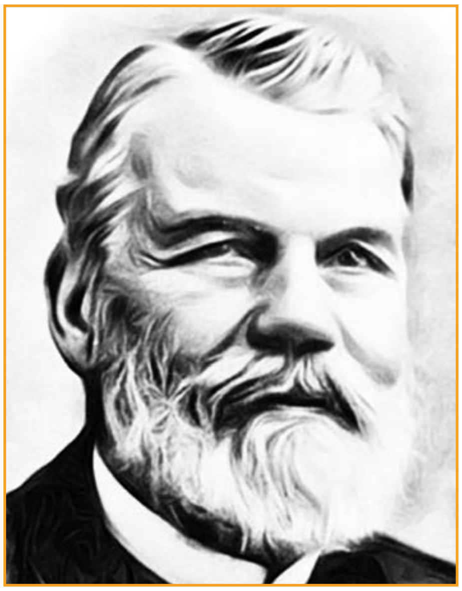
Unit 9 Solutions



François - Marie Raoult

François - Marie Raoult was a French chemist who conducted research into the behaviour of solutions, especially their physical properties.

In his first research paper, he described the action of solutes in depressing the freezing point of the solutions. He also gave a relation between the vapour pressure of the solution with the molecular wight of the solute.

Learning Objectives

After studying this unit students will be able to

- describe the formation of different types of solutions
- express the concentration of a solution in different units
- prepare solutions of required concentrations by diluting the stock solution
- state Henry's and Raoult's Law
- explain the deviation of real solutions from Raoult's Law
- correlate colligative properties of solutions with the molar masses of their solutes
- explain the abnormal colligative properties
- define Van't Hoff factor and calculate degree of dissociation / association

9.1 INTRODUCTION

There are many chemicals that play an important role in our daily life. All these chemicals are in different physical forms, viz solid, liquid and gas. If we do close examination on their composition, we could find that most of them are mixtures and rarely pure substances. One more interesting aspect is that most of the mixtures are homogeneous irrespective of their physical state and such homogeneous mixtures are called as solutions.

Sea water is one of the naturally existing solutions which covers more than 70% of the earth's surface. We cannot imagine life on earth without sea water. It contains many dissolved solids, mostly NaCl. Another important naturally occurring solution is air. Air is a homogeneous mixture of nitrogen, oxygen, carbon dioxide, and other trace gases. Even solid material such as brass is a homogeneous mixture of copper and zinc.

In the above examples the solutions are in different physical states viz... liquid (sea water), gas (air) and solid (alloys), and one common property of all the above is their homogeneity. The homogeneity implies uniform distribution of their constituents or components throughout the mixture. In this chapter, we learn about the solutions and their properties.

9.2 Types of solutions

A solution is a homogeneous mixture of two or more substances, consisting of atoms, ions or molecules. The compound that is present in largest amount in a homogeneous mixture is called the solvent, and others are solutes. For example, when a small amount of NaCl is dissolved in water, a homogeneous solution is obtained. In this solution, Na^+ and Cl^- ions are uniformly distributed in water. Here water is the solvent as the amount of water is more compared to the amount of NaCl present in this solution, and NaCl is the solute.

The commonly used solutions are the solutions in which a solid solute is dissolved in a liquid solvent. However, solute or solvent can be in any of the three states of matter (solid, liquid, gas). If water is used as the solvent,the resultant solution is called as an aqueous solution. If solvents (Benzene, CCl_4, ether etc.,) other than water is used, then the resultant solution is called as a non-aqueous solution.

The following table illustrates the different types of solutions based on the physical state of the solute and solvent.

Table 9.1 Types and examples of solutions

S. No.	State of solution	Solute	Solvent	Examples
1	Gaseous solution	Gas	Gas	Air (A mixture of nitrogen, oxygen and other gases)
		Liquid	Gas	Humid oxygen (Oxygen containing water)
		Solid	Gas	Camphor in nitrogen gas
2	Liquid solutions	Gas	Liquid	CO_2 dissolved in water (carbonated water)
		Liquid	Liquid	Ethanol dissolved in water
		Solid	Liquid	Salt water
3	Solid solutions	Gas	Solid	Solution of H_2 in palladium
		Liquid	Solid	Amalgam of potassium (used for dental filling)
		Solid	Solid	Gold alloy (of copper used in making Jewelery)

9.3 Expressing concentration of solutions

In our life we have come across many solutions of varying strengths or concentrations such as mouthwash, antiseptic solutions, household disinfectants etc... Have you ever noticed the concentration of the ingredients present in those solutions? For example, chlorhexidine mouthwash solution contains 0.2 % (w/v) chlorhexidine gluconate; The concentration of the commercially available hydrogen peroxide is 3% (w/v). Similarly, other terms such as ppm (TDS of water), molar and normal (laboratory reagents) are used to express the concentration of the solution. The concentration of a solution gives the amount of solute present in a given quantity of solvent. As we have seen, there are different ways of expressing the concentration of a solution. Let us learn the different concentration terms and to prepare a solution of a specific concentration.

Table 9.2 Different concentration units and their illustrations

S. No.	Concentration term	Expression	Illustration
1	Molality (m)	$\frac{\text{Number ofmoles of solute}}{\text{Mass of the solvent (in kg)}}$	The molality of the solution containing 45 g of glucose dissolved in 2 kg of water $\frac{\text{Number ofmoles of solute}}{\text{Mass of the solvent (in kg)}} = \frac{\left(\frac{45}{180}\right)}{2}$ $= \frac{0.25}{2} = 0.125\ \text{m}$
2	Molarity (M)	$\frac{\text{Number ofmoles of solute}}{\text{Volume of solution (in L)}}$	5.845 g of sodium chloride is dissolved in water and the solution was made up to 500 mL using a standard flask. The strength of the solution in molarity is $\frac{\text{Number ofmoles of solute}}{\text{Volume of solution (in L)}} = \frac{\left(\frac{5.845}{58.45}\right)}{0.5}$ $\frac{0.1}{0.5} = 0.2\ \text{M}$
3	Normality (N)	$\frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in L)}}$	3.15 g of oxalic acid dihydrate, is dissolved in water and the solution was made up to 100 mL using a standard flask. The strength of the solution in normality is $= \frac{\text{Number of gram equivalents of solute}}{\text{Volume of solution (in L)}}$ $= \frac{\left(\frac{\text{mass of oxalic acid}}{\text{Equivalent mass of oxalic acid}}\right)}{\text{volume of solution (inL)}} = \frac{\left(\frac{3.15}{63}\right)}{0.1}$ $= \frac{0.05}{0.1} = 0.5\ \text{N}$

S. No.	Concentration term	Expression	Illustration
4	Formality (F)	$\frac{\text{Number of Formula mass of solute}}{\text{Volume of solution (in L)}}$	5.85g of sodium chloride is dissolved in water and the solution was made up to 500 mL using a standard flask. The strength of the solution in formality is $\text{formality} = \frac{\text{Number of Formula mass of solute}}{\text{Volume of solution (in L)}}$ $= \frac{5.85}{58.5 \times 0.5\text{L}}$ $= 0.2$ F
5	Mole fraction (of a component) (x)	$\frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components present in solution}}$ Consider a solution containing two components A and B whose mole fractions are x_A and x_B, respectively. Let the number of moles of the two components A and B be n_A and n_B, respectively. $x_A = \frac{n_A}{n_A + n_B}$ and $x_B = \frac{n_B}{n_A + n_B}$ Now, $x_A + x_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1$	0.5 mole of ethanol is mixed with 1.5 moles of water. The mole fraction of ethanol in the above solution is $= \frac{\text{Number of moles of the ethanol}}{\text{Total number of moles of ethanol and water}}$ $= \frac{0.5}{1.5+0.5} = \frac{0.5}{2.0} = 0.25$ The mole fraction of water in the above solution is $= \frac{\text{Number of moles of water}}{\text{Total number of moles of ethanol and water}}$ $= \frac{1.5}{2.0} = 0.75$ The mole fraction of water can also be calculated as follows mole fraction of water + mole fraction of ethanol = 1; mole fraction of water = 1 – mole fraction of ethanol = 1-0.25 = 0.75
6	Mass percentage (% w/w)	$\frac{\text{Mass of the solute (in g)}}{\text{Mass of solution (in g)}} \times 100$	Neomycin, aminoglycoside antibiotic cream contains 300 mg of neomycin sulphate the active ingredient, in 30g of ointment base. The mass percentage of neomycin is $\frac{\text{Mass of the neomycin sulphate (in g)}}{\text{Mass of solution (in g)}} \times 100$ $= \frac{0.3\text{ g}}{30\text{ g}} \times 100 = 1\%\ \text{w/w}$

S. No.	Concentration term	Expression	Illustration
7	Volume percentage (% v/v)	$\frac{\text{Volume of the solute (in mL)}}{\text{Volume of solution (in mL)}} \times 100$	50 mL of tincture of benzoin, an antiseptic solution contains 10 mL of benzoin. The volume percentage of benzoin $= \frac{\text{Volume of the benzoin (in mL)}}{\text{Volume of solution (in mL)}} \times 100$ $= \frac{10}{50} \times 100 = 20\% \text{ v / v}$
8	Mass by volume percentage (% w/v)	$\frac{\text{Mass of the solute (in g)}}{\text{Volume of solution (in mL)}} \times 100$	A 60 mL of paracetamol paediatric oral suspension contains 3g of paracetamol. The mass percentage of paracetamol is $\frac{\text{Mass of the paracetamol (in g)}}{\text{Volume of solution (in mL)}} \times 100 =$ $= \frac{3}{60} \times 100 = 5\% \text{ w / v}$
9	Parts per million (ppm)	$\frac{\text{Number of parts of the component}}{\text{Total number of parts of all components}} \times 10^6$ $= \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 10^6$	50 g of tap water contains 20 mg of dissolved solids. The TDS value in ppm is $\frac{\text{Mass of the dissolved solids}}{\text{Mass of the water}} \times 10^6$ $\frac{20 \times 10^{-3} \text{ g}}{50 \text{ g}} \times 10^6 = 400 \text{ ppm}$

Evaluate Yourself

1) If 5.6 g of KOH is present in (a) 500 mL and (b) 1 litre of solution, calculate the molarity of each of these solutions.

2) 2.82 g of glucose is dissolved in 30 g of water. Calculate the mole fraction of glucose and water.

3) The antiseptic solution of iodopovidone for the use of external application contains 10 % w/v of iodopovidone. Calculate the amount of iodopovidone present in a typical dose of 1.5 mL.

4) A litre of sea water weighing about 1.05 kg contains 5 mg of dissolved oxygen (O_2). Express the concentration of dissolved oxygen in ppm.

The concentration of a solution is expressed in different units. The choice of unit depends on the type of measurement applied. For example,in complexometric titrations involving

EDTA, the reaction between EDTA and the metal ions takes place in the 1:1 mole ratio and hence molar solutions are used in this titrations. In the redox and neutralisation titrations we use normal solutions. The mole fraction is used to calculate the partial pressure of gases and the vapour pressure of solutions. The percentage units are used to express the active ingredients present in therapeutics, and the ppm is used to express the quantity of solutes present in small amounts in solutions.

9.3.1 Standard solutions and working standards

A standard solution or a stock solution is a solution whose concentration is accurately known. A standard solution of required concentration can be prepared by dissolving a required amount of a solute, in a suitable amount of solvent. Its done by (i) transforming a known amount of a solute to a standard flask of definite volume. (ii) a small amount of water is added to the flask and shaken well to dissolve the solute. (iii) then water is added to the flask to bring the solution level to the mark indicated at the top end of the flask. (iv) the flask is stoppered and shaken well to make concentration uniform.

At the time of experiment, the solution with required concentration is prepared by diluting the stock solution. This diluted solution is usually called working standard. A known volume of stock solution is transferred to a new container and brought to the calculated volume. The necessary volumes of the stock solution and final volume can be calculated using the following expression.

$$C_s V_s = C_w V_w \text{ ----------(9.1)}$$

Where the C_s & V_s are concentration and volume of the stock solution and C_w & V_w are concentration and volume of the working standard, respectively.

9.3.2 Advantages of using standard solutions:

1. The error in weighing the solute can be minimised by using concentrated stock solution that requires large quantity of solute.

2. We can prepare working standards of different concentrations by diluting the stock solution, which is more efficient since consistency is maintained.

3. Some of the concentrated solutions are more stable and are less likely to support microbial growth than working standards used in the experiments.

Example Problem 1

1. What volume of 4M HCl and 2M HCl should be mixed to get 500 mL of 2.5 M HCl?

Let the volume of 4M HCl required to prepare 500 mL of 2.5 MHCl = x mL

Therefore, the required volume of 2M HCl = (500 - x) mL

We know from the equation (9.1)

$$\begin{aligned} C_1V_1 + C_2V_2 &= C_3V_3 \\ (4x)+2(500-x) &= 2.5 \times 500 \\ 4x+1000-2x &= 1250 \\ 2x &= 1250 - 1000 \\ x &= \frac{250}{2} \\ &= 125 \text{ mL} \end{aligned}$$

Hence, volume of 4M HCl required = 125 mL

Volume of 2M HCl required = (500 - 125) mL= 375 mL

Evaluate Yourself

5) Describe how would you prepare the following solution from pure solute and solvent

   (a) 1 L of aqueous solution of 1.5 M $CoCl_2$.

   (b) 500 mL of 6.0 % (V/V) aqueous methanol solution.

6) How much volume of 6 M solution of NaOH is required to prepare 500 mL of 0.250 M NaOH solution.

9.4 Solubility of the solutes

Solubility of a solute is the maximum amount of solute that can be dissolved in a specific amount of solvent at a specified temperature. When maximum amount of solute is dissolved in a solvent, any more addition of solute will result in precipitation at a given temperature and pressure. Such a solution is called as a saturated solution. The solubility of a substance at a given temperature is defined as the amount of the solute that can be dissolved in 100 g of the solvent at a given temperature to form a saturated solution.

9.4.1 Factors influencing the solubility

The solubility of a solute generally depends on the nature of the solute and the solvent in which it is dissolved. It also depends on the temperature and pressure of the solution.

Nature of solute and solvent:

Sodium chloride, an ionic compound, dissolves readily in a polar solvent such as water, but it does not dissolve in non-polar organic solvents such as benzene or toluene. Many organic compounds dissolve readily in organic solvents and do not dissolve in water. Different gases dissolve in water to different extents: for example, ammonia is more soluble than oxygen in water.

Effect of temperature:

Solid solute in liquid solvent:

Generally, the solubility of a solid solute in a liquid solvent increases with increase in temperature. When the temperature is increased, the average kinetic energy of the molecules of the solute and the solvent increases. The increase in kinetic energy facilitates the solvent molecules to break the intermolecular attractive forces that keep the solute molecules together and hence the solubility increases.

When a solid is added to a solvent, it begins to dissolve. i.e. the solute leaves from the solid state (dissolution). After some time, some of the dissolved solute returns back to the solid state (recrystallisation). If there is excess of solid present, the rate of both these processes becomes equal at a particular stage. At this stage an equilibrium is established between the solid solute molecules and dissolved solute molecules.

$$\boxed{\text{Solute (solid)} \leftrightarrows \text{Solute (dissolved)}}$$

According to Le-Chatelier principle, if the dissolution process is endothermic, the increase in temperature will shift the equilibrium towards right i.e solubility increases. for an exothermic reaction, the increase in temperature decreases the solubility. The solubilities of ammonium nitrate, calcium chloride, ceric sulphate nano-hydrate and sodium chloride in water at different temperatures are given in the following graph.

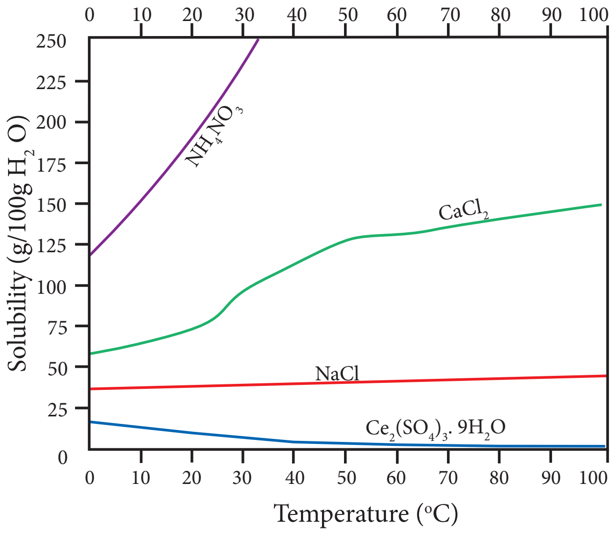


Figure 9. 1 Plot of solubility versus temperature for selective compounds

The following conclusions are drawn from the above graph.

- The solubility of sodium chloride does not vary appreciable as the maximum solubility is achieved at normal temperature. In fact, there is only 10 % increase in solubility between 0 ˚ to 100 ˚C.
- The dissolution process of ammonium nitrate is endothermic, the solubility increases steeply with increase in temperature.
- In the case of ceric sulphate, the dissolution is exothermic and the solubility decreases with increase in temperature.
- Even though the dissolution of calcium chloride is exothermic, the solubility increases moderately with increase in temperature. Here, the entropy factor also plays a significant role in deciding the position of the equilibrium.

Gaseous solute in liquid solvent:

In the case of gaseous solute in liquid solvent, the solubility decreases with increase in temperature. When a gaseous solute dissolves in a liquid solvent, its molecules interact with solvent molecules with weak intermolecular forces. When the temperature increases, the average kinetic energy of the molecules present in the solution also increases. The increase in kinetic energy breaks the weak intermolecular forces between the gaseous solute and liquid solvent which results in the release of the dissolved gas molecules to the gaseous state. Moreover, the dissolution of most of the gases in liquid solvents is an exothermic process, and in such processes, the increase in temperature decreases the dissolution of gaseous molecules.

Activity:

Open the soda bottle and put a balloon over it. The balloon will inflate with the released carbon dioxide from the soda. Carry out the same experiment by placing the soda bottle in a container of hot water. You will observe the balloon is inflated much faster now. This shows the decrease in solubility of gases in solution with increase in temperature. In the rivers where hot water is discharged from industrial plants, the aquatic lives are less sustained due to the decreased availability of dissolved oxygen.

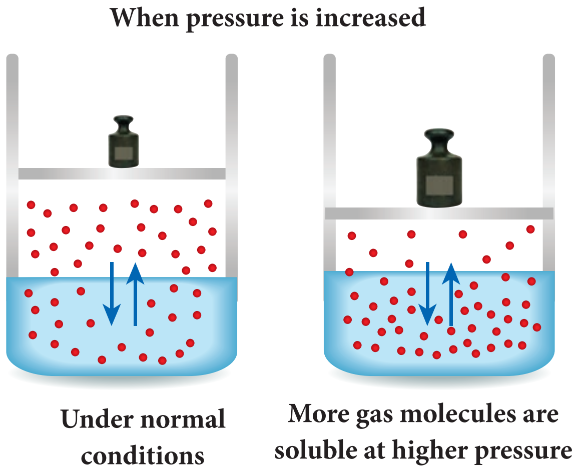


Figure 9.2 Effect of pressure on solubility

Effect of pressure:

Generally the change in pressure does not have any significant effect in the solubility of solids and liquids as they are not compressible. However, the solubility of gases generally increases with increase of pressure.

Consider a saturated solution of a gaseous solute dissolved in a liquid solvent in a closed container. In such a system, the following equilibrium exists.

$$\boxed{\text{Gas (in gaseous state)} \leftrightarrows \text{Gas (in solution)}}$$

According to Le-Chatelier principle, the increase in pressure will shift the equilibrium in the direction which will reduce the pressure. Therefore, more number of gaseous molecules dissolves in the solvent and the solubility increases.

9.5 Henry's law

William Henry investigated the relationship between pressure and solubility of a gaseous solute in a particular solvent. According to him, "the partial pressure of the gas in vapour phase (vapour pressure of the solute) is directly proportional to the mole fraction(x) of the gaseous solute in the solution at low concentrations". This statement is known as Henry's law.

Henry's law can be expressed as,

$p_{solute} \propto x_{solute\ in\ solution}$

$p_{solute} = K_H x_{solute\ in\ solution}$

Here, p_{solute} represents the partial pressure of the gas in vapour state which is commonly called as vapour pressure. x_{solute} in solution represents the mole fraction of solute in the solution. K_H is a empirical constant with the dimensions of pressure. The value of 'K_H' depends on the nature of the gaseous solute and solvent. The above equation is a straight-line in the form of y=mx. The plot partial pressure of the gas against its mole fraction in a solution will give a straight line as shown in fig 9.3. The slope of the straight line gives the value of K_H.

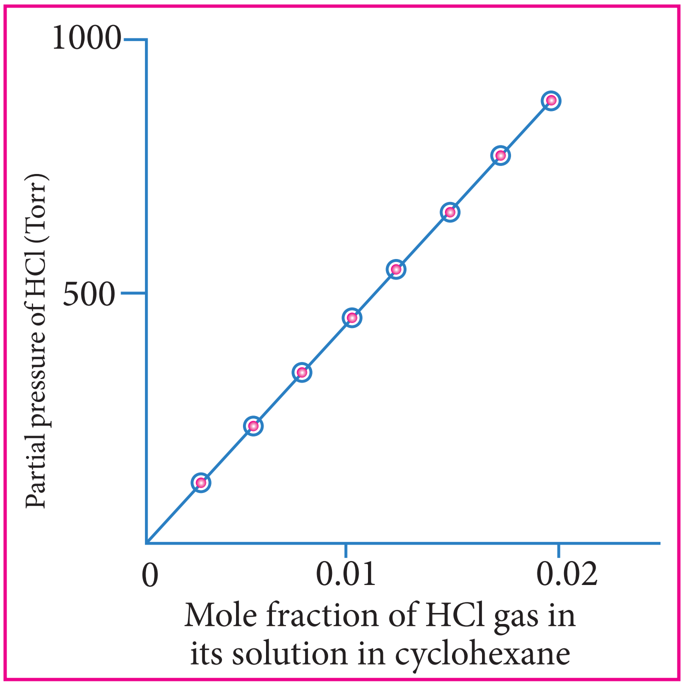


Figure 9.3 Solubility of HCl gas in cyclohexane at 293 K.

Why the carbonated drinks are stored in a pressurized container?

We all know that the carbonated beverages contain carbon dioxide dissolved in them. To dissolve the carbon dioxide in these drinks, the CO_2 gas is bubbled through them under high pressure. These containers are sealed to maintain the pressure. When we open these containers at atmospheric pressure, the pressure of the CO_2 drops to the atmospheric level and hence bubbles of CO_2 rapidly escape from the solution and show effervescence. The burst of bubbles is even more noticeable, if the soda bottle is in warm condition.

DO YOU KNOW?

Why deep-sea divers use air diluted with helium gas in their air tanks?

The professional deep-sea divers carry a compressed air tank for breathing at high pressure under water. The normal compressed air contains nitrogen and oxygen and these gases are not very soluble in blood and other body fluids at normal pressure. As the pressure at that depth is far greater than the surface atmospheric pressure, more nitrogen dissolves in the blood and other body fluids when the diver breathes from tank. When the diver ascends to the surface, the pressure decreases, the dissolved nitrogen comes out of the blood and other body fluids quickly forming bubbles in the blood stream. These bubbles restrict blood flow, affect the transmission of nerve impulses and can even burst the capillaries or block them. This condition is called “the bends”, which are painful and dangerous to life. Now a days, to avoid such dangerous condition, the professional divers, use air diluted with helium gas (about 11.7% Helium, 56.2% Nitrogen and 32.1% Oxygen), because of lower solubility of helium in the blood than nitrogen. Moreover, because of small size of helium atoms they can pass through cell walls without damaging them. The excess oxygen dissolved in the blood is used in metabolism and does not cause the condition of bends

9.5.1 Limitations of Henry’s law

- Henry’s law is applicable at moderate temperature and pressure only.
- Only the less soluble gases obeys Henry’s law
- The gases reacting with the solvent do not obey Henry’s law. For example, ammonia or HCl reacts with water and hence does not obey this law.

$$\boxed{NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-}$$

- The gases obeying Henry’s law should not associate or dissociate while dissolving in the solvent.

Example Problem 2:

0.24 g of a gas dissolves in 1 L of water at 1.5 atm pressure. Calculate the amount of dissolved gas when the pressure is raised to 6.0 atm at constant temperature.

$p_{solute} = K_H x_{solute\ in\ solution}$

At pressure 1.5 atm,

$p_1 = K_H\ x_1$------------(1)

At pressure 6.0 atm,

$p_2 = K_H\ x_2$------------(2)

Dividing equation (1) by (2)

From equation $p_1/p_2 = x_1/x_2$

$1.5/6.0 = 0.24/x_2$

Therefore $x_2 = 0.24 \times 6.0/1.5 = 0.96$ g/L

Evaluate Yourself

7) Calculate the proportion of O_2 and N_2 dissolved in water at 298 K. When air containing 20% O_2 and 80% N_2 by volume is in equilibrium with water at 1 atm pressure. Henry's law constants for two gases are $K_H(O_2) = 4.6 \times 10^4$ atm and $K_H\ (N_2) = 8.5 \times 10^4$ atm.

8) Explain why the aquatic species are more comfortable in cold water during winter season rather than warm water during the summer.

9.6 Vapour pressure of liquid

Generally, liquids have a tendency to evaporate. If the kinetic energy of molecules in the liquid state overcomes the intermolecular force of attraction between them, then the molecules will escape from the liquid state. This process is called 'evaporation' and it happens on the surface of the liquid.

If evaporation is carried out in a closed container then the vapour remains in contact with the surface of the liquid. These vapour molecules are in continuous random motion during which they collide with each other and also with the walls of the container. As the collision is inelastic, they lose their energy and as result the vapour returns back to liquid state. This process is called as 'condensation'.

Evaporation and condensation are continuous processes. If the process is carried out in a closed system, a stage is reached when the rate of evaporation becomes equal to the rate of condensation. Thus, an equilibrium is established between liquid and its vapour. The pressure of the vapour in equilibrium with its liquid is called vapour pressure of the liquid at the given temperature. The vapour pressure of a liquid depends on its nature, temperature and the surface area. The following simple apparatus demonstrates the measurement of vapour pressure of a liquid.

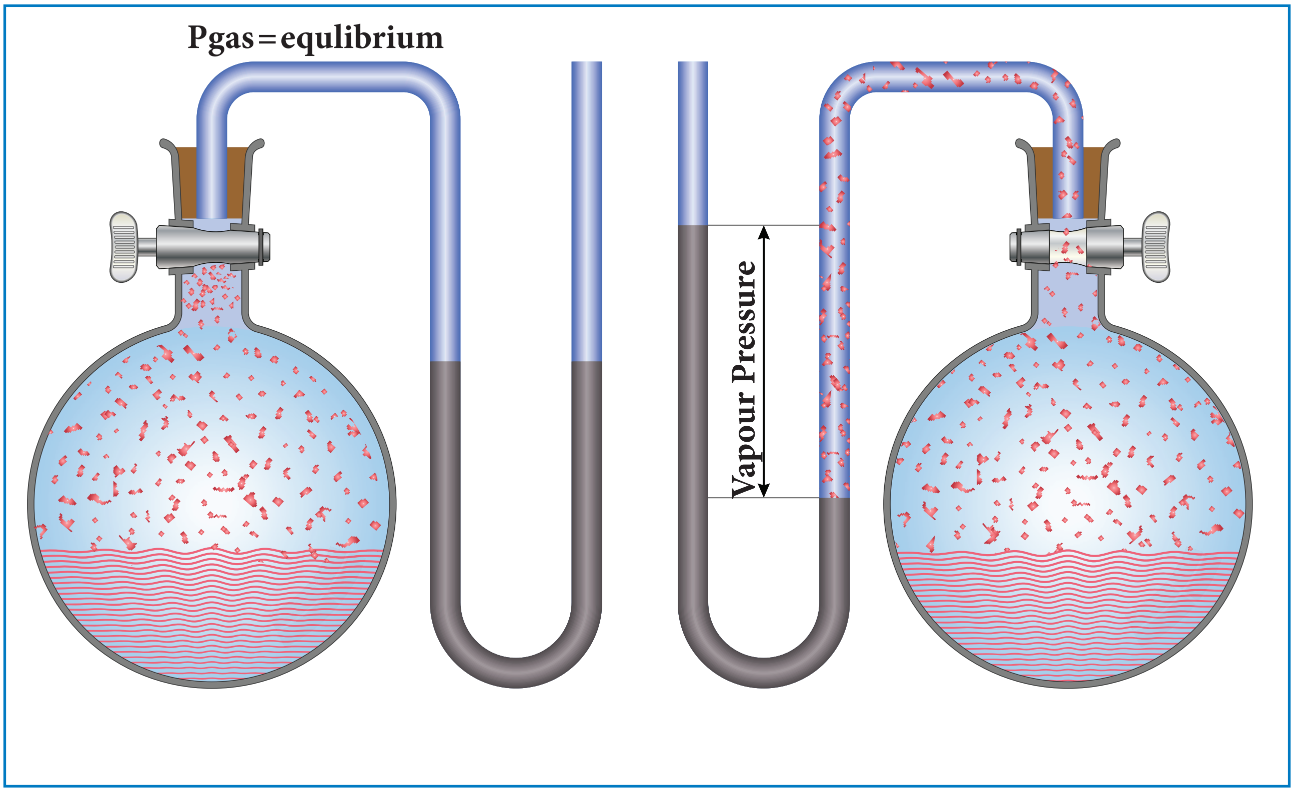


Figure 9.4 : a) A closed round bottomed flask in which ethanol is in equilibrium with its vapour. b) In the same setup the vapour is allowed to escape through a U tube filled with mercury. The escaped vapour pushes the mercury in the U tube and the difference in mercury level gives the vapour pressure of ethanol present in the RB flask.

9.7 Vapour pressure of liquid solutions

When a solute (of any physical state - solid, liquid or gas) is dissolved in a liquid solvent the resultant solution is called a liquid solution. The solution which contains only two components (one solvent and one solute) is called a binary solution. We have already discussed the solution of a gaseous solute in liquid solvent under Henry's law.

9.7.1 Vapour pressure of binary solution of liquid in liquids

Now, let us consider a binary liquid solution formed by dissolving a liquid solute 'A' in a pure solvent 'B' in a closed vessel. Both the components A and B present in the solution would evaporate and an equilibrium will be established between the liquid and vapour phases of the components A and B.

The French chemist Raoult, proposed a quantitative relationship between the partial pressures and the mole fractions of two components A & B, which is known as Raoult's Law. This law states that "in the case of a solution of volatile liquids, the partial vapour pressure of each component (A & B) of the solution is directly proportional to its mole fraction".

According to Raoult's law,

$$p_A \alpha\ x_A \text{----------}(9.3)$$

$$p_A = k\, x_A$$

when $x_A = 1,\ k = p^{\circ}_A$

where p°_A is the vapour pressure of pure component 'A' at the same temperature.

Therefore,

$$p_A = p^{\circ}_A x_A \text{----------} (9.4)$$

Similarly, for component 'B'

$$p_B = p^{\circ}{}_B\, x_B \text{----------}(9.5)$$

x_A and x_B are the mole fraction of the components A and B respectively.

According to Dalton's law of partial pressure the total pressure in a closed vessel will be equal to the sum of the partial pressures of the individual components.

Hence,

$$P_{total} = p_A + p_B \text{----------}(9.6)$$

Substituting the values of p_A and p_B from equations (9.4) and (9.5) in the above equation,

$$P_{total} = x_A p^{\circ}_A + x_B p^{\circ}_B \quad (9.7)$$

We know that $x_A + x_B = 1$ or $x_A = 1 - x_B$

Therefore,

$$P_{total} = (1 - x_B)\, p^{\circ}_A + x_B\, p^{\circ}_B \text{----------}(9.8)$$

$$P_{total} = p^{\circ}_A + x_B(p^{\circ}_B - p^{\circ}_A) \text{----------}(9.9)$$

The above equation is of the straight-line equation form y = mx+c. The plot of P_{total} versus x_B will give a straight line with $(p^{\circ}_B - p^{\circ}_A)$ as slope and p°_A as the y intercept.

Let us consider the liquid solution containing toluene (solute) in benzene (solvent).

The variation of vapour pressure of pure benzene and toluene with its mole fraction is given in the graph.

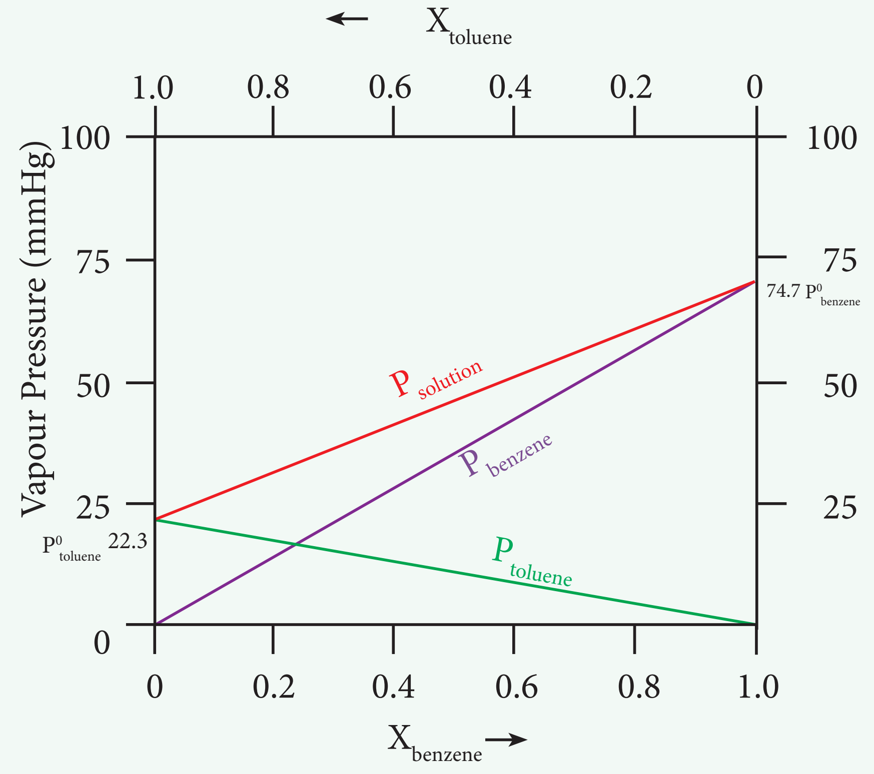


Figure 9.5 Solution of benzene in toluene obeying Raoult's law.

The vapour pressures of pure toluene and pure benzene are 22.3 and 74.7 mmHg, respectively. The above graph shows, the partial vapour pressure of the pure components increases linearly with the increase in the mole fraction of the respective components. The total pressure at any composition of the solute and solvent is given by the following straight line (represented as red line) equation.

$$P_{solution} = p^{\circ}_{toluene} + x_{benzene}(\, p^{\circ}_{benzene} - p^{\circ}_{toluene}) \text{ ---------- } (9.10)$$

9.7.2 Vapour pressure of binary solution of solids in liquids

When a nonvolatile solute is dissolved in a pure solvent, the vapour pressure of the pure solvent will decrease. In such solutions, the vapour pressure of the solution will depend only on the solvent molecules as the solute is nonvolatile.

For example, when sodium chloride is added to the water, the vapour pressure of the salt solution is lowered. The vapour pressure of the solution is determined by the number of molecules of the solvent present in the surface at any time and is proportional to the mole fraction of the solvent.

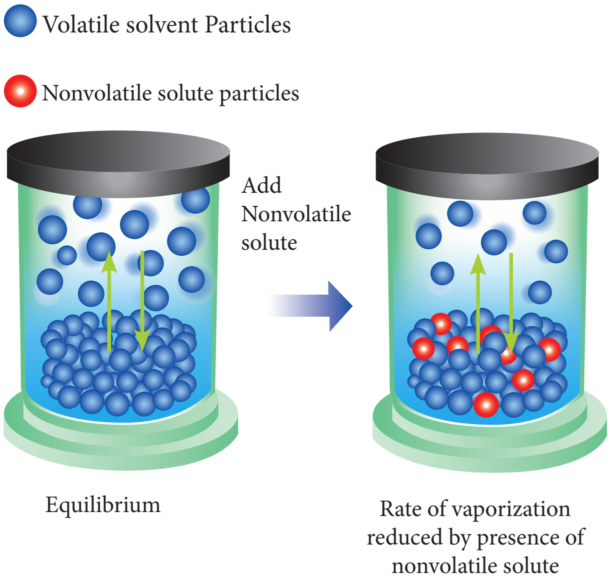


Fig 9.6 Rate of vapourization reduced by presence of nonvolatile solute.

$$P_{solution}\ \alpha\ x_A \quad \text{----------} \ (9.11)$$

Where x_A is the mole fraction of the solvent

$$P_{solution} = k\, x_A \quad \text{----------} \ (9.12)$$

When $x_A = 1, \quad K = P^{o}_{solvent}$

($P^{o}_{solvent}$ is the partial pressure of pure solvent)

$$P_{solution} = P^{o}_{solvent}\, x_A \quad \text{----------}(9.13)$$

$$\frac{P_{solution}}{P^{o}_{solvent}} = x_A \quad \text{----------}(9.14)$$

$$1 - \frac{P_{solution}}{P^{o}_{solvent}} = 1 - x_A \quad \text{----------}(9.15)$$

$$\frac{P^{o}_{solvent} - P_{solution}}{P^{o}_{solvent}} = x_B \quad \text{----------} \quad (9.16)$$

Where x_B is the mole fraction of the solute

$(\because x_{A} + x_B = 1, x_B = 1 - x_A)$

The above expression gives the relative lowering of vapour pressure. Based on this expression, Raoult's Law can also be stated as "the relative lowering of vapour pressure of an ideal solution containing the nonvolatile solute is equal to the mole fraction of the solute at a given temperature".

Comparison of Raoult's law and Henry's law

According to Raoult's law, for a solution containing a nonvolatile solute

$$p_{solute} = p^{o}_{solute}\, x_{solute} \quad \text{----------} \ (9.17)$$

According to Henry's law:

$$p_{solute} = K_H\, x_{solute\ in\ solution} \quad \text{----------} \ (9.18)$$

The difference between the above two expressions is the proportionality constant p°_{A} (Raoults Law) and K_H.(Henry's Law). Henry's law is applicable to solution containing gaseous solute in liquid solvent, while the Raoult's Law is applicable to nonvolatile solid solute in a liquid solvent. If the solute is non volatile then the Henry's law constant will become equal to the vapour pressure of the pure solvent (p°_{A}) and thus, Raoult's law becomes a special case of Henry's law. For very dilute solutions the solvent obeys Raoult's law and the solute obeys Henry's law.

9.8 Ideal and non-ideal solutions

9.8.1 Ideal Solutions:

An ideal solution is a solution in which each component i.e. the solute as well as the solvent obeys the Raoult's law over the entire range of concentration. Practically no solution is ideal over the entire range of concentration. However, when the concentration of solute is very low, the dilute solution behaves ideally. If the two components present in the solution (A and B) are identical in size, structure, and having almost similar intermolecular attractive forces between them (i.e. between A-A, B-B and B-A) and then the solution tends to behave like an ideal solution.

For an ideal solution

1. There is no change in the volume on mixing the two components (solute & solvents). ($\Delta V_{mixing} = 0$)
2. There is no exchange of heat when the solute is dissolved in solvent ($\Delta H_{mixing} = 0$).
3. Escaping tendency of the solute and the solvent present in it should be same as in pure liquids.

Examples for ideal solutions: (Benzene & Toluene) ; (n-hexane & n-heptane) ; (Ethyl bromide & Ethyl iodide) ; (Chlorobenzene & Bromobenzene).

9.8.2 Non-ideal solutions

The solutions which do not obey Raoult's law over the entire range of concentration, are called non-ideal solutions. For a non-ideal solution, there is a change in the volume and enthalpy upon mixing. i.e. $\Delta H_{mixing} \neq 0$ & $\Delta V_{mixing} \neq 0$. The deviation of the non-ideal solutions from the Raoult's law can either be positive or negative.

Non-ideal solutions - positive deviation from Rauolt's Law:

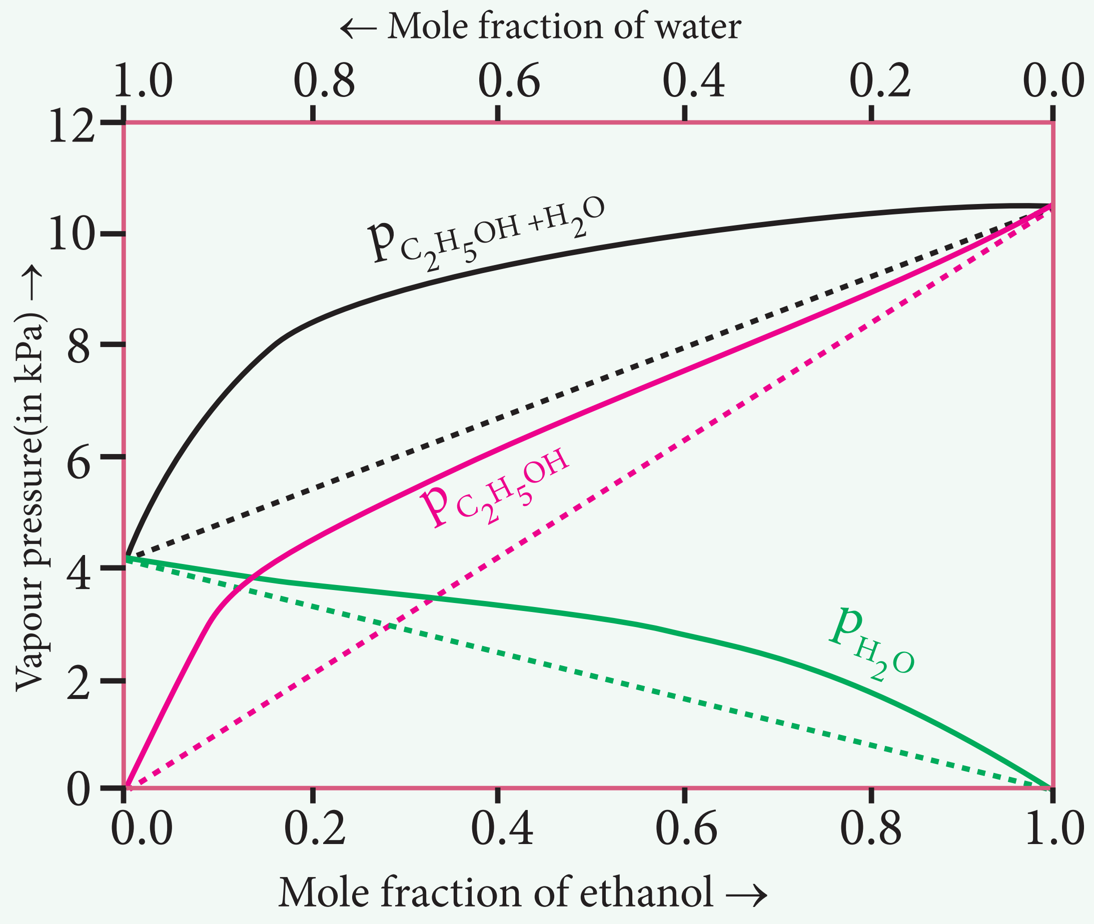
The nature of the deviation from the Rauolt's law can be explained in terms of the intermolecular interactions between solute (B) and solvent (A). Consider a case in which the intermolecular attractive forces between A and B are weaker than those between the molecules of A (A-A) and molecules of B (B-B). The molecules present in such a solution have a greater tendency to escape from the solution when compared to the ideal solution formed by A and B, in which the intermolecular attractive forces (A-A, B-B, A-B) are almost similar. Consequently, the vapour pressure of such non-ideal solution increases and it is greater than the sum of the vapour pressure of A and B as predicted by the Raoult's law. This type of deviation is called positive deviation.

Here, $p_A > p^\circ_A x_A$ and $p_B > p^\circ_B x_B$.

Hence $p_{total} > p^\circ_A x_A + p^\circ_B x_B$ ----------(9.19)

Let us understand the positive deviation by considering a solution of ethyl alcohol and water. In this solution the hydrogen bonding interaction between ethanol and water is weaker than those hydrogen bonding interactions amongst themselves (ethyl alcohol-ethyl alcohol and water-water interactions). This results in the increased evaporation of both components (H_2O and C_2H_5OH) from the aqueous solution of ethanol. Consequently, the vapour pressure of the solution is greater than the vapour pressure predicted by Raoult's law. Here, the mixing process is endothermic i.e. $\Delta H_{mixing} > 0$ and there will be a slight increase in volume ($\Delta V_{mixing} > 0$).

Examples for non-ideal solutions showing positive deviations: Ethyl alcohol & cyclohexane, Benzene & acetone, Carbon tetrachloride & chloroform, Acetone & ethyl alcohol, Ethyl alcohol & water.



Vapour pressure diagram showing positive deviation

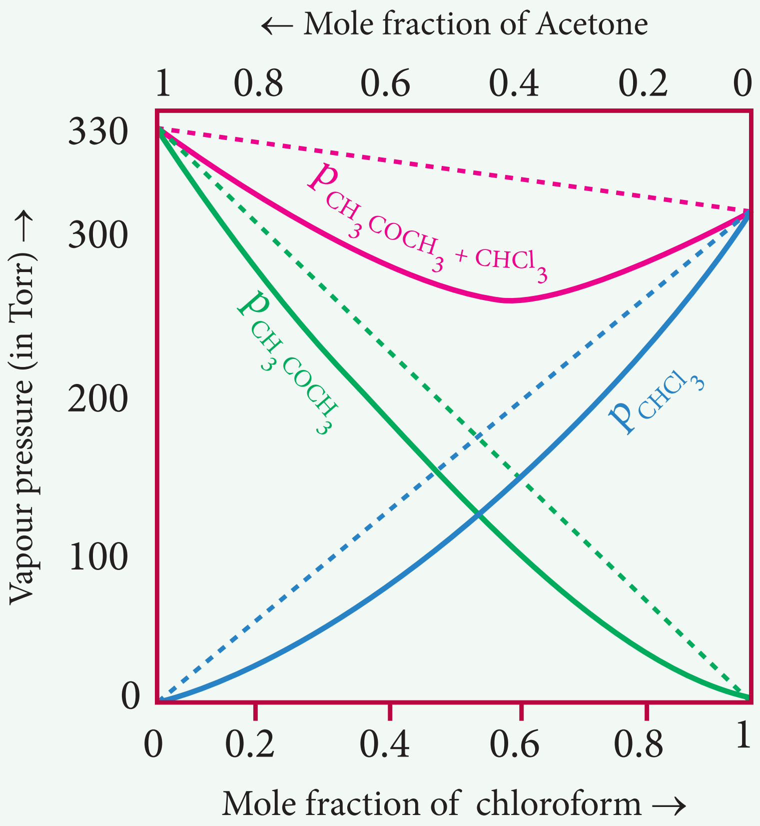
Figure 9.7 Positive deviations from Raoult's law. The dotted line (-----) is ideal behavior and the solid lines (_____) is actual behaviour

Non-ideal solutions - negative deviation from Rauolt's Law:

Let us consider a case where the attractive forces between solute (A) and solvent (B) are stronger than the intermolecular attractive forces between the individual components (A-A & B-B). Here, the escaping tendency of A and B will be lower when compared with an ideal solution formed by A and B. Hence, the vapour pressure of such solutions will be lower than the sum of the vapour pressure of A and B. This type of deviation is called negative deviation. For the negative deviation $p_A < p^\circ_A x_A$ and $p_B < p^\circ_B x_B$.

Let us consider a solution of phenol and aniline. Both phenol and aniline form hydrogen bonding interactions amongst themselves. However, when mixed with aniline, the phenol molecule forms hydrogen bonding interactions with aniline, which are stronger than the hydrogen bonds formed amongst themselves. Formation of new hydrogen bonds considerably reduce the escaping tendency of phenol and aniline from the solution. As a result, the vapour pressure of the solution is less and there is a slight decrease in volume ($\Delta V_{mixing} < 0$) on mixing. During this process evolution of heat takes place i.e. $\Delta H_{mixing} < 0$ (exothermic)

Examples for non-ideal solutions showing negative deviation: Acetone + chloroform, Chloroform + diethyl ether, Acetone + aniline,Chloroform + Benzene.



Vapour pressure diagram showing negative deviation

Figure 9.8 Negative deviation from Raoult's law. The dotted line (-----) is ideal behavior and the solid lines (____) is actual behaviour

9.8.3 Factors responsible for deviation from Raoult's law

The deviation of solution from ideal behavior is attributed to the following factors.

i) Solute-solvent interactions

For an ideal solution, the interaction between the solvent molecules (A-A),the solute molecules (B-B) and between the solvent & solute molecules (A-B) are expected to be similar. If these interactions are dissimilar, then there will be a deviation from ideal behavior.

ii) Dissociation of solute

When a solute present in a solution dissociates to give its constituent ions, the resultant ions interact strongly with the solvent and cause deviation from Raoult's law.

For example, a solution of potassium chloride in water deviates from ideal behavior because the solute dissociates to give K^+ and Cl^- ion which form strong ion-dipole interaction with water molecules.

$KCl\ (s) + H_2O\ (l) \rightarrow K^+(aq) + Cl^-(aq)$

iii) Association of solute

Association of solute molecules can also cause deviation from ideal behaviour. For example, in solution, acetic acid exists as a dimer by forming intermolecular hydrogen bonds, and hence deviates from Raoult's law.

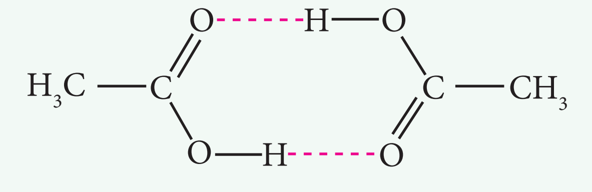


Fig 9.9 Acetic acid (dimer)

iv) Temperature

An increase in temperature of the solution increases the average kinetic energy of the molecules present in the solution which causes decrease in the attractive force between them. As a result, the solution deviates from ideal behaviour.

v) Pressure

At high pressure the molecules tend to stay close to each other and therefore there will be an increase in their intermolecular attraction. Thus, a solution deviates from Raoult's law at high pressure.

vi) Concentration

If a solution is sufficiently dilute there is no pronounced solvent-solute interaction because the number of solute molecules are very low compared to the solvent. When the concentration is increased by adding solute, the solvent-solute interaction becomes significant. This causes deviation from the Raoult's law.

Evaluate Yourself

9) Calculate the mole fractions of benzene and naphthalene in the vapour phase when an ideal liquid solution is formed by mixing 128 g of naphthalene with 39 g of benzene. It is given that the vapour pressure of pure benzene is 50.71 mmHg and the vapour pressure of pure naphthalene is 32.06 mmHg at 300 K.

9.9 Colligative properties

Pure water is tasteless. When you add sugar it becomes sweet, while addition of salt makes it salty. It implies that the properties of a solution depend on the nature of solute particles present in the solution. However, for an ideal dilute solution, the properties, namely, relative lowering of vapour pressure, elevation of boiling point, depression in freezing point and osmotic pressure do not depend on the chemical nature of the solute but depends only on the number of solute particles (ions/molecules) present in the solution. These four properties are known as colligative properties. Though the magnitude of these properties are small, they have plenty of practical applications. For example the osmotic pressure is important for some vital biological systems.

Relative lowering of vapour pressure

The vapour pressure of a solution containing a nonvolatile, non-electrolyte solute is always lower than the vapour pressure of the pure solvent. Consider a closed system in which a pure solvent is in equilibrium with its vapour. At equilibrium the molar Gibbs free energies of solvent in the liquid and gaseous phase are equal ($\Delta G = 0$). When a solute is added to this solvent, the dissolution takes place and its free energy (G) decreases due to increase in entropy. In order to maintain the equilibrium, the free energy of the vapour phase must also decrease. At a given temperature, the only way to lower the free energy of the vapour is to reduce its pressure. Thus the vapour pressure of the solution must decrease to maintain the equilibrium.

We know that from the Raoult's law the relative lowering of the vapour pressure is equal to the mole fraction of the solute (equation 9.16)

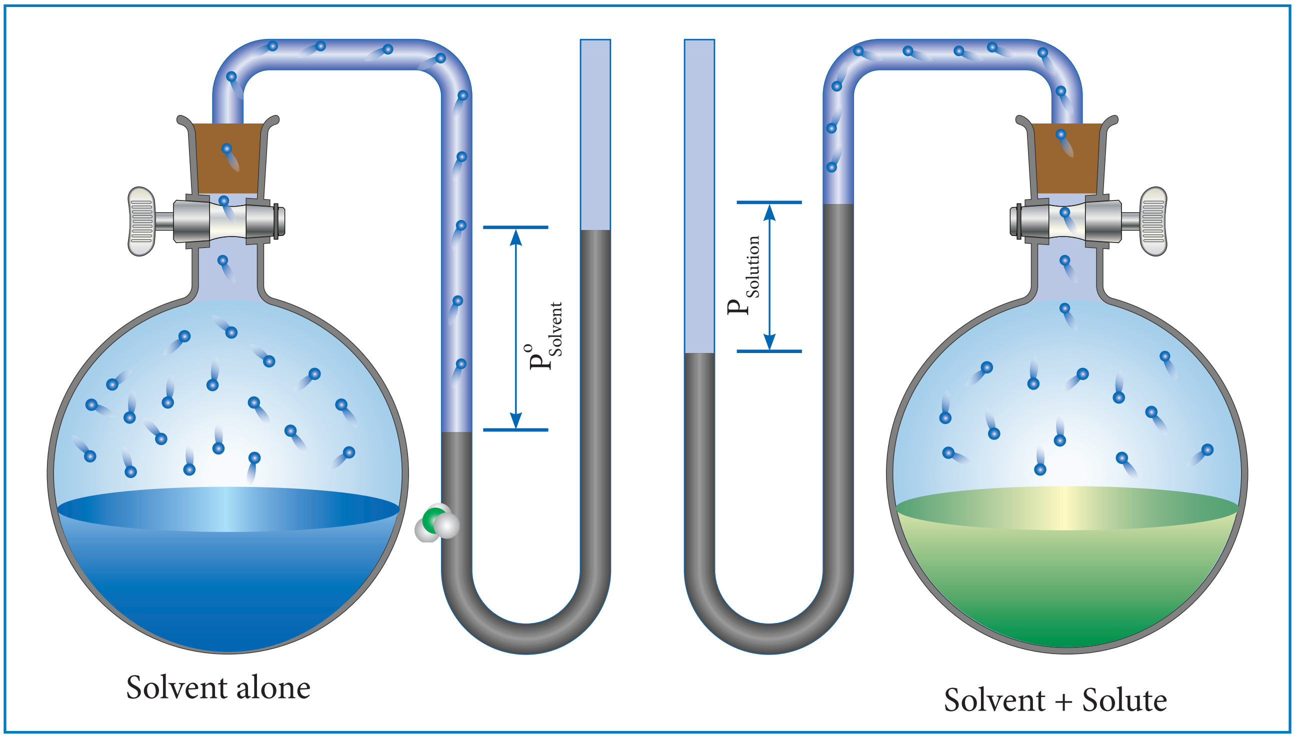


Figure 9.10 Measuring relative lowering of vapour pressure

From the above equation,it is clear that the relative lowering of vapour pressure depends only on the mole fraction of the solute (x_B) and is independent of its nature. Therefore, relative lowering of vapour pressure is a colligative property.

Determination of molar mass from relative lowering of vapour pressure

The measurement of relative lowering of vapour pressure can be used to determine the molar mass of a nonvolatile solute. In this method, a known mass of the solute is dissolved in a known quantity of solvent. The relative lowering of vapour pressure is measured experimentally.

According to Raoult’s law the relative lowering of vapor pressure is,

$$\frac{P^0_{solvent} - P_{solution}}{P^0_{solvent}} = x_B$$

Let w_A and w_B be the weights of the solvent and solute respectively and their corresponding molar masses are M_A and M_B, then the mole fraction of the solute x_B is

$$x_B = \frac{n_B}{n_A + n_B} \qquad (9.20)$$

Here, n_A & n_B are the moles of the solvent and the solute respectively. For dilute solutions $n_A >> n_B$. Hence $n_A + n_B \approx n_A$. Now

$$x_B = \frac{n_B}{n_A}$$

Number of moles of solvent and the solute are,

$$n_A = \frac{w_A}{M_A}, \; n_B = \frac{w_B}{M_B}$$

$$\text{Therefore, } x_B = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}} \qquad \text{------ (9.21)}$$

Thus,

$$\frac{P^\circ_{solvent} - P_{solution}}{P^\circ_{solvent}} = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}}$$

$$\frac{\Delta P}{P^\circ_A} = \frac{w_B \times M_A}{w_A \times M_B} \qquad \text{------ (9.22)}$$

From the equation (9.22) the molar mass of the solute (M_B) can be calculated using the known values of w_A, w_B, M_A and the measured relative lowering of vapour pressure.

Example Problem3:

An aqueous solution of 2 % nonvolatile solute exerts a pressure of 1.004 bar at the boiling point of the solvent. What is the molar mass of the solute when P°_A is 1.013 bar?

$$\frac{\Delta P}{P^\circ_A} = \frac{W_B \text{ x } M_A}{M_B \text{ x } W_A}$$

In a 2 % solution weight of the solute is 2 g and solvent is 98 g

$\Delta P = P^\circ_A - P_{solution} = 1.013 - 1.004 \text{ bar} = 0.009$ bar

$$M_B = \frac{P^\circ_A \text{ x } W_B \text{ x} M_A}{\Delta P \text{ x } W_A}$$

$M_B = 2 \text{ x } 18 \text{ x } 1.013/(98 \text{ x } 0.009)$

$= 41.3 \text{ g mol}^{-1}$

Evaluate Yourself

10) Vapour pressure of a pure liquid A is 10.0 torr at 27°C . The vapour pressure is lowered to 9.0 torr on dissolving one gram of B in 20 g of A. If the molar mass of A is 200 g mol^{-1} then calculate the molar mass of B.

Elevation of boiling point

Boiling point is an important physical property of a liquid. The boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure (1 atm). When a nonvolatile solute is added to a pure solvent at its boiling point, the vapour pressure of the solution is lowered below 1 atm. To bring the vapour pressure again to 1 atm, the temperature of the solution has to be increased. As a result,the solution boils at a higher temperature (T_b) than the boiling point of the pure solvent (T°_b). This increase in the boiling point is known as elevation of boiling point. A plot of vapour pressure versus temperature for water and an aqueous solution is given below

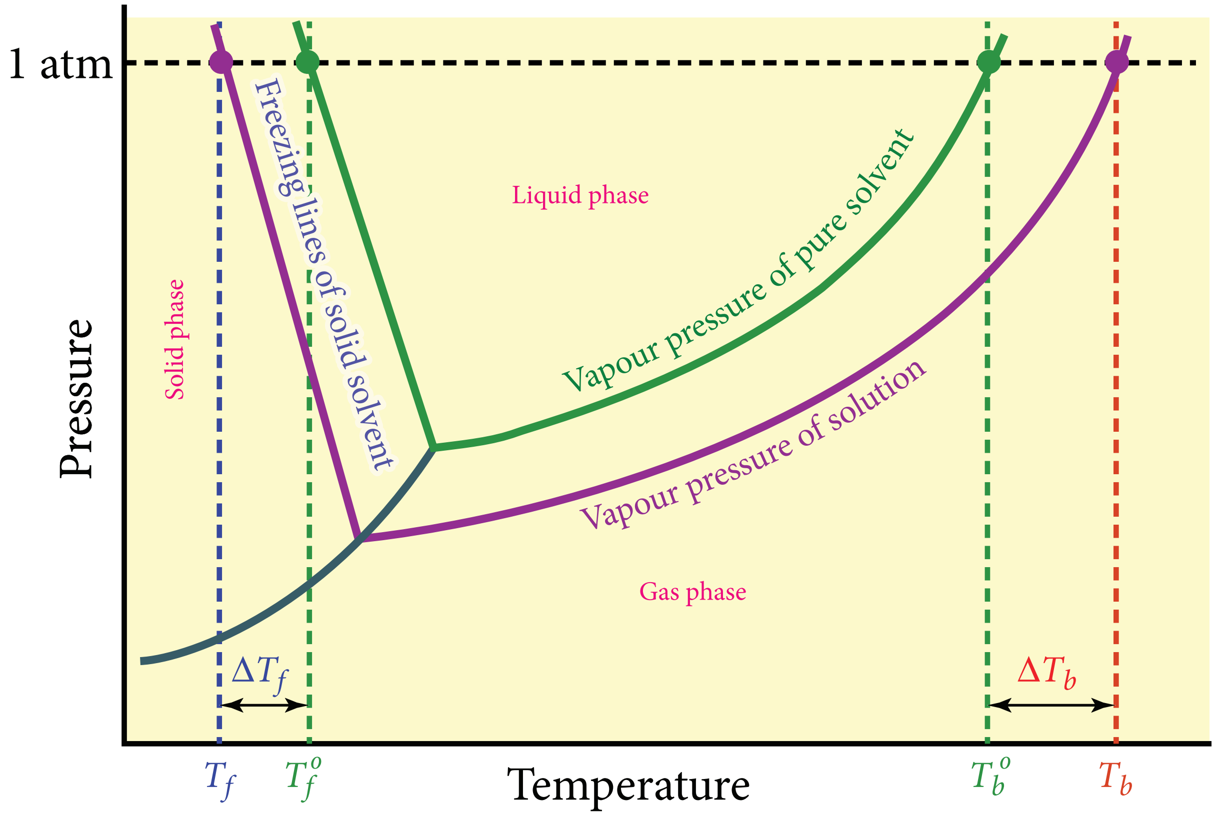


Figure 9.11 Elevation of boiling point and depression in freezing point

The vapour pressure of the solution increases with increase in temperature as shown in the above figure. The variation of vapour pressure with respect to temperature for pure water is given by the violet coloured curve. At 100 ^{0}C the vapour pressure of water is equal to 1 atm. Hence the boiling point of water is 100 ^{0}C (T_b^o). When a solute is added to water, the vapour pressure of the resultant solution is lowered. The variation of vapour pressure with respect to temperature for the solution is given by green curve. From the graph, it is evident the vapour pressure of the solution is equal to 1 atm pressure at the temperature T_b which is greater than T_b^o. The difference between these two temperatures (T_b-T_b^o) gives the elevation of boiling point.

The elevation of boiling point (ΔT_b)= T_b - T_b^o

The elevation of boiling point is directly proportional to the concentration of the solute particles.

$\Delta T_b \; \alpha \; m$ ------ (9.23)

m is the concentration of solution expressed in molality.

$\Delta T_b = K_b \, m$ ------ (9.24)

Where K_b = molal boiling point elevation constant or Ebullioscopic constant.

If m=1, then $\Delta T_b = K_b$;

Hence, K_b is equal to the elevation in boiling point for 1 molal solution. K_b is calculated by the following expression

$$K_b = \frac{RT^2 M_{solvent}}{\Delta H_{vapourisation}}$$

Determination of molar mass of solute from elevation of boiling point

If the solution is prepared by dissolving w_B g of solute in w_A g of solvent, then the molality is,

$$m = \frac{\text{Number of moles of solute} \times 1000}{\text{weight of solvent in grams}} \quad \text{............. (9.25)}$$

$$\text{Number of moles of solute} = \frac{w_B}{M_B} \quad \text{............. (9.26)}$$

Where, M_B=molar mass of the solute

Therefore,

$$m = \frac{w_B \times 1000}{M_B \times w_A} \quad \text{............... (9.27)}$$

and

$$\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A} \quad \text{...............(9.28)}$$

Molar mass can be calculated by using (9.28)

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A} \quad \text{...............(9.29)}$$

Table 9.3 Molal boiling point elevation constant 'K_b' for some solvents

S. No.	Solvent	T_b° (K)	K_b (K kg mol^{-1})
1.	Water	373.15	0.52
2.	Ethanol	351.5	1.20
3.	Benzene	353.3	2.53
4.	Chloroform	334.4	3.63
5.	Ether	307.8	2.02
6.	Carbon tetrachloride	350.0	5.03
7.	Carbon disulphide	319.4	2.42
8.	Acetic acid	391.1	2.93
9.	Cyclohexane	353.74	2.79

Example Problem 4

0.75 g of an unknown substance is dissolved in 200 g solvent. If the elevation of boiling point is 0.15 K and molal elevation constant is 7.5 K Kg mol^{-1} then, calculate the molar mass of unknown substance

$$\Delta T_b = K_b\, m$$

$$= K_b \text{ x } W_2 \text{ x } 1000 / M_2 \text{ x } W_1$$

$$M_2 = K_b \text{ x } W_2 \text{ x } 1000 / \Delta T_b \text{ x } W_1$$

$$= 7.5 \text{ x } 0.75 \text{ x } 1000 / 0.15 \text{ x } 200$$

$$= 187.5 \text{ g mol}^{-1}$$

Evaluate Yourself

11) 2.56 g of Sulphur is dissolved in 100g of carbon disulphide. The solution boils at 319. 692 K . What is the molar mass of Sulphur in solution The boiling point of CS_2 is 319. 450K. Given that K_b for CS_2 = 2.42 K Kg mol^{-1}

Depression in freezing point

Freezing point of a substance is another important physical property like boiling point. Freezing point is defined as "the temperature at which the solid and the liquid states of the substance have the same vapour pressure". At freezing point, the solid and liquid phases of the substance are in equilibrium. For example, the freezing point of water is 0 ˚C. At this temperature the ice and water are in equilibrium. When a nonvolatile solute is added to water at its freezing point, the freezing point of the solution is lowered from 0 ˚C. The lowering of the freezing point of the solvent when a solute is added is called depression in freezing point (ΔT_f).

From the above graph, we infer that the freezing point (T_f^o) is 0 ˚C as the vapour pressure at this temperature is 1 atm (atmospheric pressure). The vapour pressure versus temperature curve for the solution indicates that the freezing point (T_f) is lower than the 0 ˚C. The depression in freezing temperature (ΔT_f) can be expressed as,

$$\Delta T_f = T_f^o - T_f$$

The experimental results show that the depression in freezing point is directly proportional to the molal concentration of the solute particles.

Hence,

$$\Delta T_f \ \alpha \ m$$

$$\Delta T_f = K_f \ m \qquad \text{........(9.30)}$$

Here, 'm' = is the molality of the solution

K_f = molal freezing point depression constant or cryoscopic constant.

If m=1 then $\Delta T_f = K_f$

The K_f is equal to the depression in freezing point for 1 molal solution

Table 9.4 Molal freezing point depression constant for some solvents

S. No.	Solvent	Freezing point (K)	K_f (K.kg. mol^{-1})
1.	Water	273.0	1.86
2.	Ethanol	155.7	1.99
3.	Benzene	278.6	5.12
4.	Chloroform	209.6	4.79
5.	Carbon disulphide	164.2	3.83
6.	Ether	156.9	1.79
7.	Cyclohexane	279.5	20.0
8.	Acetic acid	290.0	3.90

Determination of molar mass of solute from depression in freezing point

If the solution is prepared by dissolving w_B g of solute in w_A g of solvent. then depression in freezing point is given by (9.31)

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A} \qquad \text{...............(9.31)}$$

molar mass of a solute can be calculated using (9.31)

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A} \qquad \text{...............(9.32)}$$

Example Problem - 5

Ethylene glycol ($C_2H_6O_2$) can be used as an antifreeze in the radiator of a car. Calculate the temperature when ice will begin to separate from a mixture with 20 mass percent of glycol in water used in the car radiator. K_f for water = 1.86 K Kg mol^{-1}

and molar mass of ethylene glycol is 62 g mol^{-1}.

Weight of solute (W_2) = 20 mass percent of solution means 20 g of ethylene glycol

Weight of solvent (water) W_1 = 100 -20 = 80 g

$$\Delta T_f = K_f m$$

$$= \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$= \frac{1.86 \times 20 \times 1000}{62 \times 80}$$

$$= 7.5\ K$$

The temperature at which ice will begin to separate is the freezing point of water after the addition of solute i.e 7.5 K lower than the normal freezing point of water (273-7.5K) = 265.5 K

Evaluate Yourself

12) 2g of a non electrolyte solute dissolved in 75 g of benzene lowered the freezing point of benzene by 0.20 K. The freezing point depression constant of benzene is 5.12 K Kg mol^{-1}. Find the molar mass of the solute.

Osmosis and osmotic pressure

Many biological processes depend on osmosis, which is a spontaneous process by which the solvent molecules pass through a semi permeable membrane from a solution of lower concentration to a solution of higher concentration. The name osmosis is derived from the Greek word '*osmos*' which means 'to push'. It is also important to know that the semipermeable membrane selectively allows certain molecules in the solution to pass through it but not others.

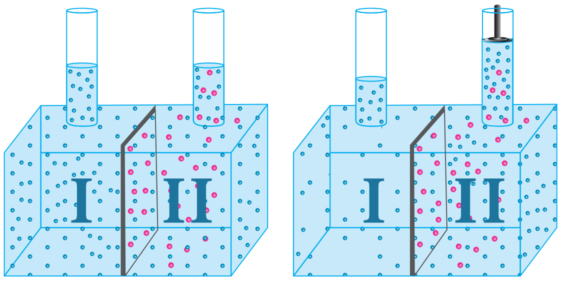


Figure 9.12 Osmosis and osmotic pressure

Let us consider a simple apparatus as shown in the above figure. A semipermeable membrane separates a chamber into two compartments. Water (pure solvent) is added to the first compartment and the aqueous NaCl (solution) is added to the second compartment such that the liquid levels on the both sides are equal. Since there is a difference in concentration between the liquids present in the two compartments, the water molecules move from first compartment to second compartment through the semipermeable membrane. The membrane allows only water molecules to pass through it in either direction but not NaCl. The net flow of water is into the sodium chloride solution and hence increases its volume. This decreases its concentration and also creates a pressure difference between the compartments. This pressure difference, push some of the water molecules back to the solvent side through the semipermeable membrane until an equilibrium is established. At the equilibrium, the rate of movement of solvent molecules on both directions are equal. The pressure difference at the equilibrium is called osmotic pressure (π). Thus, osmotic pressure can be defined as "the pressure that must be applied to the solution to stop the influx of the solvent (to stop osmosis) through the semipermeable membrane”

van’t Hoff found out that for dilute solutions, the osmotic pressure is directly proportional to the molar concentration of the solute and the temperature of the solution. He proposed the following equation to calculate osmotic pressure which is now called as van’t Hoff equation.

$$\pi = CRT \text{ ------ } 9.31$$

Here,

C = Concentration of the solution in molarity

T = Temperature

R = Gas constant

Determination of molar mass from osmotic pressure

According to van’t Hoff equation

$$\pi = CRT$$

$$C = \frac{n}{V}$$

Here, n= number of moles of solute dissolved in ‘V’ litre of the solution.

Therefore, $\pi = \frac{n}{V} RT$ or

$$\pi V = nRT \text{ ------ } (9.33)$$

If the solution is prepared by dissolving w_B g of nonvolatile solute in w_A g of solvent, then the number of moles of solute (n) is,

$$n = w_B/M_B$$

Here, M_B = molar mass of the solute

Substituting the ‘n’ in (9.33), we get,

$$\pi = \frac{w_B}{V}\frac{RT}{M_B}$$

$$M_B = \frac{w_B}{V}\frac{RT}{\pi} \text{ ------ } (9.34)$$

From the equation 9.33, molar mass of the solute can be calculated.

Significances of osmotic pressure over other colligative properties

Unlike elevation of boiling point (for 1 molal solution the elevation in boiling point is 0.512 ˚C for water) and the depression in freezing point (for 1 molal solution the depression in freezing point is 1.86 ˚C for water), the magnitude of osmotic pressure is large.

The osmotic pressure can be measured at room temperature enables to determine the molecular mass of biomolecules which are unstable at higher temperatures.

Even for a very dilute solution, the osmotic pressure is large.

Isotonic solutions

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by a semipermeable membrane, solvent flow between one to the other on either direction is same, i.e. the net solvent flow between the two isotonic solutions is zero.

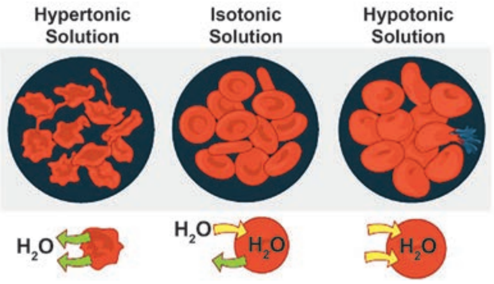


Figure 9.13 Isotonic solutions

The osmotic pressure of the blood cells is approximately equal to 7 atm at 37˚C. The intravenous injections should have same osmotic pressure as that of the blood (isotonic with blood). If the Intravenous solutions are too dilute that is hypotonic, the solvent from outside of the cells will flow into the cell to normalise the osmotic pressure and this process which is called hemolysis, causes the cells to burst. On the other hand, if the solution is too concentrated, that is hypertonic, the solvent molecules will flow out of the cells, which causes the cells to shrink and die. For this reason, the Intravenous fluids are prepared such they are isotonic to blood (0.9 % mass/volume sodium chloride solution).

9.10 Reverse osmosis (RO):

Let us consider the experimental setup (Figure 9.15) discussed in the osmosis. The pure water moves through the semipermeable membrane to the NaCl solution due to osmosis. This process can be reversed by applying pressure greater than the osmotic pressure to the solution side. Now the pure water moves from the solution side to the solvent side and this process is called reverse osmosis. It can be defined as a process in which a solvent passes through a semipermeable membrane in the opposite direction of osmosis, when subjected to a hydrostatic pressure greater than the osmotic pressure.

Application of Reverse osmosis in water purification:

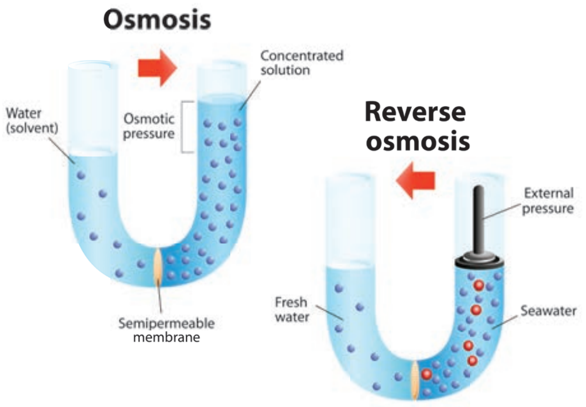


Figure 9.14 Osmosis & Reverse osmosis

Reverse osmosis is used in the desalination of sea water and also in the purification of drinking water. A simple set up used in both the process is shown in the figure 9.15. When a pressure higher than the osmotic pressure is applied on the solution side (sea water) the water molecules moves from solution side to the solvent side through semipermeable membrane (Opposite to the Osmotic flow). Pure water can be collected. There are different types of semipermeable membranes used in this process. The membrane used for reverse osmosis has to withstand high pressures. Generally, cellulose acetate or polyamide membranes are commonly used in commercial systems. The selection of membrane used for reverse osmosis will be decided based on the nature of the input water.

Example Problem-6 :

At 400K 1.5 g of an unknown substance is dissolved in a solvent and the solution is made to 1.5 L. Its osmotic pressure is found to be 0.3 bar. Calculate the molar mass of the unknown substance.

$$\text{Molar mass} = \frac{\text{mass of unknown solute} \times \text{RT}}{\text{osmotic pressure} \times \text{volume of solution}}$$

$$= \frac{1.5 \times 8.314 \times 10^{-2} \times 400}{0.3 \times 1.5}$$

$$= 110.85 \text{ gram mol}^{-1}$$

Evaluate Yourself

13) What is the mass of glucose ($C_6H_{12}O_6$) in one litre solution which is isotonic with 6 g L^{-1} of urea ($NH_2\,CO\,NH_2$) ?

9.11 Abnormal molar mass

The molar masses of the nonvolatile solutes can be calculated accurately using the experimentally determined colligative properties. In this method, we assume that the solution is very dilute and there is no dissociation or association of solute particles in the solution.

In a concentrated solution, the interaction between the solute and solvent becomes significant and reflected in the measured colligative properties. Similarly, the dissociation or association of solute molecules would alter the total number of particles present in the solution and hence affect the results of measured colligative properties. In such solutions, the value of the molar mass of the solute determined using colligative properties would be different from the actual molar mass, and it is called abnormal molar mass.

Association or dissociation of solute molecules:

Normally, the molar mass determination using measured colligative properties assumes that the solute does not dissociate or associate. In certain solvents, solute molecules associate to form a dimer or trimer etc… This reduces the total number of particles (molecules) formed in solution and as a result the calculated molar mass will be higher than the actual molar mass. Let us consider a solution of acetic acid in benzene. It is already established that acetic acid forms inter molecular hydrogen bonds as shown in the figure 9.9 and exists as a dimer in benzene.

$$2CH_3COOH \rightarrow (CH_3COOH)_2$$

The molar mass of acetic acid calculated using colligative properties is found to be around 120 g mol^{-1} is two times the actual molar mass (60 g mol^{-1}).

The electrolytes such as KCl or NaCl dissociates completely into its constitutent ions in their aqueous solution. This causes an increase in the total number of particles (ions) present in the solution. The calculated molar mass using colligative property measurement for this type of solutions will be lower than the actual molar mass. For example, sodium chloride dissociates into Na$^+$ ions and Cl$^-$ ions in aqueous solution, as shown below.

$$NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$$

When we dissolve 1 mole of NaCl (58.4 g) in water, it dissociates and gives 1 mole of Na$^+$ and 1 mole of Cl$^-$. Hence, the solution will have 2 moles of particles. Thus, the colligative properties would be double the expected value.

van't Hoff factor

We have learnt that the dissociation or association of solute molecules in a solution will result in the increase or decrease in the calculated molar mass using the colligative property. This variation is proportional to the extent of association or dissociation. To quantify the extent of association or dissociation of solutes in solution, van't Hoff introduced a term 'i' which is now called van't Hoff factor. It is defined as the ratio of the actual molar mass to the abnormal (calculated) molar mass of the solute. Here, the abnormal molar mass is the molar mass calculated using the experimentally determined colligative property.

$$i = \frac{\text{Normal (actual) molar mass}}{\text{Observed (abnormal) molar mass}}$$

$$= \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

The estimated Van't Hoff factor for acetic acid solution in Benzene is 0.5 and that of sodium chloride solution in water is 2. The degree of dissociation or association can be related to Van't Hoff factor (i) using the following relationships

$$\alpha_{\text{dissociation}} = \frac{i-1}{n-1}$$

(Where n is number ions /species formed by the dissociation of a single molecule)

$$\alpha_{\text{association}} = \frac{(1-i)n}{n-1}$$

(here, n is the number of solute involved in association.

The equations relating the four colligative properties with the concentration of the solutes can be rewritten as follows by incorporating the van't Hoff factor

Relative lowering of vapour pressure,

$$= \frac{p^{o}_{\text{solvent}} - p_{\text{solution}}}{p^{o}_{\text{solvent}}} = i\,\frac{n_{\text{solute}}}{n_{\text{solvent}}}$$

Elevation of boiling point,

$$\Delta T_b = iK_b m$$

Depression in the freezing point,

$$\Delta T_f = iK_f m$$

Osmotic pressure,

$$\pi = i\,\frac{W_{\text{solute}}}{V}\,\frac{RT}{M_{\text{solute}}}$$

For a solute that does not dissociate or associate the van't Hoff factor is equal to 1 (i = 1) and the molar mass will be close to the actual molar mass.

For the solutes that associate to form higher oligomers in solution the van't Hoff factor will be less than one (i <1) and the observed molar mass will be greater than the actual molar mass.

For solutes that dissociates into their constituent ions the van't Hoff factor will be more than one (i > 1) and the observed molar mass will be less than the normal molar mass.

Example Problem - 7

The depression in freezing point is 0.24K obtained by dissolving 1g NaCl in 200g water. Calculate van't-Hoff factor. The molal depression constant is 1.86 K Kg mol^{-1}

Molar mass of solute

$$= \frac{1000 \times K_f \times \text{mass of NaCl}}{\Delta T_f \times \text{mass of solvent}}$$

$$= \frac{1000 \times 1.86 \times 1}{0.24 \times 200}$$

$$= 38.75\text{g mol}^{-1}$$

$$= 38.75 \text{ g mol}^{-}$$

Theoretical molar mass of NaCl is =

$$i = \frac{\text{Theoretical molar mass}}{\text{Experimental molar mass}} = \frac{58.5}{38.75}$$

$$= 1.50$$

Evaluate Yourself

14. 0.2 m aqueous solution of KCl freezes at -0.68°C calculate van't Hoff factor. k_f for water is 1.86 K kg mol^{-1}.

SUMMARY

- A solution is a homogeneous mixture of two or more chemically non-reacting substances mixed uniformly. The proportion of component which is more in the solution is called solvent and the lesser component is called solute.
- The different concentration units used to prepare the solutions are formality, molality , normality, molarity, molefraction, %w/w solution, %w/v solution, %v/v solution. If the solute quantity is very minimum then ppm unit is used to express its concentration.
- The standard solutions are prepared and diluted to desired concentration (working standards). This helps in overcoming the error due to weighing and maintain efficiency and consistency in the preparation of solution.
- Solubility is defined as the amount of solute in a saturated solution per 100g of a solvent. Solubility of a solute in a solvent depends on the nature of the solute and solvent , temperature.
- The solubility of a gas in a liquid depends upon, the nature of the gas and the nature of the liquid, the temperature of the system, and the pressure of the gas.
- The effect of pressure on the solubility of a gas in a liquid is governed by Henry's Law. It states that the solubility of a gas in a liquid at a given temperature in directly proportional to the partial pressure of the gas.
- The vapour pressure of a liquid is the pressure exerted by its vapour when it is in dynamic equilibrium with its liquid, in a closed container. According to Raoults Law, the vapour pressure of a solution containing a non-volatile solute is directly proportional to the mole fraction of the solvent (X_A). The proportionality constant being the vapour pressure of the pure solvent.
- The solution shows positive deviation from Raoult's Law if its vapour pressure is higher than that predicted by Raoult's Law for example ethyl alcohol and cyclohexane.
- The solution shows negative deviation if its vapour pressure is lower than that predicted by Raoult's Law for example acetone and chloroform.
- Colligative properties of solutions are those properties which depend only upon the number of solute particles in the solution and not on their nature. Such properties are
- (a) Relative lowering in vapour pressure: On addition of a non volatile solute it is observed that the vapour pressure of the solution is lesser than the solvent. According to Raolut's law relative lowering of vapour pressure is equal to the mole fraction of the solute.
- (b) Elevation of boiling pointΔT_b: The solution boils at a higher temperature than the pure solvent. This is due to the decreased vapour pressure of solution and the temperature it reaches the atmospheric pressure on heating to boil is much higher than the solvent.
- (c) Depression of freezing point:

The freezing point of the solution is much lower than the solvent as the temperature at which the solid and the liquid have the same vapour pressure is much lower than the solvent.

- (d) Osmotic pressure: The spontaneous flow of solvent molecules from a dilute solution into a concentrated solution when the two are separated by a perfect semipermeable membrane is called osmosis.
- Osmotic pressure (π) is the pressure which must be applied to the solution side (more concentrated solution) to just prevent the passage of pure solvent into it through a semipermeable membrane.
- Abnormal colligative properties
- If solutes undergo any association or dissociation in a solutiont, they exhibit abnormal colligative properties Van't Hoft factor explains quantitatively the extent of association or dissociation of soluts in solvent.

Evaluation

I. Choose the best answer.

1. The molality of a solution containing 1.8g of glucose dissolved in 250g of water is

a) 0.2 M b) 0.01 M

c) 0.02 M d) 0.04 M

2. Which of the following concentration terms is / are independent of temperature

a) molality b) molarity

c) mole fraction d) (a) and (c)

3. Stomach acid, a dilute solution of HCl can be neutralised by reaction with Aluminium hydroxide

$Al(OH)_3 + 3HCl\,(aq) \rightarrow AlCl_3 + 3\,H_2O$

How many millilitres of 0.1 M $Al(OH)_3$ solution are needed to neutralise 21 mL of 0.1 M HCl ?

a) 14 mL b) 7 mL

c) 21 mL d) none of these

4. The partial pressure of nitrogen in air is 0.76 atm and its Henry's law constant is 7.6×10^4 atm at 300K. What is the molefraction of nitrogen gas in the solution obtained when air is bubbled through water at 300K ?

a) 1×10^{-4} b) 1×10^{-6}

c) 2×10^{-5} d) 1×10^{-5}

5. The Henry's law constant for the solubility of Nitrogen gas in water at 350 K is 8×10^4 atm. The mole fraction of nitrogen in air is 0.5. The number of moles of Nitrogen from air dissolved in 10 moles of water at 350K and 4 atm pressure is

a) 4×10^{-4} b) 4×10^4

c) 2×10^{-2} d) 2.5×10^{-4}

6. Which one of the following is incorrect for ideal solution ?

a) $\Delta H_{mix} = 0$

b) $\Delta U_{mix} = 0$

c) $\Delta P = P_{observed} - P_{\text{Calculated by raoults law}} = 0$

d) $\Delta G_{mix} = 0$

7. Which one of the following gases has the lowest value of Henry's law constant ?

a) N_2 b) He

c) CO_2 d) H_2

8. P_1 and P_2 are the vapour pressures of pure liquid components, 1 and 2 respectively of an ideal binary solution if x_1 represents the mole fraction of component 1, the total pressure of the solution formed by 1 and 2 will be

a) $P_1 + x_1 (P_2 - P_1)$

b) $P_2 - x_1 (P_2 + P_1)$

c) $P_1 - x_2 (P_1 - P_2)$

d) $P_1 + x_2 (P_1 - P_2)$

9. Osometic pressure (π) of a solution is given by the relation

a) $\pi = nRT$ b) $\pi V = nRT$

c) $\pi RT = n$ d) none of these

10. Which one of the following binary liquid mixtures exhibits positive deviation from Raoults law ?

a) Acetone + chloroform

b) Water + nitric acid

c) HCl + water

d) ethanol + water

11. The Henry's law constants for two gases A and B are x and y respectively. The ratio of mole fractions of A to B is 0.2. The ratio of mole fraction of B and A dissolved in water will be

a) $\frac{2x}{y}$ b) $\frac{y}{0.2x}$

c) $\frac{0.2x}{y}$ d) $\frac{5x}{y}$

12. At 100°C the vapour pressure of a solution containing 6.5g a solute in 100g water is 732mm. If $K_b = 0.52$, the boiling point of this solution will be

a) 102°C b) 100°C

c) 101°C d) 100.52°C

13. According to Raoults law, the relative lowering of vapour pressure for a solution is equal to

a) mole fraction of solvent

b) mole fraction of solute

c) number of moles of solute

d) number of moles of solvent

14. At same temperature, which pair of the following solutions are isotonic ?

a) 0.2 M $BaCl_2$ and 0.2M urea

b) 0.1 M glucose and 0.2 M urea

c) 0.1 M NaCl and 0.1 M K_2SO_4

d) 0.1 M $Ba(NO_3)_2$ and 0.1 M Na_2SO_4

15. The empirical formula of a non-electrolyte(X) is CH_2O. A solution containing six gram of X exerts the same osmotic pressure as that of 0.025M glucose solution at the same temperature. The molecular formula of X is

a) $C_2H_4O_2$ b) $C_8H_{16}O_8$

c) $C_4H_8O_4$ d) CH_2O

16. The K_H for the solution of oxygen dissolved in water is 4×10^4 atm at a given temperature. If the partial pressure of oxygen in air is 0.4 atm, the mole fraction of oxygen in solution is

a) 4.6×10^3 b) 1.6×10^4

c) 1×10^{-5} d) 1×10^5

17. Normality of 1.25M sulphuric acid is

a) 1.25 N b) 3.75 N

c) 2.5 N d) 2.25 N

18. Two liquids X and Y on mixing gives a warm solution. The solution is

a) ideal

b) non-ideal and shows positive deviation from Raoults law

c) ideal and shows negative deviation from Raoults Law

d) non-ideal and shows negative deviation from Raoults Law

19. The relative lowering of vapour pressure of a sugar solution in water is 3.5×10^{-3}. The mole fraction of water in that solution is

a) 0.0035

b) 0.35

c) 0.0035 / 18

d) 0.9965

20. The mass of a non-voltaile solute (molar mass 80 g mol^{-1}) which should be dissolved in 92g of toluene to reduce its vapour pressure to 90%

a) 10g

b) 20g

c) 9.2 g

d) 8.89g

21. For a solution, the plot of osmotic pressure (π) verses the concentration (c in mol L^{-1}) gives a straight line with slope 310R where 'R' is the gas constant. The temperature at which osmotic pressure measured is

a) 310×0.082 K

b) 310^oC

c) 37^oC

d) $\frac{310}{0.082}$ K

22. 200ml of an aqueous solution of a protein contains 1.26g of protein. At 300K, the osmotic pressure of this solution is found to be 2.52×10^{-3} bar. The molar mass of protein will be (R = 0.083 L bar mol^{-1} K^{-1})

a) 62.22 Kg mol–1

b) 12444g mol^{-1}

c) 300g mol^{-1}

d) none of these

23. The Van't Hoff factor (i) for a dilute aqueous solution of the strong elecrolyte barium hydroxide is (NEET)

a) 0

b) 1

c) 2

d) 3

24. What is the molality of a 10% W/W aqueous sodium hydroxide solution ?

a) 2.778

b) 2.5

c) 10

d) 0.4

25. The correct equation for the degree of an associating solute, 'n' molecules of which undergoes association in solution, is

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

b) $\alpha^2 = \frac{n(1-i)}{(n-1)}$

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

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

26. Which of the following aqueous solutions has the highest boiling point ?

a) 0.1M KNO_3

b) 0.1 MNa_3PO_4

c) 0.1 M $BaCl_2$

d) 0.1 M K_2SO_4

27. The freezing point depression constant for water is 1.86^o K $Kgmol^{-1}$. If 5g Na_2SO_4 is dissolved in 45g water, the depression in freezing point is 3.64^oC. The Vant Hoff factor for Na_2SO_4 is

a) 2.50

b) 2.63

c) 3.64

d) 5.50

28. Equimolal aqueous solutions of NaCl and KCl are prepared. If the freezing point of NaCl is -2^oC, the freezing point of KCl solution is expected to be

a) -2^oC

b) -4^oC

c) -1^oC

d) 0^oC

29. Phenol dimerises in benzene having van't Hoff factor 0.54. What is the degree of association ?

a) 0.46 b) 92

c) 46 d) 0.92

30. Assertion : An ideal solution obeys Raoults Law

Reason : In an ideal solution, solvent-solvent as well as solute-solute interactions are similar to solute-solvent interactions.

a) both assertion and reason are true and reason is the correct explanation of assertion

b) both assertion and reason are true but reason is not the correct explanation of assertion

c) assertion is true but reason is false

d) both assertion and reason are false

II. Write brief answer to the following questions.

31. Define (i) molality (ii) Normality

32. What is a vapour pressure of liquid?

What is relative lowering of vapour pressure?

33. State and explain Henry's law

34. State Raoult law and obtain expression for lowering of vapour pressure when nonvolatile solute is dissolved in solvent.

35. What is molal depression constant? Does it depend on nature of the solute ?

36. What is osmosis?

37. Define the term 'isotonic solution'.

38. You are provided with a solid 'A' and three solutions of A dissolved in water - one saturated, one unsaturated, and one super saturated. How would you determine which solution is which ?

39. Explain the effect of pressure on the solubility.

40. A sample of 12 M Concentrated hydrochloric acid has a density 1.2 gL^{-1} Calculate the molality

41. A 0.25 M glucose solution at 370.28 K has approximately the pressure as blood does what is the osmotic pressure of blood ?

42. Calculate the molality of a solution containing 7.5 g of glycine (NH_2-CH_2 -COOH) dissolved in 500 g of water.

43. Which solution has the lower freening point?10 g of methanol (CH_3OH) in 100g of water (or) 20 g of ethanol (C_2H_5OH) in 200 g of water.

44. How many moles of solute particles are present in one litre of 10^{-4} M potassium sulphate?

45. Henry's law constant for solubility of methane in benzene is $4.2x10^{-5}$ mm Hg at a particular constant temperature At this temperature. Calculate the solubility of methane at i) 750 mm Hg ii) 840 mm Hg

46. The observed depression in freezing point of water for a particular solution is 0.093^0C. Calculate the concentration of the solution in molality. Given that molal depression constant for water is 1.86 KKg mol^{-1}

47. The vapour pressure of pure benzene (C_6H_6) at a given temperature is 640 mm Hg. 2.2 g of non-volatile solute is added to 40 g of benzene. The vapour pressure of the solution is 600 mm Hg. Calculate the molar mass of the solute?

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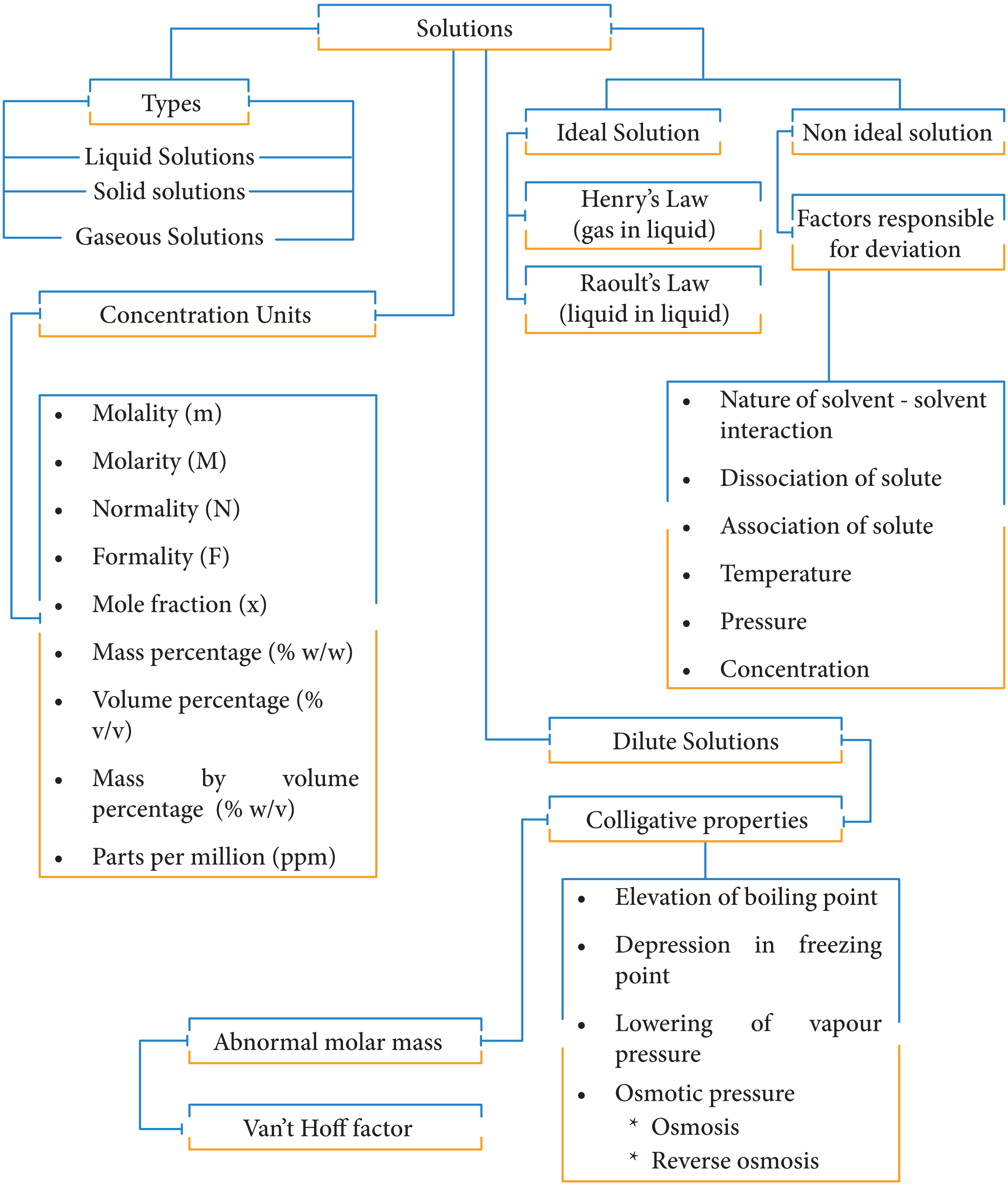

Solutions

Types
- Liquid Solutions
- Solid solutions
- Gaseous Solutions

Concentration Units
- Molality (m)
- Molarity (M)
- Normality (N)
- Formality (F)
- Mole fraction (x)
- Mass percentage (% w/w)
- Volume percentage (% v/v)
- Mass by volume percentage (% w/v)
- Parts per million (ppm)

Ideal Solution
- Henry's Law (gas in liquid)
- Raoult's Law (liquid in liquid)

Non ideal solution

Factors responsible for deviation
- Nature of solvent - solvent interaction
- Dissociation of solute
- Association of solute
- Temperature
- Pressure
- Concentration

Dilute Solutions

Colligative properties
- Elevation of boiling point
- Depression in freezing point
- Lowering of vapour pressure
- Osmotic pressure
  - * Osmosis
  - * Reverse osmosis

Abnormal molar mass

Van't Hoff factor

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