Chapter 09

Solutions

Phenol-Water System

Partial miscibility

If equal volumes of water and phenol are mixed together, they show partial miscibility.

Effect of temperature

1. Room temperature

It has been observed that around room temperature, phenol will dissolve in a lot of water giving us the upper layer and water will dissolve in a lot of phenol giving us the lower layer.

2. At 25 ⁰C

At 25 ⁰C the upper layer is 5% solution of phenol in water and the lower layer is 30% water in phenol. These two solutions are conjugate solutions to each other. The lower layer has a greater density due to greater percentage of phenol. Water acts as a solute in the lower layer while phenol is a solute in the upper layer.

3. Increase of temperature

When the temperature of water-phenol system is increased the compositions of both layers change. Water starts travelling from upper to the lower layer and phenol travels from lower to the upper layer.

4. At 65.9 ⁰C

When the temperature of this system approaches 65.9 ⁰C, a homogeneous mixture of two components is obtained. This homogeneous mixture contains 34% phenol and 66% water. The temperature of 65.9 ⁰C at which two conjugate solutions merge into one another, is called critical solution temperature or upper consulate temperature.

Partially miscible pairs of liquids

Some other partially miscible pairs of liquids have their own consulate temperatures with definite compositions. For example, water-aniline system has a single layer at 167.00 ⁰C with 15% water. Methanol-cyclohexane system has consulate temperature of 49.10 ⁰C with 29% methanol.

Raoult's Law

Statement 1

The vapour pressure of a solvent above a solution is equal to the product of the vapour pressure of pure solvent and the mole fraction of solvent in solution.

Mathematical expression

$$p = p^\circ x_1$$

..eq (1)

p =vapour pressure of solvent in the solution
p°=vapour pressure of pure solvent
x_1 =mole fraction of solvent

$$X_1 + X_2 = 1$$

(x_2 is the mole fraction of solute)

Putting the value of x_1 in eq (1)

$$X_1 = 1 - X_2$$

$$p = p^\circ(1 - X_2)$$

$$p = p^\circ - p^\circ X_2$$

$$p^\circ - p = p^\circ X_2$$

$$\Delta p = p^\circ X_2$$

…eq (2)

Statement 2

The lowering of vapour pressure is directly proportional to the mole of fraction of solute.

$$\frac{\Delta p}{p^\circ} = X_2$$

…eq (3)

$\Delta p/p^\circ$ =relative lowering of vapour pressure

Δp =actual lowering of vapour pressure

Statement 3

The relative lowering of vapour pressure is equal to the mole fraction of solute.

Factors affecting relative lowering of vapour pressure

(i) Is independent of the temperature

(ii) Depends upon the concentration of solute.

(iii) Is constant when equimolecular proportions of different solutes are dissolved in the same mass of same solvent.

Raoult's Law (when both components are volatile)

Raoult's law can be applied to understand the relationship between mole fractions of two volatile components and their vapour pressures before making the solution and after making the solution.

Explanation

Consider two liquids 'A' and 'B' with vapour pressures p°_A and p°_B in the pure state at a given temperature. After making the solution, the vapour pressures of both liquids are changed. Let the vapour pressures of these liquids in solution state be p_A and p_B with their mole fractions x_A and x_B, respectively. The liquid A is low boiling and B is high boiling.

Application of Raoult's law

$$p_A = p^\circ_A x_A$$

$$p_B = p^\circ_B x_B$$

$$P_t = p_A + p_B = p^\circ_A x_A + p^\circ_B x_B$$

P_t= total vapour pressure

$$x_A + x_B = 1$$

$$x_B = 1 - x_A$$

$$P_t = p_A^\circ x_A + p_B^\circ(1 - x_A)$$

$$P_t = p_A^\circ x_A + p_B^\circ - p_B^\circ x_A$$

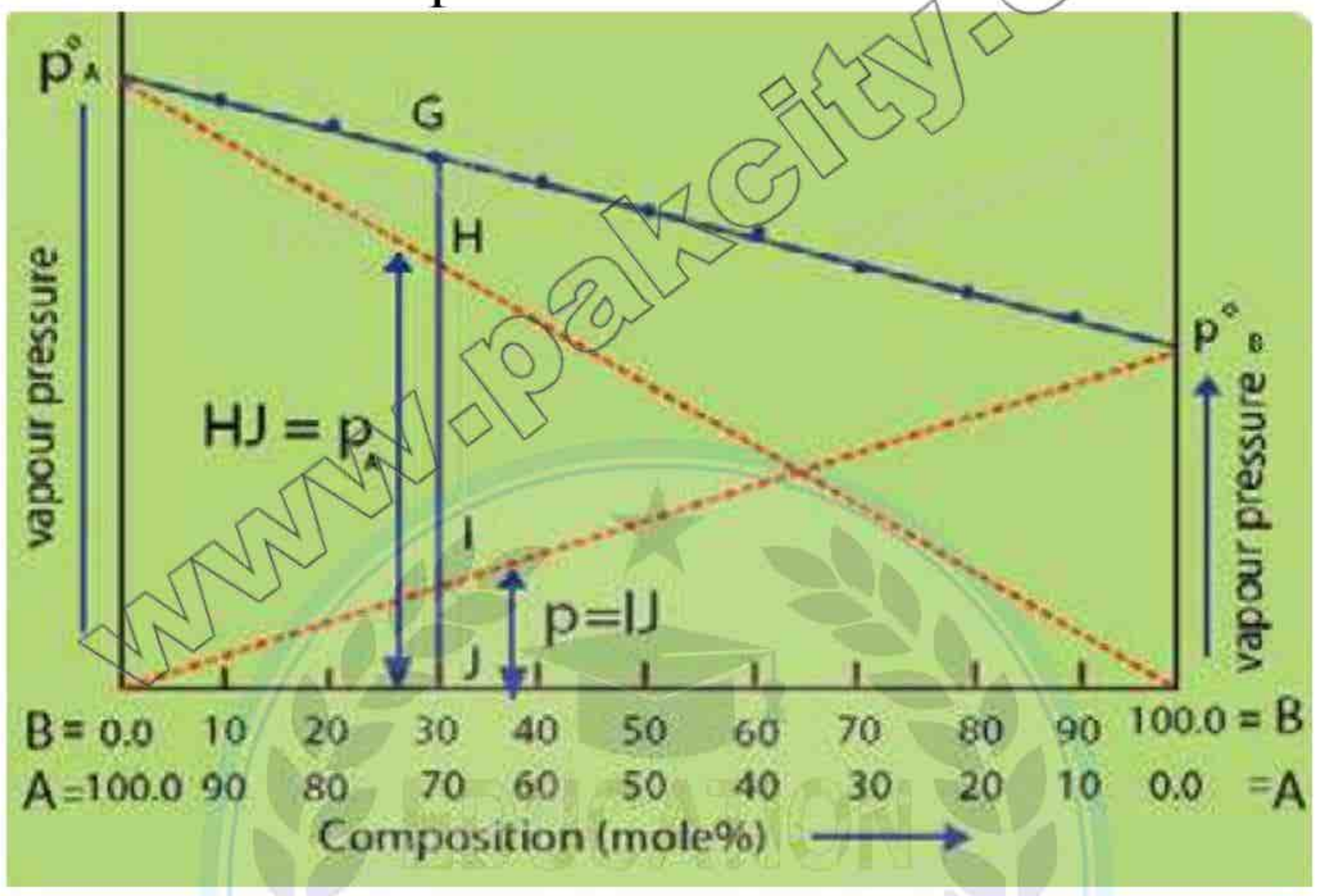
$$P_t = (p_A^\circ - p_B^\circ)x_A + p_B^\circ \qquad \text{…eq (4)}$$

Eq (4) is a straight line equation.

Plotting of graph

If a graph is plotted between x_B or mole % of B on x-axis and P_t on y-axis, a straight line will be obtained. Only those pairs of liquids give straight lines which form ideal solutions.

- Solutions of two components A and B which are ideal have their vapour pressures on the straight line connecting p°_A with p°_B.
- Each point on this straight line represents the vapour pressure of a solution, at a given temperature, with the corresponding contribution of both the components A and B.
- The two dotted lines represent the partial pressures of the individual components of solution. They show the increase of vapour pressure of a component with increase in its mole fraction in solution.

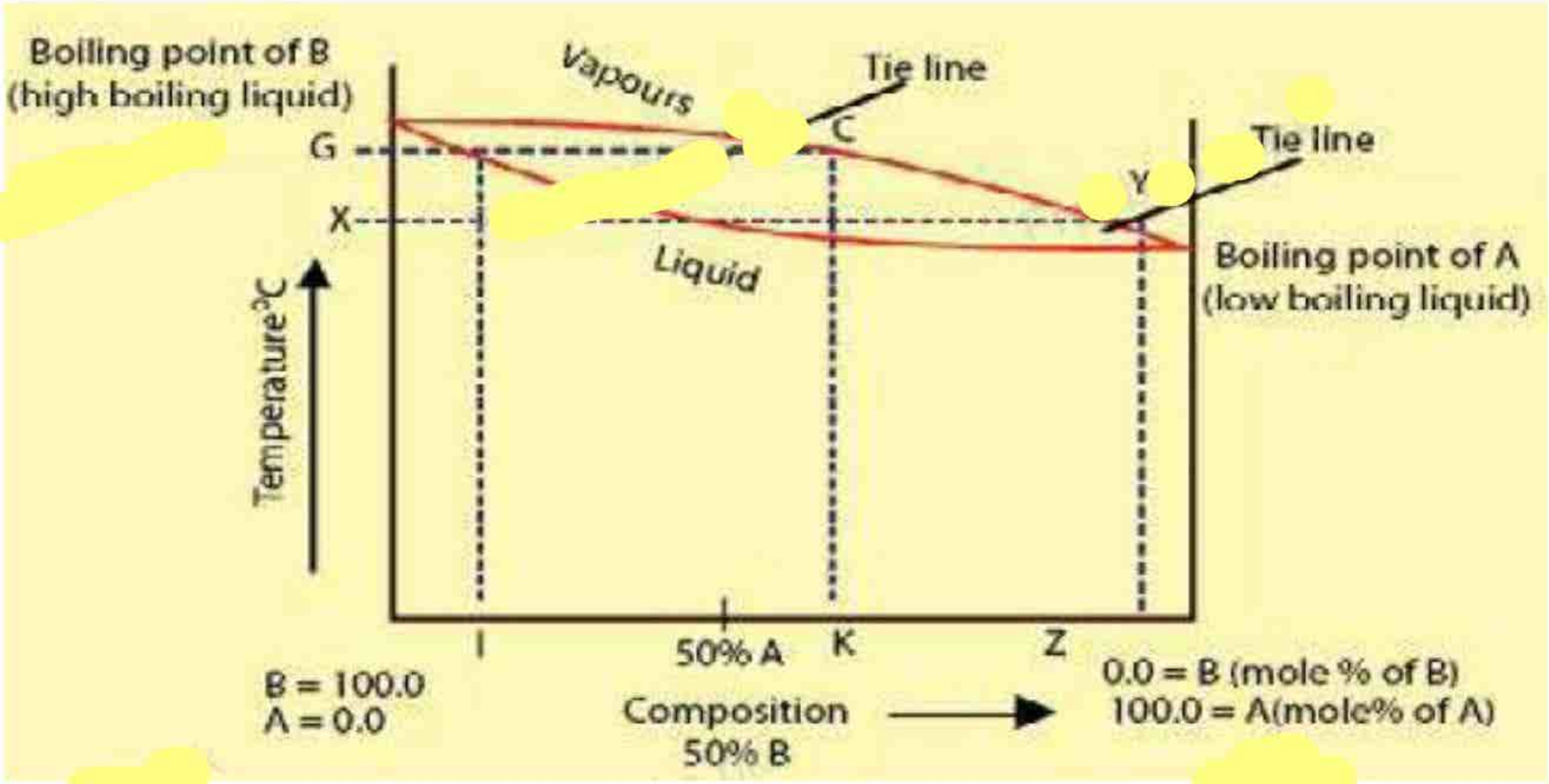


Explanation of graph

1. Consider a point G on the straight line.
2. This point represents the vapour pressure of solution with 30% moles contribution of the component B and 70% of component A.
3. Since, A is more volatile component, so its contribution towards the vapour pressure of solution is represented by p_A. The contribution of the less volatile component B is represented by p_B.
4. We can calculate the relative contributions of A and B towards the total vapour pressure of solution by taking other points along the line joining p^o_A to p^o_B.
5. The total vapour pressure of the solution (Pt) corresponding to the point G will be equal to the sum of the vapour pressures of the individual components ($p_A + p_B$).

Fractional Distillation of Ideal Mixture of Two Liquids

Let us have two liquids A and B which form a completely miscible solution. A is more volatile component so its boiling point is less than B. If we have various solutions of these two components and a graph is plotted between compositions on x-axis and temperature on y-axis, then two curves are obtained.



Explanation of graph

- The upper curve represents the composition of the vapours of different solutions while the lower curve represents the composition of the liquid mixtures.
  Reason
  At any temperature the composition of vapours is different from the composition of liquid mixture.
- The point G is the boiling point of solution corresponding to composition I. It meets liquid curve at point H and the vapour curve at point C.
- The composition of liquid mixture corresponding to point H is shown by point I. At point I the mixture has greater percentage of B and less percentage of A. At the same temperature the vapours of the mixture have the composition K.
- At point K, the percentage of A is comparatively greater than B when we compare it with composition of liquid mixture corresponding to point I. Because A is a low boiling liquid it is present in the vapour state in greater percentage than at point I.
- If the temperature of the mixture is maintained corresponding to point G the distillate will have greater percentage of A and the residue will have greater percentage of B.
  Reason
  The fraction going to distillate is that which is in vapour state and it has greater % of A.
- The distillate of composition K is again subjected to distillation. Its boiling point is X and at this temperature the distillate of composition Z is obtained.
- This distillate of composition Z is further distilled. The distillate becomes richer in A and residue is more and more rich in B.
- Process of distillation is repeated to get the pure component A.
- We can completely separate the components by fractional distillation.
  Zeotropic mixtures
  Such liquid mixtures, which distil with a change in composition, are called zeotropic mixtures.
  Example
  Methyl alcohol-water solution can be separated into pure components by distillation.

Non-Ideal Solutions (Azeotropic mixtures)

Why solutions deviate from Raoult's law

Solutions show deviations from Raoult's Law due to differences in their molecular structures i.e. size, shape and intermolecular forces. Formation of such solutions is accompanied by changes in volume and enthalpy.

Vapour pressure deviations

The vapour pressure deviations may be positive or negative in such solutions.

Azeotropic mixtures

Azeotropic mixtures are those which boil at constant temperature and distil over without change in composition at any temperature like a pure chemical compound. Such mixtures cannot be regarded as chemical compounds as changing the total pressure along with the boiling point changes their composition.

(a) Positive Deviations

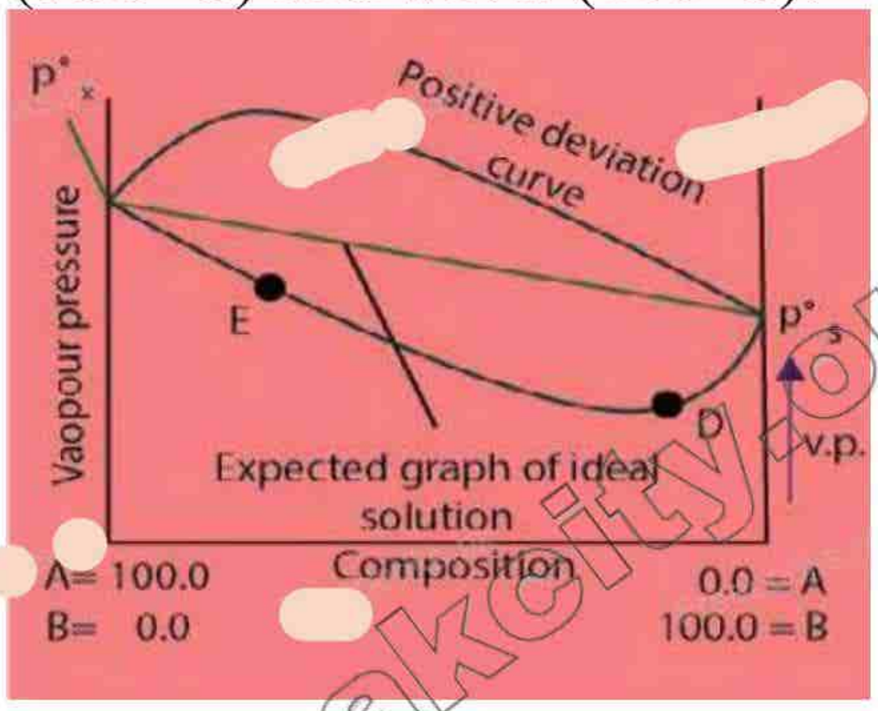
If a graph is plotted between composition and vapour pressure of a solution which shows positive deviation from Raoult's law, the total vapour pressure curve rises to a maximum. The vapour pressure of some of the solutions is above the vapour pressure of either of the pure components.

Example

Let us consider the mixture of A and B components at point C where the mixture has the highest vapour pressure and the lowest boiling point. On distilling this type of solution, the first fraction will be a constant boiling point mixture i.e. azeotropic mixture having a fixed composition corresponding to the maximum point. For this type of solution, it is not possible to bring about complete separation of components by fractional distillation.

Example

Ethanol-water mixture is an example of this type. It boils at 78.1°C with 4.5% water and 95.5 % alcohol. 78.1ºC is lower than the boiling point of ethanol (78.5°C) and water (100°C).



(b) Negative Deviations

For this type of solution, the vapour pressure curve shows a minimum.

Example

Consider a point E. The more volatile component A is in excess. On distilling this solution, the vapours will contain more of A and the remaining mixture becomes richer in less volatile component B. Finally, we reach the point D where vapour pressure is minimum and the boiling point is maximum. At this point, the mixture will distill over unchanged in composition. Therefore, it is not possible to separate this type of solution completely into its components.

Example

Hydrochloric acid solution in water. HCl forms an azeotropic mixture with water, boiling at 110 ºC and containing 20.24% of the acid.

Solubility and Solubility Curves

Solubility

Definition

The solubility is defined as the concentration of the solute in the solution when it is in equilibrium with the solid substance at a particular temperature.

Example

Saturated solution of NaCl in water at 0°C contains 37.5g of NaCl in l00g of water. The solubility of $CuSO_4$ in water at 0°C is 14.3g/100g, while at 100°C it is 75.4g/100g.

Explanation

Whenever a solute is put in a solvent then the molecules or ions break away from the surface of the solid and pass into the solvent to give a uniform solution. Some of the particles of the solute may come back towards the solid due to collisions. This is called re-crystallization or precipitation.

Dynamic equilibrium

If excess of solid is present in the solution then the rate of dissolution and rate of crystallization become equal. This is a state of dynamic equilibrium.

The concentration of the solute at equilibrium with the solution is constant for a particular solvent and at a fixed temperature. The solution is called saturated solution and the concentration is termed as its solubility.

Solubility Curves

A graphical representation between temperature and solubility of solution is called solubility curves. There are two types of solubility curves.

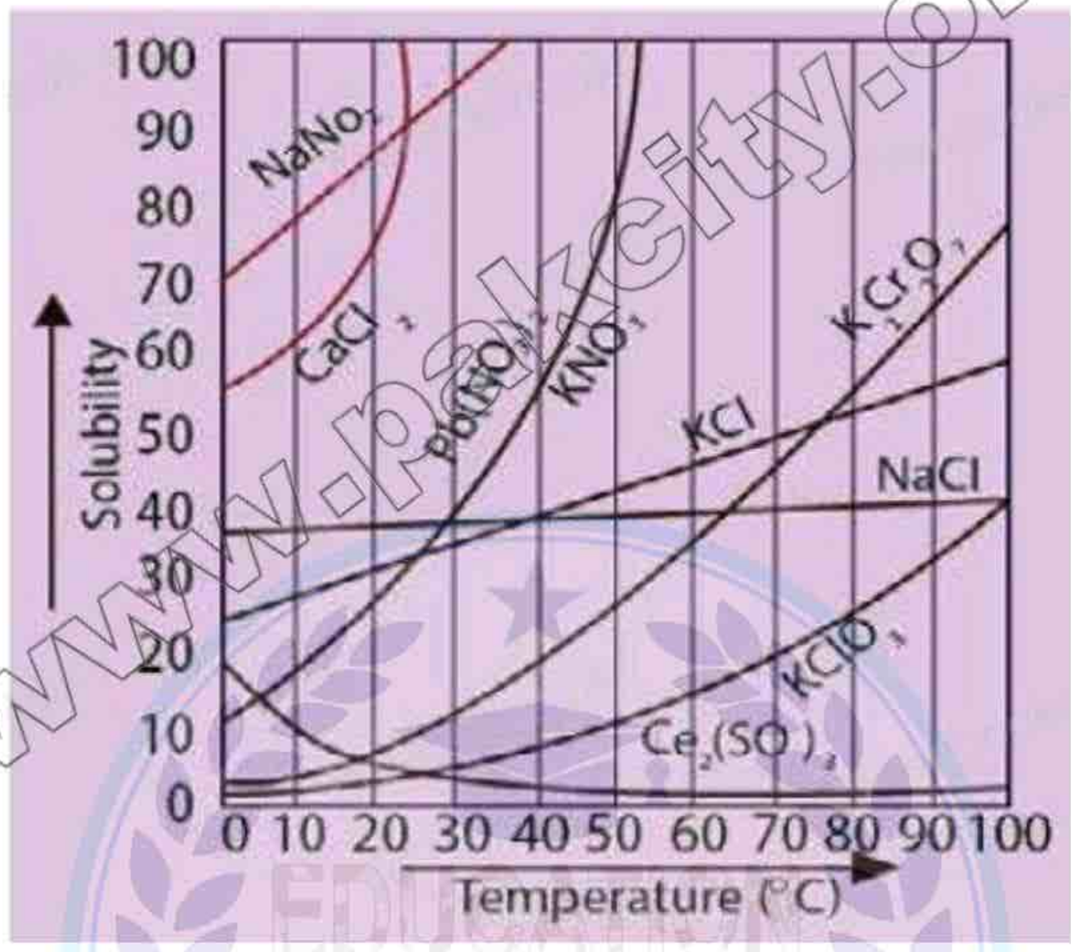
(a) Continuous solubility curves
(b) Discontinuous solubility curves

(a) Continuous Solubility Curves

Continuous solubility curves don't show sharp breaks anywhere.

Examples

- $KCIO_3$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $CaCI_2$ are showing continuous solubility curves.
- The solubility curves of KCl, NaCl and $NaNO_3$ give the straight lines.
- NaCl shows a very small change of solubility from 0°C to 100°C increase of temperature.
- $Ce_2(SO_4)_3$ shows the exceptional behaviour whose solubility decreases with the increase in temperature and becomes constant from 40°C onwards. It shows continuous solubility curve.



(b) Discontinuous Solubility Curves

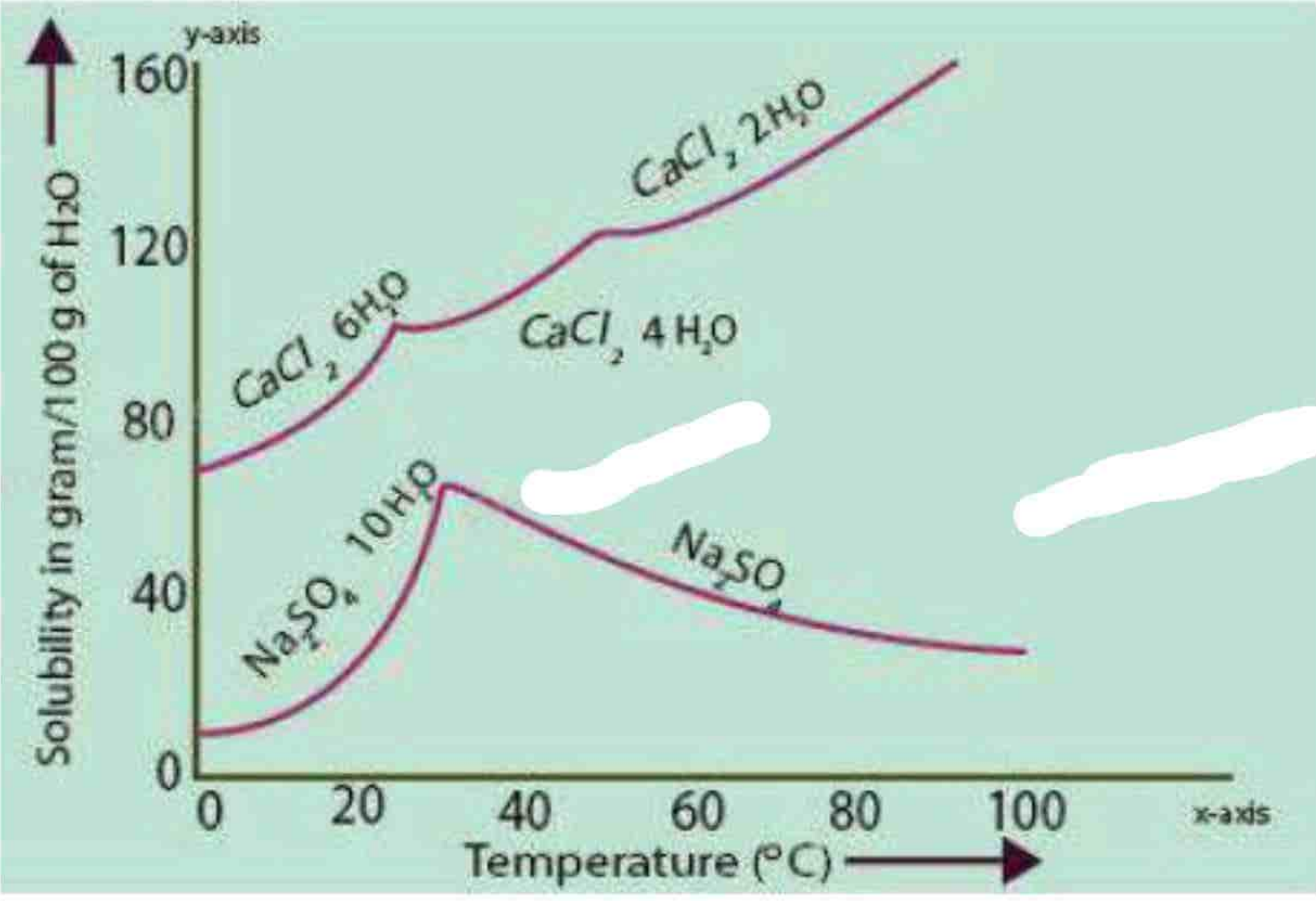
The solubility curves show sudden changes of solubilities and these curves are called discontinuous solubility curves.

Examples

$Na_2SO_4.10\ H_2O$, $CaCl_2.6\ H_2O$.

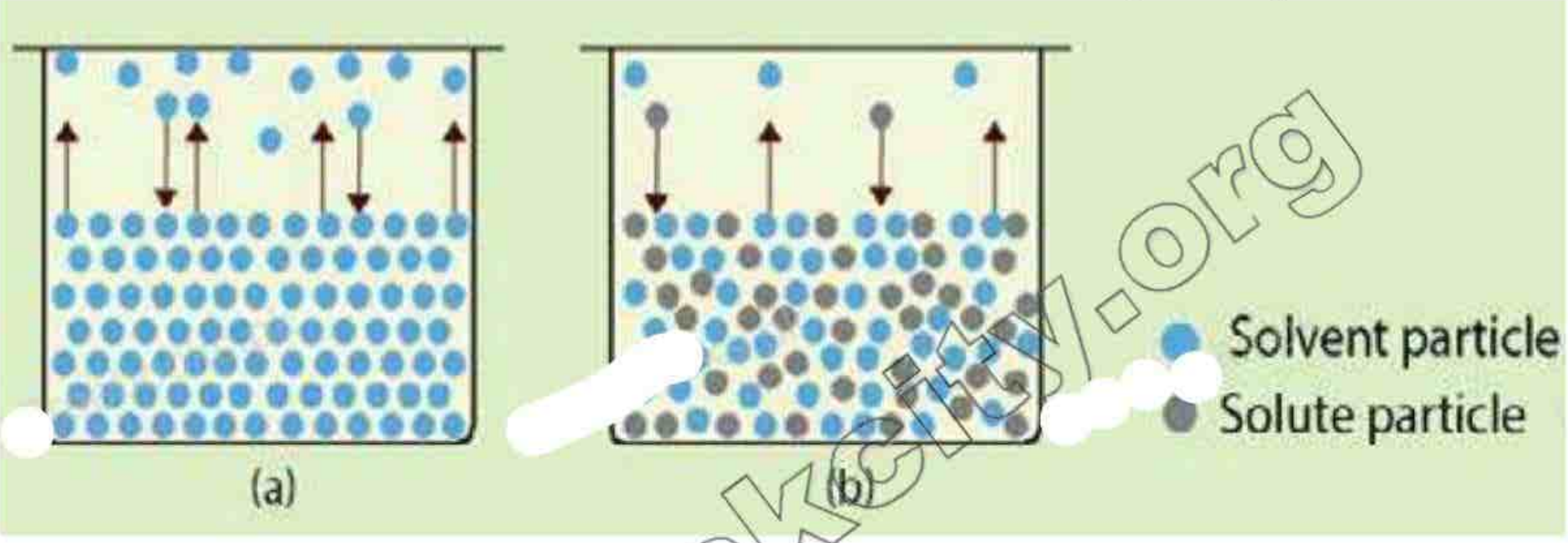
Explanation

These curves are combination of two or more solubility curves. At the break a new solid phase appears and another solubility curve of that new phase begins. It is the number of molecules of water crystallization which changes and hence solubility changes.



Lowering of Vapour Pressure

When the solvent is containing dissolved non-volatile non-electrolyte solute particles, the escaping tendency of solvent particles from the surface of the solution decreases and its vapour pressure is lowered.



Explanation through Raoult's law

A quantitative relationship between the change of vapour pressure of a solvent due to addition of non-volatile and non-electrolyte solute and the mole fraction of solute has been given by Raoult's law.

According to Raoult's law the relative lowering of vapour pressure is equal to the mole fraction of solute.

$$\frac{\Delta p}{p^\circ}=x_2$$

If n_2 and n_1 are the number of moles of a solute and solvent respectively, then

$$x_2=\frac{n_2}{n_1+n_2}$$

$$\frac{\Delta p}{p^\circ}=\frac{n_2}{n_1+n_2}$$

For a dilute solution, n_2 can be ignored in denominator

$$\frac{\Delta p}{p^\circ}=\frac{n_2}{n_1}$$

Calculation of number of moles

If W_1 and W_2 are the masses of solvent and solute while M_1 and M_2 are their relative molecular masses receptively, then

$$n_1 = \frac{W_1}{M_1} \quad \text{and} \quad n_2 = \frac{W_2}{M_2}$$

$$\frac{\Delta p}{p^\circ} = \frac{\frac{W_2}{M_2}}{\frac{W_1}{M_1}}$$

$$\frac{\Delta p}{p^\circ} = \frac{W_2}{M_2} x \frac{M_1}{W_1}$$

…eq (1)

Calculation of Molecular mass of solute

The molecular mass (M_2) of a non-volatile solute can be calculated from the equation (1).

$$M_2 = \frac{p^\circ}{\Delta p} x \frac{W_2 M_1}{W_1}$$

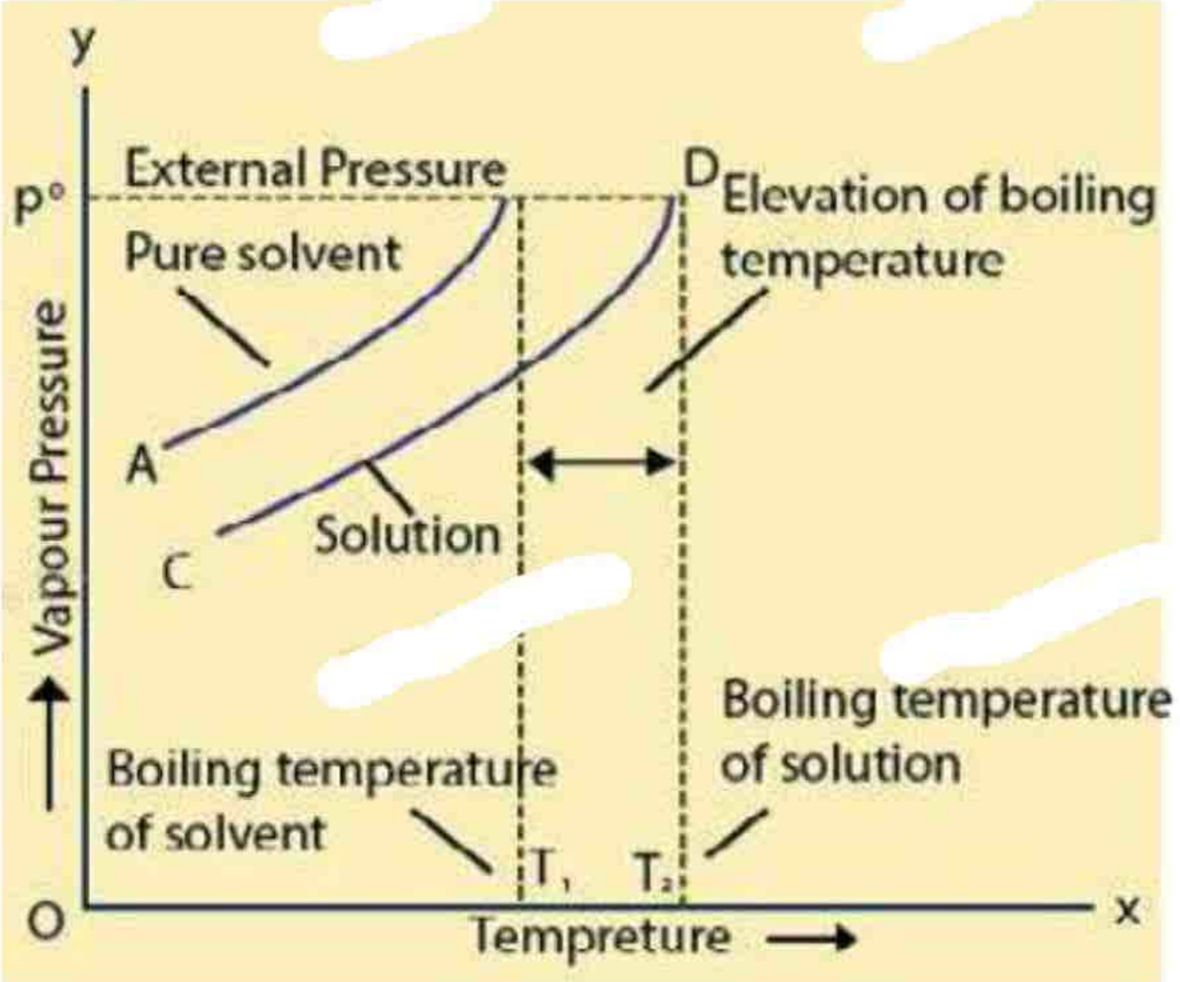
Elevation of Boiling Point

Reason for the elevation of boiling point
The presence of a non-volatile non-electrolyte solute in the solution decreases the vapour pressure of the solvent. Greater the concentration of solute greater will be the lowering of vapour pressure. The temperature at which a solvent in the solution state boils is increased.

Graph for determination of vapour pressure
Plot a graph between temperatures on x-axis and vapour pressures on y-axis.

Curve and slope

- A rising curve is obtained with the increase of temperature.
- The slope of the curve at high temperature is greater which shows that at high temperature the vapour pressure increases more rapidly.
- Temperature T_1 on the curve AB which is for the pure solvent corresponds to the boiling point of the solvent.
- The solvent boils when its vapour pressure becomes equal to the external pressure represented by p°.



Temperature vs vapour pressure

Addition of solute

- When the solute is added in the solvent then a curve CD is obtained.
- This curve is lower than the curve AB because vapour pressures of solution are less than those of pure solvent.
- Solution will boil at higher temperature T_2 to equalize its pressure to p°.
- The difference of two boiling points gives the elevation of the boiling point ΔT_b.

Expression of ΔT_b

Elevation of boiling point ΔT_b is directly proportional to the molality of solution.

$$\Delta T_b = K_b m$$

eq (1)

Where K_b is called the ebullioscopic constant or molal boiling point constant.

According to equation (1), molality of any solute determines the elevation of boiling point of a solvent.

ΔT_b is a colligative property

Dissolve 6 g of urea in 500 g of H_2O or 18 g of glucose in 500 g of H_2O. Both give 0.2 molal solution and both have same elevation of boiling points i.e. 0.1 °C which is 1/5th of 0.52 °C. Therefore, ΔT_b is a colligative property.

$$\text{Molality(m)} = \frac{\text{Mass of solute}}{\text{Molar mass of solute}} \text{x} \frac{1}{\text{Mass of solvent in kg}}$$

$$m = \frac{W_2}{M_2} \quad \frac{1}{W_1/1000} = \frac{1000\ W_2}{M_2 W_1}$$

eq (2)

Putting the value of m from equation (2) into equation (1)

$$\Delta T_b = K_b \frac{1000\ W_2}{M_2 W_1}$$

$$\text{Molecular mass } (M_2) = \frac{K_b}{\Delta T_b} \text{x} \frac{W_2}{W_1} \text{ x } 1000$$

eq (3)

Equation (3) can be used to determine the molar mass of a non -volatile and non-electrolyte solute in a volatile solvent.

Measurement of Boiling Point Elevation: Landsberger's Method

The best method for the determination of boiling point elevation of a solution is Landsberger's method.

Apparatus

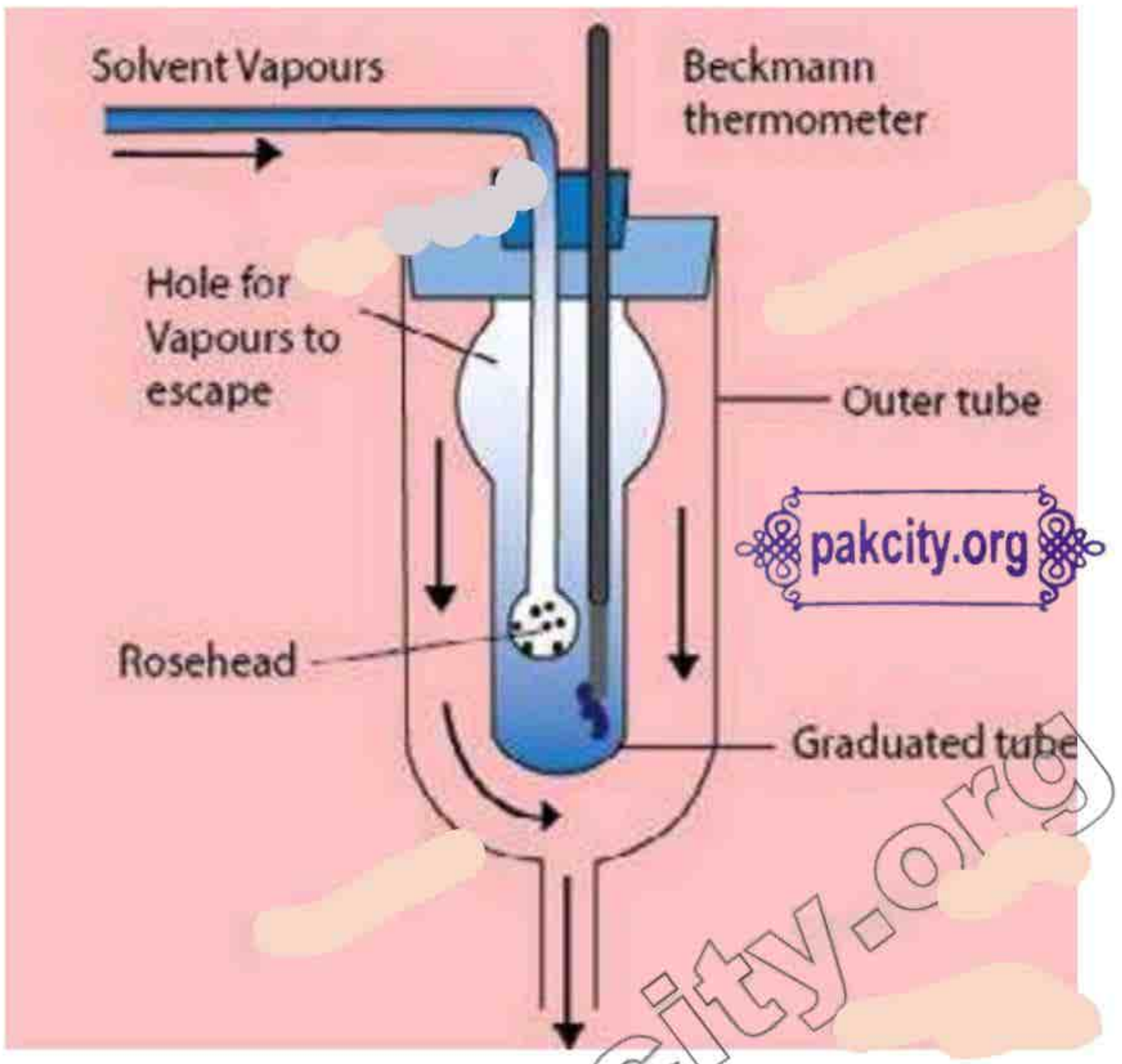
The apparatus consists of four major parts:

(a) An inner tube with a hole in its side. This tube is graduated.

(b) A boiling flask which sends the solvent vapours into the graduated tube through a rosehead.

(c) An outer tube, which receives hot solvent vapours coming from the side hole of the inner tube.

(d) A thermometer which can read up to 0.01K.



Working

1. The solvent is placed in the inner tube.
2. Some solvent is also taken in a separate flask and its vapours are sent into this tube.
3. These vapours cause the solvent in the tube to boil by its latent heat of condensation.
4. This temperature is noted which is the boiling point of the pure solvent.
5. The supply of the vapours is temporarily cut off and a weighed pellet of the solute is dropped in the inner tube.
6. The vapours of the solvent are again passed through it until the solution is boiled.
7. This temperature is again noted.
8. The supply of the solvent vapours is cut off.
9. The thermometer and the rosehead are removed and the volume of the solution is measured. The difference of the two boiling points gives the value of ΔT_b.

Formula Applied

The following formula is used to calculate the molecular mass of solute:

$$M_2 = \frac{K_b}{\Delta T_b} \frac{1000\ W_2}{W_1}$$

Measurement of Freezing Point Depression: Beckmann's Freezing Point Apparatus

An easy method to perform measurement of freezing point depression is Beckmann's freezing point apparatus.

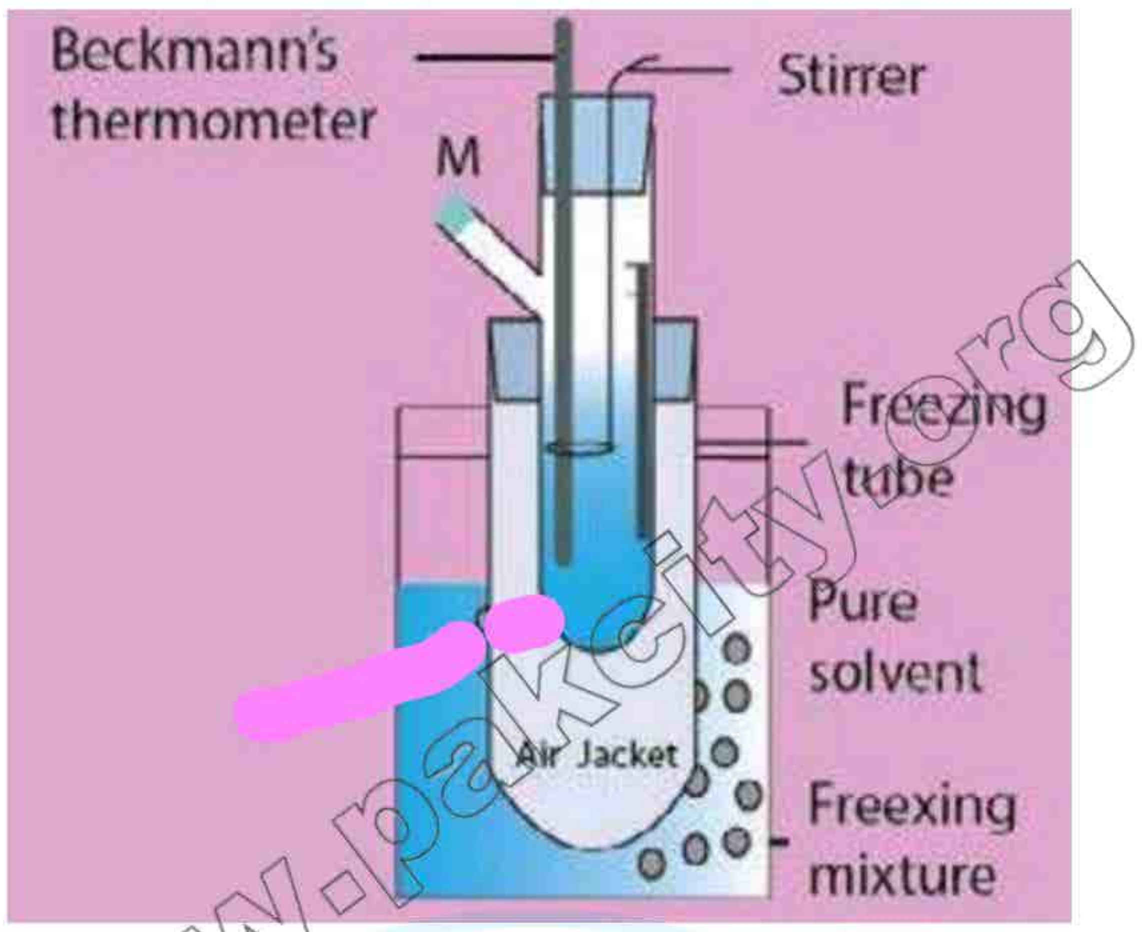
Apparatus

The apparatus consists of three major parts:

a. A freezing tube with a side arm. It contains solvent or solution and is fitted with a stirrer and a Beckmann's thermometer.

b. An outer larger tube into which the freezing tube is adjusted. The air jacket in between these tubes helps to achieve a slower and more uniform rate of cooling.

c. A large jar containing a freezing mixture.



Working

1. Around 20 to 25g of the solvent is taken in the freezing tube.
2. The bulb of the thermometer is immersed in the solvent.
3. Approximate freezing point of the solvent is measured by directly cooling the freezing point tube in the freezing mixture.
4. The freezing tube is then put in the air jacket and cooled slowly. In this way, accurate freezing point of the solvent is determined.
5. The solvent is re-melted by removing the tube from the bath and weighed amount of 0.2 to 0.3 g of the solute is introduced in the side tube.
6. The freezing point of the solution is determined while stirring the solution.
7. The difference of the two freezing points gives the value of ΔT_f

Formula Applied

The following formula is used to calculate the molar mass of solute:

$$M_2 = \frac{K_f}{\Delta T_f} \frac{1000\ W_2}{W_1}$$

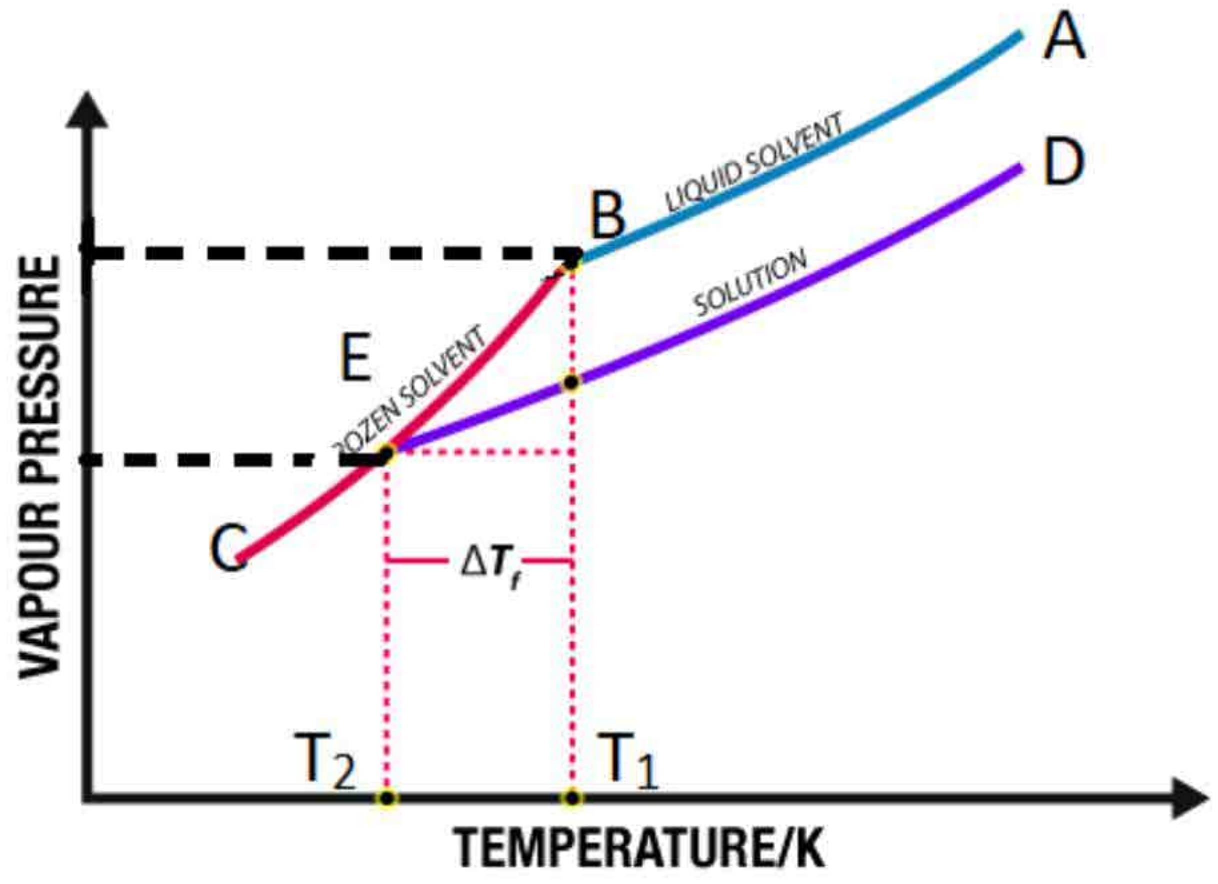
Depression of Freezing Point

Freezing point:

Temperature at which the vapour pressure of liquid becomes equal to vapour pressure of solid is called the freezing point of a substance. In order to determine the molecular mass of solute depression of freezing point is determined.

Freezing point of solvent:

- Take pure solvent.
- Note its vapour pressure change with decrease of temperature till it freezes.
- Plot a graph between temperature (X-axis) and Vapor pressure (Y-axis)
- Curve ABC is obtained.
- AB shows liquid phase and BC the solid phase.
- $T_1$is the freezing point of solvent.



FreezingPoint of solution:

- Now add a pallet of solute in solvent.
- Decrease the temperature till it freezes.
- Note the vapour pressure change with temperature.
- Plot a graph between temperature and vapour pressure.
- Curve DEC is obtained.
- $T_2$is the freezing point of solution
- Depression of freezing point $\Delta T_f = -T_1 - T_2$

Determination of molar mass of solute:

$$\Delta T_f \propto m$$

$$\Delta T_f \propto k_f m \_\_\_ \textbf{(1)}$$

k_f→Cryoscopic constant

m →Molatity

$$\text{Molatity (m)} = \frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in Kg}}$$

$$m = \frac{W_2}{M_2} \times \frac{1}{W_1/1000}$$

$$m = \frac{W_2 \times 1000}{M_2 \quad W_1} \qquad \textbf{(2)}$$

Where W_1→ mass of solvent

W_2→mass of solute

$M_2 \rightarrow$ molar mass of solute

Putting values of m in equation 1

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

$$\Delta T_f \times M_2 \times W_1 = K_f \times W_2 \times 1000$$

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

Numericals

17. (a) Calculate the molarity of glucose solution when 9g of it are dissolved in 250 cm^3 of solution

Data:

Mass of glucose = 9 g

Volume of solution = 250 cm^3

$= \frac{250}{1000} = 0.25\ dm^3$

To Find:

Molarity of glucose = ?

Formula:

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of clute}} \times \frac{1}{\text{vol. of soluton in } dm^3}$$

Calculation and Result:

Molar mass of glucose = 180g/mole

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molar mass of clute}} \times \frac{1}{\text{vol. of soluton in } dm^3}$$

$$= \frac{9}{180} \times \frac{1}{0.25} = 0.2\ M$$

(b) Calculate the mass of urea in 100g of H_2O in 0.3 molal solution

Data:

Mass of water = 100 g

$$= \frac{100}{1000} = 0.1 \text{ kg}$$

Molarity of solution = 0.3 M

To Find:

Mass of urea = ?

Formula:

$$\text{Molality} = \frac{\text{mass of urea}}{\text{molar mass of urea}} \times \frac{1}{\text{mass of solvent in kg}}$$

Calculation and Result:

Molar mass of urea, $(NH_2)_2CO$ = 60 g mol^{-1}

$$= \frac{\text{mass of urea}}{\text{molar mass of urea}} \times \frac{1}{\text{mass of solvent in kg}}$$

Mass of Urea = Molarity × molar mass × mass of solvent in kg

$= 0.3 \times 60 \times 0.1$

= 1.8 g

(c) Calculate the concentration of solution in terms of molality Kg^{-1} which is obtained by mixing 250g of 20% solution NaCl with 200g of 40% solution of NaCl.

Data:

250 of 20% NaCl, 200 g of 40% NaCl solution

To Find:

Concentration of Solution = ?

Formula applied:

$$\text{Molality} = \frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$$

Calculation and Result:

First Solution	Second Solution

250 of 20% NaCl,

Mass of NaCl = $\frac{20}{100} \times 250$

= 50g

200 g of 40% NaCl solution

Mass of NaCl = $\frac{20}{100} \times 200$

= 80 g

Total mass of NaCl in two solution = 50 + 80 = 130 g

Total mass of solution = 250 g + 200 g = 450 g

Mass of solute (NaCl) = 130g

Mass of solvent = 450 – 130 – 320 g

$= \frac{320}{1000} = 0.32$ kg

$$\text{Molality} = \frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$$

$$= \frac{130}{58.5} \times \frac{1}{0.32}$$

= **6.94 mol kg^{-1}**

18. (a) An aqueous solution of sucrose has been labeled as 1 Molar. Find the mole fraction of the solute and solvent.

Data:

Molarity of Sucrose solution = 1M

To Find:

Mole fraction of Solute and Solvent= ?

Calculation and Result:

1 Molar aqueous solution of ($C_{12}H_{22}O_{11}$) means that 1mole sucrose is present in 1000 g of water. Moles of sucrose (solute)

n_2 = 1 moles

Mass of solvent = 1000g

Moles of solvent (H_2O), n_1 = $\frac{1000}{18} = 55.5$ mol

Total moles = 1 + 55.5

= 56.5 moles

Moles fraction of solute, X_2 = $\frac{n_2}{n_1+n_2} = \frac{1}{56.6}$

$X_{sucrose}$ / X_2 = 0.0176

Moles fraction of solvent, $X_1 = \frac{n_1}{n_1+n_2}$

$= \frac{55.5}{56.5}$

$\mathbf{X_{H_2O} / X_2 = 0.98}$

(b) You are provided with 80% H_2SO_4 having density 1.8 g cm^{-3}. How much volume of this H_2SO_4 sample is required to obtain one dm^3 of 20% W/W H_2SO_4 which has a density of 1.25 g cm^{-3}

Data:

Provided solution (80% H_2SO_4 having density 1.8 g cm^{-3})

Density = 1.8 g cm^{-3}

To Find:

Volume of H_2SO_4 sample = ?

Calculation and Result:

It means that 1 cm^3 of H_2SO_4 has mass = 1.8 g

1000 cm^3 of H_2SO_4 has mass = 1.8×1000

= 1800 g

Because acid is 80% so

100 g H_2SO_4 solution has H_2SO_4 = 80 g

1 g H_2SO_4 solution has H_2SO_4 = $\frac{80}{100}$

1800 g H_2SO_4 solution has H2SO4 = $\frac{80}{100} \times 1800$

= 1440 g

Moles of H_2SO_4 = $\frac{\text{mass of } H_2SO_4}{\text{Molar mass}}$

= $\frac{1440}{98}$ = 14.7 M

Required solution (20% H_2SO_4 having density 1.25 g cm^{-3})

Density = 1.25 g/cm^{-3}

1 cm^3 of H_2SO_4 has mass = 1.25 g

1000 of H_2SO_4 has mass = 1.25×1000 = 1250 g

Because acid is 20%, so

100 H_2SO_4 solution contains H_2SO_4 = 20 g

1250 g H_2SO_4 solution contains H_2SO_4 = $\frac{20}{100} \times 1250 = 250$ g

Moles of H_2SO_4 = $\frac{250}{98} = 2.55$ mol

Provided H_2SO_4 = Requirement H_2SO_4

$M_1V_1 = M_2V_2$

$14.7 \times V_1 = 2.55 \times 1000$

$$V_1 = \frac{2.55 \times 1000}{14.7}$$

= 173.47 cm^3 (Requirement volume)

Note: Measure 173.47cm^3 of "provided solution", add water to get 1dm^3 of required solution.

19. 250 cm^3 of 0.2 molar K_2SO_4 solution is mixed with 250 cm^3 of 0.2 molar KCl solution. Calculate the molar concentration of K^+ ions in the solution.

Data:

Volume of K_2SO_4 = 250 cm^3

Molarity of K_2SO_4 = 0.2 M

Volume KCl = 250cm^3

Molarity KCl = 0.2 M

To Find:

Molar Conc. of K^+ ions = ?

Calculation and Result:

K_2SO_4 solution	**KCl solution**
Volume = 250 cm^3	Volume = 250cm^3
Molarity = 0.2 M	Molarity = 0.2 M
$K_2SO_4 \rightarrow 2K^+ + SO^-_4$	$KCl \rightarrow K^+ + Cl^-$
0.2 M 2(0.2) (0.2)	0.2 M 0.2 M

0.4 M	**0.2M**

Total concentration of K^+ ions = $0.4 + 0.2$

= 0.6 M

Total volume of two solutions = $250 + 250 = 500\ cm^3$

$$= \frac{500}{1000} = 0.5\ dm^3$$

$1\ dm^3$ solution contains K^+ ions = 0.6 mol

$0.5\ dm^3$ solution contains K^+ ions = $0.6 \times 0.5 =$ **$0.3\ mol/dm^3$**

20. 5g of NaCl are dissolved in 1000 g of water. The density of resulting solutions is $0.997\ g/cm^3$. Calculate molality, molarity and mole fraction of this solution. Assume that the volume of the solution is equal to that of solvent.

Data:

Mass of NaCl = 5 g

Mass of H_2O = 1000g

Density of solution = $0.987\ g\ cm^{-3}$

Requirement:

Molarity, Molality, Mole fraction of Solution = ?

Calculation and Result:

$$\text{Molality} = \frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{mass of solvent in kg}}$$

$$= \frac{5}{58.5} \times \frac{1}{1} = \mathbf{0.0854\ m}$$

Density of solution = $0.987\ g\ cm^{-3}$

Mass of solution = $5 + 1000 = 1005$ g

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$\text{Volume of solution} = \frac{\text{mass}}{\text{density}} = \frac{1005}{0.987} = 1018.2\ cm^3$$

$= 1.018\ dm^3$

$$\text{Molarity} = \frac{\text{mass of solute}}{\text{molar mass of solute}} \times \frac{1}{\text{volume of solvent in dm}^3}$$

= $\frac{5}{58.5} \times \frac{1}{1.018}$ = **0.084 M**

Mass of NaCl = 5 g

Moles of NaCl = $\frac{5}{58.5}$ = 0.085

Mass of H_2O = 1000g

Mole of H_2O = $\frac{1000}{18}$ = 55.5

X_{NaCl} = $\frac{0.085}{55.5 + 0.085} = \frac{0.085}{55.585}$

= **0.0015**

X_{H2O} = $\frac{55.5}{55.5 + 0.085} = \frac{55.5}{55.585}$

= **0.99**

21. 4.675 of a compound with empirical formula C_3H_8O were dissolved in 212.5 g of pure benzene. The freezing point of solution was found 1.02°C less than that of pure benzene. The molar freezing point constant of benzene is 5.1°C calculate (i) the relative molar mass and (ii) the molecular formula of the compound.

Data:

Mass of solute W_2 = 4.675 g

Mass of solvent W_1 = 212.5 g

Depression in freezing point ΔT_F = 1.02°C

Molal freezing point constant K_f = 5.1°C

To Find:

Molar mass of solute, M_2 = ?

Formula:

$$M_2 = \frac{K_f \times 1000 \times W_2}{\Delta T_1 \times W_1}$$

Calculation and Result:

$$M_2 = \frac{K_f \times 1000 \times W_2}{\Delta T_1 \times W_1}$$

$$= \frac{5.1 \times 1000 \times 4.675}{1.02 \times 212.5} = 110 \text{ g mol}^{-1}$$

Empirical formula of compound = C_3H_3O

Empirical formula mass = $36 + 3 + 16 = 55 \text{ gmol}^{-1}$

Molar mass of compound = 110 gmol^{-1}

$$n = \frac{\text{Molar Mass}}{\text{Empirical formula mass}}$$

$$= \frac{110}{55} = 2$$

Molecular formula = n (empirical formula)

= $2 \times (C_3H_3O)$

= $\mathbf{C_6H_6O_2}$

22. The boiling point of a solution containing 0.2 g of a substance A in 20 g of ether (molar mass = 74) is 0.17 K higher than that of pure ether. Calculate the molar mass of A. Molal boiling point constant of ether is 2.16 K.

Data:

Mass of solute (W_2) = 0.2 g

Mass of solvent (W_1) = 20 g

Elevation of boiling point (ΔT_b) = 0.17 K

Molal boiling point constant (K_b) = 2.16 K

To Find:

Molar mass of solute (M_2) = ?

Formula:

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{1000\, W_2}{W_1}$$

Calculation and Result:

$$M_2 = \frac{K_b}{\Delta T_b} \times \frac{1000\, W_2}{W_1}$$

$$= \frac{2.16 \times 1000 \times 0.2}{0.17 \times 20}$$

$$= \mathbf{127 \text{ g mol}^{-1}}$$

23. 3g of a non-volatile non-electrolyte solute X are dissolved in 50g of ether (molar mass = 74) at 239 K. The vapour pressure of ether falls from 442 torr to 426 torr under these conditions. Calculate the molar mass of solute X.

Data:

Mass of solute = W_2 = 3g

Mass of solvent = W_1 = 50 g

Molar mass of solvent = M_1 = 74 g mol^{-1}

Pressure of pure solvent = P^o = 442 torr

Pressure of solution = P = 426 torr

To Find:

Molar mass of solute X = ?

Formula:

$$M_2 = \frac{W_2 M_1 P^o}{\Delta P W_1}$$

Calculation and Result:

Change in pressure

$$\Delta P = P^o - P$$

$$= 442 - 426$$

$$= 16 \text{ torr}$$

$$M_2 = \frac{W_2 M_1 P^o}{\Delta P W_1}$$

$$= \frac{3 \times 74 \times 442}{16 \times 50}$$

$$= \frac{98124}{800}$$

$$= \mathbf{122.6\ g\ mol^{-1}}$$

Important long questions from past papers

23. Define Solubility curves. Explain continuous and discontinuous solubility curves.
24. Give graphical explanation of boiling point elevation of solution.
25. What are Colligative properties of solutions? Explain elevation of boiling point.
26. State and explain Raoult’s law in three forms.
27. What are ideal solutions? Explain the fractional distillation of ideal mixture of two liquids.
28. Differentiate between ideal and non-ideal solutions.
29. Describe freezing point depression method to determine the molecular mass of an organic compound.

30. Describe one method to determine the boiling elevation of a solution.
31. The boiling point of water is 99.725 ºC. To a sample of 600g of water are added 24g of solute having molar mass of 58 g.mol^{-1} to form a solution. Calculate the boiling point of solution.
32. The freezing point of pure camphor is 178.4ºC. Find the freezing point of solution containing 2 g of a non-volatile compound having molar mass of 140 gmol^{-} in 40 g of camphor. The molal freezing point constant (K_f) of camphor is 37.7 ºC. Kg^{-1}.mol^{-1}.

Any four definitions from chapter may come as long question.