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CBSE – XIIth

Chemistry

Central Board of Secondary Education (CBSE)

Quick Revision Notes + Sample Questions

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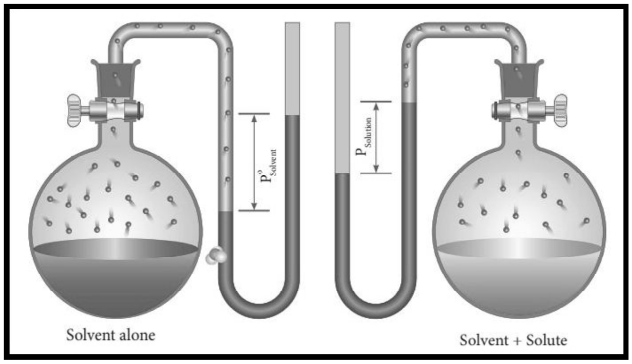
INNOVATIONS

INDEX

01

Solution & Colligative Properties



Introduction

Solution is a mixture of more than one pure substances.

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 tertiary and quaternary if it is composed of three and four components respectively.

Solution = solute + solvent

Solution

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.

Example

In a syrup (liquid solution) containing 30% sugar (a solid) and 70% 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 fixed amount 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 ($O_2 + N_2$)

(NCERT Pg. 2)

NCERT Core

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

Concentration Terms

Molarity (Molar concentration) (m)

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

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

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

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

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

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.

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

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

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.

Dependent 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.

Concentration in terms of Percentage

Percentage by weight (w/W) :

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.

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

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

Mass percent is independent of percentage

Percent by volume (Volume fraction) (v/V) :

This method is used for solutions of liquid in a liquid. The volume of liquid (solute) in mL dissolved in 100 mL of solution is called volume fraction.

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

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

Percent by strength / percentage mass by volume (w/V) :

$$\%\left(\frac{w}{V}\right) = \frac{\text{mass of solute(g)}}{\text{volume of solution(mL)}} \times 100$$

Parts per million (ppm) :

This method is used for expressing the concentration of very dilute solutions such as hardness of water, air pollution etc.

$$\text{ppm of substance} = \frac{\text{Mass of solute in gms} \times 10^6}{\text{Mass of solution(in gram)}} = \frac{\text{Volume of solute} \times 10^6}{\text{volume of solution}}$$

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

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

Mole fraction of solvent X_B is given by

$$X_B = \frac{n_B}{n_A + n_B}$$

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

$\Rightarrow [X_A + X_B = 1]$

Example

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

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

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

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

10 m. moles H_2SO_4

20 m. moles H^+

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

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

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

Relation between Molarity and Normality :

S = Molarity × molecular weight of solute

and S = Normality × equivalent weight of solute

So we can write

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

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

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

Normality = molarity × valency factor

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

Relation between Molality and Molarity :

$$\left[m = \frac{1000 \times M}{1000 \times d - M \times M_w}\right]$$

m = molality M = Molarity

d = Density (g/ml)

M_w = Molar mass of solute (g/mol)

Sp. Note

If the density of solution is approximately 1. then Molality > Molarity

Relation Between Molality (m) and Mole fraction

$$m = \frac{X_A}{X_B \times M_B} \times 1000 = \frac{X_A}{(1 - X_B) \times M_B} \times 1000$$

Since, $X_A + X_B = 1$.

X_A = mole fraction of solute

X_B = mole fraction of solvent

M_B = Molar mass of solvent (g/mol)

Concepts of Dilution :

The term dilution means addition of a solvent in a solution, where following remains unchanged after dilution and before dilution.

1. amount of solute (w_B)
2. mole of solute (M × V)
3. Number of gram equivalent of solute (N × V)

Condition of dilution :

$M_1V_1 = M_2V_2$

$N_1V_1 = N_2V_2$

Concept of Mixing of solutions

Case I- When acid acid or base base are mixed.

$$N_R = \frac{N_1V_1 + N_2V_2 + N_3V_3 + ...}{V_1 + V_2 + V_3 + ...}$$

Case II- Concept of neutralisation (when acid -base are mixed) then neutralisation will occur.

(i) Complete neutralisation

$N_AV_A = N_BV_B \begin{pmatrix} A \to \text{Acid} \\ B \to \text{Base} \end{pmatrix}; N_R = \left[\frac{N_AV_A}{V_A + V_B}\right]$ where N_R is the normality of salt

(ii) Incomplete neutralization

$N_R = \frac{N_AV_A \; ? \; N_BV_B}{V_A + V_B}$ where N_R is the normality of resultant acid or base.

NCERT Core

1. If the density of solution is approximately 1g/cc then molality > Molarity
2. ppm unit is used to represent concentration of very dilute solutions like pollutants in environment and salts present in sea water.
3. Those concentration terms which involves volume of solution are temperature dependent
4. Molarity, normality, formality, % by volume, % w/V are temperature dependent.
5. Molality, % w/W mole fraction are temperature independent

Example

Find out the molarity of 1 litre of 93% (w/W)H_2SO_4 (density = 1.84 g/ml)

Sol. $\text{Molarity} = \dfrac{\text{Moles of solute}}{\text{Volume of solution(L)}}$

$$= \frac{\text{Mass in gram} \times \text{Density} \times 1000}{\text{Molar mass} \times \text{mass of solution (g)}}$$

$$= \frac{93 \times 1.84 \times 1000}{98 \times 100} = 17.46\text{M}$$

Example

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

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

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

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

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

Example

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.

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

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

Example

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

Molarity

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

$$= \frac{0.4}{40 \times 40} \times 1000 = 0.25\text{ M} \quad \text{and}$$

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

eq. wt. of NaOH = 40

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

Second method $N = M \times n$

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

Example

The normality of 1.5M H_3PO_4 is –

Sol. Basicity of H_3PO_4 is 3

We know that $N = M \times n$

$N = 1.5 \times 3 = 4.5$

Example

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 :

$M_1V_1 = M_2V_2$

10M HCl = 5M HCl

$10 \times V_1 = 5 \times 2.00$

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

Example

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

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

wt. in gram = eq. wt × N × volume

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

Example

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

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

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

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

Example

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

$$\text{weight fraction} = \frac{3.65}{28.73} = 0.127$$

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

Example

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 $= 175\ cm^3$

$$\therefore \quad \text{volume fraction} = \frac{125}{175} = 0.714$$

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

Example

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 $= \frac{13}{98}$

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

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

$$= 1.445 \times 2 \left[n = \frac{\text{Mol. mass}}{\text{Eq. mass}} = \frac{98}{49} = 2 \right] = 2.89\ \text{N}$$

Solubility :

Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is solubility. Solubility is affected by nature of solute and solvent as well as by temperature and pressure.

(a) Solubility of solid in Liquid

Polar solutes are soluble in polar solvent and non polar solutes are soluble in non polar solvent due to similar intermolecular forces.

When solid solutes are dissolved in solvent then following equilibrium exists.

$$\text{Solute + Solvent} \underset{\text{Dissolution}}{\overset{\text{Crystallization}}{\rightleftharpoons}} \text{Solution}$$

(NCERT Pg.6)

Solubility of solids is affected by temperature and pressure according to Le-chatlier's principle. If dissolution is exothermic then solubility decreases with increase in temperature and if endothermic then solubility increases with increase in temperature. Solubility of solids is not affected by pressure significantly since solids are highly incompressible.

(b) Solubility of Gases in Liquid

Certain gases are highly soluble in water like NH_3, HCl etc. and certain gases are less soluble in water like O_2, N_2, He etc. Solubility of gases is affected by pressure and temperature. Increasing pressure increases solubility and increase in temperature decreases solubility. During dissolution of gas pressure of gas decrease and dissolution of gas is exothermic in nature.

Henry's law :

It can be stated as at constant temperature the solubility of a gas in a liquld is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

Or

Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

Or

The partial pressure of the gas in vapour phase (P) is proportional to the mole fraction of the gas (X) in the solution. (This is most common definition)

$P = K_H X$ $\quad$ K_H = Henry's Constant

Henry's Constant is not a universal constant. it depends on nature of gas and temperature. K_H increases with increase in temperature therefore solubility of gas decreases.

Effect of Temprature :

K_H values for gases increases with increase in temperature indicating that the solubility of gases increases with decrease of temperature.

Gas	Temperature / k	K_H / k bar	Gas	Temperature / k	K_H / k bar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	1.83×10^{-5}
N_2	303	88.84			
O_2	293	34.86	Methane	298	0.413
O_2	303	46.82	Vinyl chloride	298	0.611

Values of Henry's Law Constant for Some Selected Gases in Water

(NCERT Pg. 8)

Applications of Henry's law :

(i) To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

(ii) At higher altitude the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitude. Low blood oxygen causes symptoms of anoxia.

(iii) To avoid bends , in scuba divers, air is diluted with helium.

Example

Henry's law constant of CO_2 in water at 298 K is $\frac{5}{3}$K bar. If pressure of CO_2 is 0.01 bar, find its mole fraction.

Sol. $p = K_H.X$

$$\Rightarrow \quad p_{CO_{2(g)}} = K_H.X_{(CO_2)}$$

$$\Rightarrow \quad 0.01 = \frac{5}{3}\times1000\times X_{CO_2}$$

$$X_{CO_2} = 6\times10^{-6}$$

Example

Vapour pressure of CH_3Cl and CH_2Cl_2 are 540 mm Hg and 402 mm Hg respectively 101 g of CH_3Cl and 85 g of CH_2Cl_2 are mixed together. Determine

(i) The pressure at which the solution starts boiling

(ii) Molar ratio of solute v/s solvent in vapour phase in equilibrium with solution.

Sol. Boiling occures when external pressure becomes equal to the vapour pressure. SO, the boiling pressure = V.P. of solution.

$$p_A^{\circ}x_A + p_B^{\circ}x_B$$

Let A = CH_3Cl, B = CH_2Cl_2, then

$$\text{Toal pressure} \quad = 540\times\frac{2}{3} + 402\times\frac{1}{3}$$
$$= 360 + 134 = 494 \text{ mm Hg}$$

here the solute is CH_2Cl_2 as mass is less

$$x'_{CH_2Cl_2} = \frac{402\times\frac{1}{3}}{494} = \frac{134}{494},$$

$$x'_{CH_3Cl} = \frac{540\times\frac{2}{3}}{494} = \frac{360}{494}$$

$$\text{Now} \quad \frac{n'_{CH_2Cl_2}}{n'_{CHCl_3}} = \frac{n_{solute(g)}}{n_{solvent(g)}} = \frac{134}{360} = 0.372$$

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 × $P_A^0 = X_AP_A^0$

and

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

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

If total pressure be P_S, then

$$P_S = P_A' + P_B'$$

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

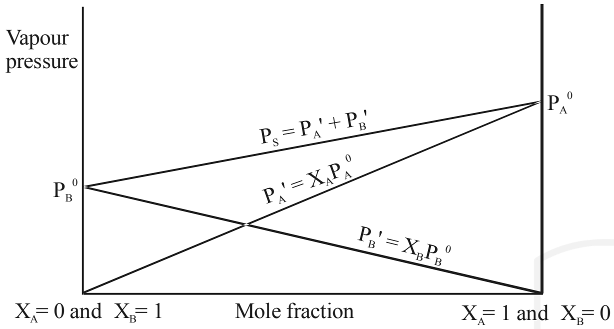
$$= X_A P_A^0 + X_B P_B^0 \quad ....(3)$$

$$P_S = X_A P_A^0 + (1 - X_A) P_B^0 \quad [?X_A + X_B = 1]$$

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

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

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



(NCERT Pg. 10)

Dalton's Law :

Partial pressure of gas = mole fraction × total pressure of gas

$$P_A = Y_A P_T$$
$$P_B = Y_B P_T$$
$$P_A + P_B = P_T$$

$$\boxed{\begin{matrix} X_A P_A^0 = Y_A P_T \\ X_B P_B^0 = Y_B P_T \end{matrix}}$$

Y_A and Y_B gives mole fraction in vapour phase (Where $P_T = P_S$)

X_A and X_B gives mole fraction in liquid phase.

Example

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

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

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

$$= 43.2 \text{ mm of Hg.}$$

Example

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 × mole fraction of C_6H_6 + 360 × [1 – mole fraction of C_6H_6]

$\therefore$ 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 [Solute]

B = volatile liquid [Solvent]

According to Raoult's law –

$$? \quad P_m = X_A P_A^0 + X_B P_B^0$$

for A, $P_A^0 = 0$

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

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

here X_B is mole fraction of solvent

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

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

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

$$\Rightarrow P_S = X_B P_B^0$$

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

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

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

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

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

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

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

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

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

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

Here n_A = moles of solute

n_B = moles of solvent

When a non - volatile solute is added to a volatile liquid its vapour pressure decrease because less number of solvent particles present in solution at surface.(as compare to pure solvent) less vapour is formed and vapour pressure of solution decreases

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

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

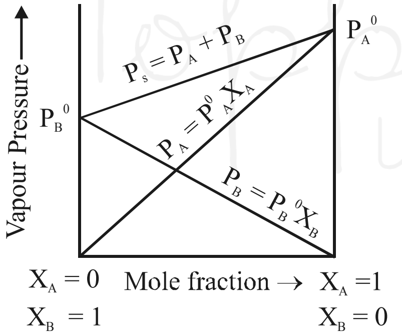
Example

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. $\frac{P^0 - P_S}{P_S} = \frac{w \times M}{m \times W}$, $\frac{1020 - 990}{990} = \frac{5 \times 78}{m \times 58.5}$, $m = 220$

Ideal Solutions (mixture of two liquids A and B) :

1. A solution which obeys Raoult's law exactly at all concentrations and at all temperatures is called an ideal solution.
2. For ideal solutions ; A-A interaction = B-B interaction = A-B interaction An ideal solution possesses the following characteristics



(NCERT Pg.13)

(a) Volume change on mixing should be zero $\Delta V_{mix} = 0$

(b) Heat change on mixing should be zero.

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

(c) There should be no chemical reaction between liquid A and liquid B.

(d) Ideal solution must obey Raoult,s law at all concentrations.

$P_A = P_A^0.x_A$, $P_B = p_B^0.x_B$

(e) Observed VP = calculated VP

(f) Observed BP = calculated BP

(g) $\Delta S_{mix} > 0$

(h) $\Delta G < 0$

Example

(i) Benzene and toluene
(ii) CCl_4 and $SiCl_4$
(iii) n-hexane and n-heptane
(iv) C_2H_5Br and C_2H_5Cl
(v) PhCl and PhBr
(vi) n-butylchloride and n-butylbromide

(NCERT Pg.13)

Non - Ideal Solutions :

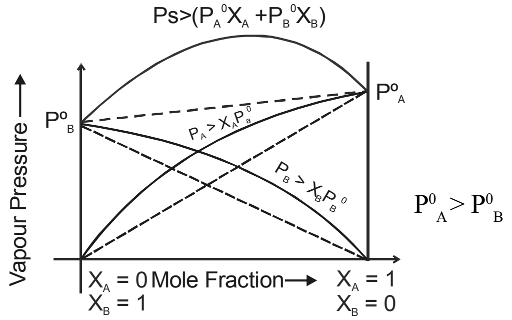
1. For non ideal solutions ; A-A interaction or B-B interaction ≠ A-B interaction.
2. Those solutions which do not obey Raoult's law are called non - ideal solutions
3. For such solutions ; $P_A \neq P_A^0 X_A$; $P_B \neq P_B^0 X_B$
4. Non ideal solutions are formed when the components differ much in their structures and polarities.
   So $\Delta H_{mixing} \neq 0$ and $\Delta V_{mixing} \neq 0$
5. Non idea solutions show either positive or negative deviations from Raoult's law.

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.



(NCERT Pg.14)

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

(iii) In these solutions A-B interaction are less than A-A and B-B molecular interaction

$$P_A > P_A^0 X_A$$
$$P_B > P_B^0 X_B$$

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

$P_{total} > (P_A^0 X_A + P_B^0 X_B)$

(v) $\Delta H_{mix} > 0$; endothermic dissolution ; heat is absorbed

(vi) $\Delta V_{mix} > 0$. ; volume increases after dissolution

(vii) 'A' and 'B' escape easily showing higher vapour pressure than the expected value.

$(B.P)_{th} > (B.P.)_{exp}$ $(\Delta S)_{mix} = +ve, \ \Delta G = -ve$

Entropy change in mixing is positive

Example

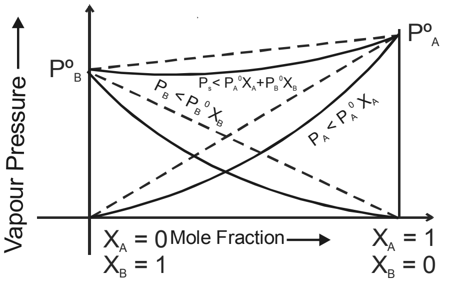
(i) Ethanol and cyclohexane
(ii) Ethanol and Water
(iii) Ethanol and Acetone
(iv) Methanol and H_2O
(v) CCl_4 and Benzene
(vi) CCl_4 and Toluene
(vii) CCl_4 and $CHCl_3$
(viii) CCl_4 and methanol
(ix) Benzene and Acetone
(x) CS_2 and Acetone
(xi) CS_2 and Acetaldehyde

Explanation : 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.**(NCERT Pg.14)**

(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

(iii) In these solutions the A-B interaction are stronger than the A-A and B-B molecular interactions

$P_A < P_A^0 X_A$; $P_B < P_B^0 X_B$

(iv) $P_{total} < (P_A^0 X_A + P_B^0 X_B)$

Total vapour pressure is less than sum of individual vapour pressure.

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

(vi) $\Delta V_{mix} < 0$; volume decreases during dissolution.

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

$(B.P.)_{th} < (B.P.)_{experimental}$; $(\Delta S)_{mix} = +ive$; $\Delta G = -ve$

More to Know

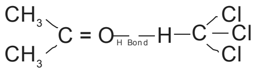
Example

(i) $CHCl_3$ and CH_3COCH_3
(ii) $CHCl_3$ and C_6H_6
(iii) $CHCl_3$ and $C_2H_5OC_2H_5$
(iv) $CHCl_3$ and HNO_3
(v) $CHCl_3$ and CH_3COOH
(vi) H_2O and HCl
(vii) H_2O and HNO_3HNO_3
(viii) CH_3COOH and CH_3OH
(ix) CH_3COOH and C_5H_5N
(x) CH_3COCH_3 and Aniline

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.

More to Know

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 $P_{T,\exp} = (x_A P_A{}^o + x_B P_B{}^o)$	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) $P_{T,\exp} < (x_A P^o_A + x_B P^o_B)$
2. Process of attraction between A-B are exactly same as A-A & B-B A--------A = A--------- B = B ----------B	(ii) A-------A B-------B >A——B	A-------A B-------B <A——B (ii)
3. $\Delta H_{mix} = 0$ 4. $\Delta V_{mix} = 0$ 5. $\Delta S_{mix} = +$ve, as for process to Proceed 6. $\Delta G_{mix} = -$ve	Weaker force of attraction between A-B than in pure A-A & B-B. (iii) $\Delta H_{mix} = +$ve energy absorbed (iv) $\Delta V_{mix} = +$ve (1L + 1L > 2L) (v) $\Delta S_{mix} = +$ ve (vi) $\Delta G_{mix} = -$ve	Stronger force of attraction between A-B than in pure A-A & B-B (iii) $\Delta H_{mix} = -$ve (iv) $\Delta V_{mix} = -$ve (1L + 1L < 2L) (v) $\Delta S_{mix} = +$ ve (vi) $\Delta G_{mix} = -$ve
eg. (1) Benzene + Toluene (2) Hexane + heptane (3) $C_2H_2Br + C_2H_2I$	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. $H_2O + HCOOH$ $H_2O + CH_3COOH$ $H_2O + HNO_3$ $CHCl_3 + CH_3COCH_3$ 

(NCERT Pg.14)

Example

1 mole heptane (V.P. = 92 mm of hg) is mixed with 4 mol. Octance (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 $X_B = 4/5$

$$P_S = X_A P_A^0 + X_B P_B^0 = \frac{1}{2} \times 92 + \frac{4}{5} \times 32 = 43.2 \text{ mm of Hg}$$

Example

At 88ºC 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 88ºC. at 1 atm pressure, benzene – toluene form an ideal solution.

Sol. $P_s = 760$ torr, because solution boils at 88ºC

$$\therefore \quad P_s = P_B^0 X_B^0 + P_t^0 X_t$$

$$760 = 900a + 360 - 360a$$

a = 0.74 where ‘a’ is mole fraction of $C_6H_6(X_B)$

Azeotropic Mixtures :

This type of liquid mixture, having a definite composition and boiling like a pure liquid is called azeotropic mixture or constant boiling mixture.

The azeotropic mixture cannot be separated by fractional distillation, such solutions are called azeotropic solutions and this phenomenon is known as azeotropy. In azeotropic conditions combination of solute and solvent (solution) starts behaving like one single molecule (with reference to boiling point). This happens due to certain inter-molecular pattern of attractive forces leaving no molecule out of this network, so no component is free to show it’s own boiling point but solution behaves like one single entity and therefore boils at a particular boiling point and therefore solution becomes inseperable by fractional distillation method as this method is only helpful when components differ in their boiling points. Two type of non-ideal solution form two different azeotropes.

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.

(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.

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 $= P^\circ - P_s$

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

According to Rault's law

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

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

$$\text{so} \quad \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B}, \qquad \frac{\Delta P}{P^0} = \frac{P^0 - P_S}{P^0} = \frac{n_A}{n_B},$$

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

or relative lowering of vapour pressure

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

Example

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

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

$P = 0.98\ V$

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

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

Example

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

Sol.

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

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

$m = 163$ gm/mol.

Example

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.

$$\frac{P^0 - P_s}{P} = \frac{w}{m} \times \frac{M}{W} \quad \Rightarrow \quad \frac{P^o - 20}{20} = \frac{6}{m} \times \frac{18}{180},$$

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

$\Rightarrow$ $P^o = 20.22$ Torr., $m = 54$ gm/mol.

(ii) *Elevation in boiling point (Ebulioscopy) :*

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_b^0 is the boiling point of pure solvent and (T_b) is the boiling point of the solution then,

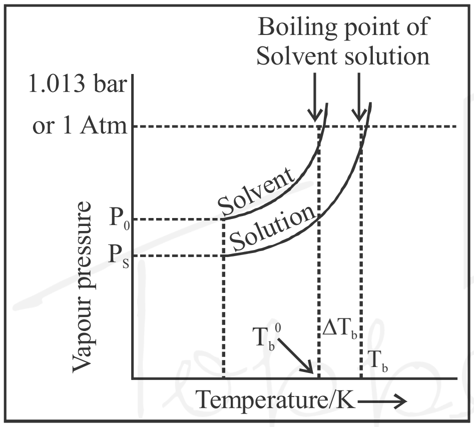
$T_b^0 > T_b^0$

and the elevation in boiling point

$\Delta T_b = T_b - T_b^0$

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

$\Delta T_b \propto P_o - P_s$ (from graph)



(NCERT Pg. 17)

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

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

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

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

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

$\Delta T_b = T_b - T_b^0$

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.

$$\mathbf{K_b = \frac{RT_b^{0^2}}{1000L_v} = \frac{MRT_b^{0^2}}{1000\Delta H_{vap}}}$$

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

where T_b^0 = Boiling point of solvent
M = Molar mass of solvent

ΔH_{vap} = Enthalpy of vapoursation per mole of solvent

L_v = latent heat of vapourisation per gram of solvent

For water

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

Example

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

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

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

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

Example

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

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

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

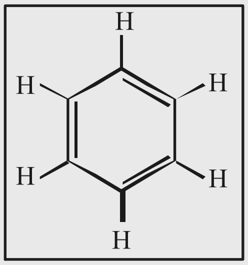
$\Delta T_b = 0.1°C$
$m = 180$
$W = 100$
$w = 1.8$

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

Example

A solution of 122 gm of benzoic acid is 1000 gm of benzene shows a b.p. elevation of 1.4º. Assuming that solute is dimerized to the extent of 80 percent (80ºC) calculate normal b.p. of benzene. given molar enthalpy of vap. of benzine = 7. 8 Kcal/mole.

Sol. $$T_b - T_o = \frac{122\times1000}{122\times1000}\times K_b\left(1+\left(\frac{1}{n}-1\right)\right)0.8$$



$$\Rightarrow \ K_b\left[\frac{1}{2}\times0.8\right]$$

$$T_b - T_o = K_b\times0.6$$

$$K_b = \frac{MRT_b^{\ 2}}{1000\times\Delta H_v}$$

$$1.4 = \frac{78\times2\times T_b^0}{1000\times7.8}$$

$$1.4 = \frac{0.4\times2}{10^5}T_b^{\ 2} \Rightarrow T_b = 418.33\ K$$

(iii) 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_b^0 is the freezing point of pure solvent and $(T_f)_s$ is the freezing point of its solution then,

$$T_f < T_f$$

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

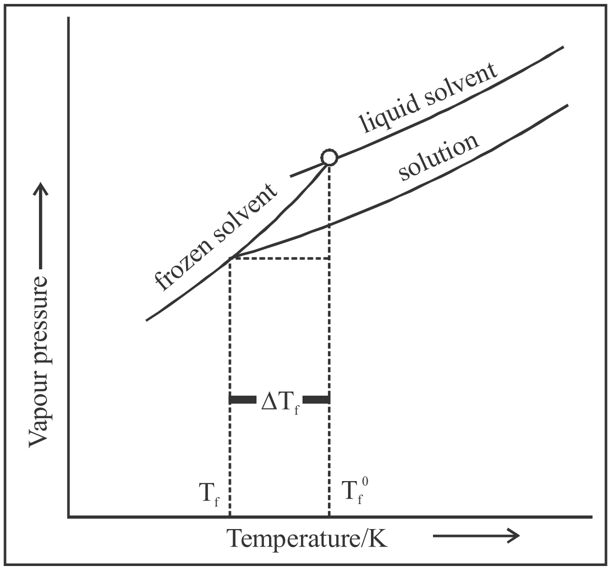
Thus,

$$T_f^0 - T_f = \Delta T_f$$

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 :



(NCERT Pg. 18)

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 only depends on nature of solvent which can be explained by thermodynamic relation

$$K_f = \frac{RT_f^{0^2}}{1000L_f} = \frac{RT_f^{0^2}M}{1000\Delta H_f}$$

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.

Where $T^0{}_f$ = Freezing point of solvent

M = Molar mass of solvent

ΔH_f = Enthalpy of fusion per mole of solvent

L_f = latent heat of fusion per gram of solvent

Solvent	b. p./K	Kb/K kg mol^{-1}	f. p./K	Kf/K kg mol^{-1}
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.79
Carbon tetrachloride	350.0	5.03	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

(NCERT Pg. 19)

Example

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 mass of the solute will be

Sol. Given : $T_f = 271.9$ K, $w = 1.25$ g, $W = 20$ g, $K_f = 1.86$

$\Delta T_f = T_b^{\,0} - T_f = 273 - 271.9 = 1.1$

$\Delta T_f = \text{Molality} \times K_f$ or $\Delta T_f = \dfrac{w}{m \times W} \times 1000 \times K_f$

$$m = \frac{w \times 1000 \times K_f}{\Delta T_f \times W} = \frac{1.25 \times 1000 \times 1.86}{1.1 \times 20} = 105.68$$

Example

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. $\Delta T_f = \text{molality} \times K_f$

$= 0.05 \times 1.86 = 0.093°C$

$T_f = T_f^{\,0} - 0.093 = 0 - 0.093$

$T_f = -0.093$

Example

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 $y < x < z$.

Example

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

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

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

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

$$\frac{\Delta T_b}{\Delta T_f} = \frac{T_b^2 \times l_f}{T_f^2 \times l_v} \qquad T_b = 100 + 273 = 373\text{ K}.$$

$T_f = 0 + 273 = 273$ K. $\quad l_f = 80$ cal g^{-1}.

$l_v = 540$ cal g^{-1}.

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

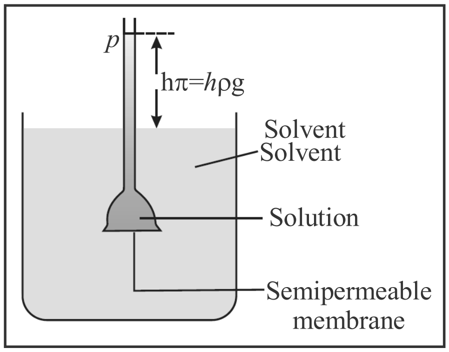
$\therefore \quad \Delta T_f = 0.362.$

$\therefore \quad T_f = 0.0 - 0.362. = \mathbf{-0.362ºC.}$

(iv) Osmosis and osmotic pressure

Osmosis :

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

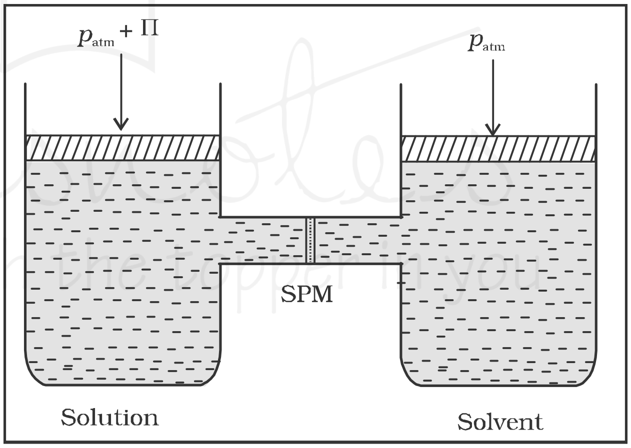


(NCERT Pg. 20) Level of solution rises in the thistle funnel due to osmosis of solvent.

Osmotic presssure (π)

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

or



(NCERT Pg. 21) The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.

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

According to it Gas equation PV = nRT is also follwed by dilute solution when pressure of gass is replaced by osmotic pressure of solution.

π = osmotic pressure of solution (atm)

V = volume of solution (L)

n = moles of solute

R = (S) gas constant / solution constant = 0.0821 L atm $mol^{-1}K^{-1}$; 0.083 L bar $mol^{-1}K^{-1}$

$$\pi = \left(\frac{n}{V}\right)RT$$

$$\pi = CRT$$

At constant temperature $\pi \propto C \therefore \pi$ is a colligative property.

On the basis of osmotic pressure solution can be classified by following ways :

(i) Isotonic solutions : Solutions having same osmotic pressure are called isotonic solution.

$\pi_1 = \pi_2$; primary condition

$C_1RT = C_2RT$; (at same temperature)

$C_1 = C_2$; (secondary condition) ; means

$\frac{n_1}{V_1} = \frac{n_2}{V_2}$; such solutions known as **isotonic**

(ii) $\pi_1 > \pi_2$ or $C_1 > C_2$ then solution I is called **hypertonic** and solution II is called **hypotonic**

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.

Example

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

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

Example

What is the osmotic pressure of 12% solution of cane sugar (molecular weight 342) at 17°C.

Sol. 12 g sugar is dissolved in 100 mL

thus 342 g sugar is dissolved in $\frac{100 \times 342}{12 \times 1000} = 2.85$ L

Now $\pi V = RT$ [? n = 1]

$$\pi = \frac{RT}{V} = \frac{0.0821 \times 290}{2.85} = 8.35\ atm$$

Example

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 $\pi_1 = \pi_2$

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

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

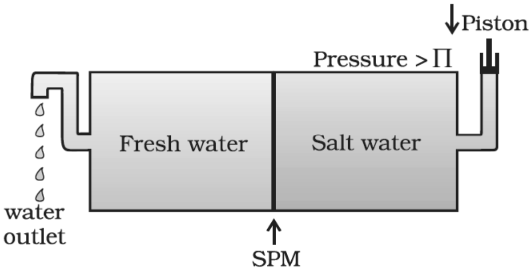
or $\left(\frac{w_1}{m_1 \times v_1}\right)_{urea} = \left(\frac{w_2}{m_2 \times v_2}\right)_{organic}$

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.



(NCERT Pg. 23) Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

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.

CASE I. 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 molecule 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.

CASE II. 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

$$\mathbf{i = \frac{observed\ colligative\ property}{Normal\ colligative\ property}},$$

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

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

$$A_xB_y \longrightarrow x\,A^{y+} + yB^{x-}$$

	A_xB_y	A^{y+}	B^{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 $\propto 1$

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

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

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

but $i = \dfrac{\text{Normal (calculated) molecular mass}}{\text{Observed molecular mass}} = \dfrac{M_C}{M_O}$

$$\alpha = \frac{M_C - M_O}{M_O(n-1)}$$

$i = (I-\alpha+2\alpha)/I$ (for AB type solute) in general

$$\Rightarrow \frac{M_C}{M_O} = 1+\alpha$$

$$\alpha = \frac{M_C - M_O}{M_O}$$

where n is the total number of ions produced per molecules of electrolyte.

Special Point

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

(2) $i = 1+\left(\dfrac{1}{n}-1\right)\alpha$

(3) Comparision of various properties :

(a) Value of colligative property $(C.P.) \propto (i) \propto \dfrac{O.C.P.}{C.C.P.} \propto \dfrac{C.M.M.}{O.M.M.}$

[MM = Molar mass, O = Observed / Experimental, C = calculated / Normal]

(b) Osmotic pressure $(\pi) \propto i$

(c) Elivation in boiling point $\propto$ i, $(\text{Boiling point} \propto i)$

(d) Depression in freezing point $\propto$ i,

$(\text{Freezing point} \propto \frac{1}{i})$

(e) Relative lowering pressure $\propto$ i,

$(\text{Vapour pressure of solution} \propto \frac{1}{i})$

Example

(a) 0.1 m Glucose (aq) i = 1

(b) 0.1 m $CaCl_2$ (aq) i = 3

(c) 0.1 m $Al_2(SO_4)_3$ (aq) i = 5

(d) 0.1 m $[Co(NH_3)_6]Cl_3$ (aq) i = 4

Arrange the above solutions in their increasing order of Osmatic pressure.

Sol. (a) < (b) < (d) < (c)

Example

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 (M_w of $CaCl_2$) will be present in $\frac{100 \times 111}{5 \times 1000} = 2.22$ L

Now $\pi V = ST$ (? n = 1) or

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

We know that Van't Hoff factor

$$i = \frac{\text{observed colligative property}}{\text{Normal colligative property}} = \frac{15}{10.09}$$

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

$$\alpha = \frac{\frac{15}{10.09} - 1}{3 - 1} = \frac{4.91}{10.09 \times 2} = 0.2433 \text{ or } 24.33\%$$

Example

Calculate the osmotic pressure of 20% (wt/Vol.) anhydrous $CaCl_2$ solution at 0°C assuming 100% ionisation.

Sol.

$CaCl_2 \longrightarrow$	Ca^{2+} +	$2Cl^-$	
Before dissociation	1	0	0
After dissociation	$1 - \alpha$	α	2α

Given, w = 20 g, V = 100 mL, T = 273 K,

mol, wt. of $CaCl_2$ = 111

$$\pi_{Normal} = \frac{w}{mV} \times S \times T = \frac{20 \times 1000 \times 0.0821 \times 273}{111 \times 100} = 40.38 \text{ atm.}$$

Now, $i = \frac{1 + 2\alpha}{1} = 1 + 2 = 3$ (? $\alpha = 1$)

$$\pi_{exp} = i \times \pi_{Normal}$$

$\therefore$ $\pi_{exp} = 40.38 \times 3 = 121.14$ atm

Example

for complex compound

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

n = 5

If α = 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

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

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

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

Salt	*Values of i			van't Hoff Factor i for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2:00
KCl	1.85	1.94	1.98	2:00
$MgSO_4$	1.21	1.53	1.82	2:00
K_2SO_2	2.32	2.70	2.84	3:00
represent i values for incomplete dissociation.				

(NCERT Pg. 25) Values of van't Hoff factor, i, at Various Concentrations for NaCl, KCl, $MgSO_4$ and K_2SO_4.

Example

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

$$\frac{100\times111}{5\times1000} = 2.22 \text{ lit.}$$

Now $\pi V = ST$ {? ?n = 1}

or $\pi = \frac{0.082\times273}{2.22} = \frac{22.47}{2.22} = 10.09$ 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 $n = 3$

$$\alpha = \frac{\frac{15}{10.09}-1}{3-1} = \frac{4.91}{10.09\times2}$$

$\alpha = 0.2433$ or 24.33%

Example

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

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

$\pi = CRT$

$\pi = 0.1 \times 0.082 \times 300$

$\pi = 2.46$ atm.

Example

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. $1.23 = \frac{10\times1000}{M\times500} \times 0.082 \times 300$

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

Example

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

$\pi = C \times 0.082 \times 300$

$\pi = \frac{0.3\times1000\times0.082\times300}{500} \Rightarrow 14.76$ atm