SOLUTIONS

A solution is defined as a homogeneous mixture of two or more substances having uniform properties throughout. The substances of which a solution is made are called its components. The solute is the component present in smaller proportion while the solvent, on the other hand, is the component present in larger proportion in which the solute dissolves.

TYPES OF SOLUTIONS:

Depending upon the state of solute and solvent, there are 9 types of solutions which are listed in the table below:

Solute	Solvent	Final phase	Examples
Gas	Gas	Gas	Air , Water
Liquid	Gas	Gas	Moisture in air
Solid	Gas	Gas	Naphthalene in air
Gas	Solid	Solid	Occlusion of H2 in Pd
Liquid	Solid	solid	Mixing of liquid mercury with solid gold to give solid amalgam
Solid	Solid	Solid	Alloys
Gas	Liquid	Liquid	O2 dissolved in water
Liquid	Liquid	Liquid	Ethanol and water mixture
Solid	Liquid	Liquid	Salt in water

RAOULT'S LAW:

Francois Marie Raoult, a French Chemist studied vapour pressure of a number of binary solutions of volatile liquids at constant temperature and gave the following generalization in 1887 which is known as Raoult's law.

The law states that: " Partial pressure of a volatile component in an ideal solution at a given temperature is equal to the product of the mole fraction of that component in the solution and vapour pressure of that component in the pure state at the same temperature."

Mathematically the law may be expressed as follows:

$$P_i = x_i P_i^o$$

Where, P_i = partial pressure of the component i and P_i^o = vapour pressure of the pure component i, at the same temperature.

VAPOUR PRESSURE OF BINARY SOLUTIONS:

Let us consider two volatile liquids A and B which are completely miscible in all proportions. If both the components of the binary mixture obey Raoult's law, then,

Partial pressure of the component A = $P_A = x_A P_A^o$

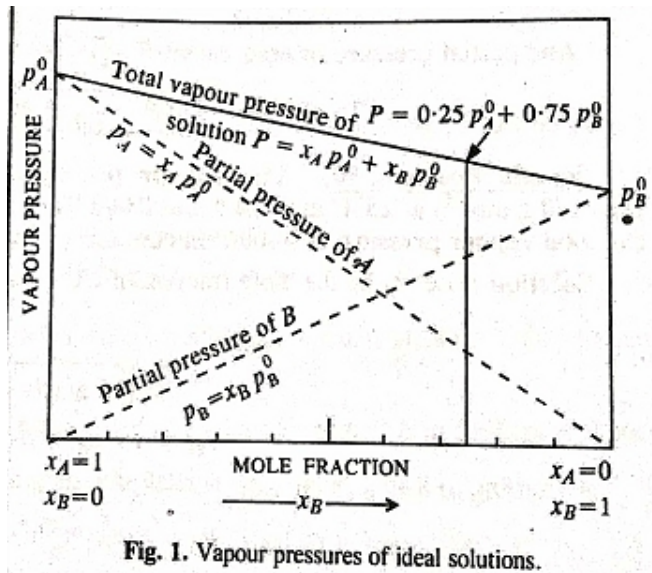Partial pressure of the component B = $P_B = x_B P_B^o$

Fig. 1. Vapour pressures of ideal solutions.

Where x_A and x_B are mole fractions of the two components A and B respectively in the liquid phase and P_A^0 and P_B^0 are their respective vapour pressures when pure at the temperature of the solution.

If the vapours behave like an ideal gas, then according to Dalton's law of partial pressures, total pressure P is given by:

$P = x_A P_A^0 + x_B P_B^0$

Since, $x_A + x_B = 1$

∴ $P = (1 - x_B) P_A^0 + x_B P_B^0$

$P = P_A^0 + x_B (P_B^0 - P_A^0)$ …………………….(1)

When $x_B = 1$, i.e. for pure component B, equation (1) reduces to,

$P = P_A^0 + 1 (P_B^0 - P_A^0) = P_B^0$

When $x_B = 0$, i.e. for pure component A

$P = P_A^0$

Equation (1) is the equation of a straight line. When total pressure P is plotted against mole fraction x_B, a straight line will be obtained with slope = $(P_B^0 - P_A^0)$ and intercept = P_A^0. Thus, when for a binary solution, the plot of total vapour pressure versus mole fraction is a straight line, the solution is ideal and obey Raoult's law. e.g. Binary mixtures of :

a) Ethylene bromide and ethylene chloride.
b) n-hexane and n-heptane
c) Benzene and toluene.
d) Carbon tetrachloride and silicon tetrachloride.
e) n-butyl chloride and n-butyl bromide.

COMPOSITION OF THE VAPOUR (GAS) PHASE:

The composition of the vapor phase may be estimated by the application of Raoult's law to the liquid phase, according to which:

Vapour pressure of the component A, $P_A = x_A P_A^o$

Vapour pressure of the component B, $P_B = x_B P_B^o$

Now, the number of moles of a component in the vapour phase which behave ideally is proportional to its partial pressure.

Since, $PV = nRT$ or $n = VP/RT$

$\therefore n_A(g) \propto P_A$

And $n_B(g) \propto P_B$

$\therefore$ mole fraction of component A is the gas phase.

$y_A = n_A (g)/ [n_A (g) + n_B (g)] = P_A/ (P_A + P_B)$

$= x_A P_A^o/ (x_A P_A^o + x_B P_B^o)$

Since, the mixture is binary ,

$y_B = 1- y_A$

or $y_B = P_B/ (P_A + P_B)$

or $y_B = x_B P_B^o/ (x_A P_A^o + x_B P_B^o)$

VAPOUR PRESSURES OF REAL AND NON-IDEAL SOLUTIONS:

Most of the solutions show appreciable deviations from the ideal behavior in their vapour pressures. The deviations from Raoult's law arise from the non-ideality or either the vapour phase or the solution. Such solutions are called real or non-ideal solutions. It can be divided into three types:

Type 1: The solutions of type 1 (fig.3) show small positive deviations from ideal behavior, the vapour pressure of each component being only slightly greater than that predicted by Raoult's law. The total vapour pressure in such cases remains always within the vapour pressures of the pure components. e.g. Cyclohexnae-Carbon tetrachloride system.

Type 2: The solutions of type 2 (fig 4) show large positive deviations from ideal behavior, the vapour pressure of each component being considerably greater than that predicted by Raoult's law. The total vapour pressure curve rise to maximum which is above the vapour pressure of each of the pure components. e.g. Acetaldehyde- Carbon disulphide , water-propyl alcohol and ethyl alcohol- chloroform mixtures.

Type 3: The solutions of type 3 (fig 5) show large negative deviations from ideal behavior and the vapour pressure of each component is considerably less than that predicted by Raoult's law. The total vapour pressure curve dips to a minimum ,i.e. for a certain composition, the total vapour pressure of the mixture is below the vapour pressure of eithr of the pure components.
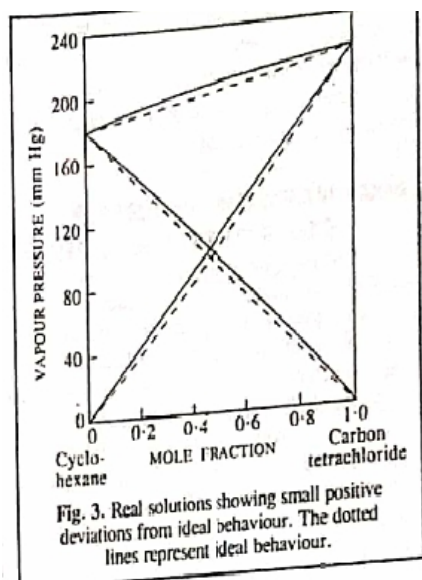
Fig. 3. Real solutions showing small positive deviations from ideal behaviour. The dotted lines represent ideal behaviour.
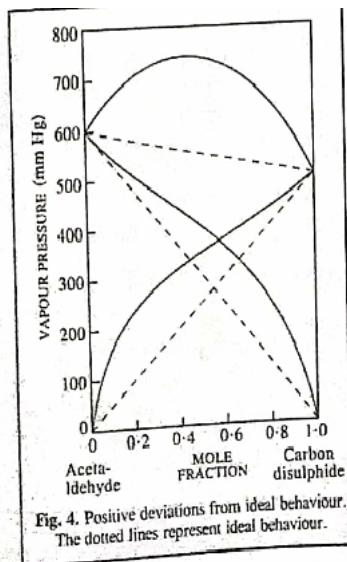
Fig. 4. Positive deviations from ideal behaviour. The dotted lines represent ideal behaviour.
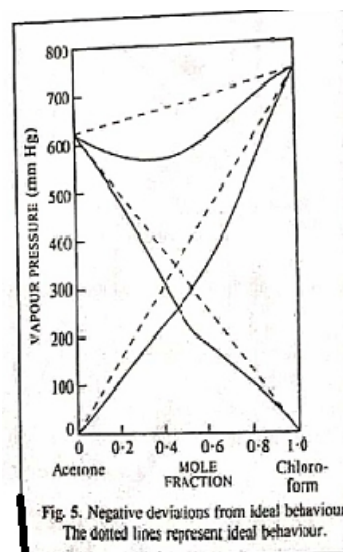
Fig. 5. Negative deviations from ideal behaviour. The dotted lines represent ideal behaviour.

SOLUBILITY OF GASES IN LIQUIDS:

The solubility of gases in liquids is generally expressed in terms of absorption coefficient (a). This is defined as the volume of gas reduced to N.T.P dissolved by unit volume of solvent at the temperature of the experiment and under a pressure of 1 atmosphere of the gas.

Factors influencing the solubility of a gas:

1) **Nature of the gas and nature of the solvent**: The gases which are easily liquefied are more soluble in common solvents. The gases which are capable of forming ions in aqueous solution are much more soluble in water than in other solvents.

2) **Effect of temperature:** under a constant pressure, the solubility of a gas diminishes with rise in temperature.

3) **Effect of pressure: Henry's law:** William Henry in 1805 found that the solubility of a gas at a given temperature decreases directly as the pressure. Thus, Henry's law states that, " The mass of a gas dissolved per unit volume of a solvent is proportional to the pressure of the gas in equilibrium with the solution at constant temperature."

   If m is the mass of a gas dissolved per unit volume of a solvent and P is the pressure of the gas in equilibrium with the solution, then at constant temperature,
      $m \alpha P$ or $m = kP$
   where k is the proportionality constant.

APPLICATIONS OF HENRY'S LAW:

1) **In the production of carbonated beverages**: In order to increase the solubility of CO_2 in cold drinks, beer, etc. the bottles are sealed under high pressure.
2) **At high altitudes :** The partial pressure of oxygen at high altitudes is less than the ground level, this results in low concentration of oxygen in the blood and tissues of the people.

3) For deep drivers, oxygen diluted with less soluble He gas is used as breathing gas and it minimizes the painful effects due to higher solubility of N2 gas in blood.
4) In lungs, where oxygen is present in air with high partial pressure, haemoglobin combines with O2 to form oxyhaemoglobin. In tissues where partial pressure of O2 is low, oxyhaemoglobin releases the oxygen for utilization in cellular activities.

ASSIGNMENTS:

1) Write the expressions for: 7x2=14
   a) Mass or weight percent
   b) Volume percent
   c) Molarity
   d) Molality
   e) Normaliy
   f) Mole fraction
   g) Mole percent
2) Distinguish between diffusion and osmosis.   3
3) Concentrated HCl contains 37% HCl by mass. The density of iys solution is 1,18 g/ml. Calculate the molarity and molality of the solution.   3