

## Solutions

Solution is a homogeneous mixture of two or more substances in same or different physical phases. The substances forming the solution are called components of the solution. On the basis of number of components a solution of two components is called binary solution.

### Solute and Solvent

In a binary solution, solvent is the component which is present in large quantity while the other component is known as solute.

### Composition of Solutions

S.No.	Solute	Solvent	Examples
<b>Solid solutions</b>			
1.	Solid	Solid	Alloys
2.	Liquid	Solid	Hydrated salts, Amalgam of Hg with Na
3.	Gas	Solid	Dissolved gases in mineral
<b>Liquid solutions</b>			
4.	Solid	Liquid	Salt/sugar solution in water
5.	Liquid	Liquid	Alcohol in water
6.	Gas	Liquid	Aerated drinks, O <sub>2</sub> in water
<b>Gaseous solutions</b>			
7.	Solid	Gas	Iodine vapour in air
8.	Liquid	Gas	Water vapour in air
9.	Gas	Gas	Air (O <sub>2</sub> + N <sub>2</sub> )

### Mole fraction (X)

It is defined as the ratio of the number of moles of a component to the total number of moles of all the components. For a binary solution, if the number of moles of A and B are  $n_A$  and  $n_B$  respectively, the mole fraction of A will be

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

Similarly,

$$\chi_B = \frac{n_B}{n_A + n_B} \quad \therefore \chi_A + \chi_B = 1$$

### Raoult's Law

The Raoult's law states "For a solution of two volatile liquids, the vapour pressure of each liquid in the solution is less than the respective vapour pressure of the pure liquids and the equilibrium partial vapour pressure of the liquid is directly proportional to its mole fraction.

For a solution containing two liquids A and B, the partial vapour pressure of liquid A is

$$p_A \propto \chi_A \quad \text{or} \quad p_A = k\chi_A$$

where,  $\chi_A = \frac{n_A}{(n_A + n_B)}$  = mole fraction of liquid A

The proportionality constant is obtained by considering the pure liquid when  $\chi_A = 1$  then  $k = P_A^\circ$ , the vapour pressure of pure liquid, hence

$$p_A = P_A^\circ \chi_A$$

Similarly,

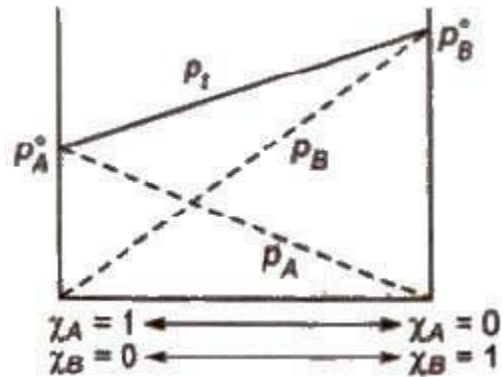
$$p_B = P_B^\circ \chi_B$$

The total vapour pressure of the solution,

$$\begin{aligned} p_T &= p_A + p_B = P_A^\circ \chi_A + P_B^\circ \chi_B \\ &= P_A^\circ + (P_B^\circ - P_A^\circ) \chi_B \end{aligned}$$

### Ideal Solutions

Those solutions in which solute-solute (B-B) and solvent-solvent (A-A) interactions are almost similar to solvent solute (A-B) interactions are called ideal solutions. These solutions satisfy the following conditions.



(i) Solution must obey Raoult's law, i.e.,

$$p_A = p_A^{\circ} \chi_A, p_B = p_B^{\circ} \chi_B$$

(ii)  $\Delta H_{\text{mix}} = 0$  (No energy evolved or absorbed)

(iii)  $\Delta V_{\text{mix}} = 0$  (No expansion or contraction on mixing)

Some solutions behave like nearly ideal solutions, e.g., benzene + toluene, n-hexane + n-heptane, ethyl iodide + ethyl bromide, chlorobenzene + bromobenzene.

### Non-ideal Solutions

Those solutions which show deviation from Raoult's law are called non-ideal solutions.

For such solutions,

$$\Delta H_{\text{mix}} \neq 0$$

$$\Delta V_{\text{mix}} \neq 0$$

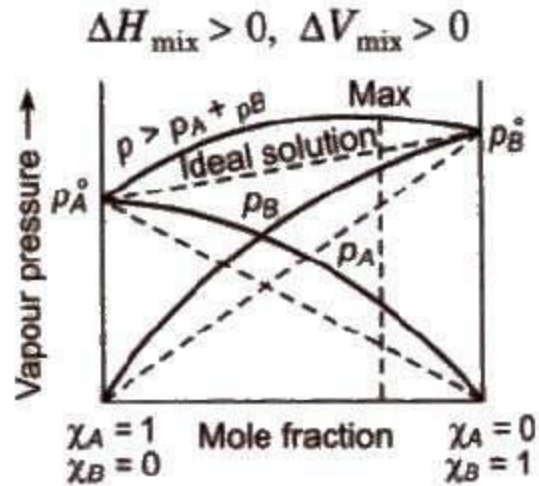
#### (a) Non-ideal solutions showing positive deviation

In such a case, the A – B interactions are weaker than A – A or B – B interactions and the observed vapour pressure of each component and the total vapour pressure are greater than that predicted by Raoult's law.

$$p_A > p_A^{\circ} \chi_A, p_B > p_B^{\circ} \chi_B$$

$$p_{\text{total}} > p_A^{\circ} \chi_A + p_B^{\circ} \chi_B$$

For such solutions



**Examples :** Ethanol + water,  $\text{CS}_2$  + acetone,  $\text{CCl}_4$  +  $\text{C}_6\text{H}_6$ ,  
 $\text{CCl}_4$  +  $\text{C}_6\text{H}_5\text{CH}_3$ , ethanol + cyclohexane,  $\text{CCl}_4$  +  $\text{CHCl}_3$ .

**(b) Non-ideal solution showing negative deviation**

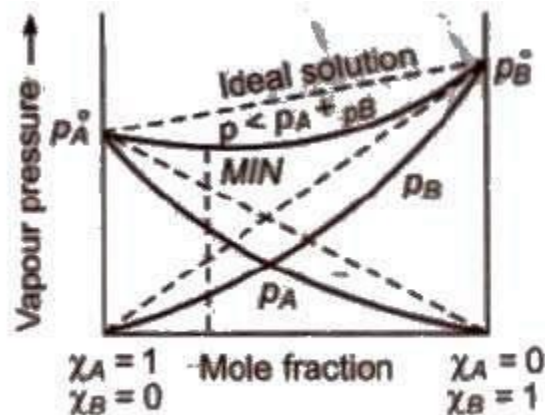
In such a case, the A – B interactions are stronger than A – A or B – B interactions and the observed vapour pressure of each component and the total vapour pressure are lesser than that predicted by Raoult's law.

$$p_A < p_A^\circ \chi_A, p_B < p_B^\circ \chi_B$$

$$p_{\text{total}} < p_A^\circ \chi_A + p_B^\circ \chi_B$$

For such solutions,

$$\Delta H_{\text{mix}} < 0, \Delta V_{\text{mix}} < 0$$



**Non-ideal solution showing negative deviation**

**Examples :**  $\text{CHCl}_3 + \text{CH}_3\text{COCH}_3$ ,  $\text{CHCl}_3 + \text{C}_6\text{H}_6$ ,  $\text{H}_2\text{O} + \text{HCl}$ ,  
 $\text{H}_2\text{O} + \text{HNO}_3$ , methanol + acetic acid.

### Azeotropic Mixture

A mixture of two liquids which boils at a particular temperature like a pure liquid and distils over in the same composition is known as constant boiling mixtures. These are formed by nonideal solutions.

#### (i) Minimum boiling azeotropes

are formed by those liquid pairs which show positive deviation from ideal behaviour. Such azeotropes have boiling points lower than either of the components, e.g.,  $\text{C}_2\text{H}_5\text{OH}$  (95.57%) +  $\text{H}_2\text{O}$  (4.43%) (by mass).

#### (ii) Maximum boiling azeotropes

are formed by those liquid pairs which show negative deviation from ideal behaviour. Such azeotropes have boiling points higher than either of the components. e.g.,  $\text{H}_2\text{O}$  (20.22%) +  $\text{HCl}$  (79.78%) by mass.

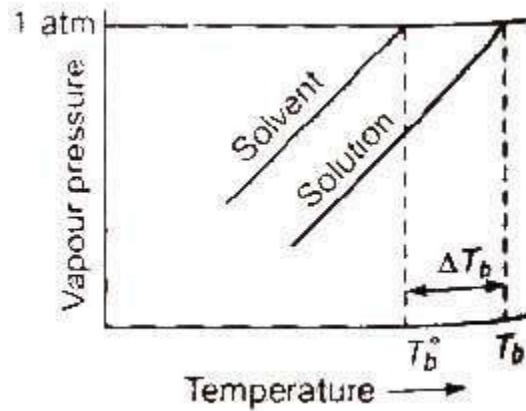
### Colligative Properties

[Colligative : from Latin. = Co mean „together”; ligare means „to bind“.]

Colligative properties are those properties which depend only upon the number of solute particles in a solution irrespective of their nature.

#### Elevation in Boiling Point ( $\Delta T_b$ )

Boiling point of a liquid is the temperature at which its vapour pressure becomes equal to the atmospheric pressure. As the vapour pressure of a solution containing a nonvolatile solute is lower than that of the pure solvent, its boiling point will be higher than that of the pure solvent as shown in figure. The increase in boiling point is known as elevation in boiling point,  $\Delta T_b$



$$\Delta T_b = T_b - T_b^0 \quad \Delta T_b = K_b m \quad (\text{where; } m = \text{molality})$$

$K_b$  is molal elevation constant or ebullioscopic constant. Molecular mass of solute can be calculated as

$$\Delta T_b = \frac{K_b \cdot W_B \times 1000}{M_B \times W_A}$$

$$M_B = K_b \cdot \frac{W_B}{W_A} \times \frac{1000}{\Delta T_b}$$

where,  $W_B$  and  $W_A$  = mass of solute and solvent respectively.

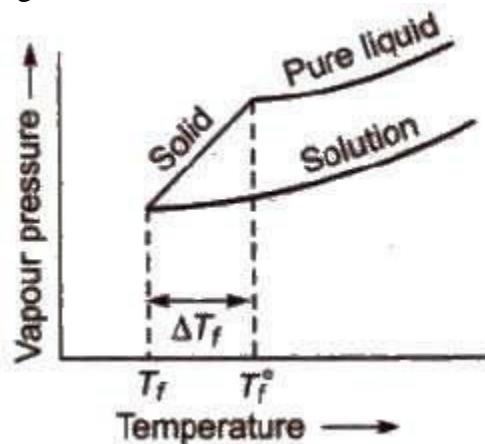
$K_b$  has units of  $K / m$  or  $K \text{ kg mol}^{-1}$ , for water,  $K_b = 0.52 \text{ K kg mol}^{-1}$

The boiling point elevation of a solution is determined by

- (i) Landsberger's method
- (ii) Cottrell's method

### Depression in Freezing Point ( $\Delta T_f$ )

Freezing point of a liquid is the temperature at which vapour pressure of the solvent in its liquid and solid phase become equal. As we know that vapour pressure of solution containing non-volatile solute is lower than that of pure solvent, solid form gets separated out at a lower temperature as shown in the figure.



This decrease in freezing point of a liquid is known as depression in freezing point.

Depression in freezing point ( $\Delta T_f$ ) =  $T_f^\circ - T_f$

$$\Delta T_f = K_f \cdot m = K_f \frac{W_B}{M_B} \times \frac{1000}{W_A}$$

To find molecular mass of solute,

$$M_B = \frac{K_f \cdot W_B \times 1000}{\Delta T_f \cdot W_A}$$

where,  $K_f$  is molal depression constant or cryoscopic constant.

$K_f$  has units of  $K / m$  or  $K \text{ kg mol}^{-1}$ .

Ethylene glycol is usually added to water in the radiator to lower its freezing point. It is called antifreeze solution.

[Common salt (NaCl) and anhydrous  $\text{CaCl}_2$  are used to clear snow on the roads because they depress the freezing point of water. The freezing point depression is determined by Beckmann method or Rast method.]

Calculations of molal elevation constant ( $K_b$ ) and molal depression constant ( $K_f$ )

$$K_b = \frac{M_A R (T_b^\circ)^2}{\Delta H_v}, \quad K_f = \frac{M_A \cdot R (T_f^\circ)^2}{\Delta H_f}$$

$T_b^\circ$  = boiling point of solvent

$T_f^\circ$  = freezing point of solvent

$\Delta H_f$  = molar enthalpy of fusion

$\Delta H_v$  = molar enthalpy of vaporisation

### Osmotic Pressure ( $\pi$ )

**Osmosis** is the phenomenon of spontaneous flow of the solvent molecules through a semipermeable membrane from pure solvent to solution or from a dilute solution to concentrated solution. It was first observed by Abbe Nollet.

Some natural semipermeable membranes are animal bladder, cell membrane etc.

$\text{Cu}_2[\text{Fe}(\text{CN})_6]$  is an artificial semipermeable membrane which does not work in non-aqueous solutions as it dissolves in them.

Osmosis may be

#### (i) Exosmosis

It is outward flow of water or solvent from a cell through semipermeable membrane.

#### (ii) Endosmosis



It is inward flow of water or solvent from a cell through a semipermeable membrane. The hydrostatic pressure developed on the solution which just prevents the osmosis of pure solvent into the solution through a semipermeable membrane is called **osmotic pressure**.

$$\text{Osmotic pressure } (\pi) = RCT; \left( C = \frac{n_B}{V} = \frac{W_B}{M_B V} \right)$$

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

$$\pi = \frac{dRT}{M_B} ; \left( d = \frac{W_B}{V} \right)$$

where, d = density, R = solution constant, T = temperature,  $M_B$  = molar mass of solute  
Osmotic pressure can be determined by anyone of the method listed below

- (i) Pfeffer's method
- (ii) Berkeley and Hartley's method (very good method)
- (iii) Morse and Frazer's method

On the basis of osmotic pressure, -the solution can be

#### (i) Hypertonic solution

A solution is called hypertonic if its osmotic pressure is higher than that of the solution from which it is separated by a semipermeable membrane.

When a plant cell is placed in a hypertonic solution, the fluid from the plant cell comes out and cell shrinks, this phenomenon is called plasmolysis.

#### (ii) Hypotonic solution

A solution is called hypotonic if its osmotic pressure is lower than that of the solution from which it is separated by a semipermeable membrane.

#### (iii) Isotonic solution

Two solutions are called isotonic if they exert the same osmotic pressure. These solutions have same molar concentration. 0.91% solution of pure NaCl is isotonic with human RBC's.

Two solutions are isotonic if they have the same molar concentration, e.g., if x % solution of X is isotonic with y % solution of Y, this means molar concentration of X = Molar concentration of Y

$$\frac{x}{100} \times \frac{1000}{M_X} = \frac{y \times 1000}{100 \times M_Y} \Rightarrow \frac{x}{M_X} = \frac{y}{M_Y}$$

Osmotic pressure method is the best method for determining the molecular masses of polymers since observed value of any other colligative property is too small to be measured with reasonable accuracy.

#### Reverse osmosis

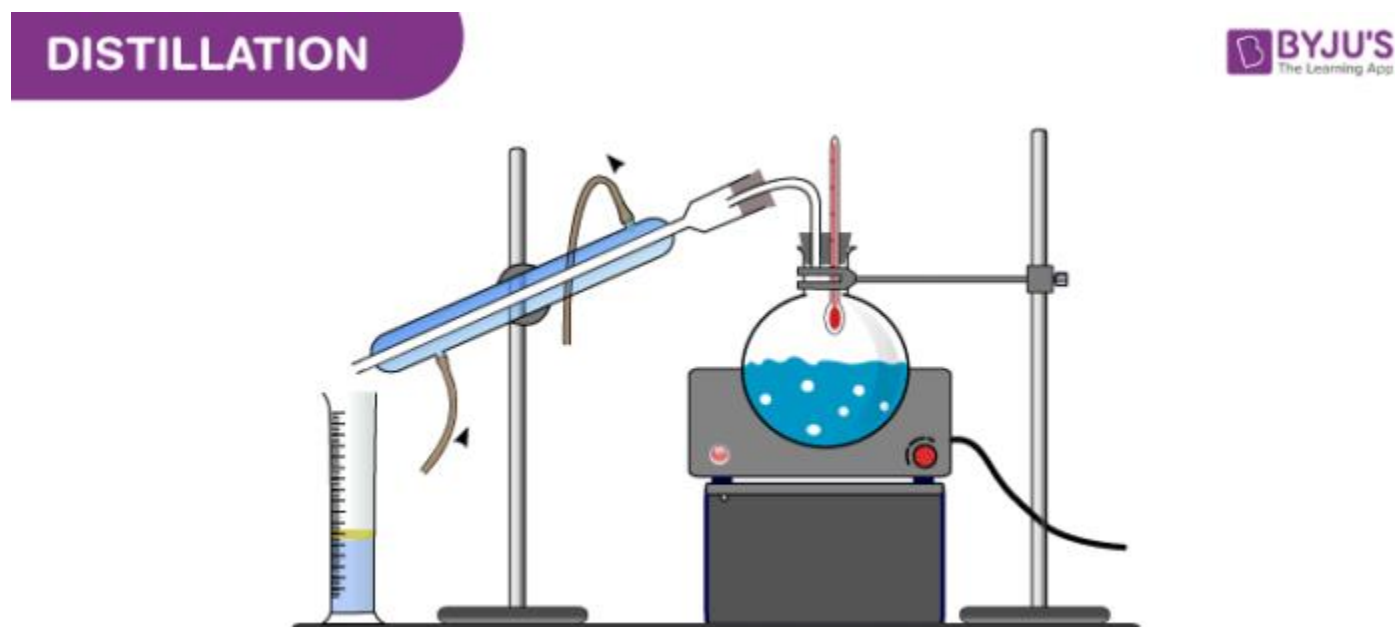


When the external pressure applied on the solution is more than osmotic pressure, the solvent flows from the solution to the pure solvent, which is called reverse osmosis. Desalination of sea water is done by reverse osmosis.

## Distillation

Distillation refers to the selective boiling and subsequent condensation of a component in a liquid mixture. It is a separation technique that can be used to either increase the concentration of a particular component in the mixture or to obtain (almost) pure components from the mixture. The process of distillation exploits the difference in the boiling points of the components in the liquid mixture by forcing one of them into a gaseous state.

It is important to note that distillation is not a chemical reaction but it can be considered as a physical separation process. An illustration describing the laboratory setup that is generally used to execute this process is provided below.



The distillation performed on a laboratory scale often uses batches of the liquid mixture whereas industrial distillation processes are generally continuous, requiring a constant composition of the mixture to be maintained.

### Why is it Impossible to Completely Purify a Mixture by Distillation?

At the boiling point of a mixture of liquids, all the volatile constituents boil. However, the quantity of a constituent in the resulting vapor is based on its contribution to the total vapor pressure of the mixture. This is why the compounds with higher partial pressures can be concentrated in the vapors whereas the compounds having low partial pressures can be concentrated in the liquid.

Since a component in the mixture cannot have zero partial pressure, it is impossible to obtain a completely pure sample of a component from a mixture via distillation. However, samples of high

purity can be obtained when one of the components in the mixture has a partial pressure which is close to zero.

### **Types of Distillation**

Some important types of distillation include:

- Simple distillation
- Fractional distillation
- Steam distillation
- Vacuum distillation
- Air-sensitive vacuum distillation
- Short path distillation
- Zone distillation

Simple distillation involves heating the liquid mixture to the boiling point and immediately condensing the resulting vapors. This method is only effective for mixtures wherein the boiling points of the liquids are considerably different (a minimum difference of 25°C). The purity of the distillate (the purified liquid) is governed by Raoult's law