

1 CHAPTER



DILUTE SOLUTIONS

- * Homogeneous Mixtures
- * Ideal and Non-ideal Solutions
- * Vapour Pressure
- * Colligative Properties

HOMOGENEOUS MIXTURES

Pure substances are very rare. In normal life we come across mixtures containing two or more substances. The properties of brass (mixture of copper with zinc) are different from that of bronze (mixture of copper with tin). A homogeneous mixture of two or more substances is called a solution. Almost all processes in body occur in some kind of liquid solutions. A solution is sometimes also called solution state. Solution state is not a true physical state but a pseudo state. Formation of a solution involves only physical mixing.

1.1.1

Types of solutions

*Binary solution
contains two
components*

The composition and the properties are uniform throughout the homogeneous solution. The component that is present in larger quantity is generally called solvent and in minor quantity is called solute. A binary solution contains only two components. Solvent determines physical state in which the solution exists. Based on the physical state, solutions are three types. Types of solutions and examples are listed in Table 1.1.

Table 1.1 Types of solutions and common examples

Type of solution	Solute	Solvent	Common example
Gaseous solutions	Solid	Gas	Camphor in nitrogen gas
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Gas	Gas	Mixture of oxygen and nitrogens
Liquid solutions	Solid	Liquid	Sucrose dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Gas	Liquid	Carbon dioxide dissolved in water
Solid solutions	Solid	Solid	Copper dissolved in gold
	Liquid	Solid	Amalgam of mercury with sodium
	Gas	Solid	Solution of hydrogen in palladium

Among different types of solutions, solid in liquid type solutions are most frequently studied. Solution unless otherwise referred is aqueous solution, prepared using water as solvent. Alcoholic solutions use ethyl alcohol as solvent. Non-aqueous solutions use benzene, chloroform, ether, carbontetrachloride, etc., as solvents.

1.1.2

Methods of concentration

*Solutions
prepared using
water as solvent
are called
aqueous solutions*

Concentration is usually a measure of the amount of solute present in a solution. It is also called strength of the solution. The concentration of a solution can be expressed quantitatively in several ways.

Mass fraction : It is the ratio of mass of solute to mass of solution. One hundred times mass fraction is mass percentage. Mass percentage is expressed in two ways. Mass of the solute present in 100g of solution is denoted as %(w/w).

Mass of the solute present in 100mL of solution is denoted as %(w/v). %(w/w) and %(v/v) are inter convertible through density of solution.

Volume fraction : It is the ratio of volume of solute to volume of solution. The volume of solute present in 100mL of solution is called volume percentage, which is denoted as %(v/v). Solutions containing liquids are expressed in this method. This method is less common.

Mole fraction : It is the ratio of number of moles of a component to the total number of moles of a solution. It is denoted by the symbol 'X'. If number of moles of component substances A and B in a solution are respectively n_A and n_B ,

$$\text{Mole fraction of component A} = X_A = \frac{n_A}{(n_A + n_B)}$$

$$\text{Mole fraction of component B} = X_B = \frac{n_B}{(n_A + n_B)}$$

The sum of the mole-fractions of all components in a solution is unity. Mole fraction is very useful in calculations involving gas mixtures and also in relating some physical properties like vapour pressure.

One hundred times mole fraction is called mole percentage. Mole fraction and mole percentage have no units. They do not vary with a change in temperature of solution.

Molality : It is defined as the number of gram moles of the solute present in one kilogram of solvent. It is denoted by 'm'. Units of molality are mol kg^{-1} . It is independent of temperature. Molality is most accurate and theoretically the best method of expressing concentration.

Molality (m) is given as,

$$m = \frac{\text{number of moles of solute}}{\text{number of kg of solvent}} \quad (\text{or}) \quad m = \frac{w}{\text{GMW}} \times \frac{1000}{W}$$

Here w and W are mass of solute and solvent, respectively in grams. GMW is the gram molecular mass of solute.

Molarity : It is defined as the number of gram moles of the solute present in one litre of solution. It is denoted by 'M'. Units of molarity are mol L^{-1} . It is dependent on temperature. As the temperature increases, volume of the solution increases and molarity decreases.

Molarity (M) is given as,

$$M = \frac{\text{number of moles of solute}}{\text{number of litres of solution}} \quad (\text{or}) \quad M = \frac{w}{\text{GMW}} \times \frac{1000}{V}$$

Here w is mass of solute in grams and V is volume of solution in millilitres.

A molar solution is that in which one gram mole of solute is present in one litre of solution. One millimole of solute present in one millilitre solution is also called one molar. Molar (M), semimolar (0.5M), decimolar (0.1M), centimolar (0.01M), millimolar (0.001M), etc., are in common use.

The mass of solute (w) in grams, present in V litres of a solution, can be calculated from molarity of the solution (M) as,

$$w = M \times V \times \text{GMW}$$

Normality : It is defined as the number of gram equivalents of the solute present in one litre of solution. It is denoted by 'N'. Units of normality are eq L⁻¹. It is dependent on temperature. As the temperature increases, volume increases and normality decreases.

Gram molar weight = n × gram equivalent weight, where 'n' is the acidity of a base, basicity of an acid, valency of an element, change in the oxidation number of a redox reagent or number of Faradays in electrochemical reaction.

Normality (N) is given as,

$$N = \frac{\text{number of equivalents of solute}}{\text{number of litres of solution}} \quad (\text{or}) \quad N = \frac{w}{\text{GEW}} \times \frac{1000}{V}$$

Normality is related to molarity as, $N = n \times M$

The mass of a solute (w) in grams, present in V litres of a solution, can be calculated from normality of the solution (N) as,

$$w = N \times V \times \text{GEW}$$

Here GEW is the gram equivalent weight of solute.

1.1.3

Solubility

Number of grams of solute that saturates 100 grams of solvent is called solubility

Solubility of a substance is its maximum amount that can be dissolved in a given quantity of solvent. It depends on the nature of solute and solvent. It is also dependent on temperature and pressure. Solubility is defined as the number of grams of the solute that saturates 100 grams of solvent at a given temperature. It has no units.

Common salt or cane sugar dissolve readily in water, but not in benzene. Naphthalene or camphor dissolve readily in benzene, but not in water. In general a solute dissolves in a solvent if intermolecular interactions are similar in the two substances. 'Like dissolves like' is the principle of solubility.

The solubility of a solid or liquid in a liquid is markedly influenced by temperature. This influence can be explained based on Le Chatelier's principle. In a nearly saturated solution, if dissolution process is exothermic (ΔH solution is negative), solubility decreases with increase in temperature. If the dissolution process is endothermic (ΔH solution is positive), solubility increases with increase in temperature.

Since solids and liquids are highly incompressible, pressure has no effect on the dissolution of solids or liquids in liquid solvents.

Many gases are soluble in water. Dissolved oxygen is very less (5ppm) in water, but this amount of oxygen sustains all aquatic life. Solubility of a gas in water generally decreases with increase in temperature and increases with increase in pressure.

With an increase in the pressure, the number of gaseous molecules per unit volume over the solution increases (Fig 1.1). The rate at which the gaseous molecule striking the surface of solution to enter into the solution increases. The solubility of gas increases until a new equilibrium is reached.

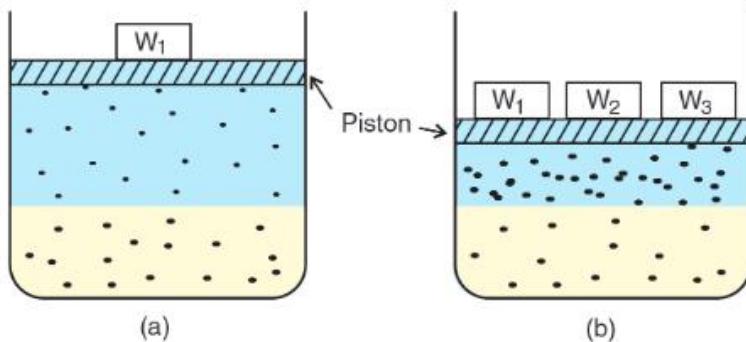


Fig 1.1 Pressure increases the solubility of a gas

Henry's law is stated as, the solubility of a gas in a liquid is directly proportional to the pressure of the gas

Increase in the solubility of CO_2 in soda water is due to high pressure of the gas

Henry's law constant is the slope of partial pressure Vs mole fraction curve

Henry was first to give a quantitative relationship between the solubility and pressure of gas, which is known as Henry's law. The law is stated as, at a constant temperature the solubility of a gas in a liquid is directly proportional to the pressure of the gas. Dalton concluded that the solubility of a gas in a liquid is a function of partial pressure of the gas. The partial pressure of the gas in vapour phase (p) is directly proportional to the mole fraction of gas (X) in the solution.

$$p = K_H X, \text{ where } K_H \text{ is Henry's law constant.}$$

Solubility of hydrogen chloride in cyclohexane is shown in Fig 1.2. The slope of the straight line is K_H . Different gases have different K_H values at the same temperature as listed in Table 1.2. It is to be noted that the higher the value of Henry's law constant, lower is the solubility of the gas in the liquid. With an increase in the temperature, Henry's law constant increases and solubility of gas in liquid decreases.

Henry's law finds several applications in industry and in biological processes. Increase in the solubility of carbondioxide in soda water and soft drinks is due to high pressure of gas. Bottles are sealed under high pressure.

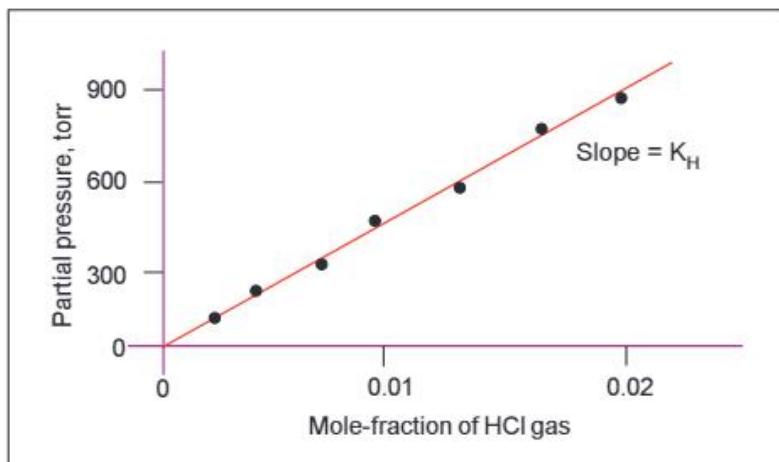


Fig 1.2 Solubility of HCl in cyclohexane at 293K

Table 1.2 Henry's law constants for some gases in water

Gas	Temperature, K	K_H , kbar	Gas	Temperature, K	K_H , kbar
Helium	293	144.97	Argon	298	40.3
Nitrogen	293	76.48	Carbondioxide	298	1.67
Nitrogen	303	88.84	Formaldehyde	298	1.83×10^{-5}
Oxygen	293	34.86	Methane	298	0.413
Oxygen	303	46.82	Vinyl chloride	298	0.611

At higher altitudes the partial pressure of oxygen is less. This leads to lower concentration of oxygen in blood and tissues of mountain climbers and people living at higher altitudes. Persons become weak and unable to think properly, due to lower pressure of oxygen. These symptoms are called 'anoxia'.

Deep sea divers will suffer with higher dissolution of atmospheric gases, under water, at high pressure. To avoid toxic effects of higher concentrations of nitrogen, the respiration tanks of air are diluted with helium (56% N₂, 32% O₂ and 12% He).

Effect of temperature : Solubility of gases in liquid decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt in the last section that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature.

1.1.4

Working with solutions

Homogeneous solutions find important applications in pharmaceuticals and industrial preparation. Aqueous homogeneous solutions are commonly used in laboratory.

Molality (m) of a solution is obtained in terms of solubility (S) as,

$$m = 10S/GMW.$$

The relationship between molality (m) of an aqueous solution and the mole fraction (X) of the solute is, $X = m/(m + 55.5)$.

If 'x' is the percent weight by volume (w/v), 'y' is the percent weight by weight (w/w) and 'd' is the density of solution,

$$M = \frac{10x}{GMW} \text{ (or)} M = \frac{10yd}{GMW} \text{ and } N = \frac{10x}{GEW} \text{ (or)} N = \frac{10yd}{GEW}$$

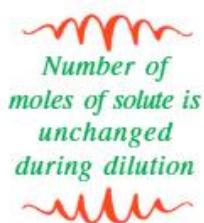
Molarity (M) is related to molality (m) in terms of density (d) as,

$$m = \frac{1000M}{1000d - (M \times GMW)} \text{ (or)}$$

$$\frac{m}{M} = \frac{\text{volume of solution (in ml)}}{\text{weight of solvent (in g)}}$$

Product of normality (N) and volume (V) in litres is a direct measure of number of equivalents. Number of equivalents of any two reactant substances is always in the ratio, 1:1.

*Ratio of
number of
equivalents of
two reactants
is always 1:1*



The formula used in volumetric titrations of two solutions is, $V_1N_1 = V_2N_2$.

Number of moles = VM , volume V is in litres.

Number of equivalents = VN , volume V is in litres.

Number of milliequivalents = VN , volume V is in millilitres.

Dilution is a process of adding more solvent to the solution. During dilution, the amount of solute is unchanged. The volume of solution increases upon dilution and concentration of solution decreases.

The number of equivalents or the number of gram moles of the solute is unchanged upon dilution. Hence, the equation useful for change in concentration during dilution of a solution is, $V_1M_1 = V_2M_2$ (or) $V_1N_1 = V_2N_2$.

The volume of the solution before and after dilution are respectively V_1 and V_2 , molarities are M_1 and M_2 and normalities are N_1 and N_2 .

When two solutions of similar nature are mixed, their milliequivalents are additive and when solutions of opposite nature are mixed, their milliequivalents are subtractive.

The normality of a mixture of solutions two acids, or bases, or oxidants, or reductants is given as,

$$N = \frac{V_1N_1 + V_2N_2}{V_1 + V_2}$$

The normality of a mixture of solutions of an acid and a base or an oxidant and a reductant is given as,

$$N = \frac{V_1N_1 - V_2N_2}{V_1 + V_2}$$



- P.1.1** 3.15 grams of oxalic acid crystals are present in a 500 mL aqueous solution. Calculate (a) molarity and (b) normality.

Solution Molarity, $M = \frac{w}{GMW} \times \frac{1000}{V} = \frac{3.15}{126} \times \frac{1000}{500} = \frac{6.3}{126} = 0.05 \text{ mol L}^{-1}$

Basicity of oxalic acid = $n = 2$

Normality, $N = n \times M = 2 \times 0.05 = 0.1 \text{ eq L}^{-1}$.



- P.1.2** What mass of sodium chloride is present in 500mL of 0.2 N solution?

Solution Mass of solute in V L solution = $N \times V \times GEW$

$$\text{Mass of sodium chloride present in solution} = 0.2 \times \frac{500}{1000} \times 58.5 = 5.86 \text{ g.}$$



- P.1.3** Calculate the molality of 10% (w/w) aqueous caustic soda. What is the mole fraction of water in the solution?

Solution 100 grams solution = 10 grams of NaOH + 90 grams of water

$$\text{Molality (m)} = \frac{10}{40} \times \frac{1000}{90} = \frac{100}{36} = 2.78 \text{ mol kg}^{-1}$$

Number of moles of NaOH = $n_1 = 10/40 = 0.25$

Number of moles of $H_2O = n_2 = 90/18 = 5.0$

$$\text{Mole-fraction of water in the solution} = n_2 / (n_1 + n_2) = \frac{5.0}{5.25} = 0.9523.$$



- P.1.4** The specific gravity of 84% (w/w) H_2SO_4 is 1.752. Find (a) molarity and (b) normality of the solution.

Solution Molarity, $M = \frac{10 \times \% \times d}{GMW} = \frac{10 \times 84 \times 1.752}{98} = 15 \text{ mol L}^{-1}$

Normality, $N = \frac{10 \times \% \times d}{GEW} = \frac{10 \times 84 \times 1.752}{49} = 30 \text{ eq L}^{-1}$.



- P.1.5** Henry's law constant for nitrogen at 20°C is 76.48 k bar. Assuming the partial pressure as 0.987 bar, calculate mass of nitrogen dissolved in one litre water at 20°C.

Solution Partial pressure (p) = $K_H \times$ mole fraction of gas (X)

$$X = \frac{p}{K_H} = \frac{0.987}{76.480} = 1.29 \times 10^{-5}$$

Number of moles (n) of nitrogen in aqueous solution is related to mole fraction (X) as

$$X = \frac{n}{n + 55.5} = \frac{n}{55.5} = 1.29 \times 10^{-5} \quad (\text{because } n \text{ is small, } n + 55.5 = 55.5)$$

$$n = 1.29 \times 10^{-5} \times 55.5 = 7.16 \times 10^{-4} \text{ mol}$$

$$\text{Mass of nitrogen dissolved} = n \times GMW = 7.16 \times 10^{-4} \times 28 = 20 \times 10^{-2} \text{ g.}$$



- P.1.6** Find the ratio of volumes of 2M HNO_3 and 5M HNO_3 required to mix in order to prepare one litre of 3M HNO_3 solution.

Solution Resultant concentration of the mixture, $N = \frac{V_1N_1 + V_2N_2}{V_1 + V_2}$

$$3 = \frac{x \times 2 + (1000 - x)5}{x + 1000 - x} = \frac{2x + 5000 - 5x}{1000}$$

$$3000 = 5000 - 3x ; 3x = 2000 ; x = 667 \text{ ml} ; 1000 - x = 333 \text{ ml}$$

The ratio of the volumes of 2N HNO_3 and 5N HNO_3 = 667 : 333 = 2 : 1.



- P.1.7** 20ml of 10M HCl and 10ml of 18M H_2SO_4 are mixed and sufficient water is added to make upto one litre. Calculate the molarity of proton in the mixture.

Solution V_1 = volume of HCl solution = 20 mL

V_2 = volume of H_2SO_4 solution = 10 mL

V = volume of mixture = 1000 mL

N_1 = Normality of HCl solution = $1 \times M = 10 \text{ N}$

N_2 = Normality of H_2SO_4 solution = $2 \times M = 36 \text{ N}$

$$\text{Normality of acid in the mixture, } N = \frac{V_1N_1 + V_2N_2}{V} = \frac{20 \times 10 + 10 \times 36}{1000} = 0.56 \text{ N}$$

Molarity of proton (H^+) in the mixture = 0.56 mol L^{-1} .



- P.1.8** 50mL of normal sulphuric acid neutralises 10mL of potash solution. Calculate the strength of potash in mol L^{-1} and g L^{-1} .

Solution In volumetric titration of H_2SO_4 with KOH solution,

$$V_1N_1 = V_2N_2 \text{ (or) } 50 \times 1 = 10 \times N \text{ (or) } N = 1.25 \text{ mol L}^{-1}$$

For KOH, $n = 1$. Hence strength of KOH = 1.25 mol L^{-1}

Strength of given potash solution = $1.25 \times 56.1 = 70.125 \text{ g L}^{-1}$.



- P.1.9** It is desired to prepare one litre of decimolar aqueous aluminium sulphate. Find the amount of solute to be weighed. Calculate the number of gram ions of sulphate in the solution.

Solution Gram formula weight of aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3$ is 342 g mol^{-1}

One litre of one molar solution requires to dissolve $342 \text{ g of Al}_2(\text{SO}_4)_3$

One litre of 0.1 molar solution requires to dissolve $34.2 \text{ g of Al}_2(\text{SO}_4)_3$

One mole of $\text{Al}_2(\text{SO}_4)_3$ = Three gram ions of SO_4^{2-} (sulphate)

Number of gram ions of sulphate = $3 \times 0.1 = 0.3$.



P.1.10 Calculate the molality of one litre aqueous one molar NaOH solution, whose density is 1.01g per mL.

Solution Weight of one litre solution = $1000 \times 1.01 = 1010\text{g}$

Weight of one mole solute, NaOH = 40 g mol^{-1}

Weight of solvent, water, used in preparing solution = $1010 - 40 = 970\text{g}$

$$\text{Molality, } m = \frac{40}{40} \times \frac{1000}{970} = \frac{100}{97} = 1.03 \text{ mol kg}^{-1}.$$



P.1.11 The solubility of a substance X at 25°C and 50°C in water is respectively 35 and 50. If 300 grams of saturated solution at 50°C is cooled to 25°C , calculate the maximum mass of 'X' separated out.

Solution 300 grams of solution at 50°C = 200g of solvent + 100g of solute. The solubility of 'X' in each 100g of solvent decreases from 50g to 35g from higher temperature 50°C to lower 35°C . The mass of 'X' may be retained in 200g solvent at 25°C = $2 \times 35 = 70\text{ g}$.

Maximum mass of 'X' that may be separated = $100 - 70 = 30\text{g}$.

EXERCISE - 1.1.1

1. Write the different types of solutions with suitable examples.
2. Define (a) mole fraction, (b) molality, (c) molarity and (d) normality. Write their units.
3. What is solubility. Discuss the factors influencing solubility.
4. State and explain Henry's Law.
5. How much water is to be added to prepare 0.12M solutions from 100mL of 0.3M solution? (Ans : 500 ml)
6. Calculate the mass of caustic soda present in 225 mL of 0.556M solution.
7. What is the weight of urea required in making 2.5kg of 0.25 molar aqueous solution? (Ans : 37.5g)
8. Calculate the weights of solutes required to prepare one litre each of (a) 0.45M KMnO_4 solution and (b) 0.25M CuSO_4 solution. (Ans : 71.1g and 38.88g)
9. A gaseous mixture has 7g of N_2 , 8g of He and 22g of CO_2 . Calculate the mole-fractions of component gases in the mixture. (Ans : 0.091, 0.727 and 0.182)
10. Concentrated hydrochloric acid has 38% of HCl by weight with a density of 1.1885g per mL. Calculate the molarity of the acid. What volume of the acid on dilution to one litre gives finally decimolar solution? (Ans : 12.37 mol L^{-1} ; 8.084 mL)
11. Calculate the weight of sodium oxalate present in 250mL of seminormal solution. (Ans : 16.8g)
12. 1.032 kg of aqueous one molal methanol is added with 500mL water. Calculate the molality of dilute solution. (Ans : 0.667 mol kg $^{-1}$)
13. 0.5g of Ba(OH)_2 , 0.01 mol Ba(OH)_2 and 0.01 eq Ba(OH)_2 were together diluted to one litre. Calculate the normality of basic solution. (Ans : 0.036 eq L^{-1})
14. Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution. (Ans : 37g)
15. Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene. (Ans : 0.556 mol kg $^{-1}$)

16. Calculate the volume of 0.1N potassium permanganate that can be decolourised by 22.5 mL of 0.25N ferrous ammonium sulphate solution in acidic medium.
(Ans : 56.25mL)
17. Mass percentage (w/w) of ethylene glycol, ($\text{HOCH}_2\text{--CH}_2\text{OH}$) in an aqueous solution is 20. Calculate (a) mole fraction of solute, (b) mole percentage of water and (c) molality of solution.
(Ans : 0.068, 93.2% and 4.03 mol kg^{-1})
18. Calculate mole fraction of alcohol in 2 molal aqueous ethanol.
(Ans : 0.0348)
19. If N_2 gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 kbar.
(Ans : 0.72 mmol)

VAPOUR PRESSURE

1.2.1

Vapourisation

*Vapourisation
is a surface
phenomenon*

*Rapid
vapourisation
of liquid results
in lowering of
liquid
temperature*

In an open vessel if a liquid is present, it gradually escapes into vapour state. The phenomenon of a liquid converting into its vapours spontaneously is called vapourisation or evaporation. Vapourisation is a surface phenomenon and takes place at all temperatures.

According to kinetic molecular theory, different molecules of liquid have different velocities. A certain fraction of molecules at the surface of the liquid possessing high kinetic energy overcome the attractive forces of the neighbouring molecules. These molecules escape into the space above the liquid. The liquid keeps on evaporating and evaporation continues till the liquid disappears.

The number of molecules escaping from the liquid surface in one second is called rate of evaporation. The rate of evaporation depends on nature of liquid, temperature, surface area of liquid and flow of air current over the surface.

Rapid vapourisation of a liquid from its surface results in lowering of the liquid temperature. This technique is used in the liquification of air of real gases.

In a closed vessel, with some free space above the liquid, the evaporated molecules cannot escape to the atmosphere. As shown in Fig 1.3, the vapour fills the space available over the surface of the liquid in the container.

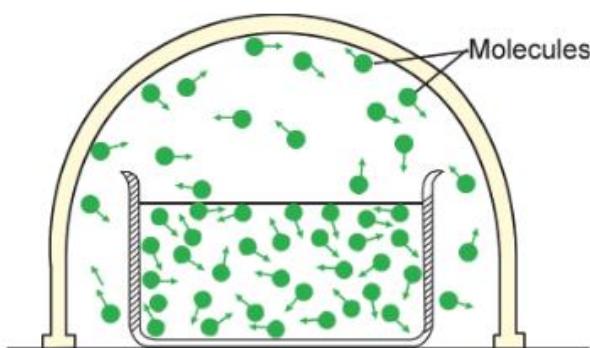


Fig 1.3 Vapourisation of a liquid in a closed vessel

The molecules of the vapour collide with other molecules, inner walls of the container and surface of liquid. Some of these molecules having lesser kinetic energy are attracted into the liquid when they come nearer to the liquid surface. The capturing of the vapour molecules of the liquid by the surface of the liquid is called condensation. Number of molecules condensing on the liquid surface in unit time is known as rate of condensation.

At any temperature, in a closed vessel both evaporation and condensation take place simultaneously. After certain time the rate of evaporation is equal to the rate of condensation. This state is called equilibrium state of liquid and vapour.

1.2.2

Vapour pressure

The pressure exerted by vapour molecules of a liquid in equilibrium, on the surface of the liquid at a given temperature is called vapour pressure. Vapour pressure of liquids is measured in barometric method.

The vapour pressure of a liquid, in general, is more if the rate of evaporation is more. Vapour pressure of a liquid depends upon nature of liquid, temperature and purity of liquid. Vapour pressure of a liquid at a given temperature is independent on the quantity of liquid, the surface area and on the shape of the vessel in which it is kept.

Vapour pressure of a liquid will be more, if the intermolecular forces of the liquid are less. Such liquids are called volatile liquids. Acetaldehyde, diethylether, pentane, etc., are examples of volatile liquids. On the other hand, intermolecular forces are strong in a metallic liquid like mercury. Vapour pressures of such liquids are less and are commonly called non-volatile liquids.

When a liquid is heated, the average kinetic energy of molecules increases. Large number of molecules possess sufficient energy to overcome the intermolecular attractions and escape into the vapour state. Therefore the rate of evaporation increases and vapour pressure increases exponentially. Variation of vapour pressures of some liquids with temperature is given in Fig 1.4.

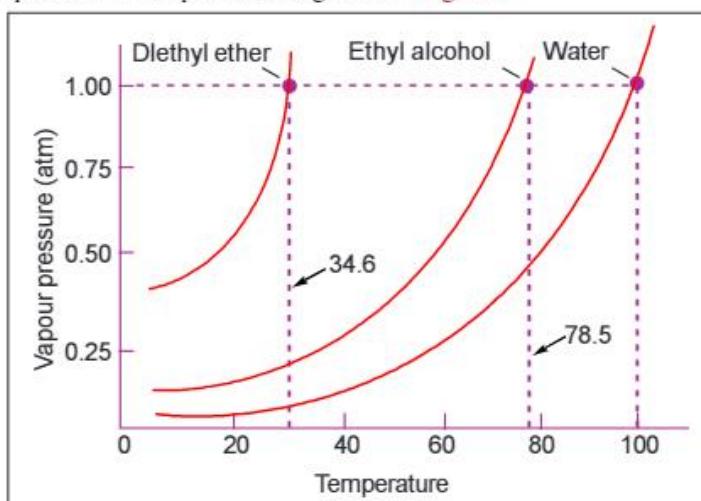


Fig 1.4 Vapour pressure curves of some liquids

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called boiling point of the liquid. Evaporation occurs at all temperatures but boiling occurs only at boiling point. The boiling point of a

*At boiling point
of the liquid,
vapour pressure
becomes equal to
atmospheric
pressure*

liquid changes with a change in external pressure and also adding another substance, volatile or non-volatile. Clausius and Clapeyron theoretically predicted the dependence of vapour pressure of liquids on temperature. A graph of log of vapour pressure (P) versus inverse of absolute temperature (T) is a straight line, as shown in Fig 1.5, with a negative slope. If P_1 and P_2 are the vapour pressure of liquid at $T_1\text{K}$ and $T_2\text{K}$,

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

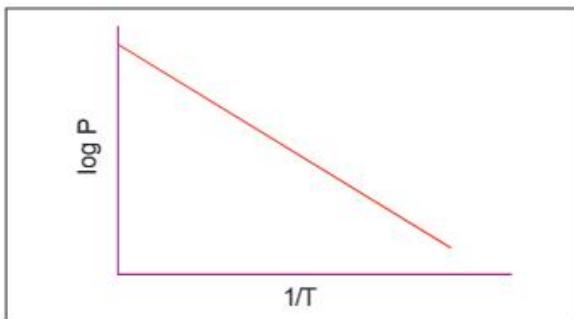


Fig 1.5 Clausius and Clapeyron graph of vapour pressure

1.2.3

Liquid-liquid solutions

*In a liquid mixture,
the vapour
pressure of each
component is
proportional to
its mole fraction
in the solution
phase*

Consider a binary solution of two volatile liquids and denote the components as 'a' and 'b'. In a closed vessel, both the components would evaporate and finally an equilibrium would be established between liquid and vapour phase. The vapour pressure is due to both components and the total pressure is the sum of the partial pressures. The partial pressures are related to the mole fractions X_a and X_b of the two components a and b respectively. This relationship is known as Raoult's law.

For a solution of volatile liquids, Raoult's law is stated as, the vapour pressure of each component in the solution is directly proportional to its mole fraction.

For component 'a', $p_a \propto X_a$ and $p_a = p_a^0 X_a$

For component 'b', $p_b \propto X_b$ and $p_b = p_b^0 X_b$

p_a^0 and p_b^0 are respectively, the vapour pressures of pure components a and b, at the same temperature of the mixture.

According to Dalton's law of partial pressures, the total vapour pressure (p_T) is the sum of partial pressures.

$$p_T = p_a + p_b = X_a p_a^0 + X_b p_b^0 = (1 - X_b)p_a^0 + X_b p_b^0$$

$$p_T = p_a^0 + X_b(p_b^0 - p_a^0)$$

The following conclusions can be drawn from the above equation.

1. Total vapour pressure over the solution can be related to the mole fraction of any one of the two components.
2. Total vapour pressure over the solution linearly varies with the mole fraction of component 'b'.
3. Total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component 'a' depending on p_a^0 and p_b^0 .


**Partial pressure
vs mole fraction
gives a
linear plot**


A graph of partial pressure versus mole fractions for a solution gives a linear plot as shown in Fig 1.6. Graph of total vapour pressure and mole fraction is also linear reflecting that it is the sum of partial pressures.

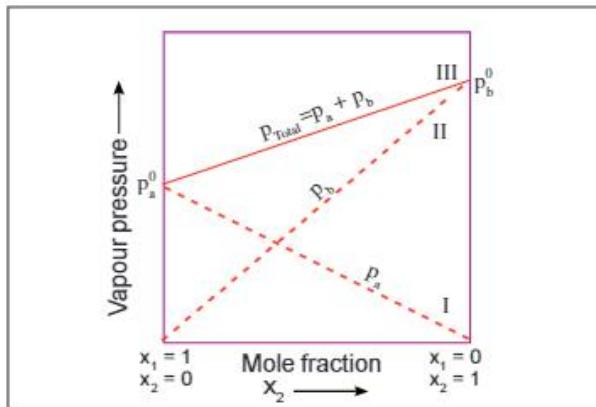


Fig 1.6 Vapour pressure versus mole fraction of components

As per Dalton's law, mole fraction of a component in vapour phase is the ratio of partial pressure of the component to the total vapour pressure.

If X_a' and X_b' are the mole fractions of components a and b in vapour phase.

$$X_a' = P_a / P_T \text{ and } X_b' = P_b / P_T$$

1.2.4

Solution of a solid in a liquid


**Properties of
solutions are
different from pure
solvent**


Consider a solution of cane sugar or glucose or urea or a salt in water and a solution of sulphur or iodine or naphthalene dissolved in carbon disulphide. These are solutions of a solid in a liquid. Some physical properties of such solutions are quite different from those of pure solvent.

In a pure liquid, the entire surface is occupied by the molecules of the liquid as shown in Fig 1.7a. If a non-volatile solute is added to a solvent, a homogeneous solution is formed. The vapour pressure of the solution is solely from the solvent alone. The number of solvent molecules is relatively less at the surface (Fig 1.7b) in a solution. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced. The vapour pressure is also reduced.

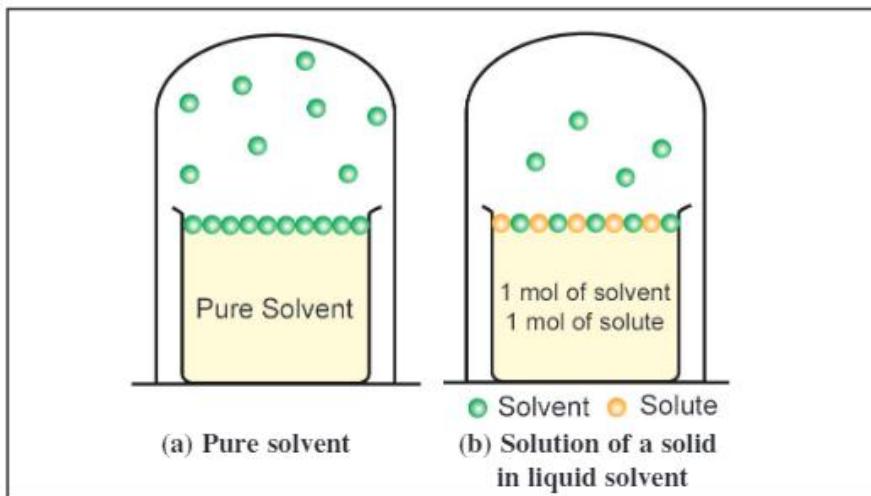


Fig 1.7 Illustration of decrease in vapour pressure

CHEMISTRY IID


Raoult's law is stated as, the relative lowering of vapour pressure is equal to mole fraction of non-volatile solute in solution


Raoult's equation for ideal solution,
$$\frac{p^0 - p}{p^0} = \frac{wM}{Wm}$$

Let, p^0 is the vapour pressure of pure solvent and p is the vapour pressure of solution ($p < p^0$)

$$(p^0 - p) \propto X_s \text{ (or)} (p^0 - p) = p^0 X_s$$

$(p^0 - p)/p^0$ is called relative lowering of vapour pressure (RLVP). According to van Babo, RLVP is constant for a dilute solution at a given temperature.

This is Raoult's law. The law is stated as, the relative lowering of vapour pressure of a dilute solution of a non-volatile solution is equal to the mole-fraction of solute in the solution.

In a dilute solution, number of moles of solute (n_1) is very less compared to number of moles of solvent (n_2). $(n_1 + n_2) = n_2$.

$$\frac{p^0 - p}{p^0} = \frac{n_1}{n_1 + n_2} = \frac{n_1}{n_2} \text{ (or)}$$

$$\frac{p^0 - p}{p^0} = \frac{wM}{Wm}$$

This is the simplified Raoult's law for a dilute solution, where w and W are masses of solute and solvent, m and M are molecular weights of solute and solvent respectively.

A plot of vapour pressure versus mole fraction of a solvent is linear with a positive slope, as shown in Fig 1.8.

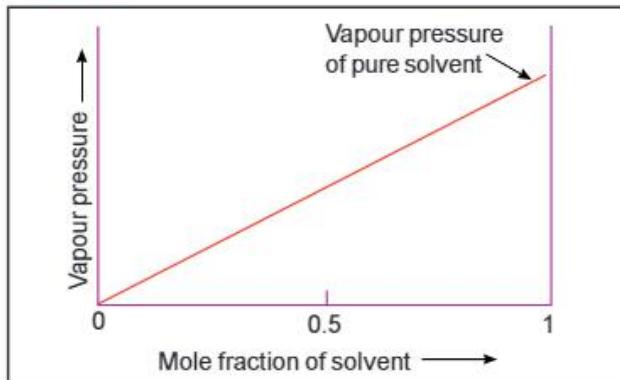


Fig 1.8 Verification of Raoult's law for all concentrations

In a solution containing a non-volatile solute, vapour pressure is directly proportional to the mole fraction of solvent.

$$p = p^0 X, \text{ where } p^0 \text{ is vapour pressure of pure solvent.}$$

Raoult's law is applicable for dilute solutions only. It is applicable if the solute is non-volatile and is in molecular state. Raoult's law is applicable only if the solution behaves as an ideal solution.



P.1.12

Raoult's law is a special case of Henry's law. Explain.

Solution According to Raoult's law, the vapour pressure of a volatile component is given as, $p = p^0 X$.

According to Henry's law, the partial solubility of a component is given as, $p = K_H X$.

Comparing these equations, partial pressure is directly proportional to the mole fraction of component in solution. Only the proportionality constants p^0 and K_H differ.

When K_H becomes equal to p^0 , Henry's law becomes Raoult's law.



P.1.13 At 70°C vapour pressure of pure benzene and pure toluene are 500 torr and 200 torr, respectively. In a homogeneous mixture of toluene with benzene at 70°C, the mole fraction of benzene is 0.4. Calculate the vapour pressure of the mixture.

Solution Vapour pressure of the mixture (P) is the sum of the total partial pressures of the components.

$$P = p_1 X_1 + p_2 X_2 = 500 \times 0.4 + 200 \times 0.6$$

$$\text{Vapour pressure of mixture} = 200 + 120 = 320 \text{ torr.}$$



P.1.14 p^o and p are vapour pressure of pure liquid and solution respectively. Among (a) p^o , (b) p/p^o and (c) $(p^o-p)/p^o$, which are temperature independent. Why?

Solution p/p^o and $(p^o-p)/p^o$ are temperature independent. p/p^o is mole fraction of solvent and $(p^o-p)/p^o$ is mole fraction of solute. Mole-fraction of a component is not dependent on temperature.



P.1.15 Drinking a hot beverage is easy and quick from a saucer than that from a cup. Why?

Solution Evaporation is an endothermic process and is a surface phenomenon. The rate of evaporation is more if surface area is more. The hot beverage will be cooled quickly in a saucer, as the surface area is high and heat is transferred from the liquid moving to the vapour state. Hence drinking is easy and quick.



P.1.16 Vapour pressure of pure water at 23°C is 19.8 torr. Calculate the vapour of 3m aqueous solution.

Solution According to Raoult's law, relative lowering vapour pressure for a dilute solution is given as

$$\frac{p^o - p}{p^o} = \frac{n_{(\text{solute})}}{n_{(\text{solvent})}} ; \frac{19.8 - p}{19.8} = \frac{3}{55.5}$$

$$\text{Vapour pressure of solution, } p = 19.8 \times \frac{52.55}{55.55} = 18.73 \text{ torr.}$$



P.1.17 Vapour pressure of pure water at 27°C is 3000 k Pa. By dissolving 5g of a non volatile molecular solid in 100g of water the vapour pressure is decreased to 2985 k Pa. What is the molecular weight of solute?

Solution According to Raoult's law,

$$\frac{p^o - p}{p^o} = \frac{WM}{Wm} ; \frac{3000 - 2985}{3000} = \frac{5 \times 18}{100 \times m} . \text{ Molecular weight of solute, } m = \frac{5 \times 18 \times 30}{100 \times 15} = 180 .$$



P.1.18 Calculate the vapour pressure of 10% (w/w) aqueous glucose solution at 30°C, if vapour pressure of pure water is 31.8 mm.

Solution 100 grams solution = 10 grams glucose + 90g water.

$$\text{Number of moles of glucose, } n_1 = 10/180 = 1/18.$$

$$\text{Number of moles of water, } n_2 = 90/18 = 5$$

$$\frac{p^o - p}{p^o} = \frac{n_1}{n_1 + n_2} ; \frac{31.8 - p}{31.8} = \frac{1/18}{5 + 1/18}$$

$$\text{Vapour pressure of solution, } p = 31.8 (1 - 1/91) = 31.45 \text{ mm.}$$

EXERCISE - 1.1.2

- What are vapourisation and condensation? On what factors rate of evaporation depends upon?
- Define vapour pressure. How is it dependent on nature of solvent and temperature?
- Explain Raoult's law for a solution containing non-volatile solute.
- What are the applications and limitations of Raoult's law.
- Calculate the relative lowering of vapour pressure of a 10% aqueous caustic soda solution.
(Ans : 0.048)

6. The vapour pressure of 4% solution of a non-volatile solute in water at 100°C is 745mm. What is the molecular weight of solute? (Ans : 36.5)
7. At room temperature, write the ascending order of volatility and vapour pressures of (A) water, (B) hexane and (C) ethanol. Explain the reasons. (Ans : Order of volatility; B>C>A)
8. 1.2g of a non-volatile solute is added to 320g of methyl alcohol at certain temperature. The vapour pressure is decreased from 400mm to 399.2 mm Hg. Calculate the molecular weight of solute. (Ans : 60)
9. Vapour pressure of chloroform (CHCl_3) and dichloromethane (CH_2Cl_2) at 298 K are 200 mm Hg and 415 mm Hg respectively. (i) Calculate the vapour pressure of the solution prepared by mixing 25.5 g of CHCl_3 and 40g of CH_2Cl_2 at 298 K. (Ans : 348 mmHg)
10. Relative lowering of a solution containing a non volatile solute (X) in a solvent (Y) is 3%. What is the mole percentage of component 'Y' in the solution. (Ans : 97%)
11. Calculate the vapour pressure, if 0.083 mole of a non-volatile solute is present in 80g of ethanol at 25°C. Vapour pressure of ethanol is 22.45 mm. (Ans : 21.38 mm)

IDEAL AND NON-IDEAL SOLUTIONS

1.3.1

Ideal solutions


Solution that
obeys Raoult's
law is called
ideal solution


Ideal solution is defined as that solution which obeys Raoult's law over the entire range of concentration. Ideal solutions are not really known. Only dilute solutions obey Raoult's law and behave nearly ideal.

An ideal solution has two other important properties. The enthalpy of mixing of pure components to form the solution is zero and the volume of mixing the components in getting the solution is also zero.

$$\Delta H_{(\text{mix})} = 0 \text{ and } \Delta V_{(\text{mix})} = 0$$

The enthalpy of mixing zero means that no heat is absorbed or evolved when the components are mixed. The volume of mixing zero means that the volume of solution would be equal to the sum of volumes of the components mixed.

At molecular level, ideal behaviour of the solutions can be explained by considering two components 'X' and 'Y'. In pure components, the intermolecular attractive interactions are of the types X-X and Y-Y. In the binary solutions of X and Y, additional X-Y type of attractions are also present. An ideal solution is formed if the intermolecular attractive forces between X-X and Y-Y are nearly equal to those between X-Y.

Ideal solutions are possible if molecules of solute and solvent are almost of same size and have identical polarity. Solution of benzene and toluene, n-hexane and n-heptane, chloroethane and bromoethane, etc., almost behave as ideal solutions.

A solution which does not obey Raoult's law is called non-ideal solution. Non-ideal solution is accompanied by change in enthalpy and change in volume during their formation.

$$\Delta H_{(\text{mix})} \neq 0 \text{ and } \Delta V_{(\text{mix})} \neq 0$$

Non-ideal solutions are of two types, showing positive deviations and showing negative deviations from ideal behaviour.

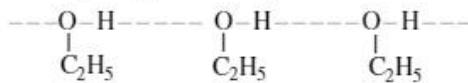
1.3.2

Solutions with positive deviation

In a solution, if solute-solute and solvent-solvent interactions are stronger than solute-solvent interactions, the solution deviates from ideal behaviour. Such solutions show positive deviations. For the binary liquid mixture, the partial vapour pressure of each component (X and Y) of the solution is greater than the vapour pressure as expected according to Raoult's law.

The interactions among molecules become weaker, as a result of which their escaping tendency of molecules increases. Hence, their partial vapour pressures increase. The total vapour pressure of the solution is greater than the vapour pressure obtained from the Raoult's law. Thus, solution mixture which shows higher experimental value of vapour pressure than those calculated from Raoult's law are said to show positive deviation.

An example of a solution with positive deviations is a binary mixture of ethanol and hexane. Other examples are: ethanol and water, acetone and benzene, acetone and carbondi-sulphite, etc. In ethanol, the molecules are associated through intermolecular hydrogen bonding.



A mixture of ethanol and hexane shows positive deviation from Raoult's law

In a mixture of ethanol and hexane, molecules of hexane come in between ethanol molecules which weaken intermolecular forces. This results in the increase in vapour pressure. The molecules are loosely held in solution, due to the decrease in the magnitude of intermolecular forces. This leads to an increase in volume. $\Delta V_{(\text{mix})}$ is positive.

Vapour pressure curves for solutions showing positive deviations are given in Fig 1.9a.

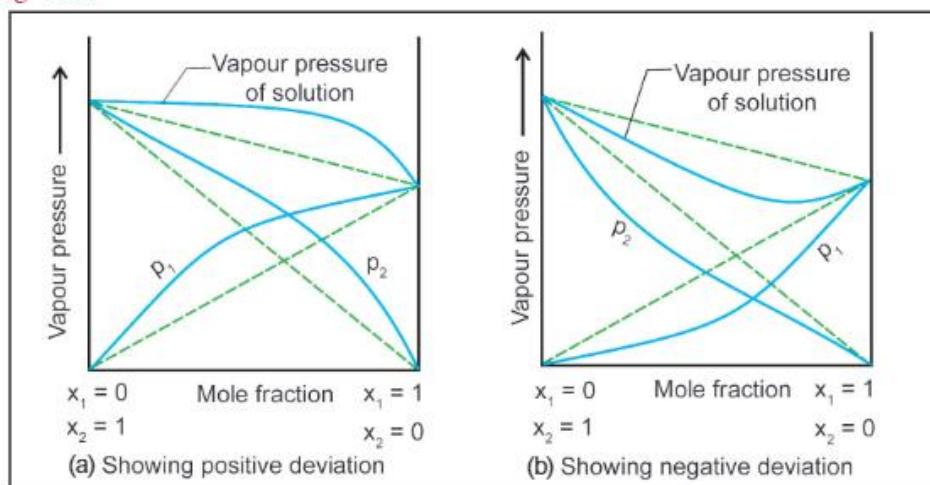


Fig 1.9 Vapour pressure of binary solutions

1.3.3

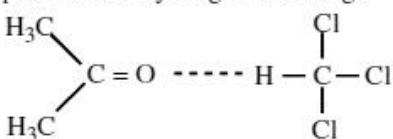
Solutions with negative deviation

In a solution, if solute-solute and solvent-solvent interactions are weaker than solute-solvent interactions, the solution deviates from ideal behaviour. Such solutions show negative deviations.

For the binary liquid mixture, the partial vapour pressure of each component (X and Y) of the solution is less than the vapour pressure as expected according to Raoult's law (Fig 1.9b).

The interactions among molecules become stronger, as a result of which the escaping tendency of molecules decreases. Hence, their partial vapour pressures decrease. The total vapour pressure of the solution is less than the vapour pressure obtained from the Raoult's law. Thus, solution mixture which shows lower experimental value of vapour pressure than those calculated from Raoult's law are said to show negative deviation.

An example of a solution with negative deviation is a binary mixture of acetone and chloroform. Other examples are : Chloroform and ether, water and nitric acid, acetone and aniline, etc. Between acetone and chloroform molecules attraction will be developed due to hydrogen bonding.



Carbon atom in chloroform becomes more electropositive due to the inductive effect by three chlorine atoms. Thus hydrogen atom of chloroform acquires more partial positive charge to develop hydrogen bonding with carbonyl oxygen atom of acetone. Evolution of heat takes place. $\Delta H_{(mix)}$ is negative. This results in the decrease in vapour pressure of each component.

Solutions with positive and negative deviations are compared for their characteristic properties in Table 1.3.

Table 1.3 Difference in the characteristics of two types of non-ideal solutions

Characteristic property of mixture	Solution with positive deviations	Solutions with negative deviations
Experimental vapour pressure	Greater than that predicted by Raoult's law	Less than that predicted by Raoult's law
Volume of mixing, $\Delta V_{(max)}$	Mixture has more volume than the sum of components	Mixture has less volume than the sum of components
Enthalpy of mixing, $\Delta H_{(max)}$	Energy is absorbed during mixing of components	Energy is released during mixing of components
Boiling point of the mixture	Less than the calculated value	More than the calculated value

1.3.4

Azeotropic mixtures

A binary mixture, which can't be resolved into components by distillation is called azeotrope

A solution which distills without a change in composition at a particular temperature is called azeotropic mixture or azeotrope. Azeotrope is a binary mixture of a particular composition, which cannot be resolved by distillation. Azeotropic mixtures are basically non-ideal solutions. They have same composition in liquid phase and vapour phase.

They are of two types: (a) minimum boiling point azeotropes and (b) maximum boiling point azeotropes (Table 1.4). The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotropes. Rectified spirit obtained from fermented sugars contain about 95% ethanol by volume is an example of minimum boiling azeotrope.

Table 1.4 Some examples of azeotropic mixtures

Components		Present mass of X	Boiling point at 1 atm (in K)			Type of azeopope
X	Y		X	Y	mixture	
Water	Ethanol	4.4	373.0	351.3	351.2	Minimum boiling
Water	Ethylacetate	11.3	373.0	352.6	346.4	Minimum boiling
Chloroform	Methanol	87.4	334.2	337.7	326.4	Minimum boiling
Chloroform	Acetone	78.5	334.2	329.1	337.5	Maximum boiling
Phenol	Aniline	42.0	455.2	457.4	459.2	Maximum boiling
Water	Nitric acid	32.0	373.0	359.0	393.5	Maximum boiling

The solutions which show a large negative deviation from Raoult's law form maximum boiling azeotropes at a specific composition. An azeotrope of nitric acid and water with about 68% nitric acid by mass is an example of maximum boiling azeotrope.



P.1.19 Methanol and ethanol are liquids of similar nature, but a mixture of them is a non-ideal solution. Why?

Solution Both methanol and ethanol are individually associate liquids, due to intermolecular hydrogen bonding. Upon mixing these alcohols, a homogeneous solution is formed. In the solution also intermolecular hydrogen bonds are present, but compared to those present in the components is less. Hence, the mixture shows positive deviation from Raoult's law.



P.1.20 Vapour pressure of pure liquids P and Q are 700 and 450 mm Hg respectively at 330K. What is the composition of the liquid mixture at 330 K, if the total vapour pressure is 600 mm Hg?

Solution Vapour pressure of the mixture = 600 mm Hg

$$= 700 \times \text{mole fraction of P} + 450 \times \text{mole fraction of Q}$$

$$= (700 \times X) + 450(1-X)$$

Mole fraction of component liquid, P = X = 0.6

Mole fraction of component liquid, Q = 1-X = 0.4.

EXERCISE - 1.1.3

- What are ideal solutions? Give examples.
- Write the differences between Ideal and non-ideal solutions.
- Which mixtures show positive deviations from Raoult's law? Why?
- Which mixtures show negative deviations from Raoult's law? Why?
- What are azeotropic mixtures? Discuss with suitable examples.

Properties which depend on the number of solute particles are called colligative properties

COLLIGATIVE PROPERTIES

Vapour pressure of a liquid decreases when a non volatile solute is added. Many other properties are also connected to the decrease in vapour pressure. Properties which depend on the number of particles of solute, irrespective of their nature relative to the total number of particles present in the solution are called colligative properties. Colligative (in Latin language) means together bind.

There are four colligative properties. The list of these four colligative properties are:

- A. Relative lowering of vapour pressure of solvent.
- B. Depression of freezing point of solvent
- C. Elevation of boiling point of solvent and
- D. Osmotic pressure of solvent.

1.4.1

Relative lowering of vapour pressure

Vapour pressure of a solvent in solution is less than that of the pure solvent. The lowering of vapour pressure depends only on the concentration of solute particles and is not dependent on their identity. If p^o is vapour pressure of pure solvent, X_1 and X_2 are mole fractions of solvent and solute in a solution respectively, the vapour pressure of solution p is given by Raoult's law as

$$p = X_1 p^o \dots \quad (1)$$

The lowering in the vapour pressure of solvent (Δp) is given as

$$\Delta p = p^o - p = p^o - p^o X_1 = p^o (1 - X_1) \dots \quad (2)$$

But the sum of mole fractions in a solution is unity, hence

$$\Delta p = X_2 p^o \dots \quad (3)$$

$$\frac{\Delta p}{p^o} = X_2 = \frac{p^o - p}{p^o} \dots \quad (4)$$

This is the Raoult's law. Since Raoult's law is applicable for dilute solutions, only dilute solutions behave as ideal solutions. The equation for ideal solutions is given as explanation of, masses and molar masses : w, m, W and M.

$$\frac{p^o - p}{p^o} = \frac{wM}{Wm} \dots \quad (5)$$

If solute undergoes association or ionisation, the above equation (5) cannot be applied. The lowering of vapour pressure is almost twice for a solution containing 58.5g (one mole) of sodium chloride in one litre aqueous solution than for a solution containing 342g (one mole) of sucrose in one litre water. This is because number of solute particles in 342g of sucrose is N_o , but the number in 58.5g of sodium chloride is $2N_o$, as sodium chloride ionises almost freely in aqueous solutions.

1.4.2

Depression of freezing point

Freezing point is the temperature at which vapour pressures of substance in liquid phase and in solid phase are equal

Lowering of vapour pressure of a solution causes decrease of the freezing point compared to that of pure solvent. At the freezing point of a substance, the solvent in solid phase is in dynamic equilibrium with the solvent in liquid phase. The freezing point is defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to that in solid phase.

A solution freezes when its vapour pressure equals the vapour pressure of the pure solid solvent as shown in Fig 1.10. When a non-volatile solute is added to the solvent, its vapour pressure decreases and it would become equal to that of a solid solvent at lower temperature. The freezing point of solvent decreases.

If T_f^o is the freezing point of pure solvent and T_f is the freezing point when non-volatile solute is dissolved in it, the decrease in freezing point (ΔT_f) is called depression in freezing point.

$$\Delta T_f = T_f^o - T_f \dots \quad (6)$$

The depression of freezing point of a dilute solution is directly proportional to molality (m) of the solution.

$$\Delta T_f \propto m \text{ (or)} \quad \Delta T_f = K_f m \dots \quad (7)$$

The proportionality constant, K_f is dependent on the nature of the solvent and is called molal freezing point depression constant or cryoscopic constant. Cryoscopic constant is the depression in the freezing point observed in one molal solution of a non-volatile solute.

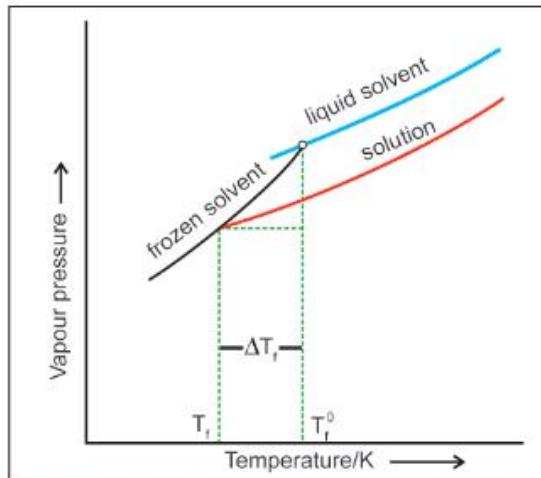


Fig 1.10 Illustration showing depression of freezing point

Equation (8) is rewritten to get expressions for cryoscopic constant and gram molecular weight (M) of the solute, in terms of weight of solute (w) and weight of solvent (W). A known mass of solute is taken in a known mass of solvent and ΔT_f is experimentally determined.

$$K_f = \frac{\Delta T_f \times M \times W}{W \times 1000} \quad (\text{or}) \quad M = \frac{K_f \times W \times 1000}{\Delta T_f \times W} \quad \dots \dots (9)$$

1.4.3

Elevation of boiling point

$$\frac{Molecular weight (M) is}{K_f \times w \times 1000} = \frac{\Delta T_f \times W}{}$$

Vapour pressure of a pure solvent decreases in the presence of a non-volatile solute. In order to achieve the condition, that the vapour pressure is equal to atmospheric pressure, the temperature of the solution must be raised. Accordingly, the boiling point increases. Similar to lowering of vapour pressure, depression of freezing point, elevation of boiling point also depend upon the quantity of non-volatile solute present in the solution.

The boiling point of a solution, as shown in Fig 1.11, is always higher than that of pure solvent with which the solution is prepared.

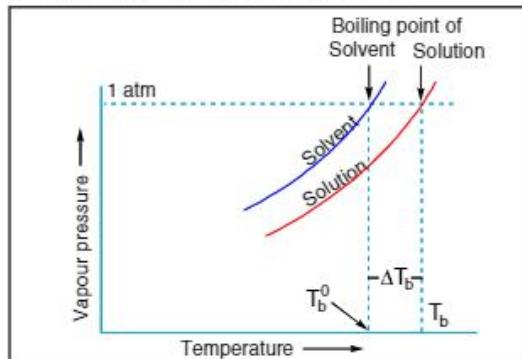


Fig 1.11 Illustration showing elevation of boiling point

If T_b^0 is the boiling point of pure solvent and T_b is the boiling point when a non-volatile solute is dissolved in it, the increase in boiling point (ΔT_b) is called elevation of boiling point.

Like the depression of freezing point, the elevation of boiling point of a dilute solution is directly proportional to molality (m) of the solution.

The proportionality constant, K_b is dependent on the nature of solvent and is called molal boiling point elevation constant or ebullioscopic constant. Ebullioscopic constant is elevation in boiling point in one molal solution of a non-volatile solute.

Molecular weight of solute or ebullioscopic constant can be calculated by the experimental determination of ΔT_b for a solution of known masses of solute and solvent.

Equation (12) is rewritten to get expressions for ebullioscopic constant and gram molecular weight of solute.

$$K_b = \frac{\Delta T_b \times M \times W}{W \times 1000} \text{ (or) } M = \frac{K_b \times W \times 1000}{\Delta T_b \times W} \dots\dots(13)$$

The units of molal depression and molal elevation constants are same and are K_b kgmol^{-1} . While K_f is related to enthalpy of fusion (ΔH_f) of the solvent, K_b is related to enthalpy of vapourisation (ΔH_v) of the solvent. If R is the molar gas constant, M_s is the molar mass of solvent, T_f and T_b denote the freezing and boiling points of solvent,

$$K_f = \frac{R \times M_s \times T_f^2}{1000 \times \Delta H_f} \quad \dots \dots \dots (14)$$

$$K_b = \frac{R \times M_s \times T_b^2}{1000 \times \Delta H_v} \quad \dots \dots \dots \quad (15)$$

Cryoscopic and ebullioscopic constants of some solvents are listed in Table 1.5.

Table 1.5 Freezing point (f.b.), boiling point (b.p.) cryoscopic constant (K_f) and ebullioscopic constant (K_b) of some solvents

Solvent	f.p., K	K_p , K kg mol ⁻¹	b.p., K	K_b , K kg mol ⁻¹
Water	237.15	1.86	373.15	0.52
Ethanol	155.7	1.99	351.5	1.20
Cyclohexane	279.55	2.00	353.74	2.79
Benzene	278.6	5.12	353.3	2.53
Chloroform	209.6	4.79	334.4	3.63
Carbon tetrachloride	250.5	31.8	350.0	5.03
Carbon disulphide	164.2	3.83	319.4	2.34
Diethyl ether	156.9	1.79	307.8	2.02
Acetic acid	290.0	3.90	391.1	2.93

1.4.4

Osmotic pressure


Process of solvent flowing into solution through semi-membrane is called osmosis


When a dilute solution of a solute is separated from its solvent by a semipermeable membrane, the solvent flows into the solution through the membrane slowly. Such phenomenon also occurs when two solutions of the same solutes with different concentrations are separated by a semipermeable membrane.

The process of solvent flowing into the solution when the solution and solvent are separated by a membrane is called osmosis. In other words, osmosis is inflow of solvent from dilute solution to concentrated solution.

Osmosis is also called endosmosis because of the inflow of solvent molecules. The osmosis process can be illustrated, as shown in Fig 1.12, when a thistle funnel to whose mouth, a semipermeable membrane is tied. Level of solution rises in the funnel due to osmosis of solvent.

The membrane which allows only the molecules of solvent to pass through it, but not the solute molecules, is called a semipermeable membrane. Parchment paper, cellophane paper, some animal membranes and inorganic precipitate membranes are commonly used in osmosis.

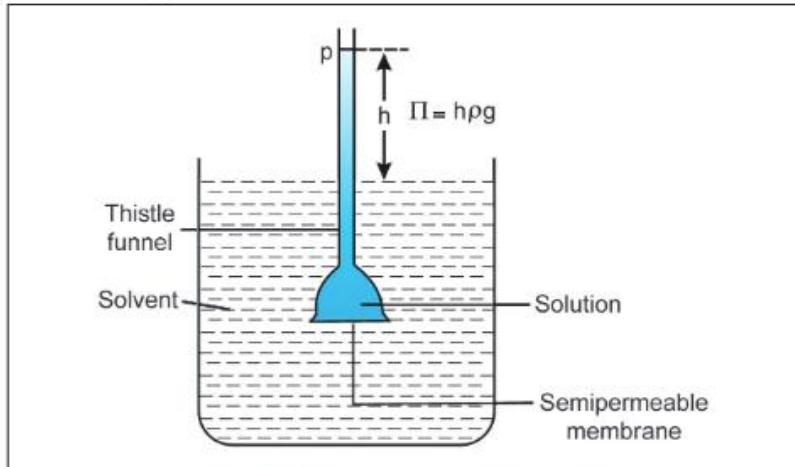


Fig 1.12 Phenomenon of osmosis

Application of osmosis : Plants take-up water from the soil through the phenomenon of osmosis through root hairs. A raw mango placed in concentrated salt solution loses water due to osmosis, which is called pickel. Haemolysis is a process of entering of contents into the cell. The cell bulges and finally bursts. Plasmolysis is a process of losing contents from the cell. The cell collapses.

The flow of solvent molecules, through the membrane, continues from solvent to solution, till equilibrium is attained. The flow of the solvent from its side to solution side can be stopped if some extra pressure is applied on the solution.

The pressure that just stops the flow of solvent is called osmotic pressure of the solution. The osmotic pressure has been found to depend on the concentration of the solution.

Osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis. Osmotic pressure is illustrated in Fig 1.13. Osmotic pressure is denoted by ‘ π ’ and is proportional to molarity (C) of the solution at a given temperature (T).

$$\text{Osmotic pressure, } \pi = (CRT) \dots\dots\dots(16)$$


Osmotic pressure is the excess pressure applied to a solution to prevent osmosis


R is the gas constant. Similar to this van't Hoff proposed 'S' as solution constant, which has values equal to R. If V is the volume of solution in litres containing 'w' grams of the solute of molar mass 'M'.

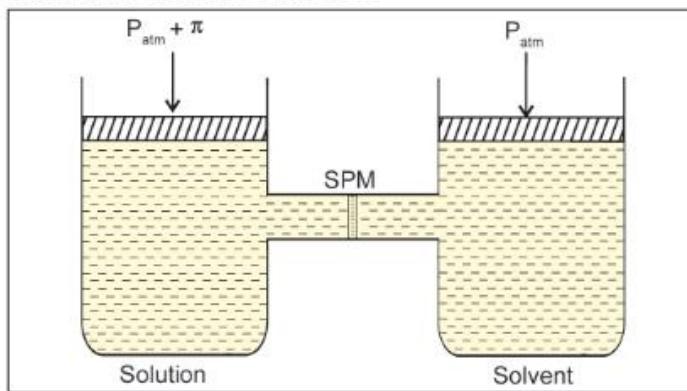


Fig 1.13 Illustration of osmotic pressure

$$\pi = (n/V)ST \text{ (or)} \quad \pi V = (wST)/M \quad \pi \dots\dots\dots(17)$$

$$M = \frac{wST}{\pi V} \dots\dots\dots(18)$$

Equation (16) and equation (18) are called van't Hoff's equations.

Molar mass of the solute can be calculated, from the experimental determination of osmotic pressure(π). Osmotic pressure method is used for determining molecular masses of proteins, polymers and other macromolecules.

Solutions having same osmotic pressure at a given temperature are called isotonic solutions. No osmosis occurs when such solutions are separated. Osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (w/v) sodium chloride solution, called normal saline solution. This solution is safe to inject intravenously.

If we place cells in a solution containing more than 0.9% (w/v) sodium chloride, water will flow out of the cells and cells would shrink. Such a solution is called hypertonic. If the salt concentration is less than 0.9% (w/v), the solution is called hypotonic. In this case, water will flow into the cells and they would swell.

The direction of osmosis can be reversed, if pressure higher than the osmotic pressure is applied to the solution side. Solvent will flow out of the solution. This process is called reverse osmosis. Reverse osmosis is used in desalination of sea water.

A schematic set up is shown in Fig 1.14 for desalination. When pressure more than osmotic pressure is applied, pure water is squeezed out of salt water through the membrane. A film of cellulose acetate placed on polymer membrane prevents impurities and ions in desalination.

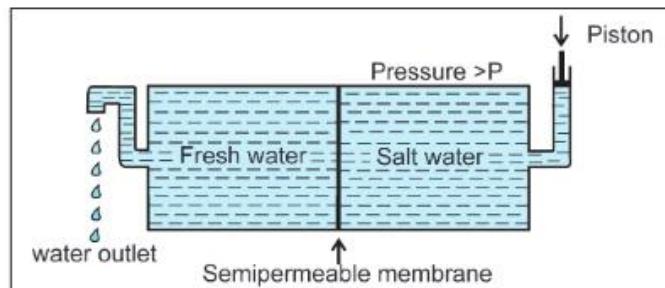


Fig 1.14 Desalination using reverse osmosis process

1.4.5**Abnormal molar masses**

Colligative properties are shown by dilute solutions. Dilute solutions obey ideal behaviour because the intermolecular forces in the solvent are negligible. But in non-ideal solutions intermolecular forces are considerable and Raoult's law is deviated.

Ionic compounds when dissolved in water dissociate into cations and anions. If we dissolve one formula weight of sodium chloride, 58.5g in water, we expect one mole each of Na^+ and Cl^- ions to be released in the solution. If this happens, there would be two moles of solute particles in the solution.

If interionic attractions are ignored, one mole of sodium chloride in one kg of water would be expected to increase the boiling point by 1.04K instead of 0.52K. If we assume that NaCl is completely dissociated in water and increase in boiling point of water is 1.04k, the molar mass of NaCl would be 29.25g mol⁻¹. This conclusion brings into light that experimentally determined molar mass is always lower than the true value when there is dissociation of solute into ions.

Similarly some solute when dissolved in solvents, may associate to form dimers or polymers. Therefore the number of solute particles decreases. Molar masses of solute determined from such solutions will be higher than that of true mass.

Molar mass that is determined either lower or higher than the expected or normal value is called abnormal molar mass. A factor 'i', known as the van't Hoff factor was introduced to account for the extent of dissociation or association. This factor is defined as the ratio of observed colligative property and calculated colligative property.

$$\text{van't Hoff factor, } i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}}$$

$$i = \frac{\text{total number of moles of particles after dissociation or association}}{\text{number of moles of particles before dissociation or association}}$$

For association :

If a solute is dissociated or ionised in solutions to give 'n' ions and ' α ' is the degree of ionisation,

$$\text{Number of particles before ionisation} = 1$$

$$\text{Number of particles after ionisation} = 1 - \alpha + n\alpha = 1 + (n - 1)\alpha$$

$$\text{van't Hoff factor, } i = 1 + (n - 1)\alpha$$

$$\text{Degree of ionisation, } \alpha = \frac{i - 1}{n - 1}$$

For dissociation :

If a solute is associated in solutions, n molecules associate and ' α ' is the degree of association,

$$\text{Number of particles before association} = 1$$

$$\text{Number of particles after association} = 1 - \alpha + (\alpha/n)$$

$$\text{van't Hoff factor, } i = 1 - \alpha + (\alpha/n)$$

$$\text{Degree of association, } \alpha = \frac{1 - i}{1 - (1/n)}$$

Inclusion of van't Hoff factor modifies equations for colligative properties as,


Colligative properties are modified using van't Hoff factor

van't Hoff factor increases upon dilution


$$\text{Relative lowering of vapour pressure of solvent, } \frac{p^o - p}{p^o} = \frac{n_1 i}{n_1 i + n_2}$$

$$\text{Depression of freezing point, } \Delta T_f = i m K_f$$

$$\text{Elevation of boiling point, } \Delta T_b = i m K_b$$

$$\text{Osmotic pressure of solution, } \pi = i C S T$$

The van't Hoff factor increases upon dilution and approaches 2 for electrolytes like NaCl and MgSO₄. It gets close to 3 for K₂SO₄ and 5 for K₄Fe(CN)₆. The van't Hoff factor for some electrolytes are listed in Table 1.6.

Table 1.6 The van't Hoff factor, i for some electrolytes

Salt	Values of i			van't Hoff factor, i for complete dissociation of solute
	0.1 m	0.01 m	0.001m	
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 ₂ SO ₄	2.32	2.70	2.84	3.00

1.4.6

Determination of molar masses


Ostwald's dynamic method is based on measuring vapour pressure


Molar mass can be determined using the experimental results and corresponding mathematical equations which relate the molar mass (m) to the colligative property.

Ostwald's dynamic method is based on the measurement of relative lowering of vapour pressure of a solution. Molar mass (m) of a non-volatile solute is determined as:

$$\frac{p^o - p}{p^o} = \frac{wM}{Wm} \quad (\text{or}) \quad m = \frac{wM}{W} \times \frac{p^o}{p^o - p}$$

Here, p^o and p are vapour pressures of solvent and solution, w and W are masses of solute and solvent and M is molar mass of solvent.

Rast's method is generally for solid solutions, since it was developed using camphor as a solvent. Rast's method is based on depression of freezing point.

A known weight of camphor (W) is finely grinded in a dry mortar and powdered. A known weight of solid solute (w) is added to this. The mixture is melted to form a homogeneous solution, cooled and powdered dry. The melting point of mixture is conventionally determined. The melting point of pure camphor is separately determined. The difference gives depression of freezing point (ΔT_f).

$$\Delta T_f = K_f \times \frac{w}{m} \times \frac{1000}{W} \quad (\text{or}) \quad m = \frac{K_f \times w \times 1000}{\Delta T_f \times W}$$

Molar mass (m) of the solid is obtained by substituting the experimental data and molal depression constant (K_f) of camphor.

Cotterill's method of determination of molar masses is based on the elevation of boiling point. Molar masses are also determined based on the depression of freezing. Since the elevation or depression values are small, conventional thermo-meters are not useful. Beckmann designed a thermometer which measures only small changes

$$\text{Molar mass} = \frac{K_b \times w \times 1000}{\Delta T_b \times W}$$

occurring in reference to freezing or boiling points. The elevation or depression is measured, but not absolute boiling and freezing temperatures.

Molar mass of the solute (m) is determined by substituting the experimental data and molal elevation constant (K_b) of the solvent.

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

Berkely-Hartley's method is based on determination of osmotic pressure. Pressure is applied on the solution to just prevent osmosis, when the solution and the solvent are separated by semipermeable membrane. This pressure applied on solution is numerically equal to osmotic pressure of the solution.

The molar mass of solute (m) is calculated from the experimental osmotic pressure (π) at temperature (T), volume of the solution (V) and mass of the solute (w) as,

$$m = \frac{wRT}{\pi V} \quad (\text{or}) \quad m = \frac{wST}{\pi V}$$

Here 'R' is molar gas constant and 'S' is molar solution constant.



- P.1.21** 1.2 mL of acetic acid having density 1.06 g mL^{-1} is dissolved in 2 L water. If the depression in freezing point was 0.0205°C , calculate (a) van't Hoff factor and (b) proton concentration of acid solution.

Solution Number of moles of acetic acid, $n = \frac{1.2 \times 1.06}{60} = 0.0212$

$$\text{Molality of acid solution, } C = \frac{0.0212}{2} = 0.0106 \text{ mol kg}^{-1}$$

$$\Delta T_f \text{ expected for this strength} = k_f \times m = 1.86 \times 0.016 = 0.0997\text{K}$$

$$\text{Van't Hoff factor (i)} = \frac{\text{observed freezing point}}{\text{expected freezing point}} = \frac{-0.0205}{-0.0197} = 1.041$$

Acetic acid is ionised as, $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+$.

If ' α ' is the extent of ionisation, total number of particles = $n(1 + \alpha)$

$$\text{van't Hoff factor} = i = \frac{n(1 + \alpha)}{n} = 1 + \alpha = 1.04; \alpha = 0.041$$

$$\text{Proton concentration} = C\alpha = 0.0106 \times 0.041 = 4.35 \times 10^{-4} \text{ mol L}^{-1}$$



- P.1.22** One litre solution X has x grams of urea dissolved in it. Another one litre solution Y has x grams of KCl dissolved in it. Find the ratio of lowering of vapour pressures of the solutions X and Y.

Solution The ratio of concentration = The ratio of number of moles

$$\text{The mole ratio} = \frac{x}{60} : \frac{x}{74.6} = 7.46 : 6$$

Urea is unionised even in dilute solutions and hence, van't Hoff factor, $i = 1$

KCl is almost ionised in dilute solutions and hence, van't Hoff factor, $i = 2$

Hence the ratio of particles in two solutions = $7.46 : 6 \times 2 = 7.46 : 12 = 1:1.6$

Since lowering of vapour pressure is a colligative property, the ratio of lowering = $1 : 1.6$



- P.1.23** What is the influence of added non-volatile solute on the boiling point of solvent ?

Solution The vapour pressure of solvent in a solution is less. Therefore temperature must be raised to make the vapour pressure of the solution equal to the atmospheric pressure.

Hence, boiling point of solution will be greater than that of the solvent.



P.1.24 K_b and K_f for water are respectively 0.52 and 1.80 kg mol⁻¹ respectively. For an aqueous glycollic solution freezing point is 3.72°C. What is the boiling point of the solution?

Solution Depression of freezing point = $\Delta T_f = 3.72^\circ\text{C}$

$$\Delta T_f = K_f \times m; \text{ molality } m = \Delta T_f / K_f = 3.72 / 1.80 = 2 \text{ mol kg}^{-1}$$

$$\text{Elevation of boiling point} = \Delta T_b = K_b \times m = 0.52 \times 2 = 1.04^\circ\text{C}$$

$$\text{Boiling point of the solution} = 100 + 1.04 = 101.04^\circ\text{C}$$



P.1.25 K_b for diethylether is 2.16 K kg mol⁻¹. Calculate the molar mass of solute when 0.4g of solute present in 40 g of ether, increased the boiling point of ether by 0.17 K.

Solution Weight of solute = $w = 0.4\text{g}$; Weight of solvent = $W = 40\text{g}$

$$K_b = 2.16 \text{ K kg mol}^{-1}; \Delta T_b = 0.17\text{K}$$

$$\text{Molar mass of solute} = \frac{w \times K_b \times 1000}{W \Delta T_b} = \frac{0.4 \times 2.16 \times 1000}{0.17 \times 40} = 127 \text{ g mol}^{-1}$$



P.1.26 1.06 Kg of urea aqueous solution is cooled to -2.33°C . Find out of the amount of ice separated. (K_f for water is $1.86 \text{ K.Kg.mol}^{-1}$)

Solution Assume that in 1060 g of urea solution x g urea and $(1060 - x)$ g water is present

$$1 = \frac{x}{60} \times \frac{1000}{1060 - x} \Rightarrow x = 60\text{g}$$

Thus in 1060 g urea aqueous solution 60 g urea and 1000 g water is present.

When this solution is cooled to -2.33°C , some ice is separated and w g of liquid water left. Since no solute will be present in the separated ice, 60 g urea will be present in the remaining solution. F.P. of remaining solution is -2.33°C . The depression in freezing point is 2.33°C .

$$2.33 = 1.86 \times \frac{60}{60} \times \frac{1000}{w} \Rightarrow w = 800\text{g}$$

$$\text{Weight of ice separated} = 1000 - 800 = 200\text{ g}$$



P.1.27 In living cells which is dangerous, plasmolysis or haemolysis ?

Solution Both plasmolysis and haemolysis are dangerous.

Contents will come out of the cell during plasmolysis and the cell collapses.

Contents will enter into the cell during haemolysis and the cell bursts.



P.1.28 7g of a solute are dissolved in 200g of solvent (mol.wt. = 78) to prepare a solution. At a certain temperature dry air is sent into a solution and solvent continuously. The loss in weights of containers containing solution and solvent are 0.975 g and 0.025g. Calculate the molar mass of solute.

Solution Lowering of vapour pressure ($P^0 - P$) is proportional to y ; $y = 0.025\text{g}$

Vapour pressure (P) is proportional to x ; $x = 0.975\text{ g}$

$$\text{Vapour pressure of pure solvent} = P^0 = x + 4 = 0.975 + 0.025 = 1\text{g}$$

$$\frac{y}{x+y} = \frac{P^0 - P}{P^0} = \frac{wM}{Wm} = \frac{0.025}{1.0}$$

$$\text{Molar mass of solute, } m = \frac{7 \times 78}{0.025 \times 200} = 100 \text{ g mol}^{-1}$$



P.1.29 2% of aqueous urea and 6% of aqueous 'X' are isotonic. If 'X' is a molecular solid, calculate its molar mass.

Solution For isotonic solutions, osmotic pressures are same, $\pi_1 = \pi_2$.
Hence, concentrations of solutions are also same, $C_1 = C_2$

$$\text{Since moles are equal ; } \frac{W_1}{M_1} = \frac{W_2}{M_2} \text{ (or) } \frac{2}{60} = \frac{6}{M_2}$$

Molar mass of solute X = $M_2 = 180 \text{ g mol}^{-1}$.



P.1.30 AT 10°C , the osmotic pressure of 1% (w/v) solution of 'X' is $7.87 \times 10^4 \text{ N m}^{-2}$. What is the molecular weight of solute X ?

Solution Osmotic pressure of the given solution = $\pi = 7.87 \times 10^4 \text{ N m}^{-2}$

Volume of the solution = $V = 100 \text{ mL} = 10^{-4} \text{ m}^3$

Solution constant = $S = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Temperature = $2.73 + 10 = 283 \text{ K}$; weight of solute = $w = 1 \text{ g}$

$$\text{Molecular weight of solute} = \frac{wST}{\pi V} = \frac{1 \times 8.314 \times 283}{7.87 \times 10^{-4} \times 10^{-4}} = 299 \text{ g mol}^{-1}$$



P.1.31 Molar masses of solutes are best measured from osmotic pressures. Why ?

Solution Compared to other colligative properties, magnitude of osmotic pressure is large, even for very dilute solutions. Determination of molar masses is particularly useful for polymers as they have poor solubility and biomolecules as they are unstable at higher temperatures.



P.1.32 If extent of dissociation of both KCl and BaCl₂ of some concentrations with identical value of α as 0.9, what is the ratio of their van't Hoff factors ?

Solution van't Hoff factor is given as, $i = \frac{1 + (n - 1)}{1} \alpha$

$n = 2$ for KCl ; $i = 1 + (2 - 1) \alpha = 1 + \alpha = 1 + 0.9 = 1.9$

$n = 3$ for BaCl₂ ; $i = 1 + (3 - 1) \alpha = 1 + 2 \alpha = 1 + 1.8 = 2.8$

The ratio of van't Hoff factors for KCl and BaCl₂ = $1.9 : 2.8 = 1 : 1.473$

EXERCISE - 1.1.4

- What are colligative properties? Discuss.
- Compare the lowering of vapour pressures of equimolar calcium bromide and glucose in aqueous solutions. (Ans : 3:1)
- Discuss the depression of freezing point of a solution.
- Boiling point of a liquid increases upon dissolving a non-volatile solute. Discuss.
- At certain temperature, the vapour pressure of pure benzene is 0.85 bar. 0.5 g of non-volatile and non-electrolyte solid 'X' is dissolved in 39 g of benzene. The vapour pressure is reduced by 0.005 bar. Calculate the molar mass of 'X'. (Ans : 170)
- Vapour pressure of pure water at 298 K is 23.8 mm Hg. 50 g of urea (NH₂CONH₂) is dissolved in 859 g of water. Calculate the vapour pressure of water for this solution and its relative lowering. (Ans : 0.0168)
- 2.0 g of a non-electrolyte solute dissolved in 100 g of benzene lowered the freezing point of benzene by 0.4°C . If the freezing point depression constant of benzene is $5.12 \text{ K kg mol}^{-1}$, calculate the molar mass of solute . (Ans : 250 g mol⁻¹)

8. When 0.9g of a non-volatile solute was dissolved in 45g of benzene, the elevation of boiling point is 0.88°C . If K_b for benzene is 2.53K kg mol^{-1} , Calculate the molar mass of solute. (Ans : 58 g mol^{-1})
9. Cryoscopic constant for benzene is 4.9 K kg mol^{-1} . Freezing point of benzene is 278.6 K . 4 grams of benzoic acid when dissolved in 50g of benzene, the freezing point is 276.98K . Calculate the extent of association of benzoic acid. (Ans : 0.99)
10. At 750 torr water has a boiling point 372.63 K . How much sucrose is to be added to one kg of water such that water boils at 373K and 750 torr? (Ans : 3.72 g)
11. What are : (a) osmosis and (b) osmotic pressure?
12. Discuss on reverse osmosis and water purification.
13. Molar mass of polymer is 185000g mol^{-1} . Calculate the osmotic pressure exerted when 10g of polymer is in 4.5 L of water at 310 K . (Ans : 23.4 mm Hg)
14. One litre aqueous solution contains $2 \times 10^{-2}\text{ kg glucose}$ at 25°C . Calculate the osmotic pressure of the solution. (Ans : 2.72 atm)
15. The osmotic pressure of a non-volatile solute 'X' in benzene at 25°C is 20.66Nm^{-2} . If the concentration of solution is 2 gL^{-1} , what is the molecular weight of X? (Ans : 240)
16. 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be $2.57 \times 10^{-3}\text{ bar}$. Calculate the molar mass of the protein. (Ans : $61,022\text{ g mol}^{-1}$)
17. Discuss the van't Hoff factor.
18. What are abnormal molar masses? Why are the molar masses abnormal?



1. A solution is a homogeneous mixture of two or more components. Component in larger proportion is called solvent and in minor proportion is solute.
2. The ratio of number of moles of a component to the total number of moles of all the components in a solution is called mole-fraction.
3. Molality is defined as the number of gram moles of solute present in one kilogram solvent.
4. Molarity is defined as the number of gram moles of solute present in one litre solution.
5. Normality is defined as the number of gram equivalents of solute present in one litre solution.
6. The amount of solute that saturates 100 g of solvent at a given temperature is called solubility.
7. Henry's law is stated as, the solubility of a gas in a given liquid at constant temperature is directly proportional to the pressure exerted by the gas.
8. Adding more solvent to a solution is called dilution. During dilution, the concentration of solution decreases, but the number of moles of the solute remains constant.
9. The pressure exerted by vapour molecules of the liquid, on the surface of the liquid, at equilibrium is called vapour pressure.

10. Vapour pressure increases exponentially with an increase in temperature.
11. The temperature where the vapour pressure becomes equal to the atmospheric pressure is defined as boiling point of the liquid.
12. The difference between vapour pressure of pure solvent and vapour pressure of solution is called lowering of vapour pressure.
13. Raoult's law is stated as, the relative lowering of vapour pressure of a non-volatile solute is equal to the mole fraction of the solute in the solution.
14. For a solution of volatile liquids, the partial vapour pressure of each component in the solution is directly proportional to its mole-fraction.
15. Solution which obeys Raoult's law over the entire range of concentration is known as ideal solution.
16. Solutions with weaker solute-solvent interactions show positive deviation and stronger solute-solvent interactions show negative deviation from Raoult's law.
17. Azeotropic mixtures are the binary mixtures having same composition in liquid and vapour phase and boil at constant temperature.
18. Properties depend on the number of solute particles irrespective of their nature are called colligative properties.
19. A solution containing a non-volatile solute has lower freezing point and higher boiling point compared to the pure solvent.
20. Depression of freezing point and elevation of boiling point are directly proportional to molality.
21. Flow of solvent molecules through semipermeable membrane into the solution is known as osmosis.
22. Pressure that just stops the flow of solvent molecules into the solution through membrane is called osmotic pressure.
23. At a given temperature osmotic pressure is directly proportional to molarity of the solution.
24. Molar mass that is either lower or higher than the expected value is called abnormal molar mass.
25. van't Hoff factor is the ratio of observed colligative property and calculated colligative property.
26. Abnormal molar masses are due to dissociation or association of solute particles. Association leads to a van't Hoff factor less than unity and dissociation leads to a van't Hoff factor greater than unity.

EXERCISE - 1.2

1. What is solubility? Discuss the factors influencing solubility.
2. Aerated water bottles are kept under cold water during summer. Why?
3. Explain the lowering and relative lowering of vapour pressures.
4. Write the units of cryoscopic constant and ebullioscopic constant?

CHEMISTRY IID

5. How is osmotic pressure useful in determining molar masses?
6. How is the principle of reverse osmosis used for desalination?
7. The molar concentration of proton obtained by mixing equal volumes of 1 M HNO_3 and 1 M H_2SO_4 is not equal to 1 M. Explain.
8. Mixing n-pentane and n-hexane, an ideal solution is formed. Substantiate.
9. A fresh grape fruit dipped in brine solution shrinks. Why?
10. Vapour pressures of benzene and toluene are 160 and 60 torr. What will be the vapour pressure of a mixture of equal masses of benzene and toluene. (Ans : 114 torr)
11. How water can be made boiling without heating?
12. Write the reason of abnormality in molar masses.
13. Calculate the weight of anhydrous sodium carbonate present in 200 mL of 0.2 M solution. (Ans : 4.24 g)
14. Calculate the normality of 10.6% (w/v) Na_2CO_3 in aqueous solutions. (Ans : 2 eq L^{-1})
15. How many mL of 0.1M ferrous oxalate can reduce 10 mL of 0.2M potassium dichromate solution in acidic medium? (Ans : 40 mL)
16. 250mL of 0.2M NaOH and 100 mL of 0.25M $\text{Ba}(\text{OH})_2$ are mixed. Calculate the molarity of hydroxyl ion in the mixture. (Ans : 0.29 mol L^{-1})
17. The density of 8.653% (w/v) Na_2CO_3 solution is 1.018 g mL^{-1} . Calculate the molarity of solution. (Ans : 0.876 mol kg^{-1})
18. 100 mL of ethanol (density 0.8g /cc) is diluted to one litre using water. Calculate (a) molality and (b) mole fraction. (Ans : 1.93 mol kg^{-1} ; 0.0336)
19. The density of 3M $\text{Na}_2\text{S}_2\text{O}_3$ is 1.25 g /cc. Calculate the mole fraction of $\text{Na}_2\text{S}_2\text{O}_3$ and molality of thiosulphate. (Ans: 0.065; 3.86 mol kg^{-1})
20. Partial pressure of ethane over a saturated solution containing 6.56×10^{12} g of ethane is 1 bar. If the solution contains 5×10^{-2} g of ethane, what is the partial pressure of gas? (Ans : 0.76 bar)
21. Vapour pressures of para xylene and methylbenzene at 90°C are respectively 150 mm and 400 mm. Calculate the mole fraction of dimethyl benzene in the mixture that boils at 90°C , when the pressure is 0.5 atm. (Ans : 0.08)
22. What weight of a non-volatile solute (molar mass 40 g) should be dissolved in 114 g of octane to reduce its vapour pressure by 20%. (Ans : 10 g)
23. Vapour pressure of pure water at 298K is 23.8 mm Hg. Calculate the lowering of vapour pressure caused by adding 5g of sucrose in 50g of water. (Ans : 0.124 mm Hg)
24. Non ideal solutions exhibit either positive (or) -ve deviations from Raoult's law. What are these deviations and why are they caused. Explain with one example for each type.
25. Define the terms osmotic and osmotic pressure. What is the advantage of using osmotic pressure as compared to their colligative properties for the determination of molar masses of solute in solutions?
26. What is the vapour pressure of one molal glucose solution at 100°C ? (Ans : 746.3 mm Hg)
27. Vapour pressure of water at certain temperature is 155 mm Hg and that of the another solvent 'X' is 'p' mm Hg. Molecular weight of 'X' is 128. An aqueous solution of 'X' (64% by wt) has a vapour pressure of 145 mm Hg. What is 'p'? (Ans : 105)
28. At 100°C vapour pressures of heptane and octane are respectively 105.2 and 46.8 kPa. Calculate the vapour pressure of 60 grams of the mixture of two liquids, in which the mass of octane is 35g. (Ans : 73 kPa)

29. Vapour pressure of aqueous glucose at 373 K is 750 mm Hg. Calculate the molality of solute present dissolved solution. (Ans : 0.74 mol kg⁻¹)
30. A mixture of two immiscible liquids water and nitrobenzene boiling at 372 K has partial vapour pressures of water 733 mm and nitrobenzene 27 mm. Calculate the weight ratio of liquid components in distillate. (Ans : 1 : 4)
31. State the law co-relating the pressure of a gas and its solubility in a liquid. State one application for this law.
32. Define the following terms : (i) Ideal solution (ii) Azeotrope and (iii) Osmotic pressure
33. If 0.869 g of cholesterol is dissolved in 4.4 g of diethyl ether the vapour pressure of ether lowers from 0.526 to 0.507 atm at 20°C. Calculate the molecular weight of cholesterol. (Ans : 390)
34. Calculate the cryoscopic constant of a solvent, if its latent heat of fusion is 180. 75 Jg⁻¹ and freezing point 16.6°C. (Ans : 3.86K kg mol⁻¹)
35. Freezing point depression of millimolar $K_nFe(CN)_6$ is 7.1×10^{-3} K. If $K_f = 1.86\text{ k Kg mol}^{-1}$, calculate the value of n. (Ans : 3)
36. A solution of urea has boiling point 100.15°C. K_f and K_b for water are 1.87 and 0.52Kkgmol⁻¹. Calculate (a) molality and (b) freezing point of the solution. (Ans : 0.29 mol kg⁻¹ ; -0.54°C)
37. Compare the weights of methanol and glycerol, which would be required separately to lower the freezing point of one Kg water by 10°. (Ans : 8 : 23)
38. At 0°C, the vapour pressure of pure water is 4.63 mm and an aqueous solution of 8.49 g of NaNO₃ dissolved in 100 g of water is 4.483 mm. What is the extent of ionisation of NaNO₃? (Ans : 0.7)
39. 75.2g of phenol is dissolved in one kg of solvent of K_f value 14 K Kg mol⁻¹. If freezing point depression is 7K, what is the percentage dimerisation of phenol. (Ans : 75%)
40. Latent heat of fusion and vaporisation of water are respectively 80 and 540 Cal g⁻¹. If the boiling point of a solution is 100.1°C, what is its freezing point? (Ans : 0.36°C)
41. A storage battery contains a solution of sulphuric acid 38% by weight and at this concentration the Van't Hoff factor is 2.5. If K_f of water is 1.86 K Kg mol⁻¹, at what temperature the contents of battery freeze? (Ans : 243.92 K)
42. 0.5% aqueous KCl has freezing point -0.24°C. Calculate the degree of dissociation, if K_f for water is 1.86 K kg mol⁻¹. (Ans : 92%)
43. A 10% solution of sucrose is iso-osmotic with 1.754% solution of X. If X is non volatile and non-electrolyte solute, what is its molar mass? (Ans : 60 g mol⁻¹)
44. At 25°C, a solution containing 0.1 g of polyisobutylene in 50 ml. of benzene developed a rise of 2.4 mm at osmotic equilibrium. If density is 0.8 cc⁻¹, calculate the molecular weight of polyisobutylene. (Ans : 2.39×10^5)
45. 100 mL of an aqueous solution of protein contains 6.3 g of protein. Calculate the molar mass of protein if osmotic pressure of the solution at 27°C is 2.57×10^{-3} bar. (Ans : 610 g mol⁻¹)
46. A 1% (w/v) aqueous solution of potassium chloride has extent of ionisation 0.82 in water at 18°C. Calculate the osmotic pressure. (Ans : 5.84 atm)
47. Give one example each for non-ideal solution showing positive deviation and non-ideal solution showing negative deviation.
48. Why is the osmotic pressure of sodium chloride solution higher than glucose solution?
49. What happens to the vapour pressure of a liquid when a non-volatile solute is dissolved in it?

