EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [1 of 48]



# CHEMISTRY LECTURE NOTES (2014-15)

**COURSE : VIJETA (JP)** 

(LECTURE No. 1 TO 6)

**TOPIC : SOLUTIONS & COLLIGATIVE PROPERTIES** 

Solution & Colligative Properties #1

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EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [2 of 48] Topics to be covered:

## Lecture # 1

#### Section (A) :

1. General Introduction

#### 2. Types of solutions

- 2.1 Solids solutions (solid solvent)
- 2.2 Liquid solutions (liquid solvent)
  - 2.2.1 Types of liquid-liquid solution (liquid solute-liquid solvent)
    - (a) completely miscible liquids.
    - (b) completely immiscible liquids.
    - (c) partially miscible liquids.
- 2.3 Gaseous solutions (gaseous solvent)

#### Section (B) :

#### 3. Expressing cocentration of solutions

- Various types of concentration terms
- **3.1** Percentage (%) composition

(a) 
$$\frac{w}{w}$$
%, (b)  $\frac{v}{v}$ %, (c)  $\frac{w}{v}$ %

- **3.2** Strength of solution
- 3.3 Molarity
- 3.4 Molality
- 3.5 Normality
- 3.6 Mole fraction
- 3.7 Parts per million

# Lecture # 2

#### Section (C) :

#### 4. Solutions of solids in liquids

- 4.1 Solubility of solids in liquids
- 4.2 Factors affecting the solubility of solids in liquids
  - 4.2.1 Nature of solute
  - 4.2.2 Nature of solvent
  - 4.2.3 Effect of temperature (solubility curves)
  - 4.2.4 Effect of pressure (no effect)

#### 5. Solutions of gases in liquids

- 5.1 Solubility of gases in liquids
- 5.2 Factors affecting the solubility of a gas in liquids
  - 5.2.1 Nature of gas.
  - 5.2.2 Nature of solvent.
  - 5.2.3 Effect of temperature
  - 5.2.4 Effect of pressure (Henry's law)

#### Section (D) : 6. Vapo

#### Vapour pressure of a pure liquid or pure solid

- 6.1 Origin of saturated vapour pressure: Evaporation and condensation
- 6.2 Important points regarding vapour pressure
  - 6.2.1 Definition of vapoure pressure
  - 6.2.2 Factors affecting vapour pressure
  - 6.2.3 Effect of Temperature on vapour pressure (Clausius-clapeyron equation)
  - 6.2.4 Boiling point and Vapour pressure
  - 6.2.5 Vapour pressure does not depend on
    - (i) amount of liquid (ii) surface area of liquid (iii) volume or shape of the container
  - Phase diagram of pure substance and Triple point (For Olympiad, Not for Boards)

## Lecture # 3

7.1

6.3

Vapour pressure of liquid-liquid solutions (volatile solute + volatile solvent)

- 7.1.1 Staement of Raoult's law for volatile solutes.
- 7.1.2 Derivation of total pressure over solution using Raoult's law and Dalton's law

 $y_1 P = x_1 p_1^{o}$ ;  $P_T = x_1 p_1^{o} + x_2 p_2^{o}$ 

Solution & Colligative Properties # 2

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**7.1.3** Determining composition of vapour phase:  $\overline{P}$ 

$$= \frac{1}{P_T} + \frac{y_2}{p_2^0}$$

7.1.4 Graphical representation of Raoult's law

#### Section (E) :

- 7.2 Application of Raoult's law for volatile solute
  - 7.2.1 Phase diagram (Bubble and dew points)
  - 7.2.2 Fractional

#### 7.3 Limitations of Raoult's Law

- 7.3.1 Molecular structure: Ideal & non-ideal solution
- 7.3.2 Positive deviation from Raoult's law.
- 7.3.3 Negative deviation from Raoult's law.

#### 7.4 Azeotropic or constant boiling mixture.

- Azeotropes (Maximum & minimum boiling azeotropic mixture).
- 7.4.2 Explanation of azeotropes with graphs.
- 7.5 Vapour pressure of completely immiscible liquids and steam distillation

#### Lecture # 4

7.4.1

#### Section (F) :

#### 8.1 Introduction to colligative properties.

- 8.1.1 Types of colligative properties.
- 8.1.2 Van't Hoff's factor
  - (a) When electrolyte dissociates.
  - (b) Electrolyte associates.

#### 8.2 Vapour pressure of solutions of solids in liquids and Raoult's law.

- 8.2.1 Relative lowering in vapour pressure.
- 8.2.2 Raoult's law as a special case of Henry's law.
- 8.2.3 Determination of molecular masses of solute from lowering of vapour pressure.
- 8.2.4 Measurement of RLVP (Ostwald-Walker dynamic method).

## Lecture # 5

#### Section (G) :

- 8.3 Elevation of boiling point.
  - 8.3.1 Concept of boiling point.
  - **8.3.2** Expression for the elevation in boiling point.
  - **8.3.3** Determination of molecular mass of solute.
  - 8.3.4 Calculation of molal elevation constant from enthalpy of vaporisation.

#### 8.4 Depression in freezing point.

- 8.4.1 General discussion.
- **8.4.2** Expression for the depression in freezing point.
- 8.4.3 Calculation of molecualr mass of solute.
- 8.4.4 Calculation of molal depression constant from enthalpy of fusion.
- 8.4.5 Application of depression in freezing point.
- 8.4.6 Rast method.

## Lecture # 6

#### Section (H):

- 8.5 Osmotic pressure.
  - **8.5.1** Definition of osmosis.
  - **8.5.2** Osmotic pressure.
  - 8.5.3 Expression for the osmotic pressure.
  - **8.5.4** Experimental measurement of osmotic pressure.
  - **8.5.5** Isotonic solution.
  - 8.5.6 Determination of molecular mass (polymer and colloidal solution).
  - **8.5.7** Explanation of some phenomena (biological) on the basis of osmosis.
  - 8.5.8 Osmotic pressure of mixture of two or more than two solution.

SOLUTION & COLLIGATIVE PROPERTIES #3

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# EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [4 of 48] LECTURE # 1

#### Section : (A)

#### 1. General Introduction :

In normal life we rarely come across pure substances. Most of these are mixtures containing two or more pure substances. Their utility or importance in life depends on their composition. For example, the properties of brass (mixture of copper and zinc) are quite different from those of German silver (mixture of copper, zinc and nickel) or bronze (mixture of copper and tin); 1 part per million (ppm) of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentrations of fluoride ions can be poisonous (for example, sodium fluoride is used in rat poison); intravenous injections are always dissolved in water containing salts at particular ionic concentrations that match with blood plasma concentrations and so on. In this Unit, we will consider mostly liquid solutions and their formation. This will be followed by studying the properties of the solutions, like vapour pressure and colligative properties. We will begin with types of solutions and then various alternatives in which concentrations of a solute can be expressed in liquid solution.

#### 2. Types of solutions :

**Solution** : A solution is a homogeneous mixture of two or more chemically non-reacting substances whose composition can be varied within certain limits.

**Solvent** : A solvent is that component of the solution which is present in the largest amount by mass. A solvent determines the physical state of solution in which it exists.

Solute : One or more components present in the solution other than the solvent are called solutes. Binary solution : A solution containing only one solute dissolved in given solvent is called Binary Solution. Ternary solutions : Those solutions which contain three components are called ternary solutions, ez.g., ethanol + water + acetic acid.

Type of solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

#### Types of Solutions :

#### 2.2.1 Types of liquid-liquid solution (liquid solute-liquid solvent) :

(a) Completely miscible liquids : When both the liquids are polar (e.g., ethyl alcohol and water) or both are non-polar (e.g., benzene and hexane), they mix completely in all proportions to form a homogeneous mixture. They are said to be completely miscible.

(b) Completely immiscible liquids : When one liquid is polar and the other is non polar, e.g., benzene and water or cyclohexane and water etc., they do not mix at all and form separate layers. They are said to be completely immiscible.

(c) Partially miscible liquids : When two liquids are not exactly similar in nature and also not completely dissimilar in nature, e.g., ether and water, they dissolve in each other to a limitied extent only. They are said to be partially miscible. Simillarly, we have phenol and water or nitrobenzene and hexane.

SOLUTION & COLLIGATIVE PROPERTIES # 4

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**EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [5 of 48]** {Though we are defining all the concentration terms once again in first lecture but try and give minimum time in the class on this section and try to move directly to second lecture you should move according to the class requirement}

Section : (B)

#### **Concentration Terms :**

3.1. % Concentration

(a) % w/w =  $\frac{\text{weight of solute (gm)}}{\text{weight of solution (gm)}}$ 

wt of solute/100 gm of solution.
% wt/wt (w/w) does not depends on temp.

Ex.10% w/w urea sol.= 10 gm of urea is present in 100 gm of solution.= 10 gm of urea is present in 90 gm of water.

(b) % wt/vol. (w/v)

% w/v = no. of gm of solute/100 mL of solution

% w/v =  $\frac{\text{gm of solutes}}{\text{vol. of solution in mL}} \times 100$ 

Ex. 10% (w/v) urea solution. = 10 gm of urea is present in 100 mL of solution. But not 10 gm of urea present in 90 ml of water for dilute solution : vol. solution = vol. solvent.

(c) % v/v : If both solute & solvent are liquids = volume in (mL) of solute per 100 mL of soln.

**Ex.** 10% v/v alchol ethanol aq solution = 10 ml of ethanol in 100 ml of sol.  $\neq$  10 ml of C<sub>2</sub>H<sub>5</sub>OH in 90 ml of H<sub>2</sub>O

#### 3.2. Strength of solution in gm/L

wt. of solute (in gms) per litre (1000 mL) of solution.

Ex. 10% (w/v) sucrose soln, then specify its conc. in gm/L 100 mL ....... 10 gm

∴ 1000 mL ...... 
$$\frac{10}{100} \times 1000 = 100$$
 gm/L

Ex. If we have 6% w/w urea soln with density 1.060 gm/mL then calculate its strength in g/L.6 gm in 100 gm solution.

$$6 \text{ gm in } \frac{100}{1.060} \text{ mL}$$

$$\frac{100}{1.060} \text{ mL} \longrightarrow 6 \text{ gm.}$$

$$000 \text{ mL} = \frac{6 \times 1.060 \times 1000}{100} = 10.6 \times 6 = 63.6$$

**3.3.** Molarity (Depends on temp.) = No. of moles of solute per litre of soln.

So<mark>luite mo</mark>les = n Solvent moles = N

$$M = \frac{n}{V(in L)} = \left(\frac{W}{M}\right) \times \frac{1000}{Vin(mL)}$$

no. of moles of solute = molarity x volume ( in L) no. of m. moles of solute = molarity x volume ( in mL) If  $V_1$ mL of  $C_1$ M solution is mixed with  $V_2$  mL of  $C_2$ M solution (same substance or solute)  $\therefore C_f (V_1+V_2) = C_1V_1 + C_2V_2$ 

Solution & Colligative Properties # 5

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$$C_{f} = \left\lfloor \frac{C_{1}V_{1} + C_{2}V_{2}}{V_{1} + V_{2}} \right\rfloor = \frac{\text{Total moles}}{\text{Total volume}}$$

**Ex.** If 20 ml of 0.5 M Na<sub>2</sub>SO<sub>4</sub> is mixed with 50 ml of 0.2 M H<sub>2</sub>SO<sub>4</sub> & 30 ml of 0.4 M Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution calculate. [Na<sup>+</sup>], [H<sup>+</sup>], [SO<sub>4</sub><sup>2–</sup>], [Al<sup>3+</sup>]. Assuming 100% dissociation

 $= \frac{\text{moles}}{\text{volume}} = 10 \text{ m. moles of Na}_2\text{SO}_4$  $\Rightarrow 20 \text{ m. moles of Na}^+$ 

(P) 
$$\therefore$$
 [Na<sup>+</sup>] =  $\frac{20}{100}$  = 0.2 M

(ii)  $[H^+] = ?$ 10 m. moles  $H_2SO_4$ 20 m. moles  $H^+$ 

$$[H^+] = \frac{20}{100} = 0.2 \text{ M}$$

(iii) 
$$SO_4^{2-} = \frac{10+10+36}{100} = \frac{56}{100} = 0.56 \text{ M}$$

(iv) 
$$AI^{3+} = \frac{24}{100} = 0.24 \text{ M}$$

**3.4.** Molality (Does not depends on temp.) = No. of moles of solute per 1 kg(1000 gm). If solvent of w gm of solute (Molar mass = m gm/mole) is dissolved in 'W' of solvent.

molality = 
$$\left(\frac{w}{M}\right) \times \frac{1000}{W(gm)}$$

molality =  $\frac{\text{moles} \times 1000}{\text{solvent W(gm)}}$ 

Derive a relationship between moalaity & molarity of a solution in which w gm of solute of molar mass m gm/mol is dissolved in W gm solvent & density of resulting solution = 'd' gm/ml.

say 1 L solution taken,

mass of 1 lit solution = (1000 d) gm moles of solute = (molarity) mass of solute = (molarity) x m mass of solvent = W = 1000 d - (molarity) x m

(molarity)×1000

$$\therefore$$
 molality = (no. of moles of solte) 1000 d-molarity  $\times$  M.Wt

**Ex.** Calculate molarity of 1.2 M H<sub>2</sub>SO<sub>4</sub> solution if its  $\rho = 1.4$  gm/mL

Molarity =  $\frac{1.2 \times 1000}{1000 \times 1.4 - 1.2 \times 98}$  = 0.865

3.5. Normality

No. of equivalents per litre of solution

volume of solution (inL)
no. of equivalents = normality × volume (in L)

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(Normality = n \times molarity)
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#### 'n' factor

(i) For oxides/reducing agents :

no. of  $e^-$  involved in ox/red half per mole of O.A./Red.

$$5e^{-} + 8H^{+} + MnO_{4}^{-} \rightarrow Mn^{2+} + H_{2}O$$

no. of H<sup>+</sup> ions displaced/ OH<sup>-</sup> ions displaced per mole of acid/ base.

(iii) For salt:

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n = Total charge on cations. or

total charge on anions

Simple salts

3.6. Mole Fraction

$$X_{\text{solute}} = \frac{\text{moles of solute}}{\text{total moles in solutions}} = \frac{n}{n+N}$$
$$X_{\text{solvent}} = \frac{\text{moles of solvent}}{n+N}$$

$$X_{solute} + X_{Solvent} = 1$$

- Ex. If we have 10 molal urea soln calculate
  - (i) Mole faction of urea in this solution & also calculate % w/w of urea.

10 moles urea in 1000 gm of water

$$X_{urea} = \frac{10}{10 + \frac{1000}{18}} = \frac{10}{65.55}$$

% w/w weight of urea = 10 x 60 = 
$$600 = \frac{10 \times 60}{10 \times 60 + 1000}$$
 x

100%

(iii) 
$$\rho = 1.5 \text{ gm/mL}$$
 : molarity = % w/v & strength in gm/L of the solution  
10 moles urea in 1000gm H<sub>2</sub>O = (1000 + 600) gm of solution

$$=\frac{1600}{1.5}$$
 mL of solution

molarity =  $\frac{10 \times 1.5}{1600}$  x 1000 =  $\frac{150}{16}$  = 9.3 M

strength in  $gm/L = (9.3 \times 60) gm/L$ 

% w/v = 
$$\frac{600 \times 1.5}{1600}$$
 x 100% =  $\frac{60 \times 15}{16}$  =  $\frac{225}{4}$  = 56.25%

Note : For dil. aq. solution molality ≈ molarity

molality = 
$$\frac{\text{molarity} \times 1000}{1000 \times d - \text{molarity} \times m} \approx (1 \text{ gm/ml})$$

3.7. ppm (Parts Per Million).

(a) ppm (w/w) = 
$$\frac{\text{wt.of solute (ingm)}}{\text{wt.of solution (ingm)}} \times 10^6 = 1 \text{ million}$$

(b) ppm (w/v) = 
$$\frac{\text{wt.of solute (in gm)}}{\text{vol. of solution (inmL)}} \times 10^6$$

ppm (moles/moles) =  $\frac{\text{moles of solute}}{\text{moles of solution}} \times 10^6$ 

**Ex.** Calculate molarity of  $CaCO_3(aq.)$  soln which has conc of  $CaCO_3 = 200$  ppm.

**Ex.** Molality of urea soln. which has  $X_{urea} = 0.2$ 

n = 0.20.2 moles of urea in 0.8 moles water

$$\Rightarrow \frac{0.2}{0.8 \times 18} \times 1000 = \frac{250}{18} = \frac{125}{9}$$

(c)

SOLUTION & COLLIGATIVE PROPERTIES #7

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# EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [8 of 48] LECTURE # 2

#### Section : (C)

4. Solubility : Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent (generally 100 g of solvent) at a specified temperature to form a saturated solution.

Solubility of one substance into another depends on (i) nature of the solute and solvent. (ii) Temprature (iii) Pressure

#### 4.1 Solubility of a solid in a liquid :

Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say like dissolves like.

**Dissolution :** When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution.

**Crystallisation :** Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation.

A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

Solute + Solvent  $\implies$  Solution

At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution. An unsaturated solution is one in which more solute can be dissolved at the same temperature and pressure is called a saturated solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its solubility. Earlier we have observed that solubility of one substance into

another depends on the nature of the substances. In addition to these variables, two other parameters, i.e., temperature and pressure also control this phenomenon.

**Saturated solution :** A solution in which no more solute can be dissolved at the same temperature is called saturated solution.

Solubility : It is defined as amount of solute dissolved in 100 g of solvent to form saturated solution.

**Unsaturated solution :** It is a solution in which more amount of solute can be dissolved at the same temperature.

**Supersaturated solution :** It is a solution which contains more mass of the dissolved solute than the saturated solution at the same temperature and pressure. It should be prepared in a dust-free vessel and at a higher temperature. It is metastable. Mechanical stress, such as shaking or addition of solute, causes deposition of solute.

#### 4.2 Effect of temperature on solubility of a solid in a liquid

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium

Solution & Colligative Properties #8

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## <u>EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [9 of 48]</u>

## ChemINFO-1.3

Daily Self-Study Dosage for mastering Chemistry

I. Supersaturation, Super cooling and Super Heating

**Special Concentration Units** 

I. Supersaturation, Super cooling and Super Heating

Supersaturation : - Refers to a solution that contains more of the dissolved material than could



be dissolved by the solvent under normal circumstances. It can also refer to a vapour of a compound that has a higher partial pressure than the vapour pressure of that compound. Super saturated solution of water and sugar commonly used to make rock candy as shown in figure.

**Supercooling** :- is also known as undercooling. It is a process of lowering the temperature of a liquid or gas below its freezing point without it becoming a solid. A liquid below its standard freezing point will crystallize in the presence of nucleation around the crystal structure can form creating a solid. In supercooling, creation of a nucleation means the formation of an interface at the boundaries of a new phase. Creation of liquid droplets in saturated vapor is characterized by nucleation. Some plants are able to supercool the fluid in their cells cytosol and vacuole and they survive temperatures down to -40°C.

**Superheating** :- is phenomenon in which a liquid is heated to a temperature higher than its boiling point, without boiling. Superheating is achieved by heating a homogenous substance free of nucleation sites.



For boiling to occur, the vapor pressure must exceed the ambient pressure plus a small amount of of pressure induced by surface tension

Memorize this theory as soon as you get the DPP. Revise it regularly and master this concept by practice.

4.

- 1. Which of the following is correct statement
  - (A) Carbonated water is a supersaturated solution of  $CO_2$  gas in water.
  - (B) In supersaturation the solution contains more than the dissolved material than it could dissolved.
  - (C\*) Both (A) & (B) are correct
  - (D) None of these.
- 2. Which of the following in correct statement.
  - (A\*) Refrigeration is an example of super cooling process in which freezer cools drinks to a super cooled level.
  - (B) Supercooling is process of lowering the temperature of a liquid below its freezing point with becoming a solid.
  - (C) Both (A) & (B) are correct
  - (D) None of these
  - Which of the following is correct option related to superheating
  - (A) Superheating refers to vapour of a compound that has lower partial pressure than the

vapour pressure of the compound.

- (B) Surface tension suppress the superheating due to additional forces of surface tension, that decrease the growth of bubbles.
- (C) Adding sand or gases to the liquid provides nucleation sites which minimize the super heating.
- (D\*) Both B & C are correct
- Which of the following is correctly matched.
  - (A) Supersaturation The vapour of a compound that has higher partial pressure than the vapour pressure of the compound.
  - (B) Super cooling The process of lowering the temperature of liquid or gas below freezing point without it become solid
  - (C) Super heating The process of liquid is heated to temperature higher than its boiling point without boiling
  - (D\*) All are correctly matched

3.

Solution & Colligative Properties #9

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#### EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [10 of 48] represented by equation. Solute + Solvent 🛁 Solution. This, being dynamic equilibrium, must follow Le Chateliers Principle. In general, if in a nearly saturated solution, the dissolution process is endothermic ( $\Delta_{sol}$ H > 0), the solubility should increase with rise in temperature and if it is exothermic ( $\Delta_{sol}$ H > 0) the solubility should decrease. These trends are also observed experimentally. If above process is exothermic i.e. $\Delta H < 0$ , then as T increases, solubility decreases. If above process is endothermic i.e. $\Delta H > 0$ , then as T increases, solubility increases. Graph of solubility of solids in solution vs T 200 180 KNO<sub>2</sub> 160 Solubility (g/100 g of water) 140 120 100 NaNO 80 60 40 NaCI 20 $Ce_2(SO_4)_3$ 100 60 0 20 40 80

#### 4.3 Effect of pressure (no effect)

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

Temperature (°C)

#### 5. Solubility of gases in liquids :

#### 5.1 Factors Affecting Solubility of Gas In Liquid : (i) Nature of gas (ii) Nature of liquid (iil) Temperature (iv) Pressure

#### 5.2 Henry Law (Effect of pressure on solubility of gases in liquids) :

Henry law deal with effect of pressure on the solubility of gas in a liquid.

#### Statement :

Let

or

or

The solubility of a gas in a liquid at a given temperature is directly proportional to the pressure at which it is dissolved.

X = Mole fraction of gas at a given temperature as a measure of its solubility.

p = Partial pressure of gas in equilibrium with the solution.

Then according to Henry's law.

X∞p p∞X

 $p = K_{\mu}X$ 

or  $X = \frac{p}{K_H}$ 

where  $K_{H} =$  Henry law constant.

5.3 Characteristics of Henry law constant ( $K_{\mu}$ ).

(i) unit same as those of pressure torr or bar.

Solution & Colligative Properties #10

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# **EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [11 of 48]** (ii) Different gas have different value of K<sub>H</sub> for the same solvent.

(iii) The  $\mathbf{K}_{\mu}$  value of a gas is different in different solvents and it increase with the increase in temperature.

(iv) Higher the value of  $\mathbf{K}_{H}$  of a gas, lower will be its solubility. Since,  $X = \frac{p}{K_{H}}$ .

Plot of p Vs X is a straight line passing through the origin with slope equal to  $\mathbf{K}_{\mu}$ .



Plot of p Vs X for solution of HCl in cyclohexane.

**Note:** (i) If a mixture of gases is brought in contact with solvent each constituent gas dissolves in proportion to its partial pressure. It means Henry's law applies to each gas independent of the pressure of other gas.

(ii) Henry's law can also be applied by expressing the solubility of the gas in terms of mass per unit volume. Mass of the gas dissolved per unit volume of a solvent at a given temperature is directly proportional to the pressure of a gas in equilibrium with the solution.

 $m \propto p, m = K \times p$ where,

m = mass of gas dissolved in unit volume of solvent.

p = pressure of gas in equilibrium with solution.

Where K is the constant of proportional that depends on nature of gas, temperature & unit of pressure.

Ex. The Henry's law constant for the solubility of N₂ gas in water at 298 K is 1.0 × 10<sup>5</sup> atm. The mole fraction of N, in air is 0.8. The number of moles of N, from air dissolved in 10 moles of water of 298 K and 5 atm pressure is : [JEE - 2009] (B) 4.0 × 10<sup>-5</sup>

(A\*) 4 × 10<sup>-4</sup>

(C) 5.0 × 10<sup>-4</sup> (D) 4.0 × 10<sup>-6</sup>

 $\mathsf{P}_{\mathsf{N}_2} = \mathsf{K}_{\mathsf{H}} \times \mathsf{X}_{\mathsf{N}_2}$ Sol.

 $x_{N_2} = \frac{1}{10^5} \times 0.8 \times 5 = 4 \times 10^{-5}$  per mole

In 10 mole solubility is  $4 \times 10^{-4}$ .

#### 5.4 Effect of temperature :

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's principle. As dissolution of gases in liquids is an exothermic process, the solubility should decrease with increase of temperature.

**Note**: K<sub>4</sub> values for both N<sub>2</sub> and O<sub>2</sub> increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature. It is due to this reason that aquatic spcies are more comfortable in cold wasters rather than warm water.

#### Solubility of gases in solution vs T (P=constant)

SOLUTION & COLLIGATIVE PROPERTIES # 11

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#### 5.5 Application of Henry's law :

Several application in biological and industrial phenomena.

(i) To increase the solubility of  $CO_2$  in soft drinks and soda water the bottle is sealed under high pressure. (ii) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmosphere gases in blood. When the divers come towards surface, the pressure gradually decreased. The release the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

(iii) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

#### 5.6 Limitation of Henry's law :

Henry's law is valid only under following condition.

- (i) The pressure of gas is not too high.
- (ii) The temperature is not too low.
- (iii) The gas should not undergo any chemical reaction with the solvent.
- (iv) The gas should not undergo dissociation in solution.

#### Section : (D)

Solution & Colligative Properties # 12

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## ChemINFO-1.4

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#### I. Henru's Law

(ii) Di

3.

When a gas is dissolved in a solvent the following equilibrium is established.

Gas + Solvent a solution

The relationship between solubility of gas and its pressure is expressed in terms of Henry's law, which states that the amount of gas dissolved in the given amount of a solvent at any temperature is proportional to pressure of the gas above solvent. It may also be stated as, at constant temperature the mole fraction of gas dissolved in a solvent is directly proportional to the partial pressure of gas.

Let x be the mole fraction of a gas dissolved in a definate amount of liquid at temperature T.

If the partial pressure of gas over the solvent p<sub>are</sub> then

$$x \propto P$$
;  $x = K_{H}P$  or  $P = K_{H}'X$ 

 $K_{H}$  = Proportionality constant or Henry constant.

#### Characteristics of Henry law constant (K<sub>µ</sub>)

(i) Unit same as those of pressure (mol/ L atm, L atm/mole)

	Gases	K <sub>H</sub> (mol/l.atm)
fferent gas have different value of K <sub>H</sub>	O <sub>2</sub>	1.3 × 10 <sup>-3</sup>
	N <sub>2</sub>	7 × 10 <sup>-4</sup>
	CO <sub>2</sub>	2.3 × 10 <sup>-2</sup>
	H <sub>2</sub>	8.5 × 10 <sup>-4</sup>



A diet coke shortly after mentos were dropped on it

(iii) The  $K_{\mu}$  values of a gas is different in different solvent and it increase with the increase in temperature.

(iv) Higher the value of K<sub>u</sub> of a gas lower will be its solubility

#### Application of Henry's law

(i) To increase the solubility of  $CO_2$  in soft drinks and soda water the bottle is sealed under high pressure.

(ii) At high altitude the partial pressure of oxygen is less than that at the ground level. This leads to low concentration of oxygen in the blood and tissue of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

Memorize this theory as soon as you get the DPP. Revise it regularly and master this concept by practice.

1. At 298 K and 1 atm pressure solubility of N<sub>2</sub> in water was found to be  $6.8 \times 10^{-4}$  mol/L. If partial pressure of  $N_2$  is 0.78 atm, then what is the concentration of N<sub>2</sub> dissolved in water under atmospheric conditions.

(A) 
$$2.4 \times 10^{-3}$$
 m (B\*)  $5.3 \times 10^{-4}$  m (C)  $9 \times 10^{-4}$  m (D)  $16.5 \times 10^{-4}$  m

Solubility curves of four ionic salts X, Y, Z, W 2. are given below:



In which case the value of  $\Delta H_{sol.} < 0$ (A\*) X (B) Y (C) Z (D) W.

The henry's law constant s for  $H_2 O_2$  and  $CO_2$  in water are 1282 L atm/mol, 769.2 Latm/ mol, 29.41 L atm/ Mol respectively which of these gas has highest concentration in a sample of A Reswite at 25°C when pressure over water is 1 atm.  $(A) H_2$  $(B)O_2$  $(C^*)CO_2$ (D) None of these

4. The Henry's law constant for the solubility of N<sub>2</sub> gas in water at 298 K is 2.0 × 10<sup>5</sup> atm. The mole fraction of N<sub>2</sub> in air is 0.8. The no. of moles of N<sub>2</sub> from air dissolved in 5 moles of water of 298 K and 3 atm pressure is

(A) 
$$2 \times 10^{-5}$$
(B\*)  $6 \times 10^{-5}$ (C)  $9 \times 10^{-4}$ (D)  $9 \times 10^{-5}$ 

Select correct statements : (A\*) Gases which have high value of van der Waals constant 'a' are easily liquefied (B) Easily liquefiable gases are water soluble (C\*) lons forming gases in a solvent are soluble in that solvent

(D) Under same conditions, NH, has low solubility than that of  $CO_2$ .

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5.

I. Henry's Law

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6. Vapour Pressure of a pure liquid or pure solid :

#### 6.1 The origin of saturated vapour pressure: The evaporation of a liquid

Some of the more energetic particles on the surface of the liquid move fast enough to escape from the attractive forces holding the liquid together. They evaporate. The diagram shows a small region of a liquid near its surface.



**Note:** evaporation only takes place on the surface of the liquid. That's quite different from boiling which happens when there is enough energy to disrupt the attractive forces throughout the liquid. That's why, if you look at boiling water, you see bubbles of gas being formed all the way through the liquid. If you look at water which is just evaporating in the sun, you don't see any bubbles. Water molecules are

simply breaking away from the surface layer. Eventually, the water will all evaporate in this way.

#### The evaporation of a liquid in a closed container:

Now imagine what happens if the liquid is in a closed container. Common sense tells that water in a sealed bottle doesn't disappear over time. But, there is still constant evaporation from the surface. Particles continue to break away from the surface of the liquid - but this time they are trapped in the space above the liquid.



As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and be trapped there. This is called as condensation. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it. At equilibrium, rate of evaporation becomes equal to the rate of condensation.



In this equilibrium, there will be a fixed number of the gaseous particles in the space above the liquid. When these particles hit the walls of the container, they exert a pressure. This pressure is called the **saturated vapour pressure** (or just **vapour pressure**) of the liquid.

Suppose, we take 10 gram liquid in a chamber. Initially, there are no molecules in the gaseous phase. Thus,



SOLUTION & COLLIGATIVE PROPERTIES #14

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#### EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [15 of 48] no pressure is exerted on the mercury and the level of mercury in both columns is equal. Suppose, after vapourization of 5 gram of the liquid vapour-liquid equillibrium is established. Now, molecules in the gaseous phase exert pressure on the mercury and level of mercury in the column attached to the chamber decreases. Note: From the figure, we can see that, Vapour Pressure of the liquid = h mm Hg.



Vacuum liquid (5 gm) at equilibrium

(Imagine no liquid molecule exist in vapour phase)

Note: Volatile solids (like lodine) also evaporate and have a vapour pressure at any given tempratre, just like liquids.

#### 6.1 Important Points related to vapour pressure :

Definition of vapour pressure : The partial pressure of vapours in equilibrium with pure solid or pure liquid (1) at a given temperature.

At eq. the rate of evaporation = rate of condensation

e.g. 
$$H_2O(I) = H_2O(g)$$

$$K_p = P_{H_2O,g}^{eq}$$

Hence V.P is equilibrium constant ( $K_p$ ) of the reaction, liquid  $\iff$  vapours.

- (2) Since vapour pressure is an eqlibrium constant. so it's value is dependent only on (a) Nature of liquid. (b) Temperature of the given liquid
- The value of a liquid's vapour pressure depends on the magnitude of the intermolecular forces in the liquid. (3) The smaller the intermolecular fores, higher the vapour pressure becuase loosely held molecules escape more easily into vapour phase.
- At higher temperature, more molecules from the liquid have enough KE to escape from the surface of the (4) liquid. That will increase the saturated vapour pressure.

vapour ∆H is +ve liauid

Vapourization (liquid to vapour) is always endothermic. It needs heat to convert the liquid into the vapour. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means that increasing the temperature increases the amount of vapour present, and so increases the saturated vapour pressure.

The dependence of vapour pressure with temperature is given by Clausius-Clapeyron equation



 $p_2$  = vapour pressure of the liquid at  $T_2$  and  $p_1$  = vapour pressure of the liquid at  $T_1$ .

(5) Vapour pressure of a liquid does not depend on :

(i) On the amount of liquid taken.

- (ii) On surface area of the liquid
- (iii) On volume or shape of the container
- (6) Partial pressure of vapours: If vapours of a liquid are present in a gaseous mixture then,

Pressure of vapours Partial pressure of vapours of the liquid = Total pressure

Saturation: A gas or gaseous mixture is said to be saturated with the vapours of a liquid if the partial pressure of the liquid vapours is equal to its (saturated) vapour pressure.

(7) (a) Saturated (Equillibrium) Vapour pressure of water, at a given temprature, is called aqueous tension.

SOLUTION & COLLIGATIVE PROPERTIES #15

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# **EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [16 of 48]** The value of aqueous tension is different at different temprature.

(b) Relative Humidity (R.H.) =  $\frac{Partial \text{ pressure of water vapour at given temperature}}{Vapour \text{ pressure of water at the same temperature}}$ × 100%

#### (8) Saturated vapour pressure and boiling point:

A liquid boils when its saturated vapour pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapour to form throughout the liquid. If the external pressure is higher than the saturated vapour pressure, these bubbles are prevented from forming, and we just get evaporation at the surface of the liquid.

If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapour pressure becomes equal to 1 atmosphere. This happens with water when the temperature reaches 100°C. But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C.

(a) Boiling point : The boiling point is the temperature at which the vapour pressure of a liquid is equal to the external pressure.

(b) At boiling temperature, vapour pressure of the pure liquid i.e.  $P^{\circ} = P_{ext}$ 

(c) At normal boiling point, vapour pressure of the pure liquid i.e. P° = 1atm

#### (9) Saturated vapour pressure and solids: Sublimation

Solids can also lose particles from their surface to form a vapour, except that in this case we call the effect sublimation rather than evaporation. Sublimation is the direct change from solid to vapour without going through the liquid stage.

The forces of attraction in many solids are too high to allow much loss of particles from the surface. However, there are some solids which easily form vapours.

Naphthalene (used in "moth balls") has quite a strong smell. Molecules must be breaking away from the surface as a vapour, because otherwise we wouldn't be able to smell it.

Solid carbon dioxide never forms a liquid at atmospheric pressure and always converts directly from solid to vapour. That's why it is known as dry ice.

- If partial pressure of vapours of a liquid is increased beyond the saturated (equillibrium) vapour pressure value (10) (P°), its vapours begin to condense till their partial pressure becomes equal to the saturated vapur pressure.
- (11) If the partial pressure of vapour is less than v.p. of liquid, the liquid (if present) will vaporize till (a) its v.p. is attained or

(b) the liquid completely gets vaporized

- (12) If a volatile solid/liquid is brought in contact with a gas (or vaccuum), vapours of that solid/liquid occupy the gas phase till the gas phase becomes saturated with that solid /liquid vapours.
- The vapor pressure of water at 80°C is 355 torr. A 100 ml vessel contained water-saturated oxygen at 80°C, Ex. the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 ml, vessel at the same temperature. What were the partial pressures of oxygen and of water vapor, what was the total pressure in the final equilibrated state ? Neglect the volume of any water which might condense.

#### $P_{O_2}$ = 810mm Hg, $P_{H_2O}$ = 355 mm Hg , $P_{total}$ = 1165 mm Hg Ans.

Sol. In 100 ml vessel which contained water - saturated oxygen, the pressure of O<sub>2</sub> gas = 760 – 355 = 405 torr when the contents of this vessel were pumped into 50 ml vessel, at the same temperature, the pressure of oxygen gets doubled i.e.  $P_{O_2} = 810$  torr.

But pressure of water vapour will remain constant, as some vapour in this 50 ml vessel, gets condensed. So  $P_{H_2O} = 355$  torr & Total pressure = 810 + 355 = 1165 torr.

SOLUTION & COLLIGATIVE PROPERTIES #16

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#### **EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [17 of 48]** 6.2 Phase-Diagram of a Pure substance and Triple point (NOT FOR BOARD, For Olympiad)

(1) Phase: A phase is a part of a system that is homogenous in chemical and physical state throughout and is separated from the other phases by a definite boundary.

Thus, solid, liquid and gaseous forms of a pure substance always constitute different phases since it has different physical states in these three forms. Presence of the different phases can be recognized by a boundary between them. For example, a boundary between solid ice and liquid water or bound ary between two immiscible liquids (oil and water).

(2) Phase diagram of a pure substance:

A phase diagram tells exactly what phases are present at any given temperature and pressure.



#### (3) The critical point: Point C on the diagram

The liquid-vapour equilibrium curve has a top limit that labelled as C in the phase diagram. The temperature and pressure corresponding to this are known as the critical temperature and critical pressure. Above the critical temperature, it is impossible to condense a gas into a liquid just by increasing the

pressure. All you get is a highly compressed gas.

The critical temperature varies from substance to substance and depends on the strength of the attractions between the particles. The stronger the intermolecular attractions, the higher the critical temperature.

#### (4) The triple point: Point T on the diagram

The three equilibrium lines meet at this point. They represent conditions of:

- " solid-liquid equilibrium
- liquid-vapour equilibrium
- " solid-vapour equilibrium

#### (5) The phase diagram for water

...

There is only one difference between this and the phase diagram that we've looked at up to now. The solid-liquid equilibrium line (the melting point line) slopes backwards rather than forwards. In the case of water, the melting point gets lower at higher pressures. Why?



formed occupies a smaller volume.

- " If you have this equilibrium and increase the pressure on it, according to Le Chatelier's Principle the equilibrium will move to reduce the pressure again. That means that it will move to the side with the smaller volume. Liquid water is produced.
- To make the liquid water freeze again at this higher pressure, you will have to reduce the temperature. Higher pressures mean lower melting (freezing) points.
- " Notice that the triple point for water occurs at a very low pressure. Notice also that the critical temperature is 374°C. It would be impossible to convert water from a gas to a liquid by compressing it above this temperature.

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Solution & Colligative Properties #17

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# (6) The phase diagram for carbon dioxide

- The only thing special about this phase diagram is the position of the triple point which is well above atmospheric pressure. It is impossible to get any liquid carbon dioxide at pressures less than 5.11 atmospheres.
- " That means that at 1 atmosphere pressure, carbon dioxide will sublime at a temperature of -78°C.
- " This is the reason that solid carbon dioxide is often known as "dry ice". You can't get liquid carbon dioxide under normal conditions only the solid or the vapour.



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## ChemINFO-1.1

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1. Phase diagram and triple point

I. Phase diagram and triple point

#### Comprehension

A phase is the form of the matter that is homogeneous in chemical and physical composition. Phases are solid liquid and gases. Two immiscible liquids constituent two different phases. Two miscible liquids constituent only one phase. Two differents solids constituent two different phases. Alltropes and polymorphes also consitutent two different phases. For ex. Red phosphorus and White phosphorus are different phases, Diamond and Graphite are different phases.

Phase diagram is the summary of the phases that are present at any given temperature and pressure. The phases will simply be solid, liquid or gas states of a pure substance moving from one phase to another by changing the temperature and pressure.

The three lines which meet at point T on the diagram is called the triple point. At triple point you must have unique combination of temperature and pressure where all three phases are in equilibrium together.

At the top of limit of liquid-vapour equilibrium curve, labelled as C is known as critical point. The temperature and pressure at point C is known as critical temperature and critical pressure. Above the critical temperature it is impossible to condense a gas in liquid just by increasing the pressure. All you get is highly compressed gas.



Memorize this theory as soon as you get the DPP. Revise it regularly and master this concept by practice.

4.

5.

Give the answer of following question by using above phase diagram of CO<sub>2</sub>.

- What kind of phase change will take place if solid S is kept in the open under normal condition? (A\*) Sublimation (B) Melting (C) Evaporation
  - (D) No change
- 2. Under which condition, are all the three phases of the system S in equilibrium? (A) T > 304.2k and P > 72.9 atm
  - (B\*) T = 216 K and P = 5.2 atm
  - (C) T > 304.2 K

1.

- (D) P > 72.9 atm
- 3. Temperature of the system at X<sub>1</sub> is increased at constant pressure to reach X<sub>4</sub>. Which of the following is incorrect about the phases of the system at different state.
  - (A) At  $X_1$  solid phase exists.
  - (B) At X<sub>2</sub> solid liquid equilibrium phase exists
  - $(C^*)$  At X<sub>3</sub> solid-liquid gas equilibrium phase exists.
  - (D) At X<sub>4</sub> vapour phase exists.

- If the pressure is increased, the melting temperature of solid S will
  - (A) Not change (B\*) Increase (C) Decrease (D) Can't say
- What happens to the system at  $X_5$  if pressure is changed slowly keeping temperature constant? (A) At a higher pressure, the system will become liquid
  - (B) At a lower pressure, the system will become liquid.
  - (C\*) The system will be in the same phase
  - (D) None of these

SOLUTION & COLLIGATIVE PROPERTIES #19

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# EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [20 of 48] LECTURE # 3

#### 7. Vapour Pressure of liquid-liquid solution :

SOLUTIONS CONTAINING 2 VOLATILE LIQUIDS: VOLATILE SOLVENT 7.1

7.1.1 Statement of Raoult's law (for volatile lig. mixture): In solution of volatile liguids, the partial vapour pressure of each component is directly proportional to its mole fraction

 $p_{\rm A} \propto x_{\rm A}$ 

 $p_{\Delta} = x_{\Delta} P_{\Delta}^{o}$ 

 $p_A = Partial vapour pressure of component A$ 

- $x_A^{o}$  = Mole fraction of component 'A' in solution.  $P_A^{o}$  = Vapour pressure of pure component 'A' at given temprature
- 7.1.2 Derivation of total pressure over solution using Raoult's law and Dalton's law: Let A, B be to two volatite liquids in a closed container as shown.



$$\mathbf{y}^{\mathsf{A}} \propto \mathbf{X}^{\mathsf{A}}$$

$$A = X_A P_A^o$$

Similarly, for liquid B we have,

$$p_{\rm B} \propto x_{\rm B}$$

p,

$$p_{B} = x_{B}P$$

Total pressure over the solution  $P_{\tau}$ , according to Dalton's law is  $P_{T} = p_{A} + p_{B} = x_{A} P_{A}^{0} + x_{B} P_{B}^{0}$ 

#### 7.1.3 Determinig composition of vapour phase:

Let,  $y_A =$  mole fraction of A in vapour phase above the solution and  $y_{B}$  = mole fraction of B in vapour phase above the solution

Now, we have

Thue

 $p_A = y_A P_T$  .....Daltion's law of partial pressure for a gaseous mixture  $p_A = x_A P_A$  Raoult's law  $p_A = y_A P_A = x_A P_A$ 

Thus, 
$$p_{A} = y_{A}T_{T} = x_{A}T_{A}$$
  
Also,  $p_{B} = y_{B}P_{T} = x_{B}P_{B}^{0}$   
 $x_{A} + x_{B} = 1 = \frac{y_{A}P_{T}}{P_{A}^{0}} + \frac{y_{B}P_{T}}{P_{B}^{0}}$   
Thus,  $\frac{1}{P_{T}} = \frac{y_{A}}{P_{A}^{0}} + \frac{y_{B}}{P_{B}^{0}}$ 

**Graphical Representation :** 7.1.4



Note: if  $P_A^{\circ} > P_B^{\circ}$ , A is more volatile than B. B.P. of A < B.P. of B



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SOLUTION & COLLIGATIVE PROPERTIES # 20

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#### EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [21 of 48] Section : (E)

#### 7.2 Application of Raoult's Law :

#### 7.2.1 Phase Diagrams of Two-Component Ideal Solutions: Bubble And Dew Points

The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This can be easily derived from Raouls's Law.

$$\frac{1}{P_{T}} = \frac{y_{A}}{P_{A}^{0}} + \frac{y_{B}}{P_{B}^{0}} = \frac{y_{A}}{P_{A}^{0}} + \frac{1 - y_{A}}{P_{B}^{0}}$$
$$P_{T} = \frac{P_{A}^{0} P_{B}^{0}}{P_{A}^{0} + (P_{B}^{0} - P_{A}^{0}) y_{A}}$$

From the above equation, the plot of  $P_{\tau}$  with respect to y is a curve instead of a straight line. We can superimpose this curve on the diagram for graphical representation of Raoult's Law to get following phase diagrams.

#### (A) Pressure versus Composition Phase Diagram (At constant T): P vs. x and y

In this kind of phase diagram the temperature has a fixed value. The mole fraction of one component is plotted on the horizontal axis and the pressure is plotted on the vertical axis. If A is more volatile than B, then we get following diagram.



#### Explaination:

(i) On horizontal-axis we have plotted both x and y that is both liquid composition and vapour composition.

(ii) The lower curve (Dew Point Curve) represents the total pressure as a function of the composition i.e. mole fraction in the vapor phase at equilibrium with the liquid phase. It is plotted using  $P_{\tau}$  vs.  $y_{A}$  equation:



(iii) The upper curve i.e. Bubble Point Curve (a straight line in the case of an ideal solution) represents the total pressure as a function of composition i.e. mole fraction in the liquid. It is plotted using  $P_T$  vs.  $x_A$  equation:  $P_T = (P_A^{\circ} - P_B^{\circ}) x_A + P_B^{\circ}$ 

(iv) The area between these two curves is vapour-liquid equilibrium region. Vapours cannot exist above the bubble point curve and liquid can not exist below the dew point curve.

(v) Suppose, initially the pressure over the solution is very high so that no vapour exist above the liquid. As we gradually decrease the pressure, a point (Bubble point) comes when we cross the Bubble-Point curve and first bubble of vapour starts forming. Hence, the name bubble point curve. Now we have entered the vapour-liquid equilibrium region. On further decreasing the pressure, a point (Dew Point) comes when we cross the Dew-Point curve when almost all the liquid has evaporated into vapour i.e. only the last drop of liquid (Dew) remains. Beyond this point no liquid exists in the system.

Solution & Colligative Properties # 21

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EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [22 of 48] (a) A liquid mixture of benzene and toluene is composed of 1 mol of benzene and 1 mol of toluene. If the Ex. pressure over the mixture at 300K is reduced, at what pressure does the first bubble form? (b) What is the composition of the first bubble formed. (c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear? (d) What is the composition of the last drop of liquid? (e) What will be the pressure, composition of the liquid and the composition of vapour, when 1 mol of the mixture has been vaporized? Given  $P_T^0 = 40$  mmHg,  $P_B^0 = 100$  mmHg (c) P = 400/7 = 57.14 mm (b)  $x_{h} = 5/7$ Ans. (a) 70 mmHg, (a)  $P = X_A P_A^0 + X_B P_B^0 = 0.5 \times 40 + 0.5 \times 100 = 70$ Sol. (b)  $Y_{A} = \frac{0.5 \times 40}{70} = \frac{2}{7}$   $Y_{B} = \frac{5}{7}$ (c) at last trace of liquid  $Y_{A} = 0.5$   $Y_{B} = 0.5$  $\frac{1}{P} = \frac{Y_A}{P_a^0} + \frac{Y_B}{P_a^0} = \frac{0.5}{40} + \frac{0.5}{100}$  $P = \frac{400}{7}$ (d)  $Y_A = \frac{Y_A P_A^0}{P} \Rightarrow 0.5 = \frac{X_A 40}{400/7} \qquad X_A = \frac{5}{7}$ (e) Let x mole of B be present in liquid phase. Mole of A Mole of B Liquid 1 - x х Vapour 1 - x х P = 40 (1 - x) + 100 x $\frac{1}{P} = \frac{Y_A}{P_A^0} + \frac{Y_A}{P_B} \Rightarrow \frac{1}{P} = \frac{x}{40} + \frac{1-x}{100} = \frac{100x + (1-x)40}{40 \times 100}$  $p^2 = 40 \times 100$ So  $p = 20\sqrt{10}$  $20\sqrt{10} = 40(1 - x) + 100x = 40 + 60x$  $x = \frac{20\sqrt{10} - 10}{60} = \frac{\sqrt{10} - 2}{3}$ (B) Temperature versus Composition Phase Diagrams i.e. T vs x and y diagram

(i) In this type of phase diagram the pressure is held fixed. The mole fraction of one component is plotted on the horizontal axis and the boiling temperature is plotted on the vertical axis.

(ii) The upper curve (Dew-Point curve) gives the boiling temperature at the given pressure as a function of the mole fraction in the vapor phase, and the lower curve (Bubble-Point curve) gives the boiling tempera ture at the given pressure as a function of the mole fraction in the liquid phase.

**Note:** If a liquid has a high vapour pressure at a particular temperature, it means that its molecules can escape easily from the surface. The liquid with the higher vapour pressure at a particular temperature is the one with the lower boiling point. If A is more volatile than B, then we get following diagram.

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#### 7.2.2 Distillation:

(i) The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component.

(ii) In a simple distillation, the vapour over a boiling mixture is withdrawn and condensed in a separate container. The liquid collected in the new container is called condensate and the liquid remaining in the original container is called distillate. The condensate has higher mole fraction of the more volatile component than the original mixture. The distillate has higher mole fraction of the less volatile component than the original mixture. This is the principle of distillation and is used to separate a more volatile liquid from a less volatile liquid.

(iii) In fractional distillation, the boiling and condensation cycle is repeated successively to get a condensate which gets richer in the more volatile component after each cycle.

**Ex.** An equimolar mix of benzene & toluene is prepared the total V.P. of this mix as a fraction of mole fraction of benzene is found to be

$$P_{T} = 200 + 400 X_{be}$$

(a) Calculate composition of vapours of this mix. [Assume that the no. of moles going into vapour phase is negligible in comparison to no. of moles present in liq. phase ].

(b) If the vapour above liq in part A are collected & are condensed into a new liquid calculate composition of vapours of this new liq.



Solution & Colligative Properties # 23

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#### 7.3 Limitaions of Raoult's Law:

Raoult's Law only works for ideal solutions. Very dilute solutions obey Raoult's Law to a reasonable approximation.

#### 7.3.1 Molecular Structure and Ideal Solutions:

In an ideal solution the substances have molecules of similar size, shape, and polarity. Thus, the forces of attraction between solvent and solute are exactly the same as among the original solvent molecules or among the original solute molecules.

That is, A-B interactions in solution are same as original A-A and B-B interactions. In an ideal solution, it takes exactly the same amount of energy for a solvent molecule to break away from the surface of the solution as it did in the pure solvent.

The similarity of interaction allows the molecules to mix randomly in a solution without changing the volume or the enthalpy (just like non-interacting molecules mix randomly in a dilute gas mixture).



That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

#### Non-ideal solutions:

Those solutions which do not obey Raoult's law are called non-ideal solutions.

When the forces of attraction between A — A, B — B is different from A — B then 'A' and 'B' form non-ideal solutions. For these solutions :

(i) Raoult's law is not obeyed. (ii)  $\Delta H_{mix} \neq 0$ ; (iii)  $\Delta V_{mix} \neq 0$ .

SOLUTION & COLLIGATIVE PROPERTIES # 24

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#### **EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [25 of 48]** 7.3.2 Non-Ideal Solutions Showing Positive Deviation From Raoult's Law :

(i) In this case, partial pressure of each component A and B is higher than that calculated from Raoult's law, and hence total pressure over the solution is also higher than if the solution were ideal, as shown in figure.
 (ii) Boiling point of such a solution is relatively lower than the boiling points of both A and B.



Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution

**Examples**: water and ethanol, chloroform and water, ethanol and CCI<sub>4</sub>, methanol and chloroform, benzene and methanol, acetic acid and toluene, acetone and ethanol, methanol and H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH + cyclohexane.

**Explaination:** The fact that the vapour pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids. That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

You can see this when you mix the liquids. Less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic.

#### 7.3.3 Non-Ideal Solutions Showing Negative Deviation From Raoult's Law :

(i) In this case, partial pressure of each component A and B is lower than that calculated from Raoult's law, and hence total pressure over the solution is also lower than if the solution were ideal, as shown in figure.(ii) Boiling point of such a solution is relatively higher than the boiling points of both A and B.



Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution

**Examples:** chloroform and acetone, chloroform and methyl acetate, H<sub>2</sub>O and HCI, H<sub>2</sub>O and HNO<sub>3</sub>, acetic acid and pyridine, chloroform and benzene.

**Explaination:**These are cases where the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

You can recognise this happening because heat is evolved when you mix the liquids - more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones.

Solution & Colligative Properties # 25

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	Non - Ideal solutions :		
Ideal solutions	+ ve deviation from Raoult's law	-ve deviation from Raoult's Lav	
<ol> <li>Which follow Raoul'ts law at all temp. &amp; at all compositions. P<sub>T</sub> = x<sub>A</sub>P<sub>A</sub>° + x<sub>B</sub>P<sub>B</sub>°</li> <li>Porces of attraction between A-B are exactly same as A-A &amp; B-B AB = BB.</li> </ol>	Which do not follow Rault's law (i) P <sub>Texp</sub> > (X <sub>A</sub> P° <sub>A</sub> + X <sub>B</sub> P <sub>B</sub> °) (ii) AA BB > AB Weaker force of attraction between A-B than in pure A-A & B-B.	<ul> <li>Which do not obey Raoult's law.</li> <li>(i) P<sub>T</sub> exp &lt; x<sub>A</sub>p<sup>o</sup> + x<sub>B</sub>p<sup>o</sup>B</li> <li>(ii) A A B B &gt; A B.</li> <li>Stronger force of attraction between A-B than in pure A-A &amp; B-B.</li> </ul>	
<b>3.</b> $\Delta H_{mk} = 0$ <b>4.</b> $\Delta \bigvee_{mk} = 0$	(iii) $\Delta H_{mk} = +ve$ energy absorbed (iv) $\Delta V_{mk} = +ve$ (1L + 1L > 2L) (v) $\Delta S_{mk} = +ve$ (v) $\Delta G_{mk} = -ve$	$ \begin{array}{ll} \text{(iii)} & \Delta H_{mk} = -\text{ve} \\ \text{(iv)} & \Delta V_{mk} = -\text{ve}(1\text{L}+1\text{L}<2\text{L}) \\ \text{(v)} & \Delta S_{mk} = +\text{ve} \\ \text{(vi)} & \Delta G_{-} = -\text{ve} \end{array} $	
<ul> <li>5. AS<sub>mix</sub> = + ve as for process to proceed.</li> <li>6. AG = - ve</li> </ul>	eg. $H_2O$ + $CH_3OH$ . H_O + $C_2H_2OH$	eg. H <sub>2</sub> O + HCOOH H <sub>2</sub> O + CH <sub>3</sub> COOH	
eg. (1) Benzene + Toluene. (2) Hexane + heptane. (3) C <sub>2</sub> H <sub>5</sub> Br + C <sub>2</sub> H <sub>5</sub> I.	C <sub>2</sub> H <sub>5</sub> OH + hexane C <sub>2</sub> H <sub>5</sub> OH + cyclohexane. CHCl <sub>3</sub> + CCl <sub>4</sub> → dipole dipole interac tion becomes weak	$ \begin{array}{c c} H_{2}O + HNO_{3} \\ CHCI_{3} + CH_{3}OCH_{3} \\ \hline CH_{3} \\ C = O H - C - CI \\ CH_{3} \\ CI \end{array} $	

Solution & Colligative Properties #26

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#### EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [27 of 48] ChemINFO-1.2 **Special Concentration Units** I. Non ideal solutions Daily Self-Study Dosage for mastering Chemistry I. Non ideal solution A non-ideal solution is defined as the one which does not obey Raoult's law. These are divided into two types. 1. Non-ideal positive deviation solution 2. Non-ideal negative deviation solution. **Positive deviation solution Negative deviation solution** $P_T > (X_A P_A^0 + X_B P_B^0)$ $P_T < X_{\Delta}P_{\Delta}^0 + X_B P_B^0$ (i) (i) The inter molecular interaction is more than (ii) The inter molecular interaction is weaker as (ii) the interaction found in any of the pure interaction found in any one of the pure components components. A.....B molecular interaction A.....A is more than A.....A molecular interaction is Stronger than A.....B B.....B (iii) There is decrease in volume on mixing and There is increase in volume on mixing and (iii) evolution of heat takes place on mixing absorption of heat. $\Delta V_{mix} = -ve$ $\Delta H_{mix} = -ive$ $\Delta V_{mix} = positive$ $\Delta H_{mix} = positive$ $\Delta S_{mix} = +ive$ $\Delta G_{mix} = -ive$ $\Delta G_{mix} = -ive$ $\Delta S_{mix} = +ive$ $H_2O + HCOOH,$ $H_2O + HNO_3$ H<sub>2</sub>O + CH<sub>3</sub>COOH Ex. Ex. $H_{2}O + CH_{3}OH$ $C_2H_5OH + Hexane$ CHCl<sub>3</sub> + CH<sub>3</sub>OCH<sub>3</sub> $C_2H_5OH + Cyclohexane, CHCl_3 + CCl_4$

Memorize this theory as soon as you get the DPP. Revise it regularly and master this concept by practice.

- 1. Identify the mixture that shows negative deviation 3. solutions (A) Benzene +  $(CH_3)_2CO$ (B\*)  $(CH_3)_2CO+C_6H_5NH_2$ (C)  $CHCI_3 + C_6H_6$ (D)  $(CH_3)_2CO + CS_2$
- 2. At 55°C, ethanol has a vapour pressure of 168 mm, and the vapour pressure of methyl cyclohexane is 280 mm. A solution of the two in which the mole fraction of ethanol is 0.68, has a total vapour pressure of 376 mm. This solution is formed from its components with
  - (A) The evolution of heat
  - (B\*) The absorption of heat.
  - (C) Neither absorption nor evolution of heat
  - (D) Nothing can be predicted on the basis of given information

- Total vapour pressure of mixture of 1 mole of A  $(P_A^0 = 150 \text{ mm})$  and 2 mole of B  $(P_B^0 = 240 \text{ mm})$  is 200 mm. In this case :
  - (A) There is a positive deviation from Raoult's law.
  - (B\*) There is a negative deviation from Raoult's law
  - (C) There is no deviation from Raoult's law.
  - (D) Molecular masses of A & B are also required for calculating deviation.
- Identify the mixture showing positive deviation of non-ideal solution.

 $(A^*) CH_3 COCH_3 + CS_2$ 

- (B) Hexane + Heptane
- (C) Chlorobenzene + Bromo benzene
- (D) Acetone + Chloroform

Solution & Colligative Properties #27

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4.

#### EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [28 of 48] 7.4 Azeotropic Mixtures : Very large deviations from ideality lead to a special class of mixtures known as

**Azeotropic Mixtures :** Very large deviations from ideality lead to a special class of mixtures known as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

**Azeotropes :** Liquid mixtures which distill over without changes in composition are called constant boiling mixtures or Azeotropes or Azeotropic mixtures.

A boiling liquid mixture at the azeotropic composition produces a vapour of exactly the same composition, and the liquid does not change its composition as it evaporates. Two types of azeotropes are known.

7.4.1 Minimum Boiling Azeotropes : Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes which boil at temperature lower than boiling point of its components 'A' and 'B', e.g., water and benzene, chloroform and methanol.

The figures below show the Temprature vs. composition (at constant pressure) phase diagram on the left side and Pressure vs. composition (at constant temprature) phase diagram for a minimum-boiling azeotropic mixture chloroform and methanol.

Note : The detailed values in the diagram are not important. Only the qualitative shape of the diagram is important.



The characteristic of such mixture is that the total pressure goes through a maximum (in constant temperature phase diagram), and therefore the temperature goes through a minimum (in constant pressure phase diagram). At the lowest point in the temperature vs. composition phase diagram, the concentration in the vapour phase is the same as the concentration in the liquid phase (y = x). This concentration is known as the azeotropic composition. At this point, the mixture boils at a constant temperature and without change in composition.

**7.4.2** Maximum Boiling Azeotropes : Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which boil at temperature higher than the boiling point of its components A and B respectively, e.g., a mixture of HCl and H<sub>2</sub>O containing 20.2% HCl by weight boils at 108.5°C higher than either pure HCl (– 85°C) or water (100°C).

On left side, temprature versus composition phase diagram is shown. On right side, pressure versus composition diagram is shown for maximum boiling azeotrope.



Solution & Colligative Properties # 28

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#### EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [29 of 48] Separation of Azeotropic Mixtures

Azeotropic mixtures cannot be completely separated by distillation. When the azeotropic composition has been reached, distillation cannot separate the two liquids because the condensate has the same composition as the azeotropic liquid. The vapour phase is not richer in any component than the liquid phase. Thus, azeotropic mixtures can't be separated beyond the azeotropic composition using distillation.

#### 7.5 Completely Immiscible Liquids and Steam Distillation

It is probably true that no two liquids are absolutely insoluble in each other, but with certain pairs, eg., mercury and water and carbon disulfide and water, the mutual solubility is so small that the liquids may be regarded as virtually immiscible. For systems of this type, each liquid exerts its own vapor pressure, independent of the other, and the total vapor pressure is the sum of the separate vapour pressures of the two components in the pure state at the given temperature. The composition of the vapor can be readily calculated by assuming that the gas laws are obeyed; the number of moles of each constituent in the vapor will then be proportional to its partial pressure, that is to say, to the vapor pressure of the substance in the pure state.

- (1) Immiscible Liquids : When two liquids are mixed in such a way that they do not mix at all then both liquids constitute two different phases. Hence, mole fraction of each liquid is one in it's own phase. (i)  $P_{\tau} = p_{A} + p_{B}$ 
  - (ii)  $p_{A} = P_{A}^{0} x_{A}$  But,  $x_{A} = 1$ . Thus,  $p_{A} = P_{A}^{0}$ (iii)  $p_{B} = P_{B}^{0} x_{B}$  But,  $x_{B} = 1$ . Thus,  $p_{B} = P_{B}^{0}$ (iv)  $P_{T} = P_{A}^{0} + P_{B}^{0}$  (v)  $\frac{P_{A}^{0}}{P_{B}^{0}} = \frac{n_{A}}{n_{B}}$  (vi)  $\frac{P_{A}^{0}}{P_{B}^{0}} = \frac{W_{A} M_{B}}{M_{A} W_{B}}$  (v)  $P_{A}^{0} = \frac{n_{A} RT}{V}$ ;  $P_{B}^{0} = \frac{n_{B} RT}{V}$

where  $n_A$  and  $n_B$  are the numbers of moles of each component present in the vapor phase.

(vi) To express the ratio of A to B in the vapor in terms of the actual weights  $w_A$  and  $w_B$ , the numbers of moles must be multiplied by the respective molecular weights  $M_A$  and  $M_B$ ; hence,

$$\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B} = \frac{p_A^0 M_A}{p_B^0 M_B}$$
(3)

Note: The boling point of a solution of two immiscible liquids is less than the individual boiling points of both the liquids. This concept is used in steam distillation.

(2) Steam Distillation: The boling point of a solution of two immiscible liquids is less than the individual boiling points of both the liquids. This concept is used in steam distillation.

(i) A system of two immiscible liquids will boil when the total vapor pressure P is equal to the atmospheric pressure. The boiling point of the mixture is thus lower than that of either constituent.

(ii) Further, since the total vapor pressure is independent of the relative amounts of the two liquids, the boiling point, and hence the composition of the vapor and distillate, will remain constant as long as the two layers are present.

A liquid (generally organic) that is immiscible with water, and that has a higher boiling point than water can be boiled (distilled) at a much lower temperature by passing steam through it. In this way, the organic liquid can be purified from impurities using steam distillation.



Solution & Colligative Properties # 29

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#### **EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [30 of 48]** Extra Information for Faculty :

It is seen that chlorobenzene, which has a normal boiling point of 132°C, can be distilled with steam at a temperature about 40° lower, the distillate containing over 70 percent of the organic compound. An examination of the calculation shows that the high proportion by weight of chlorobenzene in the steam distillate is due largely to the high molecular weight of this substance, viz., 112.5 as compared with that of water. In addition this case is a particularly favorable one because chlorbenzene has a relatively high vapor pressure in the region of 90° to 100°C.

In order that a liquid may be distilled efficiently in steam, it should therefore be immiscible with water, it should have a high molecular weight, and its vapor pressure should be appreciable in the vicinity of 100°C.

Attention may be called to the fact that equation (3) can be employed to determine the approximate molecular weight of a substance that is almost immiscible with water. This can be done provided the composition of the steam distillate and the vapor pressures of the two components are known.

**Phase Rule :** The various conditions of equilibrium between phases, such as the number of phases, the number of components and the degrees of freedom (or the variance), can be correlated with one another with the help of a general rule, known as the phase rule.

**Phase (P) :** A phase is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surface ; the term homogeneous means that the system has identical physical properties and chemical composition throughout the whole of the system.

Number of Components (C) : It is the smallest number of independent chemical constituents by means of which the composition of each and every phase can be expressed.

One-component system :	Solid water (ice)		liquid water	
	Solid water	$\rightarrow$	liquid vapour 🛁	water vapour

**Degree of Freedom (F) :** The degree of freedom or variance of the system is the minimum number of independent variables such as temperature, pressure and concentration, that must be ascertained so that a given system in equilibrium is completely defined.

Phase rule is a general rule which is applicable to all types of reactive and nonreactive systems.

Nonreactive system : Consider a heterogeneous system of P phases at equilibrium containing in all C components

F= C – P +2 ; F + P = C +2

Example : Let us verify the rule by calculating the variance of a one- component system :

 One phase only
 P = 1, F = C - P + 2 = 1 - 1 + 2 = 2 

 Two phase in equilibrium
 P = 2, F = C - P + 2 = 1 - 2 + 2 = 1 

 Three phase in equilibrium
 P = 3, F = C - P + 2 = 1 - 3 + 2 = 0 

**Reactive system :** Let us consider a heterogenous system composed of arbitrary amount of C constituents For the sake of simplicity we assume that four of the constituents are chemically active, capable of undergoing the reaction.

$$v_1A_1 + v_2A_2 \longrightarrow v_3A_3 + v_4A_4$$

We have F = (C –2) –P + 2

For nonreactive system :

where 'r' is the number of independent reactions that are taking place in the system.

#### Some Typical Example to Compute The Number of Components

Number components = Number of constituents

For reactive system : Number components = Number of constituents - (Number of chemical reactions) - (Number of restricting conditions)

Solution & Colligative Properties # 30

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# EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [31 of 48] LECTURE # 4

## Section : (F)

## 8.1 Introduction to Colligative properties & constitutional properties :

**Colligative properties :** The properties of the solution which are dependent only on the total no. of particles or total conc. of particles in the solution & are not dependent on the nature of particle i.e. shape, size, neutral /charge etc. of the particles.

**Constitutional Properties :** Properties which are dependent on nature of particles are constitutional properties like electrical conductence.

There are 4 colligative properties of solution

- 1. Relative lowering in vapour pressere  $\left(\frac{\Delta P}{P}\right)$
- 2. Elevation in b.p. (ΔT<sub>b</sub>)
   3. Depression in freezing pt. (ΔT<sub>t</sub>)
- 4. Osmotic pressure

#### Van't Hoff Factor :

#### **Abnormal Colligative Properties :**

If solute gets associated or dissociated in solution then experimental / observed / actual value of colligative property will be different from theoretically predicted value so it is also known as abnormal colligative property.

This abnornality can be calculated in terms of vont. hoff factor.

\_\_\_\_\_exp/observed/actual/abnormal value of colligative property

Theoritical value of colligative property

exp./observed no. of particles / conc.

Theoritical no. of particles

Theoritical mass of substance

- experimental molar mass of the substance
- i > 1 dissociation
- i < 1 association

#### Relation between i & $\alpha$ (degree of dissociation) :



SOLUTION & COLLIGATIVE PROPERTIES # 31

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EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [32 of 48] Relation b/w degree of association  $\beta \& i$ .



dimerise n = 2; trimerise n = 3; tetramerise n = 4.

e.g. CH<sub>3</sub>COOH 100% dimerise in benzene, i =  $\frac{1}{2}$ ; C<sub>6</sub>H<sub>5</sub>COOH 100% dimerise in benzene, i =  $\frac{1}{2}$ 

#### 8.2 Relative lowering in vapour pressure (RLVP) :

#### Vapour Pressure of a solutions non-volatile solute in a volatile solvent

Vapour Pressure of a solution of a non volatile solute ( solid solute ) is always found to be less than the vapour pressure of pure solvent.

**Reason**: Some of the solute molecules will occupy some surface area of the solutions so tendency of the solvent particles to go into the vapour phase is slightly decreased hence  $P^0 > P_s$ , where  $P^0$  is vapour pressure of the solution

pressure of pure solvent and P<sub>s</sub> is vapour pressure of the solution.



**Raoult's law** (For non–volatile solutes): The vapour pressure of a solution of a non-volatile solute is equal to the vapour pressure of the pure solvent at that temperature multiplied by its mole fraction. **OR** Relative Lowering in Vapour Pressure = mole fraction of the non volatile solute in solutions.

$$P_{s} = \mathbf{x}_{solvent} P^{0} = (1 - \mathbf{x}_{solute}) P^{0}$$
  
RLVP =  $\frac{P^{0} - P_{s}}{P^{0}} = \mathbf{x}_{solute} = \frac{n}{n + N}$ 

where n = number of moles of non-volatile solute and N = number of moles of solvent in the solution.

Solution & Colligative Properties # 32

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$$\frac{P^{0}}{P^{0} - P_{s}} = \frac{n + N}{n} = 1 + \frac{N}{n}$$

$$\frac{N}{n} = \frac{P^{0} - P_{s}}{P^{0}} - 1 = \frac{P_{s}}{P^{0} - P_{s}}$$

$$\frac{P^{0} - P_{s}}{P^{0}} = \frac{n}{N}$$

$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{w}{m} \times \frac{M}{W} = \frac{w}{m} \times \frac{M}{W} \times \frac{1000}{1000} = \frac{w}{m} \times \frac{1000}{W} \times \frac{M}{1000}$$

$$\frac{P^{0} - P_{s}}{P_{s}} = (\text{ molality }) \times \frac{M}{1000}$$

where w and W = mass of non-volatile solute and volatile solvent respectively m and M = molar mass of non-volatile solute and volatile solvent respectively

If solute gets associated or dissociated ; 
$$\frac{P^0 - P_s}{P_s} = \frac{i.n}{N}$$
 that is  $\frac{P^0 - P_s}{P_s} = i \times (\text{molality}) \times \frac{M}{1000}$ 

**Ex.** Calculate wt of urea which must be dissolved in 400 gm of water so final solutions has V.P. 2% less than V.P. of pure water :

let V.P be V. of water  

$$P^{0} - P_{s} = .02 V$$
  
 $P_{s} = 0.98 V$   
 $\Rightarrow \qquad \frac{0.02}{0.98} = \frac{w}{60} \times \frac{18}{400}$ ; where w = weight of urea.  
 $w = \frac{2 \times 60 \times 400}{18 \times 98}$  gm.

**Ex.** 10 gm of a solute is dissolved in 80 gm of acctone V.P. of this sol = 271 mm of Hg. If V.P. of pure acctone is 283 mm of Hg. Calculate molar mass of solute.



**Ex.** V.P. of solute containing 6 gm of non volatile solute in 180 gm of water is 20 Torr/mm of Hg. If 1 mole of water is further added in to the V.P. increses by 0.02. Torr calculate V.P of pure water & molecular wt. of non volatile solute.

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

$$\Rightarrow \frac{P - 20}{20} = \frac{6}{m} \times \frac{18}{180}$$

$$\frac{P - 20.02}{20.02} = \frac{6}{m} \times \frac{18}{198}$$

$$\Rightarrow P = 20.22 \text{ Torr.}$$

$$m = 54 \text{ gm/mol.}$$

 $\Rightarrow$ 

Solution & Colligative Properties #33

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What is the final volume of both container.

Sol.  $i_1C_1 = i_2C_2$ 0.1×2 0.1×1

 $\frac{100 + x}{100 - x} = \frac{100 - x}{100 - x}$ 200 - 2x = 100 + x. x = 33.3 ml.

If 0.1 M solutions of  $K_4$  [Fe (CN)<sub>6</sub>] is prepared at 300 K then its density = 1.2 gm/mL. If solute is 50% Ex. dissociated calculate  $\Delta P$  of solutions if P of pure water = 25 mm of Hg. (K = 39, Fe = 56)

$$\frac{P^{0} - P_{s}}{P_{s}} = i \frac{w}{m} \times \frac{M}{W}$$
$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{im \times M}{1000}$$
$$= \left(\frac{3 \times 0.1 \times 1000}{1000 \times 1.2 - 1.2 \times 368}\right) \times \frac{18}{1000}$$
$$\frac{P^{0}}{P_{s}} = 1 + 7.12 \times 10^{-3}$$
$$P_{s} = 24.82 \text{ mm of Hg}$$
$$\Delta p = 25 - 24.82 = 0.18 \text{ mm of Hg}$$

**Ostwald–Walker Method :** 



(i) Initially note down the weights of the solution set, solvent set containers & of dehydrating agent before start of experiment.

(ii) Note down the same weights after the experiment is complete.

- Loss of wt of solution containers  $\alpha$  P
- Loss of in wt of solvent containers  $\alpha (P P_s)$
- gain in wt of dehydriating agent  $\alpha$  P.

SOLUTION & COLLIGATIVE PROPERTIES # 34

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$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{loss \text{ in wt.of solvent}}{loss \text{ in wt.of solvent}}$$

$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{loss \text{ is wt.of solvent}}{gain \text{ is wt.of dehydrating agent}} = \frac{w}{m} \times \frac{M}{W} = (\text{ molality }) \times \frac{M}{1000}$$
Dry air was passed through a solution of 5 gm of a solute in 80 gm of water & then it is passed through pure water. Loss in weight of solution was 2.50 g & loss in weight of pure water was 0.04 g. Find molecular weight of the solute.
$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{loss in wt.of solvent}{loss in wt.of solvent}$$

$$\frac{P^{0} - P_{s}}{P_{s}} = \frac{0.04}{2.50} = \frac{w}{m} \times \frac{M}{W} = \frac{5}{m} \times \frac{18}{80}$$
Thus. m = molecular weight of the solute = 70 g/mol.
$$\frac{dry air}{(A_{s})} = \frac{(B_{s})}{(B_{s})} = \frac{(C_{s})}{(C_{s})} = \frac{(C$$

If same volume solution of different solute is used then what is order of (a) vapour pressure (b) moles of solute (c) molar mass of solute.

Ans.
$$P_A \propto 1 \text{ gm.}$$
; $P_A - P_B \propto 0.5 \text{ gm.}$  $P_C \sim 0.5 \text{ gm.}$  $P_C - P_B \propto 1 \text{ gm}$ ; $P_C \propto 1.5 \text{ gm.}$  $P_C > P_A > P_B$ ; $n_C < n_A < n_B$ ;

Ex.

Ex.

Solution & Colligative Properties #35

Solution & Colligative Proper JOIN IN OUR TELEGRAM CHANNEL https://t.me/AIMSKRISHNAREDDY [944 0 345 996] [35 of 48]

# EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [36 of 48] **LECTURE # 5**

#### 8.3 Third colligative property :

#### 3. Elevation in Boiling point $(\Delta T_{\rm s})$ Boiling point of a Liq. :

The temprature at which vapour pressure of a liquid becomes equal to the external pressure present at the surface of the liquid is called b.p of liquid at that pressure.



Figure

#### Boiling point of any solution :

Since V.P. of solution is smaller than V.P. of pure solvent at any temp. hence to make it equal to Part we have to increase the temp. of solution by greater amount in comparision to pure solvent.

Т-



SOLUTION & COLLIGATIVE PROPERTIES # 36

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Due to presence of solute, it is difficult to vapourise the solution (so R.L.V.P occur), it is difficult to boil (so elevation in boiling point occur), it is difficult to freeze (so depression in freezing point occur).

This diagram is related to boiling point elevation and freezing point depression of solutions is taken from 'MCMURRY FAY CHEMISTRY' for details see chapter -11 page no. 450.



Phase diagram for a pure solvent (red line) and a solution of a nonvolatile solute (green line). Because the vapor pressure of the solution is lower than that of the pure solvent at a given temperature, the temperature at which the vapor pressure reaches atmospheric pressure is higher for the solution than for the solvent. Thus, the boiling point of the solution is higher point of the solution is higher point of the solution is higher point of the solution than for the solvent, because the liquid / vapor phase transition line is lower for the solution than for the solvent, the triple point temperature  $T_t$  is lower and the solid/ liquid phase transition line is shifted to a lower temperature. As a result, the freezing point of the solution is lower than that of the pure solvent by an amount  $\Delta T_t$ .

**Derivation of formula**  $\Delta T_{b} = K_{b} \times \text{molality by Graphical Method:}$ 



Solution & Colligative Properties # 37

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$$\frac{\Delta T_{b1}}{\Delta T_{b2}} = \frac{\Delta P_1}{\Delta P_2}$$
$$\therefore \qquad \Delta T_b \alpha \Delta P$$

using Raoult's law :

$$\frac{\Delta P}{P} = \frac{n}{n+N} = \frac{w}{M} \cdot \frac{M}{W} \cdot P$$
$$\Rightarrow \Delta T_{b} \propto \frac{w}{m} \cdot \frac{M}{W} \cdot P$$
$$\propto \left(\frac{w}{M} \times \frac{1000}{W}\right) \left(\frac{M}{1000} \cdot F\right)$$

Formula for Elevation of Boiling Point  $\Delta T_{b} = K_{b} \times molality$ 

Note: (i) If solute gets associated/dissociated then  $\Delta T_{b} = i \times K_{b} \times molality$ 

(ii) Units of 
$$K_{b}$$
:  $\frac{\Delta T_{b}}{\text{molality}} = \frac{K}{\text{mol/kg}}$ .

Thus units of  $K_{b} = K \text{ kg mol}^{-1}$ 

(iii) K<sub>b</sub> is dependent on property of solvent and known as molal elevation constant of solvent

$$K_{b} = \frac{RT_{b}^{2}M}{1000 \times \Delta H_{vap}} = \frac{RT_{b}^{2}}{1000 \times L_{vap}}$$

where,  $\Delta H_{vap}$  is molar enthalpy of vaporisation  $L_{Vap}$  is Latent Heat of Vapourisation in cal/gm or J/gm M is molecular mass of the solvent in gram R = 2 cal mol<sup>-1</sup> cal<sup>-1</sup> or 8.314 J .... T<sub>b</sub> = b.p. of pure liquid solvent (in kelvin) K<sub>b</sub> = K kg mol<sup>-1</sup>

$$L_{vap} = \left(\frac{\Delta H_{vap}}{M}\right)$$

(iv)  $K_{b}$  = elevation in bp of 1 molal solution.

(v) elevation in boiling point is proprtional to the lowering of vapoure pressure i.e.  $\Delta T_{
m b} \propto \Delta P$ 

Ex. Calculate  $K_b$  of water if  $L_{vap} = 540$  Cal/gm  $T_b = 100^{\circ}$ C

$$\Rightarrow \qquad K_{\rm b} = \frac{2 \times 373 \times 373}{1000 \times 540} = K \text{ kg mol}^{-1} = 0.52 \text{ K k/gm}$$

if solute gets associated/dissociated  $\Delta t = i \times K_{b} \times molality$ 

 $K_{b} \left| \frac{1}{2} \times 0.8 \right|$ 

 $T_{b} - T_{i} = K_{b} \times 0.6$ 

**Ex.** A solution of 122 gm of benzoic acid is 1000 gm of benzene shows a b.p. elevation of 1.4°. Assuming that solute is dimerized to the extent of 80 percent (80°C) calculate normal b.p. of benzene. given molar enthalpy of vap. of benzine = 7.8 Kcal/mole.

$$T_{b} - T_{i} = \frac{122 \times 1000}{122 \times 1000} \times K_{b} \left( 1 + \left( \frac{1}{n} - 1 \right) \right) 0.8$$



Solution & Colligative Properties #38

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$$K_{b} = \frac{R T_{b}}{1000 \times L_{vap.}}$$

$$K_{b} = \frac{2 \times T_{b}^{2} \times 78}{1000 \times 7.8 \times 1000}$$

$$1.4 = \frac{0.4 \times 2}{10^{5}} T_{b}^{2}$$

$$T_{b} = 418.33 \text{ K}$$

**р**т 2

- **Ex.** 1 Lit. of aq. solution of urea having density = 1.060 gm/mL is found to have  $\Delta T_b = 0.5^{\circ}$ C, If temp. of this solution increase to 101.5°C then calculate amount of water which must have gone is vapour state up to this pt. given K<sub>b</sub> = 0.5 K kg mol<sup>-1</sup> for water
- **Sol.** mass of solution =  $1.060 \times 10^3 = 1060$  gm

 $0.5 = 0.5 \times \frac{1060}{1060} \frac{M}{60}$   $\Rightarrow 1060 \times 60 = M$ 1 Lit solution = 1060 gm (Mass of water) i = 1000 gm urea = 60 gm  $\Delta T_{b} = (\text{molality})_{i} \times K_{b}$ (Molality)<sub>i</sub>  $\Rightarrow 3 = \frac{60}{60} \times \frac{1000}{W_{water}}$ 

$$W_{water} = \frac{1000}{3}$$
 gm.

mass of water vaporised =  $1000 - \frac{1000}{3} = \frac{2000}{3}$  gm = 666.67 gm

#### 8.4 Fourth colligative property :

#### 4. Depression in freezing pt ( $\Delta T_{b}$ ) Freezing point :

Temprature at which vapour pressure of solid becomes equal to v.p of liq. is called freezing pt of liq. or melting pt. of solid.

$$Vacuum$$

$$H_{sub} = + ve$$

$$\Delta H_{sub} > \Delta H_{vap}$$

$$\Delta H_{sub} = \Delta H_{fusion} + \Delta H_{vap}$$

$$H_2O(s) \iff H_2O(g)$$

$$K_p = P_{H_2O}(g)_{req}$$

$$= V.P. \text{ of solid}$$

Solution & Colligative Properties # 39

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<b>F</b>	0.1M urea 0.1M NaCl	0.1M BaCl <sub>2</sub>
EX.	(A) , (B)	' (C)
	order of $\pi$	C > B > A.
	order of R.L.V.P	C > B > A.
	order of V.P	A > B > C.
	order of $\Delta T_{B}$	C > B > A.
	order of $T_{B}$ of solution	C > B > A.
	order of $\Delta \overline{T}_{F}$	C > B > A.
	order of $T_{F}$ of solution	A > B > C.

Ex. Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence, their (assume equal concentrations in all three cases)
(A) b.p. : X < Y < Z</li>
(B\*) f. p. Z < X < Y</li>

(C) osmotic pressure : X = Y = Z

(B\*) f. p. Z < X < Y (D) v. p. : Y < X < Z i.e., V.P. decreases y > x > z y < x < z y > x > z

- Sol. As van't Hoff factor increases RLVP increases Elevation in b.p. increases i.e., b.p. increases Depresion in f.p increases i.e., f.p decreases Osmotic pressure increases so
- **Ex.** 1000 gm  $H_2O$  have 0.1 mole urea and its freezing point is  $-0.2^{\circ}C$  and now it is freezed upto  $-2^{\circ}C$  then how much amount of ice will form.



y < x < z.

Sol. It is assume that solute do not freeze and do not vapourise

$$\Delta T_{F} = 0.2 = K_{f} \frac{0.1}{1000} \times 1000 \qquad .....(i)$$
  
$$\Delta T_{F} = 2 = K_{f} \frac{0.1}{\text{wt. of solvent}} \times 1000 \qquad .....(ii) \qquad \text{on dividing } \frac{\text{wt. of solvent}}{1000} = \frac{0.2}{2}.$$

weight of remaining H<sub>2</sub>O is 100 gm and weight of ice is 900 gm.

- **Ex.** If boiling point of an aqueous solution is 100.1°C. What is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g<sup>-1</sup> and 540 cal g<sup>-1</sup> respectively.
- Sol. For a given aqueous solution

$$\Delta I_{b} = K_{b}^{L} \times \text{molality}$$

$$\Delta T_{f} = K_{f}^{L} \times \text{molality}$$

$$\Delta T_{f} = K_{f}^{L} \times \text{molality}$$

$$\frac{\Delta T_{b}}{\Delta T_{f}} = \frac{K_{b}}{K_{f}^{L}} = \frac{RT_{b}^{2}}{1000 \text{ ly}} \times \frac{1000 \text{ lf}}{RT_{f}^{2}} .$$

$$\frac{\Delta T_{b}}{\Delta T_{f}} = \frac{T_{b}^{2} \times \text{lf}}{T_{f}^{2} \times \text{ly}}$$

$$T_{b} = 100 + 273 = 373 \text{ K}.$$

$$T_{f} = 0 + 273 = 273 \text{ K}.$$

$$I_{f} = 80 \text{ cal } \text{g}^{-1}.$$

$$I_{v} = 540 \text{ cal } \text{g}^{-1}.$$

$$\frac{0.1}{\Delta T_{f}} = \frac{373 \times 373 \times 80}{273 \times 273 \times 540}.$$

$$\Delta T_{f} = 0.362.$$

$$T_{f} = 0.0 - 0.362. = -0.362^{\circ}\text{C}.$$

Solution & Colligative Properties # 41

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#### EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [42 of 48] A 0.001 molal solution of a complex reprsented as Pt(NH<sub>2</sub>)<sub>4</sub>Cl<sub>4</sub> in water had a freezing point depression of Ex. 0.0054°C. Given K, for H<sub>2</sub>O = 1.86 molality<sup>-1</sup>. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex. Sol. Let n atoms of CI be the acting as ligand. Then formula of complex and its ionisation is : $[Pt(NH_{3})_{4}Cl_{n}]Cl_{(4-n)} \longrightarrow [Pt(NH_{3})_{4}Cl_{n}]^{+(4-n)} + (4-n)Cl^{-1}$ 0 (4 – n) Thus particles after dissocation = 4 - n + 1 = 5 - nand therefore, van't Hoff factor (i) = 5 - nNow $\Delta T_f = K'_f \times molality \times van't Hoff factor$ $0.0054 = 1.86 \times 0.001 \times (5 - n)$ $n = 2.1 \approx 2$ (integer value) .... Thus complex and its ionisation is : $[Pt(NH_3)_{4}Cl_{2}]Cl_{2} \longrightarrow [Pt(NH_3)_{4}Cl_{2}]^{2+} + 2Cl^{-}$ Ex. Depression of freezing point of 0.01 molal aq. CH, COOH solution is 0.02046°. 1 molal urea solution freezes at – 1.86°C. Assuming molality equal to molarity, pH of CH, COOH solution is : (A) 2 (B\*) 3 (C) 3.2 (D) 4.2 Sol. For urea $\Delta T_{f} = k_{f} \times m$ or $k_{f} = \frac{\Delta T_{f}}{m} = \frac{1.86}{1} = 1.86$ Now for CH<sub>2</sub>COOH $\Delta T_{f} = i k_{f} m$ $i = \frac{0.02046}{1.86 \times 0.01} = 1.1$ so Now $i = 1 + \alpha$ $\alpha = 1.1 - 1 = 0.1$ so CH<sub>3</sub>COO CH<sup>°</sup>COOH Now С 0 0 $C - C\alpha$ Cα Cα $[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$ pH = 3.so LECTURE # 6 8.5 Osmosis & Osmotic pressure : **Osmosis & Diffusion Diffusion :** Spontaneous flow of particles from high conc. region to lower conc. region. H<sub>2</sub>O Blue Cu<sup>2</sup> Ex. Saturated Uniform (Solution)blue **CuSO**

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Conclusion : After some time in (A) grape or egg will shrink and in (B) grape or egg will swell.

**Ex.** In which soluton side complex  $[Cu(NH_3)_4]^{2+}$  will form and deep blue colour will obtain.



Ans. In neither of side colour complex will form.

#### Osmosis :

The spontaneous flow of solvent particles from solvent side to soultion side or from solution of low conc. side to solution of high conc. side through a semipermeable membrane = (SPM)

SPM : A membrane which allows only solvent particles to more across it.

- (a) Natural : Semi permeable membrane
- (i) Animal/plant cell membrane formed just below the outer skins.
- (b) Artificial membranes also : A copper ferrocyanide.

 $Cu_2[Fe(CN)_6]$  & Silicate of Ni, Fe, Co can act as SPM.

#### **Osmotic Pressure :**



The equilibrium hydrostatic pressure developed by solution column when it is seperated from solvent by semipermeable membrane is called O.P. of the solution.

- $\pi = \rho g h$
- $\rho$  = density of soln.
- g = acc. due to gravity
- h = eq. height

 $1 \text{ atm} = 1.013 \text{ x} 10^5 \text{ N/m}^2$ 

Solution & Colligative Properties # 43

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#### **Definition** :

The ext pressure which must be applied on solution side to stop the process of osmosis is called osmotic pressure of the of the solution.

 $C_1 > C_2$  particle movement.

$$\mathsf{P}_{\mathsf{ext.}} = (\pi_1 - \pi_2)$$

P<sub>ext.</sub> must be applied on the higher conc. side.

#### **Remarks**:

If the pressure applied on the soln side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is reverse osmosis. Berkely : Hartely device/method uses the above pr. to measure O.P.

Vont – Hoff Formula (For calculation of O.P.)



In ideal solns solute particles can be assumed to be moving randomly without any interactions.  $\therefore$  C = total conc. of all types of particles.

$$= C_1 + C_2 + C_3 + s....$$

$$= \frac{(n_1 + n_2 + n_3 + \dots)}{V}$$

**Ex.** If  $V_1$  mL of  $C_1$  ion +  $V_2$  mL of  $C_2$  conc. are mixed.

$$C_{f} = \frac{C_{1}V_{1} + C_{2}V_{2}}{V_{1} + V_{2}}$$

$$\pi_{1} = C_{1}RT, C_{1} = \left(\frac{\pi_{1}}{RT}\right)$$

$$\pi_{2} = C_{2}RT, C_{2} = \left(\frac{\pi_{2}}{RT}\right)$$

$$\pi = \left(\frac{C_{1}V_{1} + C_{2}V_{2}}{V_{1} + V_{2}}\right)RT$$

$$\pi = \left(\frac{\pi_{1}V_{1} + \pi_{2}V_{2}}{V_{1} + V_{2}}\right)$$

Solution & Colligative Properties # 44

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#### **EVERY COMPETITIVE EXAMINATION STUDY MATERIAL WITH COMPLETE SOLUTIONS ARE AVAILABLE [45 of 48]** Type of solutions :

(a) Isotonic solution 2 solutions having same O.P.

 $\pi_1 = \pi_2$  (at same temp.)

- **(b)** Hyper tonic I<sup>st</sup> If  $\pi_1 > \pi_2$  solution is hypertonic solution w.r.t. 2<sup>nd</sup> solution.
- (c) Hypotonic 2<sup>nd</sup> solution is hypotonic w.r.t. I<sup>st</sup> solution.



#### **Conclusion :**

Pressure is applied on the hypertonic solution to stop the flow of solvent partices, this pressure become equal to  $(\pi_2 - \pi_1)$  and if hypotonic solution is replaced by pure solvent then pressure becomes equal to  $\pi_2$ .

**Ex.1** Calculate osmotic pressure of 0.1 M urea aq. solution at 300 K,

R = 0.082 lit atm K<sup>-1</sup>  $\pi$  = CRT  $\pi$  = 0.1 x 0.082 x 300

$$\pi = 2.46 \text{ atm}$$

Osmotic pressure of very dilute solns is also quite significant so its measurement in lab is very easy.

**Ex.2** If 10 gm of an unknown substance (non-electrolyic) is dissolved to make 500 mL of soln then OP at 300 K is observed to be 1.23 atm find m.wt. ?

$$1.23 = \frac{10 \times 1000}{M \times 500} \times 0.0832 \times 300$$
$$M = \frac{20}{1.23} \times \frac{0.0832}{100} \times 300 \approx 400 \text{ gm/mol}$$

**Ex.3** If 6 gm of urea, 18 gm glucose & 34.2 gm sucrose is dissolved to make 500 mL of a soln at 300 K calculate  $\pi$ 

M.W. of urea = 60 gm , Glucose = 180gm , SUcrose = 342 gm

 $\pi = C \times 0.082 \times 300$ 

 $\pi = \frac{0.3 \times 1000 \times 0.082 \times 300}{500}$  $\Rightarrow 14.76 \text{ atm}$ 

**Ex.4** If 200 mL of 0.1 M urea soln is mixed with 300 mL of 0.2 M Glucose soln. at 300 K calculate  $\pi$ . 0.02 moles urea

0.06 moles Glucose

$$\pi = \frac{0.08}{0.5} \times 0.083 \times 300 \quad \text{or} \quad \pi = \left(\frac{C_1 V_1 + C_2 V_2}{V_1 + V_2}\right) \text{RT}$$
  
3.94 atm

**Ex.5** If an urea (aq) solution at 500K has O.P. = 2.05 atm. & glucose solution at 300 K has OP = 1.23 atm. If 200 ml of I<sup>st</sup> solutions & 400 ml of 2<sup>nd</sup> soln are mixed at 400 K then cal. O.P. of resulting solution as 400 K (assume molarity is not dependent on temp.)

$$\mathrm{C}_{\mathrm{urea}} = \frac{2.05}{\mathrm{R} \times 500} = 0.05 \implies 200 \ \mathrm{mL}$$

SOLUTION & COLLIGATIVE PROPERTIES # 45

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$$C_{glucose} = \frac{1.23}{R \times 300} \implies 400 \text{ mL}$$

$$\pi_{F} = (C_{F} \times RT)$$

$$C_{F} = \frac{\left(\frac{2.05}{R \times 500}\right) \times 200 \text{ moles} + \left(\frac{1.23}{R \times 300}\right) \times 400 \text{ moles}}{600 \text{ mL}}$$

$$\Rightarrow \qquad \pi_{F} = \frac{(0.05)200 + (0.05)400}{600} \times 0.083 \times 400 = \frac{(0.05) \times 600}{600} \times 0.083 \times 400$$

$$= 0.05 \times 0.083 \times 400$$

$$= 20 \times 0.083 = 1.66 \text{ atm.}$$

#### Ex. When reaction is not taking.

Calculate  $\pi$  of a solutions having 0.1 M NaCl & 0.2 M Na<sub>2</sub>SO<sub>4</sub> and 0.5 HA (weak acid which is 20% Ex. dissociation solutions at 300 K)

$$\pi = (0.2 + 0.6) RT + i_3 C_3 RT$$
  

$$i_3 = 1 + (1).2 = 1.2$$
  

$$\Rightarrow [0.8 + 0.6] RT$$
  

$$= (1.4 \times 0.083 \times 300)$$
  

$$= 1.162 \times 30$$
  

$$= 34.86 atm$$

If 0.04 M Na<sub>2</sub>SO<sub>4</sub> solutions at 300 K is found to be isotonic with 0.05 M NaCl (100 % disscociation) Ex. solutions calculate degree of disscociation of sodium sulphate.

i 
$$C_1 RT = i_2 C_2 RT$$
  
[ 1+(2)  $\alpha$  ] 0.042 = 2 ×  $\frac{0.05}{2}$   
1 + 2  $\alpha$  =  $\frac{5}{2}$  - 1  
2  $\alpha$  =  $\frac{3}{2}$   
 $\alpha$  =  $\frac{3}{4}$  × 100 = 75 %.

If 6 gm of CH<sub>3</sub> COOH is dissolved in benzene to make 1 litre at 300 K  $\pi$  of solutions is found to be 1.64 Ex. atm. If it is known that CH<sub>3</sub>COOH in benzene forms a dimer.



)

Calculate degree of association of acetic acid in benzene

$$i = 1 + \left(\frac{1}{n} - 1\right)\beta.$$
  
1.64 = 0.0823 × 300 × [1 +  $\left(\frac{1}{n} - 1\right)\beta$ ]  
1.64 = 0.0823 × 300 [1 -  $\frac{\beta}{2}$ ] 0.1

Solution & Colligative Properties # 46

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SOLUTION & COLLIGATIVE PROPERTIES # 47

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Other	method :	
	$HgCl_2$ + 4KI $\swarrow$ K[HgI_1] + 2KCl.	
	40 400 0 0	
	0 400-160 40 80	
	$\frac{240}{1000}$ $\frac{40}{1000}$ $\frac{80}{1000}$	
	(1000 1000 1000	
	$\pi = (I_1 C_1 + I_2 C_2 + I_3 C_3) R I.$	
	$= (0.24 \times 2 + 3 \times 0.04 + 0.08 \times 2) 0.082 \times 300. = 18.69 \text{ atm.}$	
Ex.	(Note: Take this problem after co-ordination compounds have been taught)	
	Ba <sup>2+</sup> ions, CN <sup>-</sup> & Co <sup>2+</sup> ions form a water soluble complex with Ba <sup>2+</sup> ions as free cations for a 0.01 M	
	coordination number of $Co^{2+}$ ion in this complex and formula of the co-ordination compound.	
	$(T = 300 \text{ K}, \text{R} = 0.082 \text{ L} \text{ atm. mol}^{-1} \text{ k}^{-1})$	
Solution	Say C.N. = x	
	$0.984 = i 0.01 \times 0.082 \times 300 = i \times 0.246$	
	$i = 4 = 1 + (n - 1) \alpha$	
$\Rightarrow$	n = 5	
	Charge on co-ordination sphere = charge on Coblat ion - charge on x cyanide ions = - (x-2) i.e. co-ordination sphere is $[Co(CN)]^{-(x-2)}$	
	Chage on Barium ion is $+2$	
	THus, formula of the complex will be $Ba_{(x-2)}$ [Co(CN), by charge balance.	
	x - 2 + 2 = 5	
	$\therefore CN = 5$	
:.	Formula is $Ba_3[Co(CN)_5]_2$ .	

Solution & Colligative Properties #48

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