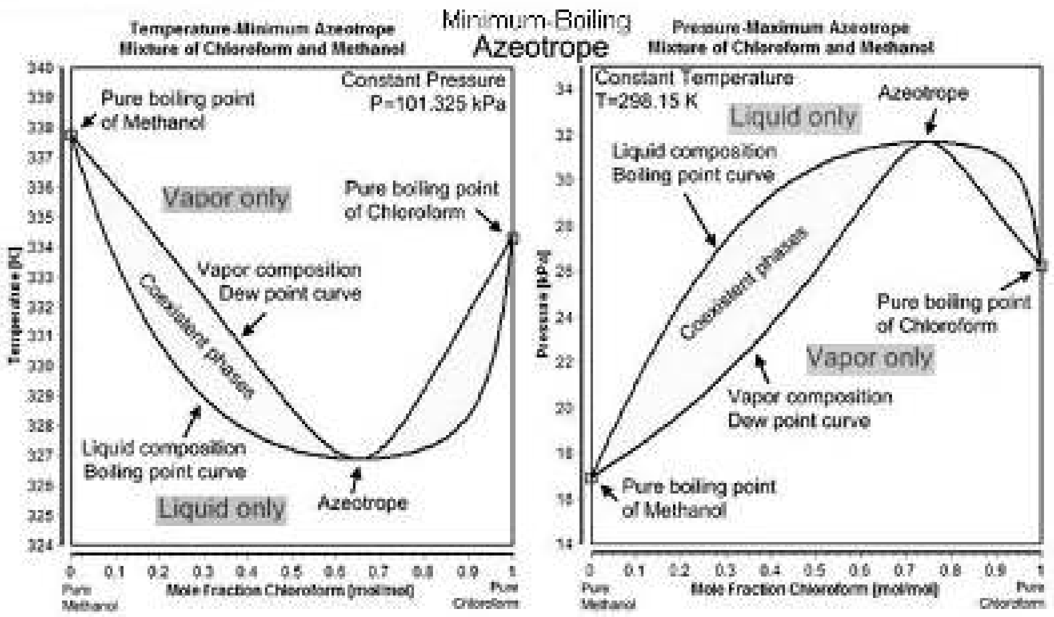
Azeotropes : Liquid mixtures which distill over without changes in composition are called constant boiling mixtures or Azeotropes or Azeotropic mixtures.

A boiling liquid mixture at the azeotropic composition produces a vapour of exactly the same composition, and the liquid does not change its composition as it evaporates. Two types of azeotropes are known.

(1) **Minimum Boiling Azeotropes :** Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes which boil at temperature lower than boiling point of its components A and B. e.g.: water and benzene, chloroform and methanol.

The figures below show the Temprature vs. composition (at constant pressure) phase diagram on the left side and Pressure vs. composition (at constant temprature) phase diagram for a minimum-boiling azeotropic mixture chloroform and methanol.

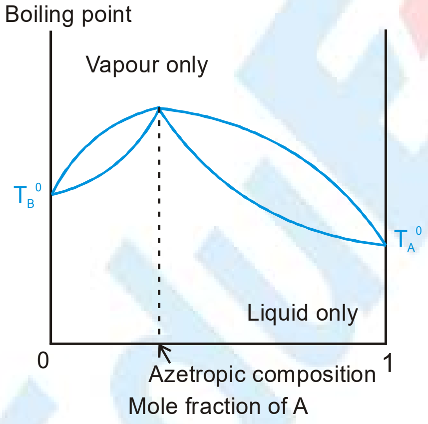
Note: The detailed values in the diagram are not important. Only the qualitative shape of the diagram is important.

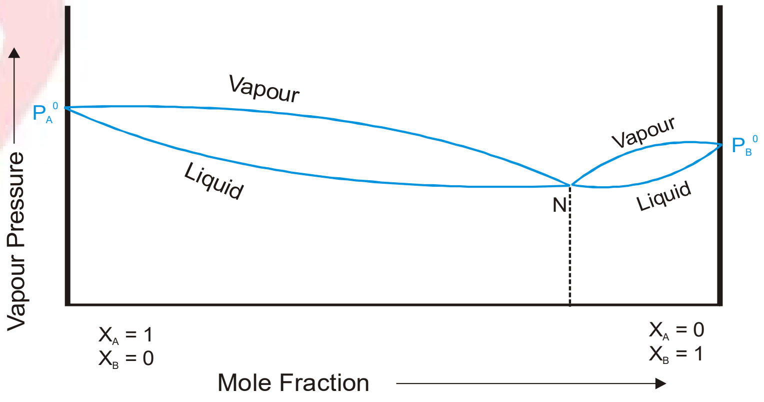


At the lowest point in the temperature vs. composition phase diagram, the concentration in the vapour phase is the same as the concentration in the liquid phase (y = x). This concentration is known as the azeotropic composition. At this point, the mixture boils at a constant temperature and without change in composition.

(2) **Maximum Boiling Azeotropes :** Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which boil at temperature higher than the boiling point of its components A and B respectively. e.g.: mixture of HCl and H_2O.

On left side, temprature versus composition phase diagram and on right side, pressure versus composition diagram is shown for maximum boiling azeotrope.





(3) **Separation of Azeotropic Mixtures**

When the azeotropic composition has been reached, the condensate has the same composition as the azeotropic liquid. The vapour phase is not richer in any component than the liquid phase. Thus, azeotropic mixtures can’t be separated beyond the azeotropic composition using distillation.

COMPLETELY IMMISCIBLE LIQUIDS AND STEAM DISTILLATION

For mixture of two completely immiscible liquids, each liquid exerts its own vapor pressure, independent of the other, and the total vapor pressure is the sum of the separate vapour pressures of the two components in the pure state at the given temperature.

(1) Immiscible Liquids

When two liquids are mixed in such a way that they do not mix at all then both liquids constitute two different phases. Hence, **mole fraction of each liquid is one in it's own phase.**

(i) $P_T = p_A + p_B$

(ii) $p_A = P_A{}^0 x_A$ But, $x_A = 1$. Thus, $p_A = P_A{}^0$

(iii) $p_B = P_B{}^0 x_B$ But, $x_B = 1$. Thus, $p_B = P_B{}^0$

(iv) $P_T = P_A{}^0 + P_B{}^0$ (v) $\dfrac{P_A^0}{P_B^0} = \dfrac{n_A}{n_B}$ (vi) $\dfrac{P_A^0}{P_B^0} = \dfrac{W_A M_B}{M_A W_B}$ (v)$P_A{}^0 = \dfrac{n_A RT}{V}$; $P_B{}^0 = \dfrac{n_B RT}{V}$

where n_A and n_B are the numbers of moles of each component present in the vapor phase.

(vi) To express the ratio of A to B in the vapor in terms of the actual weights w_A and w_B, the numbers of moles must be multiplied by the respective molecular weights M_A and M_B ; hence,

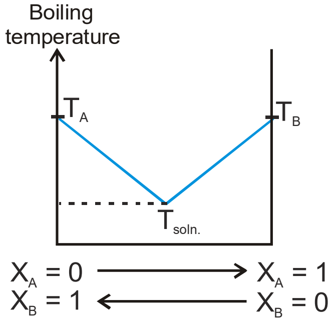
$$\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B} = \frac{p_A^0 M_A}{p_B^0 M_B}$$

(2) Steam Distillation

Steam Distillation: The boiling point of a solution of two immiscible liquids is less than the individual boiling points of both the liquids. This concept is used in steam distillation.

(i) A system of two immiscible liquids will boil when the total vapor pressure P is equal to the atmospheric pressure. The boiling point of the mixture is thus lower than that of either constituent.

(ii) Further, since the total vapor pressure is independent of the relative amounts of the two liquids, the boiling point, and hence the composition of the vapor and distillate, will remain constant as long as the two layers are present.



A liquid (generally organic) that is immiscible with water, and that has a higher boiling point than water can be boiled (distilled) at a much lower temperature by passing steam through it. In this way, the organic liquid can be purified from impurities using steam distillation.

COLLIGATIVE PROPERTIES

Those physical properties of a solution which depend upon the number of particles in a given volume of the solution or the mole fraction of the solute are called colligative properties.

The following four properties are colligative properties :

(i) Lowering of vapour pressure of the solvent.
(ii) Elevation in boiling point of the solvent.
(iii) Depression in freezing point of solvent.
(iv) Osmotic pressure.

Colligative properties $\propto$ No. of particles.
$\propto$ No. of molecules (In the solution of non electrolyte)
$\propto$ No. of ions (In the solution of electrolytes)
$\propto$ No. of moles of solute
$\propto$ Mole fraction of solute

Equimetal solutions of different substances (non valatile, non electrolyte) have the same values of colligative properties.

Colligative properties are the properties of dilute solution

(i) LOWERING OF VAPOUR PRESSURE

When a non-volatile solute is dissolved in a pure solvent, the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases (due to lesser surface area of solution available for evaporation).

If at a certain temperature P° is the vapour pressure of pure solvent, and P_s is the vapour pressure of solution then

Lowering of vapour pressure = $P° - P_s$

Relative lowering of vapour pressure $= \dfrac{P^0 - P_s}{P^0}$

from equation (8)

$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B}$$

for a more dilute solution $n_A <<< n_B$

so
$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B}$$

$$\frac{\Delta P}{P^0} = \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B}$$

$$\frac{\Delta P}{P^0} = \frac{n_A}{n_B} \qquad \text{....(11)}$$

or relative lowering of vapour pressure

$$= \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B} = \frac{w_A}{m_A} \times \frac{m_B}{w_B}$$

Ex. Calculate wt of urea which must be dissolved in 400 gm of water so final solutions has V.P. 2% less than V.P. of pure water :

Sol. Let V.P be V. of water

$P^0 - P_s = .02\,V$

$P_s = 0.98\,V$

$\Rightarrow \quad \dfrac{0.02}{0.98} = \dfrac{w}{60} \times \dfrac{18}{400}$; where w = weight of urea.

$$w = \frac{2 \times 60 \times 400}{18 \times 98}\ \text{gm.}$$

Ex. 10 gm of a solute is dissolved in 80 gm of acctone V.P. of this sol = 271 mm of Hg. If V.P. of pure acetone is 283 mm of Hg. Calculate molar mass of solute.

Sol. $\dfrac{P^0 - P_s}{P_s} = \dfrac{w}{m} \times \dfrac{M}{W}$

$$\Rightarrow \quad \frac{283 - 271}{271} = \frac{10}{m} \times \frac{58}{80}$$

m = 163 gm/mol.

Ex. V.P. of solute containing 6 gm of non volatile solute in 180 gm of water is 20 Torr/mm of Hg. If 1 mole of water is further added in to the V.P. increases by 0.02. Torr calculate V.P of pure water & molecular wt. of non volatile solute.

Sol. $$\frac{P^0 - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$$

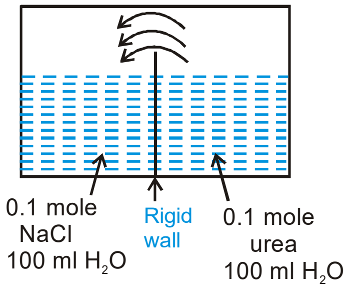
$$\Rightarrow \quad \frac{P^o - 20}{20} = \frac{6}{m} \times \frac{18}{180}$$

$$\frac{P^o - 20.02}{20.02} = \frac{6}{m} \times \frac{18}{198}$$

$\Rightarrow$ $P^o = 20.22$ Torr.

$m = 54$ gm/mol.

Ex.



What is the final volume of both container.

Sol. $i_1C_1 = i_2C_2$

$$\frac{0.1 \times 2}{100 + x} = \frac{0.1 \times 1}{100 - x}.$$

$200 - 2x = 100 + x.$

$x = 33.3$ ml.

Ex. If 0.1 M solutions of $K_4[Fe(CN)_6]$ is prepared at 300 K then its density = 1.2 gm/mL . If solute is 50% dissociated calculate ΔP of solutions if P of pure water = 25 mm of Hg. (K = 39, Fe = 56)

Sol. $$\frac{P^0 - P_s}{P_s} = i\frac{w}{m} \times \frac{M}{W}$$

$$\frac{P^0 - P_s}{P_s} = \frac{im \times M}{1000}$$

$$= \left(\frac{3 \times 0.1 \times 1000}{1000 \times 1.2 - 1.2 \times 368}\right) \times \frac{18}{1000}$$

$$\frac{P^0}{P_s} = 1 + 7.12 \times 10^{-3}$$

$P_s = 24.82$ mm of Hg

$\Delta p = 25 - 24.82 = 0.18$ mm of Hg

MEASUREMENT OF RELATIVE LOWERING IN VAPOUR PRESSURE (Ostwald and Walker Method)

The apparatus used is shown in Fig. It consists of two sets of bulbs. The first set of three bulbs is filled with solution to half of their capcity and second set of another three bulbs is filled with the pure solvent.

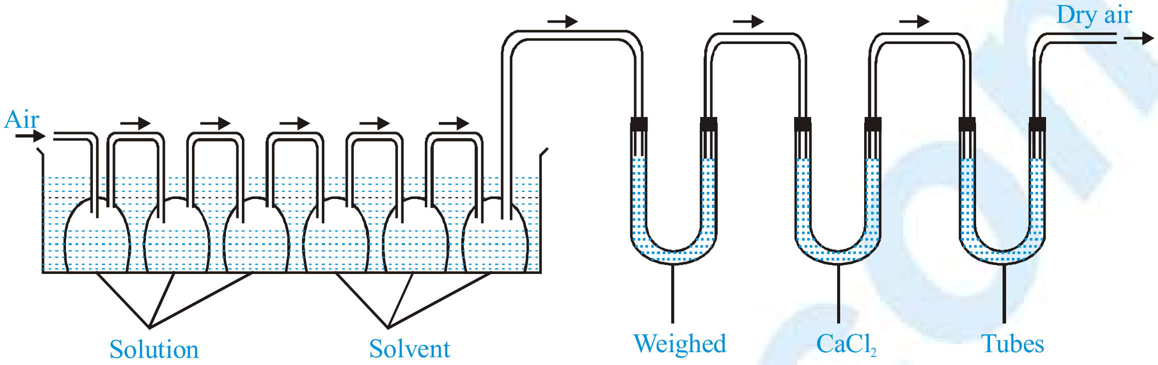


Fig. Ostwald and Walker method

Each set is separately weighed accurately. Both sets are connected to each other and then with the accurately weighed set of guard tubes filled with anhydrous calcium chloride or some other dehydrating agents like P_2O_5, conc. H_2SO_4 etc. The bulbs of solution and pure solvent are kept in a thermostat maintained at a constant temperature. A current of pure dry air is bubbled through the series of bulbs as shown in fig. The air gets saturated with the vapour in each set of bulbs. The air takes up an amount of vapours proportional to the vapour pressure of the solution first and then it takes up more amount of vapours from the solvent which is proportional to the difference in the vapour pressure of the solvent and the vapour pressure of solution, i.e., $p_0 - p_s$.

The two sets of bulbs are weighed again. The guard tubes are also weighed.

$$\text{Loss in mass in the solution bulbs} \propto p_s$$

$$\text{Loss in mass in the solvent bulbs} \propto (p_0 - p_s)$$

$$\text{Total loss in both sets of bulbs} \propto [p_s + (p_0 - p_s)]$$

$$\propto p_0$$

Total loss in mass of both sets of bulbs is equal to gain in mass of guard tubes.

Thus, $$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass in solvent bulbs}}{\text{Total loss in mass in both sets of bulbs}}$$

$$= \frac{\text{Loss in mass in solvent bulbs}}{\text{Gain in mass of guard tubes}}$$

Further, we know from Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

$$\therefore \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}} = \frac{w_A / m_A}{w_A / m_A + w_B / m_B}$$

The above relationship is used for calculation of molecular masses of non-volatile solutes.

For very dilute solutions, the following relationship can be applied :

$$\frac{p_0 - p_s}{p_0} = \frac{\text{Loss in mass of solvent bulbs}}{\text{Gain in mass of gaurd tubes}} = \frac{w_A m_B}{w_B m_A}$$

Ex. Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

Sol. According to Raoult's law,

$$\frac{p_0 - p_s}{p_0} = \frac{n}{n+N}$$

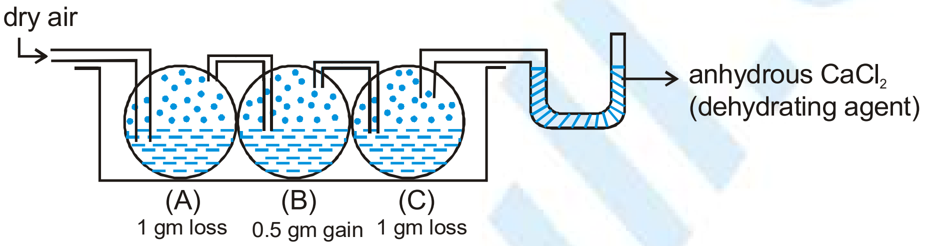
or $\Delta p = \frac{n}{n+N}.p_0$

Given : $n = \frac{50}{342} = 0.146$; $N = \frac{500}{18} = 27.78$ and $p_0 = 23.8$ mmHg

Substituting the values in the above equation,

$$\Delta p = \frac{0.146}{0.146 + 27.78} \times 23.8 = 0.124 \text{ mm Hg}$$

Ex.



If same volume solution of different solute is used then what is order of (a) vapour pressure (b) moles of solute (c) molar mass of solute.

Sol. $P_A \propto 1$ gm. ; $P_A - P_B \propto 0.5$ gm, $P_B \propto 0.5$ gm.

$P_C - P_B \propto 1$ gm ; $P_C \propto 1.5$ gm.

$P_C > P_A > P_B$; $n_C < n_A < n_B$. ; $M_C > M_A > M_B$.

Elevation in boiling point (Ebullioscopy)

The boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. i.e. 760 mm of Hg.

When a non-volatile solute is dissolved in a pure solvent, its vapour pressure is decreased. The difference ΔT_b of boiling points of the solution and pure solvent is called elevation in boiling point.

If T_0 is the boiling point of pure solvent and $(T_b)_s$ is the boiling point of the solution then,

$$(T_b)_s > T_0$$

and the elevation in boiling point

$$\Delta T_b = (T_b)_s - T_0$$

The elevation in boiling point (ΔT_b) is directly proportional to lowering of vapour pressure of the solution i.e.

$$\Delta T_b \propto P_o - P_s$$

or $\Delta T_b \propto \Delta P \propto \frac{n_A}{n_B}$

$$\therefore \quad \Delta T_b \propto \frac{n_A}{n_B} = \frac{w.M}{m.W}$$

for a solvent P^0 & M = const.

$$\therefore \quad \Delta T_b \propto \frac{w}{m.W}$$

$$\Delta T_b = \frac{Kw}{m.W}$$

where K = elevation constant

If $\frac{w}{m} = 1$ mole

and $w = 1$ g

then $\Delta T_b = K$

If $\frac{w}{m} = 1$ and $W = 100$ grams

$$\therefore \quad \Delta T_b = \frac{K}{100} = K' \quad = \text{ molecular elevation constant}$$

$$\therefore \quad K = 100\,K'$$

$$\Delta T_b = \frac{100K' \times w}{m \times W}$$

If $\frac{w}{m} = 1$ and $W = 1000$ gram

$$\therefore \Delta T_b = \frac{K}{1000} = K_b$$ (molal elevation constant or Ebulloscopic constant)

K_b is defined as the elevation in boiling point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

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

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

$$\therefore \quad \Delta T_b = \text{molality} \times K_b$$

$$\therefore \quad \Delta T_b \propto \text{molality}$$

So we can say that elevation of boiling point = boiling point of the solution – boiling point of pure solvent

$$\Delta T_b = (T_b)_s - T_0$$

The elevation in boiling point of solution of non-electrolyte is proportional to its molality and equimolal solution of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation of boiling point.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^2}{1000\,L_v}$$

where, R is molar gas constant, T_b is the boiling point of the solvent on kelvin scale and L_v the latent heat of vaporisation of solvent in calories per gram.

For water

$$K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515$$

The molal elevation constant for some common solvents are given in the following table

Solvent	B.P. (°C)	Molal elevation constant
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.67
Carbon tetra chloride	76.8	5.02
Benzene	80.0	2.70
Ethyl alcohol	78.4	1.15

Ex. 0.15 g of a substance dissolved in 15 g of solvent boiled at a temperature higher by 0.216°C than that of the pure solvent. What is the molecular weight of the substance. [K_b for solvent = 2.16°C]

Sol. Given $K_b = 2.16°C$

$w = 0.15$ g

$\Delta T_b = 0.216°C$

$W = 15$ g

$$\Delta T_b = \text{molality} \times K_b$$

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

$$0.216 = \frac{0.15}{m \times 15} \times 1000 \times 2.16$$

$$m = \frac{0.15 \times 1000 \times 2.16}{0.216 \times 15} = 100$$

Ex. The rise in boiling point of a solution containing 1.8 g glucose in 100 g of a solvent is 0.1°C. The molal elevation constant of the liquid is –

Sol. $\Delta T_b = \text{molality} \times K_b$

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

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

$\Delta T_b = 0.1°C$

$m = 180$

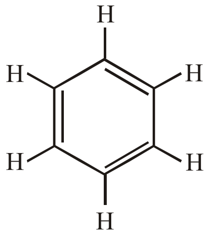
$W = 100$

$w = 1.8$

$$K_b = \frac{180 \times 0.1 \times 100}{1000 \times 1.8} = 1.0$$

Ex. A solution of 122 gm of benzoic acid is 1000 gm of benzene shows a b.p. elevation of 1.4°. Assuming that solute is dimerized to the extent of 80 percent (80°C) calculate normal b.p. of benzene. given molar enthalpy of vap. of benzine = 7.8 Kcal/mole.

Sol. $$T_b - T_i = \frac{122 \times 1000}{122 \times 1000} \times K_b \left(1 + \left(\frac{1}{n} - 1\right)\right) 0.8$$



$$\Rightarrow \quad K_b \left[\frac{1}{2} \times 0.8\right]$$

$$T_b - T_i = K_b \times 0.6$$

$$K_b = \frac{RT_b^2}{1000 \times L_{vap.}}$$

$$K_b = \frac{2 \times T_b^{\,2} \times 78}{1000 \times 7.8 \times 1000}$$

$$1.4 = \frac{0.4 \times 2}{10^5} T_b^{\,2}$$

$$T_b = 418.33\ \text{K}$$

Ex. 1 Lit. of aq. solution of urea having density = 1.060 gm/mL is found to have $\Delta T_b = 0.5^\circ C$, If temp. of this solution increase to 101.5ºC then calculate amount of water which must have gone is vapour state upto this pt. given $K_b = 0.5\ \text{K kg mol}^{-1}$ for water

Sol. mass of solution = $1.060 \times 10^3 = 1060$ gm

$$0.5 = 0.5 \times \frac{1060}{1060}\frac{M}{60} \qquad \Rightarrow \qquad 1060 \times 60 = M$$

1 Lit solution = 1060 gm

(Mass of water) i = 1000 gm

urea = 60 gm

$$\Delta T_b = (\text{molality})_i \times K_b$$

$$(\text{Molality})_i \qquad \Rightarrow \qquad 3 = \frac{60}{60} \times \frac{1000}{W_{water}}$$

$$W_{water} = \frac{1000}{3}\ \text{gm.}$$

$$\text{mass of water vaporised} = 1000 - \frac{1000}{3} = \frac{2000}{3}\ \text{gm} = 666.67\ \text{gm}$$

Depression in freezing point (Cryoscopy)

The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other.

It may be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.

When a non-volatile non-electrolyte is dissolved in a pure solvent the vapour pressure of the solvent is lowered

If T_o is the freezing point of pure solvent and $(T_f)_s$ is the freezing point of its solution then,

$$(T_f)_s < T_o$$

The difference in the freezing point of pure solvent and solution is the depression of freezing point (ΔT_f) Thus,

$$T_o - (T_f)_s = \Delta T_f$$

Depression in freezing point is directly proportional to the lowering of vapour pressure of solution.

$$\Delta T_f \propto P^0 - P_s$$

from Raoult's law for dilute solution :

$$\frac{P^0 - P_S}{P^0} = \frac{w_A}{m_A} \cdot \frac{m_B}{w_B}$$

or $$P^0 - P_S = \frac{w_A}{m_A} \cdot \frac{m_B}{w_B} . P^0$$

for the pure solvent, P^0 and m_B are constant. therefore –

$$P^0 - P_S \propto \frac{w_A}{m_A w_B}$$

or $$\Delta P \propto \frac{w_A}{m_A w_B} \propto \Delta T$$

$$\Delta T_f = K\frac{w_A}{m_A w_B}$$

Where K is a constant, called depression constant .

when $\frac{w_A}{m_A} = 1$ (one mole of solute)

and $w_B = 1g.$

then $\Delta T_f = K$

If $\frac{w_A}{m_A} = 1$ and $w_B = 100$ g

then $\Delta T_f = \frac{K}{100} = K'$

K' is called molecular depression constant.

It is defined as the depression of freezing point produced when 1 mole of the solute is dissolved in 100 g of the solvent.

Thus $K' = 100\,K$

So $$\Delta T_f = \frac{100K' \times w_A}{m_A \times w_B}$$

If $\frac{w_A}{m_A} = 1$ and $w_B = 1000$ g

$$\Delta T_f = \frac{K}{1000} = K_f$$

K_f is called molal depression constant.

K_f is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

or $\Delta T_f = \frac{1000K_f \times w_A}{m_A \times w_B}$ or $\Delta T_f = \text{molality} \times K_f$

K_f is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$K_f = \frac{0.002\,T_f^2}{L_f}$$

Where, T_f is the freezing point of solvent in absolute scale and L_f the the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86$$

the molal depression constant for some common solvents are given in the following table

Solvent	F.P.(°C)	Molal depression solvents
Water	0.0	1.86
Ethyl alcohol	– 114.6	1.99
Chloroform	– 63.5	4.70
Carbon tetra chloride	– 22.8	29.80
Benzene	5.5	5.12
Camphor	179.0	39.70

Ex. If freezing point of a solution prepared from 1.25 g of a non electrolyte and 20 g of water is 271.9 K, the molar mas of the solute will be –

Sol. Given = $(T_f)_s = 271.9$ K

$w = 1.25$ g $\quad W = 20$ g $\quad K_f = 1.86$

$\Delta T_f = T_0 - (T_f)_s$

$= 273 - 271.9$

$\Delta T_f = 1.1$

$\Delta T_f =$ molality $\times K_f$

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

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

$$m = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20}$$

$m = 105.68$

Ex. Molal depression constant for water is 1.86°C. The freezing point of a 0.05 molal solution of a non electrolyte in water is

Sol. $\Delta T_f =$ molality $\times K_f$

$= 0.05 \times 1.86 \quad = 0.093°C$

$(T_f)_S = T_0 - 0.093 \quad = 0 - 0.093$

$(T_f)_S = -0.093$

Ex. Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence, their (assume equal concentrations in all three cases)

(A) b.p. : $X < Y < Z$ **(B*)** f. p. $Z < X < Y$

(C) osmotic pressure : $X = Y = Z$ **(D)** v. p. : $Y < X < Z$

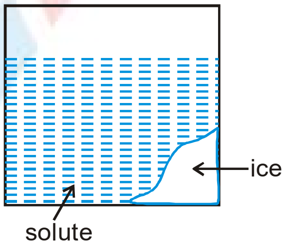
Sol. As van't Hoff factor increases RLVP increases i.e., V.P. decreases $y > x > z$

Elevation in b.p. increases i.e., b.p. increases $y < x < z$

Depression in f.p increases i.e., f.p decreases $y > x > z$

Osmotic pressure increases so $y < x < z$.

Ex. 1000 gm H_2O have 0.1 mole urea and its freezing point is – 0.2ºC and now it is freezed upto – 2ºC then how much amount of ice will form.



Sol. It is assume that solute do not freeze and do not vapourise

$$\Delta T_F = 0.2 = K_f \frac{0.1}{1000} \times 1000 \quad ....(i)$$

$$\Delta T_F = 2 = K_f \frac{0.1}{\text{wt. of solvent}} \times 1000 \quad ....(ii)$$

on dividing $\frac{\text{wt. of solvent}}{1000} = \frac{0.2}{2}$.

weight of remaining H_2O is 100 gm and weight of ice is 900 gm.

Ex. If boiling point of an aqueous solution is 100.1ºC. What is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

Sol. For a given aqueous solution

$$\Delta T_b = K_b' \times \text{molality}$$
$$\Delta T_f = K_f' \times \text{molality}$$

$$\therefore \quad \frac{\Delta T_b}{\Delta T_f} = \frac{K_b'}{K_f'} = \frac{RT_b^2}{1000\, l_v} \times \frac{1000\, l_f}{RT_f^2}.$$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{T_b^2 \times l_f}{T_f^2 \times l_v}$$

$T_b = 100 + 273 = 373$ K.
$T_f = 0 + 273 = 273$ K.
$l_f = 80$ cal g^{-1}.
$l_v = 540$ cal g^{-1}.

$$\therefore \quad \frac{0.1}{\Delta T_f} = \frac{373 \times 373 \times 80}{273 \times 273 \times 540}.$$

$\therefore \quad \Delta T_f = 0.362.$

$\therefore \quad T_f = 0.0 - 0.362. =$ **$-$ 0.362ºC.**

Ex. A 0.001 molal solution of a complex reprsented as $Pt(NH_3)_4Cl_4$ in water had a freezing point depression of 0.0054ºC. Given K_f for $H_2O = 1.86$ molality^{-1}. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

Sol. Let n atoms of Cl be the acting as ligand. Then formula of complex and its ionisation is :

$$\begin{array}{ccccc} [Pt(NH_3)_4Cl_n]Cl_{(4-n)} & \longrightarrow & [Pt(NH_3)_4Cl_n]^{+(4-n)} & + & (4-n)\, Cl^- \\ 1 & & 0 & & 0 \\ 0 & & 1 & & (4-n) \end{array}$$

Thus particles after dissociation $= 4 - n + 1 = 5 - n$

and therefore, van't Hoff factor (i) $= 5 - n$

Now $\Delta T_f = K'_f \times$ molality $\times$ van't Hoff factor

$0.0054 = 1.86 \times 0.001 \times (5 - n)$

$\therefore \quad n = 2.1 \approx 2$ (integer value)

Thus complex and its ionisation is :

$$[Pt(NH_3)_4Cl_2]Cl_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$$

Ex. Depression of freezing point of 0.01 molal aq. CH_3COOH solution is 0.02046°. 1 molal urea solution freezes at –1.86°C. Assuming molality equal to molarity, pH of CH_3COOH solution is :

(A) 2 **(B*)** 3 **(C)** 3.2 **(D)** 4.2

Sol. For urea

$$\Delta T_f = k_f \times m \qquad \text{or} \qquad k_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86$$

Now for CH_3COOH

$$\Delta T_f = i\, k_f m$$

$$\text{so} \qquad i = \frac{0.02046}{1.86 \times 0.01} = 1.1$$

Now $i = 1 + \alpha$

so $\alpha = 1.1 - 1 = 0.1$

Now
$$
\begin{array}{lccc}
CH_3COOH & \rightleftharpoons & CH_3COO^- & + \quad H^+ \\
C & & 0 & 0 \\
C - C\alpha & & C\alpha & C\alpha
\end{array}
$$

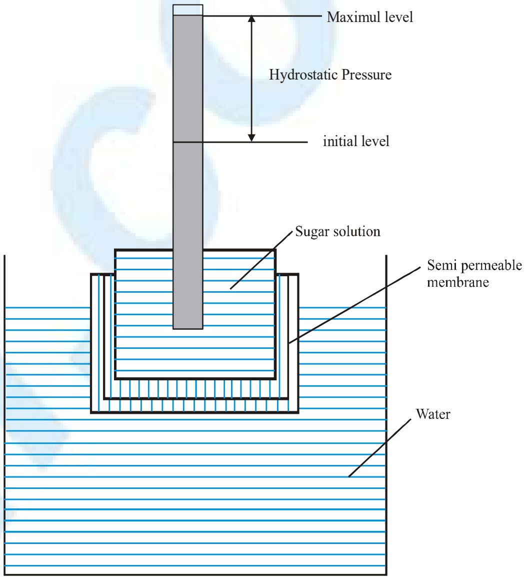
$$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$$

so $pH = 3.$

OSMOSIS AND OSMOTIC PRESSURE

Osmosis :

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a dilute solvent to a solution or from a dilute to a concentrated solution.



Osmotic presssure (π)

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution.

or

The hydrostatic pressure built up on the solution which just stops the osmosis.

osmotic pressure = hydrostatic pressure

$$\pi = hdg$$

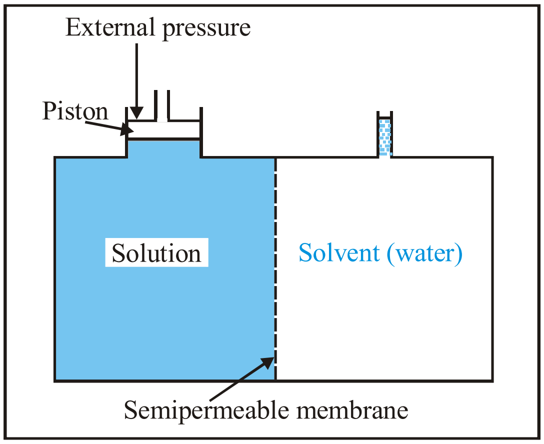
h = increase in level in the tube of unit cross section.

d = density of solution,

g = acceleration due to gravity

or

The external pressure which must be applied on the solution in order to stop the flow of the solvent into the solution through semipermeable membrane is equal to osmotic pressure.



Van't Hoff law for dilute solution

The osmotic pressure (P or π) of a solution is directly proportional to its concentration(C) when the temperature is kept constant. The concentration of the solution containg in one gram mole in V litres is equal to 1/V.

thus $P \propto C$ (when temperature is constant)

or $P \propto \frac{1}{V}$

$PV = \text{constant}$ or $\pi V = \text{constant}$

Gay – Lussac – Van't Hoff law (Pressure - Temperature law)

Concentration remaining same, the osmotic pressure of a dilute solution directly proportional to its absolute temperature (T), i.e.,

$P \propto T$

or $\frac{P}{T}$ = consant

or $\frac{\pi}{T}$ = consant

Combining the two laws, i.e., when concentration and temperature both are changing, the osmotic pressure will be given by :

$P \propto CT$

or $P = kCT$

or $P = k.\frac{1}{V}.T$ $\left(\text{since, } C = \frac{1}{V}\right)$

or $PV = ST$ or $\pi V = ST$

S is called molar solution constant.

Here, V is the volume solution containing one gram mole of the solute. The value of S comes out to 0.082 litre atm K^{-1} mol^{-1} which is in agreement with the value of R, the molar gas constant. In case, the solution contains n gram moles in V litre, the general equation would become :

$PV = nST$

or $\pi V = nST$

Ex. A cane sugar solution has an osmotic pressure of 2.46 atm at 300 K. What is the strength of the solution.

Sol. $\pi V = nST$

or $\pi = \frac{n}{V}ST = CST$

or $C = \frac{\pi}{ST} = \frac{2.46}{300 \times 0.0821} = 0.1\ M$

Isotonic or iso-osmotic solution

Solutions which have the same osmotic pressure are termed isotonic or iso-osmotic solutions

$\pi_1 = \pi_2$

i.e. $C_1ST = C_2ST$

$C_1 = C_2$

Hypertonic solution

A solution having higher osmotic pressure than some other solution is said to be called hypertonic solution.

Hypotonic solution

A solution having a lower osmotic pressure relative to some other solution is called hypotonic solution.

Semipermeable Membrane

A membrane which allows the passage of solvent molecules but not that of solute. When a solution is separated from the solvent by it is known as semipermeable membrane.

Some example of it are as follows

(a) Copper ferrocyanide $Cu_2[Fe(CN)_6]$;

(b) Calcium phosphate membrane; and

(c) Phenol saturated with water.

Ex. A solution containing 8.6 g urea in one litre was found to be isotonic with 0.5% (wt./vol.) solution of an organic, non-volatile solution. The molecular weight of latter is

Sol. Solutions are isotonic

so $\pi_1 = \pi_2$

$$\frac{n_1}{V_1}ST = \frac{n_2}{V_2}ST \qquad \{S \ \& \ T \text{ are constant}\}$$

so, $\frac{n_1}{V_1} = \frac{n_2}{V_2}$

or $\left(\frac{w_1}{m_1 \times v_1}\right)_{urea} = \left(\frac{w_2}{m_2 \times v_2}\right)_{organic}$

or $\frac{8.6}{60 \times 1000} = \frac{0.5}{m_2 \times 100}$

$m_2 = 34.89$

Reverse Osmosis

If external pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis.

* Reverse osmosis is used for the desalination of sea water for getting fresh drinking water.

Ideal Solutions

A solution which obeys Rault's law exactly at all concentrations and at all temperatures is called an ideal solution.

An ideal solution possesses the following characteristics :

(i) Volume change of mixing shoule be zero.

$\Delta V_{mix} = 0 ; V_{solvent} + V_{solute} = V_{solution}$

(ii) Heat change on mixing should be zero.

$\Delta H_{mix} = 0$ (Heat is neither absorbed nor evolved)

(iii) There should be no chemical reaction between solvent and solute.

(iv) Solute molecules should not dissociate in the ideal solution.

(v) Solute molecules should not associate in ideal solution.

(vi) Ideal solution must obey Raoult's law at all concentrations.

Ex. : (i) Benzene and toluene

(ii) Carbon tetrachloride and silicon tetra chloride.

(iii) n - Hexane and n - heptane

(iv) Ethylene dibromide and ethylene dichloride.

Non Ideal solutions

Those solutions which do not obey Rault's law are called non-ideal solutions.

For such solutions $P_A \neq P_A^o \cdot X_A$

$P_B \neq P_B^o \cdot X_B$

Non ideal solutions are formed when the components differ much in their structures and polarities.

$\Delta H_{mixing} \neq \text{zero}$

$\Delta V_{mixing} \neq \text{zero}$

Non ideal solutions show either positive or negative deviations from Rault's law.

Ex. Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 mole of B is 550 mm of Hg. At the same temperature, if one more mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

Sol. Let the vapour pressure of pure A be = p_A^0 ; and the vapour pressure of pure B be = p_B^0 .

Total vapour pressure of solution (1 mole A + 3 mole B)

$= X_A.p_A^0 + X_B.p_B^0$ [X_A is mole fraction of A and X_B is mole fraction of B]

$$550 = \frac{1}{4}p_A^0 + \frac{3}{4}p_B^0 \quad \text{or} \quad 2200 = p_A^0 + 3p_B^0 \qquad \text{.......(i)}$$

Total vapour pressure of solution (1 mole A + 4 mole B) = $\frac{1}{5}p_A^0 + \frac{4}{5}p_B^0$

$$560 = \frac{1}{5}p_A^0 + \frac{4}{5}p_B^0$$

$$2800 = p_A^0 + p_B^0 \qquad \text{.......(ii)}$$

Solving eqs. (i) and (ii)

p_B^0 = 600 mm of Hg = vapour pressure of pure B

p_A^0 = 400 mm of Hg = vapour pressure of pure A

Positive deviation from Rault's law

This deviation is shown when the forces of attraction between A – B molecules are less than forces of attraction between A – A and B – B molecules in the two liquids forming the solution.

$$P_A > P_A^o \cdot X_A$$

$$P_B > P_B^o \cdot X_B$$

The total vapour pressure of the solution will be greater than the corresponding vapour pressure expected in case of ideal, an ideal solution of same composition. i.e.

$$P_{total} > P_A^o \cdot X_A + P_B^o \cdot X_B$$

— $\Delta H_{mix} > 0$. Endothermic dissolution ; heat is absorbed.

— $\Delta V_{mix} > 0$. volume is increased after dissolution.

— 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

Ex. (i) Ethanol and cyclohexane

(ii) Acetone and benzene

(iii) Water and methanol.

(iv) acetone + ethanol

(v) acetone + CS_2

(vi) water + ethanol

(vii) CCl_4 + toluene

(viii) CCl_4 + $CHCl_3$

Negative deviation from Rault's law

In these solutions the A–B interaction are stronger than the A–A and B–B molecular interactions present in the two liquids forming the solution. For thus solutions showing –ve deviation.

$$P_A < P_A^o \cdot X_A$$

$$P_B < P_A^o \cdot X_B \quad \text{and} \quad P_{total} < P_A^o \cdot X_A + P_B^o \cdot X_B$$

– $\Delta H_{mix} < 0$; exothermic dissolution heat is evolved.

– $\Delta V_{mix} < 0$; volume is decreased during dissolution.

Escaping tendency of both components 'A' and 'B' is lowered showing lower vapour pressure than expected ideally.

Ex. (i) Acetone and chloroform

(ii) Nitric acid and chloroform.

(iii) Water and HCl.

(iv) $CH_3OH + CH_3COOH$

(v) $H_2O + HNO_3$

(vi) Chloroform + diethyl ether

(vii) water + HCl

(viii) acetic acid + pyridine

(ix) chloroform + benezene

Relation between Dalton's Law and Raoult's Law

The composition of the vapour in equilibrium with the solution can be calculated applying Dalton's law of partial pressures. Let the mole fraction of vapours A and B be Y_A and Y_B respectively. Let p_A and p_B be the partial pressure of vapours A and B respectively and total pressure P.

$p_A = Y_A P$ ....(i)

$p_B = Y_B P$ ....(ii)

$p_A = X_A P_A^0$ ....(iii)

$p_B = X_B P_B^0$ ....(iv)

Equating eqs. (i) and (iii),

$$Y_A P = X_A P_A^0$$

or $$Y_A = \frac{X_A P_A^0}{P} = \frac{p_A}{P}$$

Similarly, equating eqs. (ii) and (iv),

$$Y_B = \frac{X_B P_B^0}{P} = \frac{p_B}{P}$$

Thus, in case of ideal solution the vapour phase is richer with more volatile component, i.e., the one having relatively greater vapour pressure.

Abnormal colligative properties

It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.

Association of solute particles

The formation of a bigger molecule by the union of two, three or more solute molecules is called association.

Let 'n' simple molecules combine to give an associated molecule as :

$$n(X) \underset{\text{solvent}}{\overset{\text{non polar}}{\rightleftharpoons}} (X)_n$$

n single molecules　　　one bigger molecule.

As a result, the total number of particles in solution becomes less than the number of molecules initially dissolved in the solution and hence the colligative properties will have lower value.

As the molar mass of solute is inversely proportional to the colligative properties, so the molar mass of solute will be greater than theoretical value.

Dissociation of solute molecules

Molecules of electrolytes undergo ionization or dissociation in ionizing solvents to give two or more particles in solution.

For example, AB ionizes in solution to give two particles.

$$AB \underset{\text{solvent}}{\overset{\text{ionizing}}{\rightleftharpoons}} A^+ + B^-$$

This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher.

As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.

Van't Hoff factor (i)

In order to express the extent of association or dissociation with certain solutes are expected to undergo in solution. Van't Hoff in 1886, introduced a factor, called Van't Hoff factor (i). The factor i is defined as

$$i = \frac{\text{observed colligative property}}{\text{Normal colligative property}}$$

$$i = \frac{\text{Normal or actual molecular weight}}{\text{observed molecular mass.}}$$

In case of association of solute particles in solution, the observed molecular weight of solute being more than the normal, the value of factor 'i' is less than unity (i.e. $i < 1$), while for dissociation the value of i is greater than unity (i.e. $i > 1$), because the observed molecular weight has lesser value than normal molecular weight.

Van't Hoff factor and degree of dissociation

The fraction of the total number of molecules which dissociates in the solution into simple ions or molecules is called the degree of dissociation.

$$i = \frac{\text{number of particles after dissociation}}{\text{Number of particles initially taken.}}$$

Calculation of 'i'

Let, solute be A_xB_y

	A_xB_y	$\longrightarrow$	$x\,A^{y+}$ +	yB^{x-}
Initial mol	1		0	0
after dissociation	$1-\alpha$		$x\alpha$	$y\alpha$

Total no. of solute particles

$= 1 - \alpha + x\alpha + y\alpha$

$= 1 - \alpha + \alpha(x + y)$

$= 1 - \alpha + n\alpha$ [where $x + y = n$ (total ions.)]

(i) observed colligative properties $\propto$ observed number of solute particles

observed colligative properties $\propto (1 - \alpha + n\alpha)$

(ii) Normal colligative properties $\propto 1$

$$\frac{\text{eq (i)}}{\text{eq (ii)}} \Rightarrow i = \frac{1 - \alpha + n\alpha}{1}$$

$$i - 1 = \alpha(n - 1)$$

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

for strong electrolytes : $\alpha = 1$ or 100% so $i = n$ (total no. of ions)

Ex. $NaCl \rightarrow Na^+ + Cl^-$ $(i = 2)$

Ex. $K_2SO_4 \rightarrow 2K^+ + SO_4^{2-}$ $(i = 3)$

Ex. for complex compound

$K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(CN)_6]^{4-}$

$n = 5$

If $\alpha = 50\%$ then find Van't hoff factor **'i'** = ?

Sol. $i = 1 - \alpha + n\alpha$

or $i = 1 - 0.5 + 5 \times 0.5 = 3$

Van't Hoff factor and degree of association

The fraction of the total number of molecules of the substance which is present as associated molecules is known as the degree of association.

$$i = \frac{\text{Number of particles after association}}{\text{Number of particles before association}}$$

Calculation of 'i'

Let, solute be nA

	$nA \longrightarrow$	$(A)_n$
Initial mol	1	0
after dissociation	$1 - \alpha$	α/n

Total no. of solute particles

$= 1 - \alpha + \alpha/n$

(i). observed colligative properties $\propto$ observed number of solute particles.

observed colligative properties $\propto 1 - \alpha + \alpha/n$

(ii). Normal colligative properties $\propto 1$

$$\frac{\text{eq (i)}}{\text{eq (ii)}} \Rightarrow i = 1 - \alpha + \alpha/n$$

$$\alpha = \frac{1 - i}{1 - \left(\frac{1}{n}\right)}$$

α = degree of assocation , n = no. of solute particles which are associated

Ex. A 5% solution of anhydrous $CaCl_2$ at 0°C developed 15 atm. Osmotic pressure. What is the degree of dissociation of $CaCl_2$.

Sol. 5 g. of $CaCl_2$ are present in 100 ml, so 111 g (mol. wt. of $CaCl_2$) will be present in

$$\frac{100 \times 111}{5 \times 1000} = 2.22 \text{ lit.}$$

Now $\pi V = ST$ {✈ $n = 1$}

or $\pi = \frac{0.082 \times 273}{2.22} = \frac{22.47}{2.22} = 10.09$ atm

Van't Hoff factor

$$i = \frac{\text{Actual no. of particles in solution}}{\text{No. of particles taken}}$$

and $\alpha = \frac{i - 1}{n - 1}$

here $n = 3$

$$\alpha = \frac{\frac{15}{10.09} - 1}{3 - 1} = \frac{4.91}{10.09 \times 2}$$

$$\alpha = 0.2433 \text{ or } 24.33\%$$

Ex. Calculate osmotic pressure of 0.1 M urea aqueous solution at 300 K ,

Sol. $R = 0.082$ lit atm K^{-1}

$\pi = CRT$

$\pi = 0.1 \text{ x } 0.082 \text{ x } 300$

$\pi = 2.46$ atm.

Ex. If 10 gm of an unknown substance (non-electrolytic) is dissolved to make 500 mL of solution, then osmotic pressure at 300 K is observed to be 1.23 atm find molecular weight ?

Sol. $1.23 = \frac{10 \times 1000}{M \times 500} \text{ x } 0.082 \text{ x } 300$

$$M = \frac{20}{1.23} \text{ x } \frac{0.082}{100} \text{ x } 300 \quad \approx 400 \text{ gm/mol}$$

Ex. If 6 gm of urea, 18 gm glucose & 34.2 gm sucrose is dissolved to make 500 mL of a solution at 300 K calculate osmotic pressure ?

Sol. molecular weight of urea = 60 gm , Glucose = 180gm , Sucrose = 342 gm

$\pi = C \text{ x } 0.082 \text{ x } 300$

$$\pi = \frac{0.3 \times 1000 \times 0.082 \times 300}{500} \quad \Rightarrow 14.76 \text{ atm}$$

Ex. If 200 mL of 0.1 M urea solution is mixed with 300 mL of 0.2 M glucose solution at 300 K, Calculate osmotic pressure ?

Sol. 0.02 moles urea

0.06 moles glucose $\quad \Rightarrow \pi = \frac{0.08}{0.5} \times 0.082 \times 300 = 3.94$ atm.

Ex. If urea (aq) solution at 500K has O.P. = 2.05 atm. & glucose solution at 300 K has OP = 1.23 atm. If 200 ml of Ist solution & 400 ml of 2nd solution are mixed at 400 K then calculate O.P. of resulting solution at 400 K (assume molarity is not dependent on temp.)

Sol. $C_{urea} = \frac{2.05}{R \times 500} = 0.05 \quad \Rightarrow \quad V_{urea} = 200\text{ mL}$

$C_{glucose} = \frac{1.23}{R \times 300} = 0.05 \quad \Rightarrow \quad V_{glucose} = 400\text{ mL}$

$C_{total} = \frac{C_1V_1 + C_2V_2}{V_1 + V_2} = \frac{0.05 \times 200 + 0.05 \times 400}{600} = 0.05$

$\pi = CRT = 0.05 \times 0.082 \times 400$

$\pi = 1.64$ atm

Ex. $\frac{0.1\text{M urea}}{(A)}, \frac{0.1\text{M NaCl}}{(B)}, \frac{0.1\text{M BaCl}_2}{(C)}$

Sol.

order of π — $C > B > A.$

order of R.L.V.P — $C > B > A.$

order of V.P — $A > B > C.$

order of ΔT_B — $C > B > A.$

order of T_B of solution — $C > B > A.$

order of ΔT_F — $C > B > A.$

order of T_F of solution — $A > B > C.$

(Calculating osmotic pressure when reaction is not taking place)

Ex. Calculate osmotic pressure of a solutions having 0.1 M NaCl & 0.2 M Na_2SO_4 and 0.5 MHA.
(Given : Weak acid is 20% dissociated at 300 K).

Sol. $\pi = \pi_{NaCl} + \pi_{Na_2SO_4} + \pi_{HA}$

$= 0.1\ RT \times 2 + 0.2\ RT \times 3 + 0.5\ RT \times 1.2$

$= 0.0821 \times 300\ (0.2 + 0.6 + 0.6)$

$= 34.482$ atm.

Ex. If 0.04 M Na_2SO_4 solutions at 300 K is found to be isotonic with 0.05 M NaCl (100 % dissociation) solutions. Calculate degree of dissociation of sodium sulphate ?

Sol. $i_1 C_1 RT = i_2 C_2 RT$

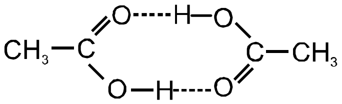
$i_1 C_1 = i_2 C_2$

$0.04\ (1 + 2\alpha) = 0.05 \times 2$

$\alpha = 0.75 = 75\%.$

Ex. If 6 gm of CH_3 COOH is dissolved in benzene to make 1 litre at 300 K. Osmotic pressure of solution is found to be 1.64 atm. If it is known that CH_3COOH in benzene forms a dimer. Calculate degree of association of acetic acid in benzene ?

Sol.



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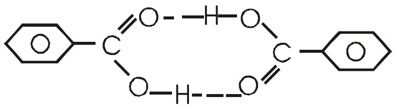


$$i = 1 + \left(\frac{1}{n} - 1\right)\beta.$$

$$1.64 = 0.0821 \times 300 \times [\,1 + \left(\frac{1}{n} - 1\right)\beta\,] \times 0.1$$

$$\Rightarrow \quad 1.64 = 0.0821 \times 300\ [1 - \frac{\beta}{2}]\,0.1$$

$$\frac{1.64}{00.821 \times 30} = \frac{2-\beta}{2}$$

$$\frac{1.64}{2.46} = \frac{2-\beta}{2} \qquad 4 = 6 - 3\beta$$

$$3\beta = 2$$

$$\beta = \frac{2}{3}$$

(Calculating osmotic pressure when reaction is taking place)

Ex. If 200 ml of 0.2 M $BaCl_2$ solution is mixed with 500 ml of 0.1 M Na_2SO_4 solution. Calculate osmotic pressure of resulting solutions ?

Sol.

$BaCl_2$ +	Na_2SO_4 →	$BaSO_4$ +	2 NaCl
0.04 moles	0.05	0	0
0	0.01	No effect	0.08
	$\frac{0.01}{0.7}$	No effect	$\frac{0.08}{0.7}$

$$\pi = (i_1C_1 + i_2C_2)\,RT.$$

$$= (3 \times \frac{0.01}{0.7} + 2 \times \frac{0.08}{0.7})\,0.082 \times 300. = \textbf{6.685 atm.}$$

Ex. If 200 ml of 0.2 M $HgCl_2$ solution is added to 800 ml of 0.5 M KI (100% dissociated) solution. Assuming that the following complex formation taken place to 100% extent.

$$Hg^{2+} + 4I^- \longrightarrow [HgI_4]^{2-}$$

0.04 0.4

Calculate osmotic pressure of resulting initially solution at 300K ?

Sol.

$HgCl_2$ +	4KI →	$K[HgI_4]$ +	2KCl.
40	400	0	0
0	400 –160	40	80
	$\frac{240}{1000}$	$\frac{40}{1000}$	$\frac{80}{1000}$

$$\pi = (i_1C_1 + i_2C_2 + i_3C_3)\,RT.$$

$$= (0.24 \times 2 + 3 \times 0.04 + 0.08 \times 2)\,0.082 \times 300. = \textbf{18.69 atm.}$$

Other method :

$$\begin{array}{cccc} HgCl_2 & + \; 4KI & \rightleftharpoons \; K[HgI_4] & + \; 2KCl. \\ 40 & 400 & 0 & 0 \\ 0 & 400-160 & 40 & 80 \\ & \frac{240}{1000} & \frac{40}{1000} & \frac{80}{1000} \end{array}$$

$\pi = (i_1C_1 + i_2C_2 + i_3C_3)\,RT.$

$= (0.24 \times 2 + 3 \times 0.04 + 0.08 \times 2)\,0.082 \times 300. =$ **18.69 atm.**

Ex. (**Note:** Attempt this problem after you have studied co-ordination compounds)

Ba^{2+} ions, CN^- & Co^{2+} ions form a water soluble complex with Ba^{2+} ions as free cations for a 0.01 M solution of this complex, osmotic pressure = 0.984 atm & degree of dissociation = 75%. Then find coordination number of Co^{2+} ion in this complex (T = 300 K, R = 0.082 L atm. $mol^{-1}\,k^{-1}$)

Sol. Say C.N. = x

$0.984 = i\,CRT$

$0.984 = i\,0.01 \times 0.082 \times 300 = i \times 0.246$

$i = 4 = 1 + (n-1)\,\alpha$

$\Rightarrow$ n = 5

Charge on co-ordination sphere = charge on Coblat ion - charge on x cyanide ions = - (x-2)

i.e. co-ordination sphere is $[Co(CN)_x]^{-(x-2)}$

Change on Barium ion is +2

Thus, formula of the complex will be $Ba_{(x-2)}\,[Co(CN)_x]_2$ by charge balance.

$x - 2 + 2 = 5$

$x = 5$

$\therefore$ CN = 5

$\therefore$ Formula is $Ba_3[Co(CN)_5)_2$.

DISTRIBUTION LAW

Nernst distribution law

(a) A solute on addition between two immiscible solvents distributes itself in such a way that the ratio of its concentration in between two solvents remains constant at constant temperature provided the solute remains in same molecular state in both solvent.

(b) Let solute A be distributed in between two phases I and II, then according to the distribution law,

$$K = \frac{[A]\text{in phase I}}{[A]\text{in phase II}} = \frac{[C_A]_I}{[C_A]_{II}}$$

or $$K = \frac{\text{Moles of A in phase I}}{\text{Volume of phase I in litre}} \times \frac{\text{Volume of phase II in litre}}{\text{Moles of A in phase II}}$$

or $$K = \frac{\text{wt. of A in phase I}}{\text{Volume of phase I in litre}} \times \frac{\text{Volume of phase II in litre}}{\text{wt. of A in phase II}}$$

Where K is distribution coefficient or partition coefficient, a characteristic constant at the given temperature for given solute-solvent - I - solvent - II system.

(c) Also,

$$K \text{ in favor of I} = \frac{[C_A]_I}{[C_A]_{II}}$$

$$K \text{ in favor of II} = \frac{[C_A]_{II}}{[C_A]_I}$$

Condition for validity of law

(a) Temperature should remain constant .

(b) Solution should be dilute.

(c) System must be heterogeneous, i.e., two solvents should be immiscible.

(d) Solute should not influence the immisicibility of two solvents.

(e) Solute neither dissociate nor associate in either of the solvent.

(f) Solute should be soluble in both solvents.

Solute showing dissociation in either of the solvent

Let AB be a solute which dissolves in solvent I during its distribution between two immiscible solvents I and II, then if C_1 is concentration of solute in phase I and C_2 its concentration of solute in phase II, according to distribution law.

$$K = \frac{C_1(1-\alpha)}{C_2}$$

Where α is the degree of dissociation of solute in solvent I.

Solute showing association either of the solvent

(a) Let AB be a solute which associates in solvent II as

$$nAB \rightleftharpoons (AB)_n$$

during its distribution in between two solvents I and II.

(b) Then, if C_1 and C_2 are concentrations of solute in phase I and II respectively then according to distribution law,

$$K = \frac{C_1}{\sqrt[n]{C_2}}$$

Where n is association number and 100% association is assumed.

Extraction of solute in multistep operations

(a) Let w g of a solute be present in V mL of solvent A. Now suppose V_1 mL of another solvent B are used to extract out solute from solvent A. Suppose n operations for extraction are made using V mL of solvent B, then

$V_1 = n \times v.$

(b) Then the amount of solute (W_n) left unextracted in A after n operation using v mL of B in each step is given by

$$W_n = \left[\frac{KV}{v + KV}\right]^n W$$

It is clear from the equation of a solute from a given solution by extracting a liquid is more efficient when small volumes of extracting liquid are used in large number of operations.

Ex. 100 mL water and 50 mL ether mixture is shaken with succinic acid. At equilibrium ether layer contains 0.127 g and water layer contains 0.127 g and water layer contains 1.843 g of succinic acid. Calculate distribution coefficient in favour of water.

Sol.

$$wK_{ether} = \frac{[\text{Succinic acid}]_{water}}{[\text{Succinic acid}]_{ether}}$$

$$wK_{ether} = \frac{1.843/100}{\frac{0.127}{50}} = \frac{1.843}{100} \times \frac{50}{0.127} = 7.26$$

Ex. An organic substance has a normal molecular weight in water but gives a higher value in C_6H_6. The following data were obtained during a distribution experiment

Conc. of subs. in water ($g\,L^{-1}$)	0.01	0.02	0.24
Conc. of subs. in C_6H_6 ($g\,L^{-1}$)	1.848×10^{-5}	2.661×10^{-3}	1.089×10^{-2}

Find the degree of complexity of the substance in C_6H_6

Sol. Let, n be the complexity of acid in C_6H_6 and C_1, C_2 are concentrations of acid in water C_6H_6.

Then $$K = \frac{C_1}{\sqrt[n]{C_2}}$$

Taking log, $\log K = \log C_1 - \frac{1}{n}\log C_2$ ....(1)

using data in eq. .... (1)

$\log K = \log 0.01 - \frac{1}{n}\log 1.848 \times 10^{-5}$ ....(2)

$\log K = \log 0.12 - \frac{1}{n}\log 2.661 \times 10^{-3}$ ....(3)

$\log K = \log 0.24 - \frac{1}{n}\log 1.089 \times 10^{-2}$ ....(4)

Solving equation (1) and (3) $n = 1.999$

Solving equation (3) and (4) $n = 2.033$

The value of $n \approx 2$, which shows that organic substance form dimer in C_6H_6

AZEOTROPIC MIXTURES

Some liquids on mixing form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. Azeotropic mixture cannot be separated by fractional distillation.

TYPES OF AZEOTROPIC MIXTURES

(i) Minimum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviation. For example (95.5%) + water (4.5%) + water boils at 351.15 K.

(ii) Maximum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point are more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.

1. **Vapour Pressure :** Pressure of any volatile substance at any given temperature.

T↑ ⇒ V.P.↑

Attractive forces ↑ ⇒ V.P. ↓

2. **Raoult's law**

Non volatile solute and volatile solvent solution.

$$\text{If} \begin{cases} B = \text{Non volatile solid} \\ P_B = 0 \end{cases}$$

$$P_A = P_A^\circ X_A$$

3. **Colligative Properties :** Properties depends on no. of particles of Non volatile solute in solution.

No. of particle of Non volatile solute ↑ Colligative Properties ↑

(1) Relative lowering of V.P.

$$\frac{P_A^\circ - P_A}{P_A^\circ} = i\frac{n_B}{n_A + n_B} \; ; \; i\frac{n_B}{n_A}$$

Where n_B = mole of Non-volatile solute.

i = Vant Hoff's factor.

(2) Elevation in B.P.

$$\Delta T_b = (T_b' - T_b) = i.\,k_b \times m.$$

where $K_b = \dfrac{RT_b^2}{1000 \times l_v}$

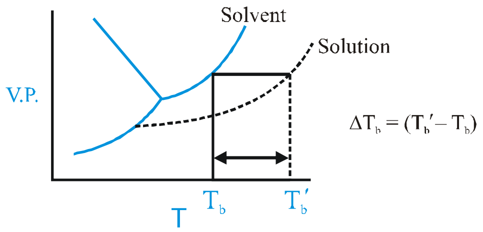
where T_b = B.P. of pure solvent.

$●_v$ = Latent heat of vapourization per gm

K_b = molal elevation constant

M = molar mass

where $●_v = \left(\dfrac{\Delta H_{vap}}{M}\right)$



(3) Depression in FP.

$$\Delta T_f = T_f - T_f' = i\,k_f \times m$$

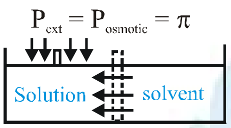
where $k_f = \dfrac{RT_f^2}{1000 \times l_f}$

T_f = f.p. of pure solvent

k_f = molal depression contsant

$●_f$ = latent heat of fusion per gm.

(4) Osmotic presssure



$\pi \propto \left(P_A^{\circ} - P_A\right)$

$\pi = iC.\,S.T.$

where π = osmotic pressure
C = molarity (mole/lit)
$S = R$ = const. for solution.

	Sol.(1)		Sol (2)	
If	π_1	=	π_2	Isotonic
If	π_1	>	π_2	$\begin{cases} \text{sol}^n(1)\text{ hypertonic} \\ \text{sol}^n(2)\text{ hypotonic} \end{cases}$

Van't Hoff factor for different Cases of solutes undergoing Ionisation and Association

Solute	Example	Ionisation/association (x degree)	y*	van'thoff factor	abnormal mol. wt. (m_1')
Non-electrolyte	urea-glucose, sucrose etc.	none	1	1	normal mol.wt. (m_1)
Binary electrolyte A^+B^-	NaCl, KCl, HCl CH_3COOH, $FeSO_4$ etc.	$\underset{1-x}{AB} \rightleftharpoons \underset{x}{A^+} + \underset{x}{B^-}$	2	$(1+x)$	$\dfrac{m_1}{(1+x)}$
Ternary electrolyte A_2B, AB_3	K_2SO_4, $BaCl_2$,	$\underset{1-x}{A_2B} \rightleftharpoons \underset{2x}{2A^+} + \underset{x}{B^{2-}}$	3	(1+2x)	$\dfrac{m_1}{(1+2x)}$
	$K_3[Fe(CN)_6]$, $FeCl_3$	$\underset{1-x}{AB_3} \rightleftharpoons \underset{x}{A^{3+}} + \underset{3x}{3B^-}$	4	(1+3x)	$\dfrac{m_1}{(1+3x)}$
Associated Solute	benzoic acid in benzene forming dimer	$2A \rightleftharpoons A_2$ $\underset{(1-x)}{A} \rightleftharpoons \underset{x/2}{\frac{1}{2}A_2}$	$\dfrac{1}{2}$	$\left(1-\dfrac{x}{2}\right) = \left(\dfrac{2-x}{2}\right)$	$\dfrac{2m_1}{(2-x)}$
	any solute forming polymer A_n	$nA \rightleftharpoons A_n$ $\underset{(1-x)}{A} \rightleftharpoons \underset{x/2}{\frac{1}{n}A_n}$	$\dfrac{1}{n}$	$\left[1+\left(\dfrac{1}{n}-1\right)x\right]$	$\left[\dfrac{m_1}{1+\left(\dfrac{1}{n}-1\right)x}\right]$
General	one mole of solute giving y mol of products	$A \rightleftharpoons yB$	y	[1+(y–1)x]	$\dfrac{m_1}{[1+(y-1)x]}$

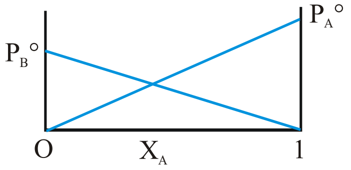
***Number of products from one mole solute**

(5) Raoult's law

Volatile binary liquid mix :

Volatile liq.	A	B
Mole fraction	X_A/Y_A	$X_B/Y_A \Rightarrow$ liq/vapour
V.P. of pure liq.	P_A°	P_B°

Binary liquid solution :

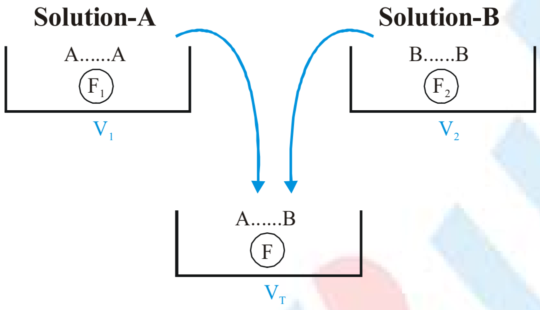


By Raoult's law $\Rightarrow P_T = P_A^{\circ}X_A + P_B^{\circ}X_B = P_A + P_B$ ......(i)

By Dalton's law $\Rightarrow P_A = Y_A P_T$ ......(ii)

$P_B = Y_B P_T$ ......(iii)

5. Ideal and Non-Ideal solution



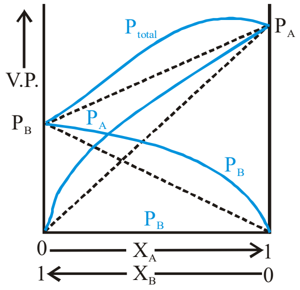
Ideal solution : $\begin{cases} F_1 \simeq F_2 \simeq F \\ V_T = V_1 + V_2 \end{cases} \Rightarrow \Delta H_{solution} = 0$

6. Non-Ideal solution

(i) Solution showing +ve deviation

$F < F_1$ & F_2

$V_T > V_1 + V_2 \Rightarrow \Delta H_{solution} > 0$

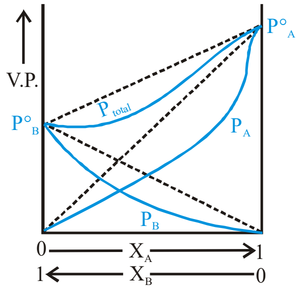


(ii) Solution showing –ve deviation

$\Rightarrow F > F_1$ & F_2

$\Rightarrow V_T < (V_1 + V_2)$

$\Rightarrow \Delta H_{solution} < 0$



DEVIATION FROM RAOULT'S LAW

	Positive deviation ($\Delta H = +ve$)	Negative deviation ($\Delta H = -ve$)	Zero deviation ($\Delta H = 0$)
(i)	ethanol + cyclohexane	acetone + chloroform	benzene + toluene
(ii)	acetone + carbon disulphide	benzene + chlorform	n-hexane + n-heptane
(iii)	acetone + benzene	nitric acid + chloroform	ethyl bromide + ethyl iodide
(iv)	ethanol + aceton	acetone + aniline	chlorobenzene + bromo benzene
(v)	ethanol + water	water + nitric acid	
(vi)	carbon tetrachloride chloroform	diethyl ether + chloroform	

7. Azeotropic mixtures

Some liquids on mixing form azeotropes which are binary mixture having same composition in liquid and vapour phase and boil at a constant temperature. Azeotropic mixture cannot be separated by fractional distillation.

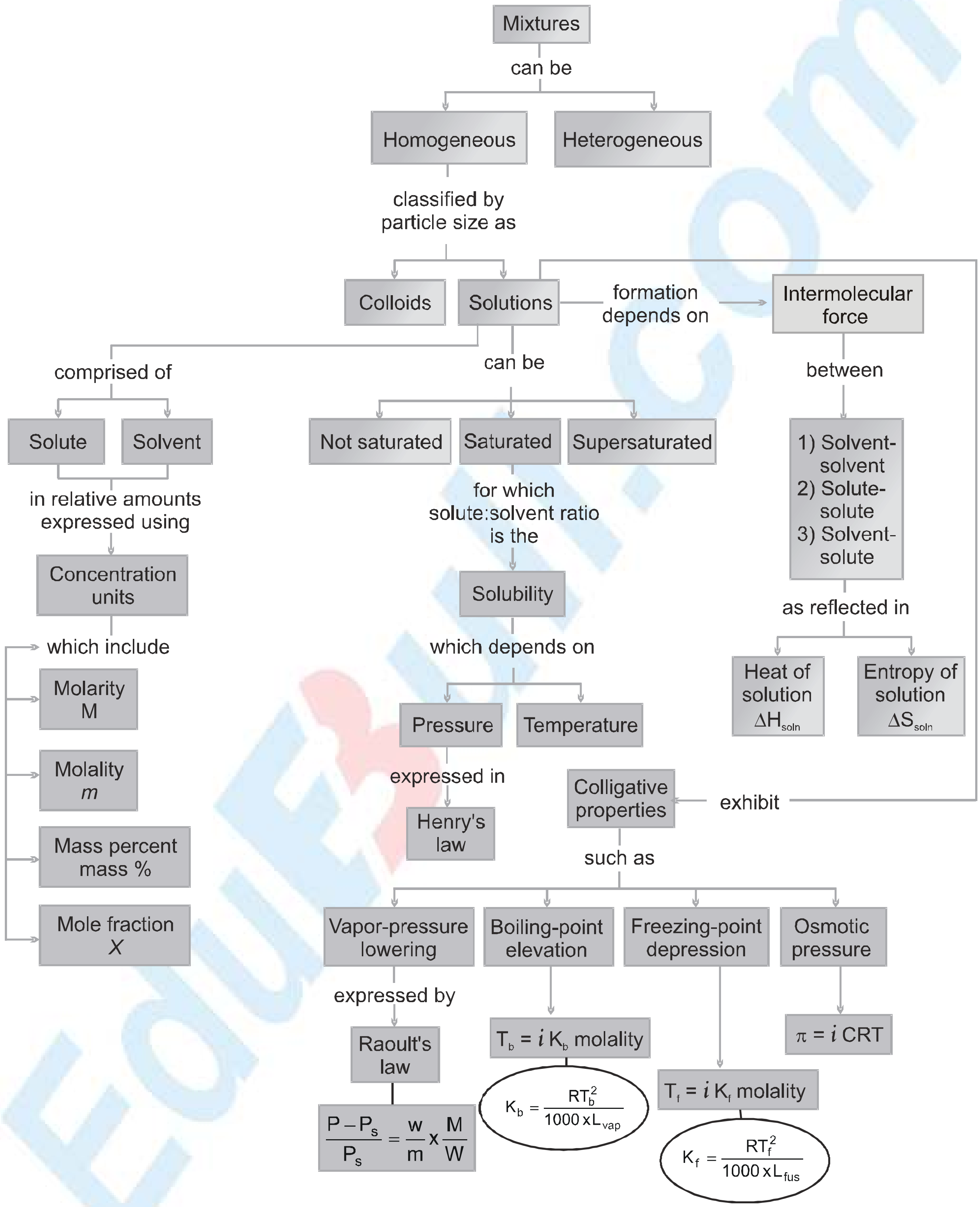
Types of Azeotropic mixtures

(i) Minimum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point is less than either of the two pure components. They are formed by non-ideal solutions showing positive deviation. For example (95.5%) + water (4.5%) + water boils at 351.15 K.

(ii) Maximum boiling Azeotropic mixtures

The mixture of two liquids whose boiling point are more than either of the two pure components. They are formed by non-ideal solutions showing negative deviation. For example HNO_3 (68%) + water (32%) mixture boils at 393.5 K.


Mixtures
can be
Homogeneous
Heterogeneous
classified by particle size as
Colloids
Solutions
formation depends on
Intermolecular force
between
1) Solvent-solvent
2) Solute-solute
3) Solvent-solute
as reflected in
Heat of solution ΔH_{soln}
Entropy of solution ΔS_{soln}
comprised of
Solute
Solvent
in relative amounts expressed using
Concentration units
which include
Molarity M
Molality *m*
Mass percent mass %
Mole fraction *X*
can be
Not saturated
Saturated
Supersaturated
for which solute:solvent ratio is the
Solubility
which depends on
Pressure
Temperature
expressed in
Henry's law
exhibit
Colligative properties
such as
Vapor-pressure lowering
Boiling-point elevation
Freezing-point depression
Osmotic pressure
expressed by
Raoult's law
$\frac{P-P_s}{P_s}=\frac{w}{m}\times\frac{M}{W}$
$T_b = i K_b$ molality
$K_b=\frac{RT_b^2}{1000\times L_{vap}}$
$T_f = i K_f$ molality
$K_f=\frac{RT_f^2}{1000\times L_{fus}}$
$\pi = i$ CRT