SOLUTIONS

Topic-2

RAOULT'S LAW, APPLICATIONS AND NUMERICALS

VERY SHORT ANSWER QUESTIONS

1. Define vapour pressure?

Ans: When a liquid is in equilibrium with its own vapour the pressure exerted by the vapour on the surface of the liquid is known as the vapour pressure of the liquid.

2. Stat Raoult's Law?

Ans: For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B}$$

Simplified (or) reduced form of Raoult's law:

3. What prediction can you make for relation between vapour pressure and temperature?

Ans: The vapour pressure of the liquid is directly proportional to the temperature of the liquid. The vapour pressure of a liquid is independent of shape of the vessel. Vapour pressure of liquid increases exponentially with increase in temperature.

4. Solutions A, B, C, D have vapour pressures 30mm, 40mm, 60mm, and 80mm of Hg at 25ºC respectively. Which is the most volatile and why?

Ans: D is the most volatile because of high vapour pressure. This is due the effect of non-volatile on the vapour pressure of the the liquid.

5. What is boiling point of liquid? How it is effected by external pressure?

Ans: The temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure is known as the boiling point of the liquid. Boiling point of a liquid can be changed by changing the external pressure. If external pressure is increased, the boiling point of a liquid is increased and vice-versa.

6. Write any two limitations of Raoult's Law?

Ans: Raoult's Law is applicable to;

1. Dilute solutions only

2. The solute must be non-volatile.
3. Solutes which does not undergo in its molecular weight.
4. to ideal solutions.

7. What is an ideal solution?

Ans: The solutions which obey Raoult's law at all concentrations of temperatures are called ideal solutions. In case of ideal solutions, $\Delta V_{mixing} = 0$ and $\Delta H_{mixing} = 0$.

8. What happens to the magnitude of the boiling point of a solvent if a non-volatile solute is dissolved in it?

Ans: The vapour pressure of solution is less than that of the solvent. Therefore the Temperature required to raise the vapour pressure of the solution to the atmospheric pressure is greater than the temperature required to raise the vapour pressure of the solvent to the value equal to the atmospheric pressure. Hence, the boiling point of solution will be greater than that of the solvent.

SHORT ANSWER QUESTIONS

1. What is vapour pressure? How does it vary with temperature?

Ans: When a liquid is in equilibrium with its own vapour the pressure exerted by the vapour on the surface of the liquid is known as the vapour pressure of the liquid.

The vapour pressure of the liquid must be called as saturated vapour pressure, because actually the atmosphere over the liquid, which is saturated with the vapour of the liquid, exerts the pressure on the liquid. The vapour pressure of the liquid is represented by P.

The vapour pressure of the liquid is directly proportional to the temperature of the liquid. Vapour pressure of liquid increases exponentially with increase in temperature.

Log P Vs $\frac{1}{T}$ gives a straight line with – ve slope.

2. State and explain Raoult's law?

Raoult's law: For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B}$$

Simplified (or) reduced form of Raoult's law:

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A}$$ (for dilute solutions, n_B is very small and it can be neglected)

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W}$$

Where,

$P°$= Vapour pressure of pure solvent

P_s= Vapour pressure of solution

X_B = mole fraction of solute
m = molecular weight of solute
M = molecular weight of solvent
w = weight of solute W = weight of solvent

3. What is the relation between the vapour pressure and its boiling point?
Ans: The vapour pressure of a liquid increases with increase in temperature. This goes on until the critical temperature of the liquid is reached. Above the critical temperature liquid state does not exist when the vapour pressure of the liquid becomes equal to the external (atmospheric) pressure the liquid is said to be boiling and the temperature at which this happens is known as **boiling point**.

Water boiling point is 100ºC at 1 atm. Pressure. If the external pressure is reduced, the liquid boils at lower temperature. The boiling point of liquid can be increased by increasing the external pressure.

4. What is the role of non-volatile solute in lowering of vapour pressure of solvent?
Ans: When a non-volatile solute is added to a solvent, the vapour pressure is lowered due to the following reasons:

- Percentage surface area occupied by the solvent decreases. Thus the rate of evaporation and vapour pressure decreases. The solute molecules occupy the surface, and so the per cent surface area occupied by the solvent decreases.
- According to Graham's law of evaporation,

Rate of evaporation $\propto 1/\sqrt{\text{density}}$

When a non-volatile solute is dissolved in a liquid, its density increases. Thus both rate of evaporation and vapour pressure are lowered.

5. What is relative lowering of vapour pressure? How is it useful in determining the molecular weight of a solute?

Ans: When a non-volatile solute is dissolved in a liquid, its density increases. Thus both rate of evaporation and vapour pressure are lowered.

If p_0 is the vapour pressure of pure solvent and **ps** is the vapour pressure of the solution,

The difference **$(p_0 - p_s)$** is termed lowering in vapour pressure, and the ratio **$[p_0 - p_s/p_0]$** is termed relative lowering in vapour pressure.

Raoult, established a relationship between relative lowering in vapour pressure and composition of the solution after a series of experiments in various solvents. Using this relationship one can determine the molecular weight of solute by using this following equation.

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W}$$

Where,

$P°$= Vapour pressure of pure solvent

P_s= Vapour pressure of solution

X_B = mole fraction of solute

m = molecular weight of solute

M = molecular weight of solvent

w = weight of solute W = weight of solvent

LONG ANSWER QUESTIONS

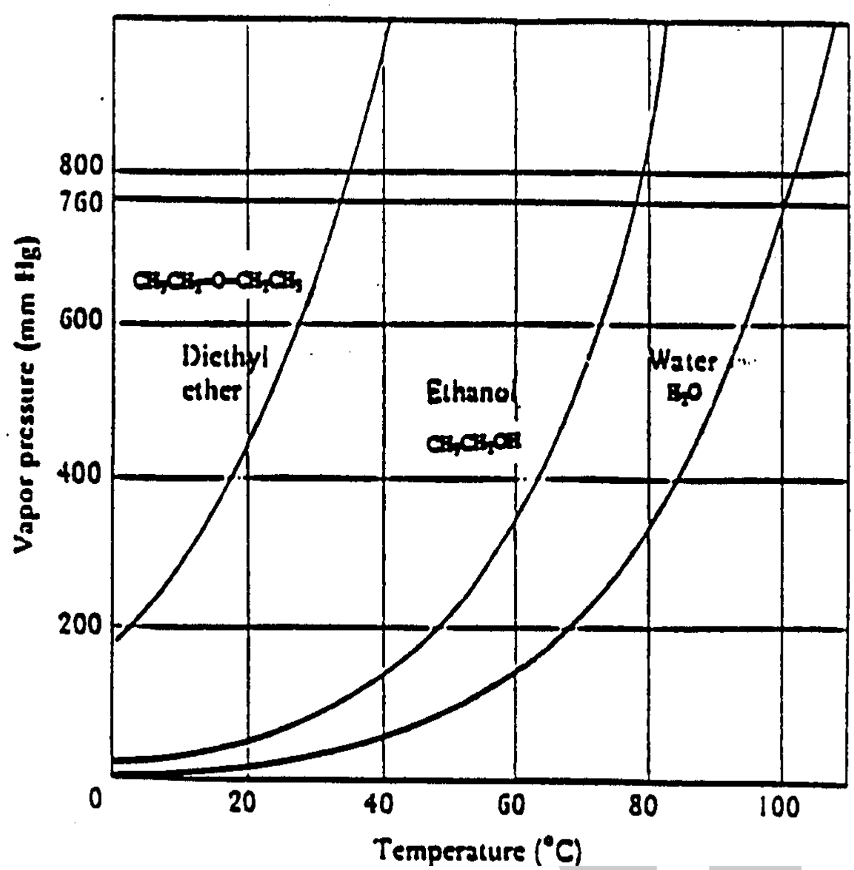
1. **What do you mean by vapour pressure of a liquid? Describe the vapoiurisation and condensation process in a closed vessel. How does vapour pressure change with pressure?**

Ans: The pressure exerted by the vapour of a liquid when it is in equilbrium with liquid is called vapour pressure.

The process of transformation of liquid into vapour is called evaporation and the process of transformation of vapour into liquic is called condensation. In a lquid present in closed vessel rate of evaporation is equal to rate of condensation. This stage is called equilibrium stage and the equilibrium is called dynamic equilibrium.

Effect of temperature: As you know, liquids will evaporate. The rate and extent to which it evaporates depends on the temperature. With rise in temperature of a liquid the average kinetic energy of liquid molecules increases. This increase in kinetic energy overcomes the attractive forces between molecules and hence molecules escape more rapidly into air. Thus the vapour pressure of a liquid increases with increase in temperature. The increase in vpour pressure of a liquid with rise in temperature in non linear but it is exponential.

The amount of evaporation increases when the temperature increases. When the temperature is such that the vapor pressure is just as high as the atmospheric pressure, the liquid boils. That temperature is called the boiling point.



2. Define and explain Raoult's law. How is it useful in determining molecular weight of a non-volatile solute?

Ans: Raoult's law:

For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

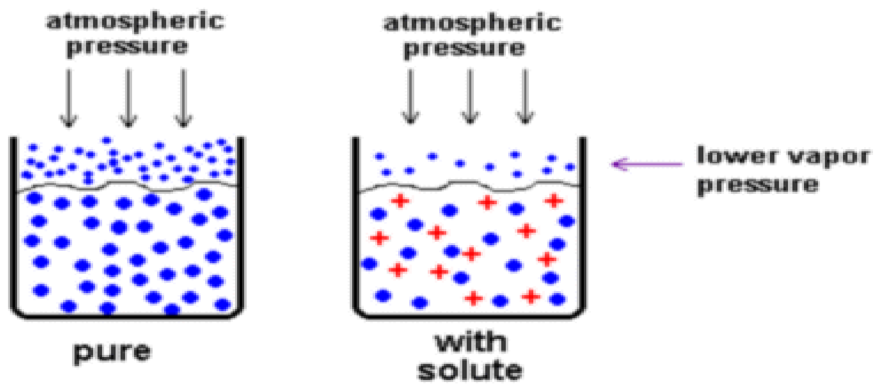
$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B} \quad \text{-------------------(1)}$$

Simplified (or) reduced form of Raoult's law is given by;

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A}$$ (for dilute solutions, n_B is very small and it can be neglected)

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W} \quad \text{-----------------------(2)}$$



From equation (2) molecular weight of solute (m) can obtained by the following equation.

$$m = \frac{p^{o} . w . M}{(p^{o} - p) W}$$

Where,

P°= Vapour pressure of pure solvent
P_s= Vapour pressure of solution
X_B = mole fraction of solute
m = molecular weight of solute
M = molecular weight of solvent
w = weight of solute W = weight of solvent

Raoult's law is applicable to :

- Ideal solutions
- dilute solutions
- solutions containing non volatile solute
- no change in the interactions before and after mixing of liquid components in case of solution containing miscible liquids.
- Solute which neither dissociates nor associates.

3. Define Raoult's law for lowering of vapour pressure. How is the law useful in determing the molecular weight of solvent when a known non-volatile solute is dissolved?

Ans: Raoult's law:

For a solution containing non volatile solute, the relative lowering of vapour pressure is equal to mole fraction of solute.

$$\frac{P^0 - P_s}{P^0} = X_B$$

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A + n_B} \quad \text{-------------------(1)}$$

Where, n_B and n_A are number of moles of solute and solvent respectively.

Simplified (or) reduced form of equation (1) is given by;

$$\frac{P^0 - P_s}{P^0} = \frac{n_B}{n_A} \text{ --------------------------(2)}$$

(for dilute solutions, n_B is very small and it can be neglected)

Where,

$P°$= Vapour pressure of pure solvent

P_s= Vapour pressure of solution

X_B = mole fraction of solute

We know that

n_B = w/m and

n_A = W/M

where,

m = molecular weight of solute

M = molecular weight of solvent

w = weight of solute

W = weight of solvent

By substituting these values in equqtion(2).

$$\frac{P^0 - P_s}{P^0} = \frac{w}{m} \times \frac{M}{W} \text{ ---------------- (3)}$$

Form the above equation the molecular weight of solvent **(M)** is given by;

$$\mathbf{M = \frac{m \cdot (p^o - p) \cdot W}{p^o \cdot w}}$$

<u>**NUMERICALS**</u>

Example: 1

Calculate the vapour pressure lowering caused by addition of 50 g of sucrose (molecular mass = 342) to 500 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

According to Raoult's law,

$\mathbf{p_0 - p_s/p_0 = n/n+N}$

or $\Delta p = (n/n+N)p_0$

Given n = 50/342 = 0.416, N = 500/18 = 27.78 and p_0 = 23.8

Substituting the values in the above equation,

$\Delta p = (0.146/0.146+27.78) \times 23.8 = 0.124$ mm Hg

Example: 2

The vapour pressure of pure benzene at a certain temperature is 640mm Hg. A non-volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular mass of the solid substance?

Solution: According to Raoult's law.

$$(p_0 - p_s)/p_0 = n/(n+N)$$

Let m be the molecular mass of the solid substance.

n = 2.175/m ; N = 39/78 = 0.5

[Molecular mass of benzene = 78]

Substituting the values in the equation

$$m = \frac{p^o \cdot w \cdot M}{(p^o - p)\, W}$$

$$m = \frac{640 \cdot 2.175 \cdot 78}{(640 - 600)\, 39}$$

m = 65.25

Thus molecular weight of solute is 65.25

Example: 3

A solution containing 30 g of a non-volatile solute in exactly 90 g of water has a vapour pressure of 21.85 mm of Hg at 25°C. Further 18 g of water is then added to the solution; the new vapour pressure becomes 22.15 mm Hg of at 25°C. Calculate (a) molecular mass o the solute and (b) vapour pressure of water at 25°C.

Solution:

Let the vapour pressure of water at 25°C be p_0 and molecular mass of the solute be m.

Using Raoult's law in the following form.

For solution (I), $\mathbf{(p_0 - 21.85)/21.85 = 30 \times 18/90 \times m}$ **…(i)**

For solution (II), $\mathbf{(p_0 - 22.15)/22.15 = 30 \times 18/108 \times m}$ **…(ii)**

Dividing Eq. (i) by Eq. (ii),

$$\mathbf{(p_0 - 21.85)/21.85 \times 22.15/(p_0 - 22.15) = 108/90 = 6/5}$$

Substituting the value of p_0 in Eq. (i) the value of m is given by;

$$\mathbf{M = 67.9}$$

Example:4

What mass of non-volatile solute (urea) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 5%. What will be the molality of solution?

Solution: Using Raoult's law in the following form,

$$\mathbf{p_0 - p_s/p_s = wM/Wm}$$

If $p_0 = 100$ mm, then $p_s = 75$ mm

$$100 - 75/75 = w \times 18/100 \times 60$$

$$w = 111.1$$

$$\text{Molality} = w \times 1000/m \times W = 111.1 \times 1000/60 \times 100 = 18.52 \text{ m}$$