

SOLUTIONS CHAPTER NO. 9

(1st Year Chemistry) Tof/s

PHASE: The sample of matter with uniform properties and a fixed composition is called PHASE.

EXAMPLE: Water at room temp. and normal pressure is in liquid phase. The properties of water are uniform throughout this liquid phase.

SOLUTION: A homogeneous mixture of two or more substances is called SOLUTION. It is also a phase whose properties are different from water.

SOLUTE: The substance which is present in relatively small quantity is called SOLUTE.

SOLVENT: The substance which is present in relatively larger quantity is called SOLVENT.

EXAMPLE: When 5.0g glucose is dissolved in 100ml of water, glucose is solute and water is solvent.

CONCENTRATION: The amount of solute dissolved in unit amount of solvent is called Concentration.

Solutions containing relatively lower concentration are called dilute solutions. Those containing relatively higher concentrations of solute are called concentrated solutions.

CONCENTRATION UNITS OF SOLUTIONS

There are different types of concentration units of solutions. These are

- 1) PERCENTAGE COMPOSITION
- 2) MOLARITY
- 3) MOLALITY
- 4) MOLE FRACTION
- 5) PARTS PER MILLION.

$\% \text{ w/v} =$ Parts by wt of solute per 100 parts by vol. of solution.
5% w/v sol. of glucose contains 5g glucose in 100ml of solution.

$\% \text{ v/v} =$ It is parts by vol. of solute in 100 parts by wt of solution.
5% v/v solution contains 5ml of solute in 100g solution. mass of solute cannot be specified.

(2)

PERCENTAGE COMPOSITION It can be w/w% or v/v% (2)

1. w/w% :- Both solute and solvent are expressed in grams. For example 5% w/w solution of NaCl contains 5g NaCl in 95g solvent. In other words it contains 5g solute per 100g solution.

(2) v/v% :- The volume of solute present per 100ml of solution. For example 5% v/v solution is a solution which contains 5ml of solute per 100ml of solution.

MOLARITY "M" It is defined as number of moles of solute per dm³ of solution. $M = \frac{\text{moles of solute}}{\text{Vol. of solution in dm}^3}$

It can be modified as follows $M = \frac{\text{wt. of solute} \times 1000}{\text{M.W. of solute} \times \text{Vol. of solution in cm}^3}$

MOLALITY "m" It is defined as number of moles of solute per kg of solvent. $m = \frac{\text{moles of solute}}{\text{wt of solvent in kg}}$

For example 1 molar solution of glucose contains 1 mole of glucose per dm³ of solution (glucose + H₂O = 1 dm³) while 1 molal solution contains 1 mole glucose in 1kg of solvent. MOLALITY is independent of Temp.

MOLE FRACTION It is defined as number of moles of a particular component divided by total number of moles in the mixture. Let these are n_A, n_B, n_C moles of component A, B and C respectively. Their moles fraction of A, B and C are $x_A = \frac{n_A}{n_A + n_B + n_C}$, $x_B = \frac{n_B}{n_A + n_B + n_C}$, $x_C = \frac{n_C}{n_A + n_B + n_C}$

The sum of mole fractions is always equal to unity. $x_A + x_B + x_C = 1$

NORMALITY "N" The number of gram equivalents of solute present per dm³ of solution. $N = \frac{\text{gram equivalent of solute}}{\text{volume of solution in dm}^3}$

PARTS PER MILLION

1 ppm = $\frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$

This unit is used for very dilute solutions.

SOLUTIONS OF SOLIDS IN LIQUIDS.

The process of dissolution can be explained in terms of forces of attraction between solute and solvent molecules.

MOLECULAR CRYSTALS IN NON POLAR SOLVENTS In molecular crystals the intermolecular forces are very weak called London forces. These forces can be easily broken. Thus molecular crystals are soluble in non polar solvents like benzene.

POLAR SOLIDS IN NON POLAR SOLVENTS In polar solids like cane sugar inter ionic or intermolecular forces are quite strong. The forces of attraction between solute and solvent molecules (non polar solvent) cannot overcome the forces of attraction between solute particles. Thus polar solids are insoluble in non polar solvents. A quite polar solvent like water is required to dissolve these solids.

IONIC SOLIDS AND POLAR SOLVENTS The inter ionic forces are very strong in ionic solids. Thus equally strong polar solvents are required to dissolve them. Such solids cannot be dissolved in moderately polar solvents e.g. Acetone. A moderately polar solvent fails to dissolve sodium chloride, because forces of attraction between solute ions (Na^{+} , Cl^{-} ions) are too strong. The forces solvent can not break these forces of attraction. Thus in general solubility principle is "LIKE DISSOLVES LIKE."

SOLUTIONS OF LIQUIDS IN LIQUIDS

The solutions of liquids in liquids may be divided into three classes.

- 1) Completely miscible liquids -
- 2) Partially miscible liquids -
- 3) Practically immiscible liquids

COMPLETELY MISCIBLE LIQUIDS Liquids like alcohol and water or alcohol and ether mix in all proportions. However

the properties of such solutions are not strictly additive. Generally, volume may increase on mixing two components. Heat may be absorbed or evolved on mixing. These solutions can be separated by fractional distillation.

PARTIALLY MISCIBLE LIQUIDS A large number of liquids dissolve into each other to a limited extent.

EXAMPLE Ether dissolves water 1.2%
water dissolves ether 6.5%.

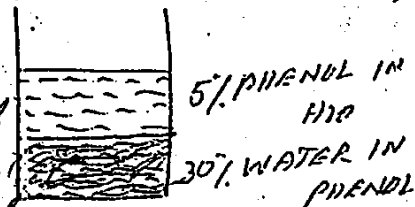
On shaking equal volumes of water and ether two layers are formed. Each layer is saturated w.r. of other layer. For example ether layer is a saturated sol. of water in ether and vice versa. Such solutions are called CONJUGATE SOLUTIONS. The mutual solubilities are affected by temp. change.

EXAMPLES

- 1) Phenol-water system (ii) Ethyl amine - water system
- 2) Nicotine - water system

PHENOL - WATER SYSTEM

When equal volumes of phenol and water are mixed at room temperature two layers are formed. The upper layer is a saturated sol. of phenol in water. The lower layer is saturated sol. of water in phenol.



When temp. of water-phenol system is increased, the composition of both layers changes. Phenol travels from lower layer to upper layer and water from upper layer moves to lower layer. At 65.9°C a homogeneous mixture of two components is obtained. This homogeneous mixture contains 34% PHENOL AND 66% WATER.

CRITICAL SOLUTION TEMPERATURE OR UPPER CONSOLUTE TEMP.

The temp. 65.9 at which two conjugate solutions merge into one another is called CRITICAL SOLUTION TEMP. OR UPPER CONSOLUTE TEMPERATURE.

Consolute temp. of some other partially miscible liq.

given below
 water - Aniline 16.7°C with 15% water
 methanol - cyclohexane 49.1° with 29% methanol

3) LIQUIDS PRACTICALLY IMMISCIBLE / Two liquids which don't dissolve into each other in any proportion are immiscible. Examples: water - Benzene, CS_2 - water.

WHAT ARE CHARACTERISTICS OF IDEAL AND NON-IDEAL SOLUTIONS

1) FORCES OF ATTRACTION / The forces of attraction between molecules of pure components are the same as forces of attractions between solute and solvent molecules. i.e. A-A, B-B and A-B forces are equally strong forces.

2) VOLUME / There should be no change in volume on mixing two components $\Delta V = \text{zero}$

3) ENTHALPY CHANGE / $\Delta H = 0$ i.e. Heat should not be absorbed or evolved on mixing two components.

4) RAOULT'S LAW / The solution which obeys Raoult's law under all conditions of conc, temp and pressure is called ideal solution.

The solutions which don't possess the characteristics are called Non-ideal solution.

$\Delta H \neq 0$
 $\Delta V \neq 0$
 $A-A \neq B-B \neq A-B$

which don't obey Raoult's law.

COLLIGATIVE PROPERTIES OF SOLUTIONS.

Q. NO. 1 STATE RAOULTS LAW? HOW TO DETERMINE MOLECULAR WT. OF SOLUTE ON THE BASIS OF

ANSWER

RAOULT'S LAW

According to Raoult's law, "The vapour pressure of a solution of a non-volatile non-electrolyte solute in a volatile solvent is directly proportional to mole fraction of solvent". Mathematically it could be written as $P_s \propto x_1$ or $P_s = P^0 x_1$ — (1)

$P_s = v.p.$ of solution, $P^0 = v.p.$ of pure solvent.
 Since $x_1 + x_2 = 1$ and $x_1 = 1 - x_2$ so eq. No. 1 could be written as

$$P_s = P^0(1 - x_2)$$

$$P_s = P^0 - P^0 x_2$$

$$P^0 x_2 = P^0 - P_s$$

$$x_2 = \frac{\Delta P}{P^0} \quad \text{--- (2)}$$

Equation (2) states that, "Relative lowering of v.p. ($\frac{\Delta P}{P^0}$) is equal to mole fraction of solute". Raoult's law can also be stated as, "This follows Lowering of vapour pressure is directly proportional to mole fraction of solute, for a solution of non-volatile non-electrolyte solute in a volatile solvent."

$$\Delta P \propto x_2 \quad \text{or} \quad \Delta P = P^0 x_2 \quad \text{--- (3)}$$

$$P^0 - P_s = P^0 x_2$$

$$\Delta P = P^0 - P_s$$

LOWERING OF V.P. = $\Delta P = P^0 - P_s$

But $x_2 = 1 - x_1$, $\therefore P^0 - P_s = P^0(1 - x_1)$

$$P^0 - P_s = P^0 - P^0 x_1$$

$$P^0 - P_s - P^0 = -P^0 x_1$$

$$+ P_s = +P^0 x_1$$

CALCULATION OF MOLECULAR WEIGHT

P-2.

Raoult's law can be used to determine molecular wt. of unknown solute by dissolving a definite amount of solute in a known quantity of a known solvent.

The lowering of v.p. of solvent is determined after dissolving unknown solute. Let it be " ΔP "

Then according to eq. No. 2 $\frac{\Delta P}{P^0} = X_2$ — (2)

$$X_2 = \frac{n_2}{n_1 + n_2} \quad \text{or} \quad X_2 = \frac{w_2/M_2}{\frac{w_1}{M_1} + \frac{w_2}{M_2}}$$

Putting value of " X_2 " in eq. 2 we get

$$\frac{\Delta P}{P^0} = \frac{w_2/M_2}{\frac{w_1}{M_1} + \frac{w_2}{M_2}} \quad \text{--- (4)}$$

For a very dilute solution $w_2 \ll w_1$, therefore $\frac{w_2}{M_2}$ can be neglected as compared to $\frac{w_1}{M_1}$ in eq. (4)

$$\frac{\Delta P}{P^0} = \frac{w_2/M_2}{w_1/M_1}$$

$$\frac{\Delta P}{P^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$M_2 = \frac{w_2 \times M_1 \times P^0}{w_1 \times \Delta P} \quad \text{--- (6)}$$

Equation No. 6 can be used to determine M.Wt. of solute.

RAOULTS LAW FOR A SOLUTION OF NON VOLATILE NON ELECTROLYTE SOLUTE IN A VOLATILE SOLVENT

For this solution Raoult's law states that, "The vapour pressure of each component in a solution of a volatile non electrolyte solute in a volatile solvent is directly proportional to mole fraction of that component."

Let there be two components "A" and "B" with respective mole fractions " X_A " and " X_B " then according to Raoult's law

P. (3)

$$P_A \propto X_A$$

ϕ

$$P_B \propto X_B$$

$$P_A = P_A^0 X_A$$

$$P_B = P_B^0 X_B$$

— (7)

" P_A " and " P_B " are partial pressures of "A" and "B" in solution and P_A^0 and P_B^0 are pressures of pure components.

The total pressure of solution is equal to sum of partial pressures of two components

$$P_s = P_A + P_B$$

$$P_s = P_A^0 X_A + P_B^0 X_B$$

— (8)

Q. No. 2 WHAT ARE IDEAL & NON-IDEAL SOLUTIONS. DISCUSS DEVIATIONS OF REAL SOLUTIONS.

IDEAL SOLUTION // The concept of ideal solution is very important to compare behavior of real solutions. The ideal solution may be defined as a solution which obeys Raoult's law under all conditions. For an ideal solution activity of each component is equal to mole fraction of that component $X_A = a_A$ and $X_B = a_B$

The ideal solution possesses following characteristics

(i) There is no enthalpy change on mixing components of an ideal solution $\Delta H = 0$

(ii) There is no volume change $\Delta V = 0$

(iii) Heat is neither absorbed nor evolved on mixing two components

(iv) The vapor pressure of each component is given by Raoult's law. According to Raoult's law, "the vapor pressure of each component is directly proportional to mole fraction of that component. And V.P. of solution is equal to sum of partial pressures of two components."

$$P_A \propto X_A$$

ϕ

$$P_B \propto X_B$$

$$P_A = P_A^0 X_A$$

$$P_B = P_B^0 X_B$$

$$P_s = P_A + P_B$$

— (9)

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

$$P = P_A^0 (1 - x_B) + P_B^0 x_B \quad \text{Since } (x_A + x_B = 1)$$

$$x_A = 1 - x_B$$

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

$$P = P_B^0 x_B - P_A^0 x_B + P_A^0 \quad \text{--- (2)}$$

At any given temperature P_A^0 and P_B^0 are constant

Hence a plot of "P" against " x_B " should give a straight line with $P = P_A^0$ at $x_B = 0$

and $P = P_B^0$ at $x_B = 1$

Eq. can be written as $P = (P_B^0 - P_A^0) x_B + P_A^0$

In figure "P" indicates v.p. of solution

and total v.p. of solution is intermediate between vapour pressures of pure components

The total v.p. of solution at composition "Y" is indicated by "Z". The v.p. of solution is equal to sum of partial pressures of two components

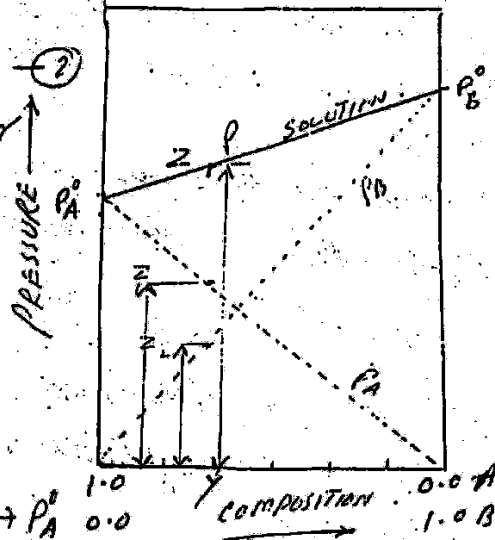
$$P = Z = Z_1 + Z_2$$

It appears from fig that for an ideal solution the partial vapour pressure of component in solution is always less than pure component v.p.

NOTE :- Dotted lines " P_A^0 " and " P_B^0 " indicate v.p. of component "A" and "B" in solution. Partial

When solution is very dilute Raoult's law is almost invariably applied to solvents. In general Raoult's law could be written as

$$P_{\text{solvent}} = P_{\text{solvent}}^0 \times x_{\text{solvent}}$$



10
WHAT ARE COLLIGATIVE PROPERTIES?

EXPLAIN LOWERING OF VAPOUR PRESSURE

The physical properties which depend upon number of solute and solvent molecules or ions and independent of their nature are called COLLIGATIVE PROPERTIES.

For example

- (i) Lowering of vapour pressure
- (ii) Elevation of boiling point
- (iii) Depression of freezing point

The colligative properties help us to determine molecular weights of unknown solutes. Further these properties have helped in development of solution theory.

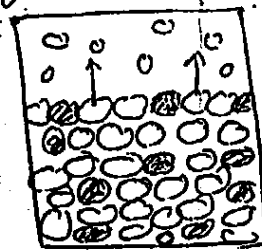
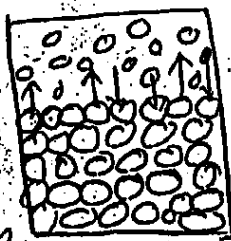
The following conditions should be fulfilled by the solutions

- 1) Solution should be dilute
- 2) Solute should be non volatile.
- 3) Solute should be non electrolyte.

LOWERING OF VAPOUR PRESSURE:

When a non volatile solute is dissolved in a volatile solvent vapour pressure of solution is always less than pure solvent.

REASON On the surface of solvent 100% molecules are volatile while in case of solution some solute molecules are also present on the surface which are non volatile.



pure solvent has higher vapour pressure than solution. Further stronger forces of attraction between solute and solvent molecules also decrease vapour pressure of solution. A quantitative relationship between amount of solute and lowering of vapour pressure is given by Raoult's Law.

According to Raoult's Law,

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

$$\Delta P \propto X_2$$
$$\Delta P = P^0 X_2 \quad \text{--- (1)}$$

$$X_2 = \frac{n_2}{n_1 + n_2}$$

For dil. solutions, " n_2 " is negligible as compared to n_1 .

$$\text{mole} = \frac{\text{wt of sub.}}{\text{M.Wt of sub.}}$$

$$\frac{\Delta P}{P^0} = X_2$$

$$\frac{\Delta P}{P^0} = \frac{n_2}{n_1 + n_2} \quad \text{--- 2}$$

$$\frac{\Delta P}{P^0} = \frac{n_2}{n_1}$$

$$\frac{\Delta P}{P^0} = \frac{w_2/M_2}{w_1/M_1} \quad \text{--- 3}$$

$$\frac{\Delta P}{P^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$M_2 = \frac{w_2 \times P^0 \times M_1}{w_1 \times \Delta P} \quad \text{--- (4)}$$

Eq (4) can be used to determine M.Wt of unknown substances (see example No. 10)

DEFINE ELEVATION OF B.P.

PROVE THAT

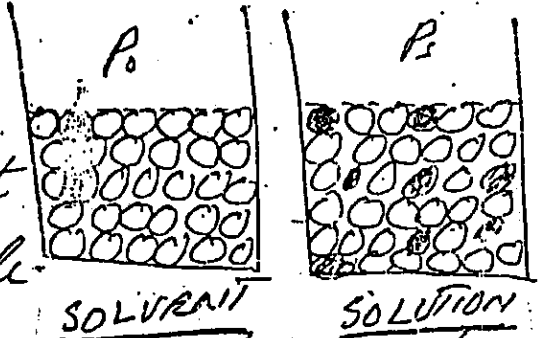
$$\Delta T_b = K_b m$$

ELEVATION OF BOILING POINT:

BOILING POINT: The temp. at which vapour pressure of a liquid becomes equal to atmospheric pressure or any other external pressure is called boiling point.

The vapour pressure of a solution is of non-volatile non-electrolyte solute in a volatile solvent is always lower than that of pure solvent. It is due to the fact that in pure solvent 100% molecules present at surface are volatile.

While in solution, solute molecules are also present at surface which are non-volatile.



Further there are more solute-solvent interactions in solution than that between pure solvent molecules.

Thus $P^0 > P_1$ i.e. vapour pressure of solution is always less than pure solvent. It is called lowering of vapour pressure denoted by " ΔP ".

The lowering of vapour pressure depends upon number of solute particles present in solution. This type of property which depends upon number of particles and independent of its nature are called "COLLIGATIVE PROPERTIES" OF SOLUTIONS.

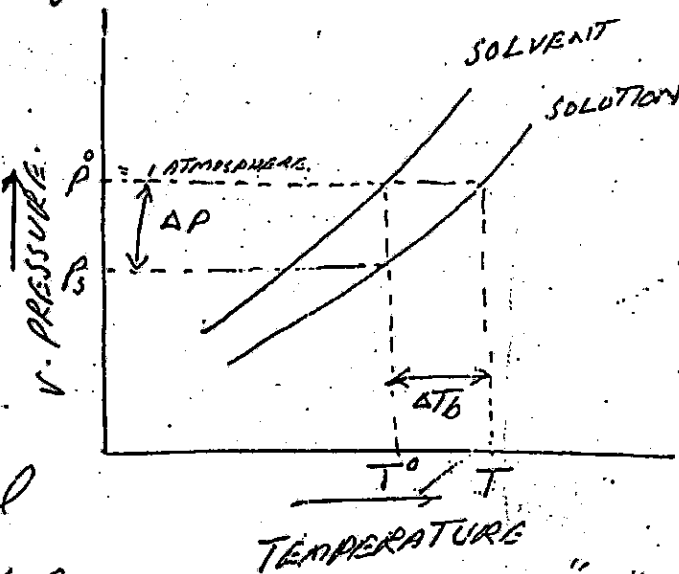
Since vapour pressure of solution is less than that of pure solvent, therefore

more heat and higher temperature will be required to bring vapour pressure of solution equal to increased external pressure. Thus B.P. of solution of non volatile non electrolyte solute is always higher than that of pure solvent. It is called ELEVATION OF BOILING POINT.

It can also be shown as follows.

It is clear from graph that v.p. of solvent

become equal to external pressure at temperature T° . It is boiling point of pure solvent. The v.p. of solution becomes equal to same external pressure at temp. T at increased pressure.



This difference $\Delta T_b = T - T^{\circ}$ is called Elevation of boiling point.

The elevation of boiling point depends upon conc. of solution. The more conc. solution will have higher elevation of B.P. $\Delta T_b \propto m$ (m = molality of solute)

$$\Delta T_b = K_b \cdot m \quad \text{--- (1)}$$

In equation (1) K_b is called ^{EBULLIOSCOPIC} ~~Ebullioscopic~~ constant (or molal elevation of boiling point constant).

It can be defined as, "ELEVATION OF BOILING POINT FOR 1 MOLAL SOLUTION OF NON-VOLATILE NON ELECTROLYTE SOLUTE IN A VOLATILE SOLVENT PROVIDED SOLUTION OBEYS RAOULTS LAW"

$$\Delta T_b = K_b \cdot m$$

$$\Delta T_b = K_b \times 1$$

$$\Delta T_b = K_b$$

(m = MOLALITY OF SOLUTION)
 m = 1 FOR 1 MOLAL SOLUTION)

CALCULATION OF MOLECULAR WEIGHT

The equation no. "1" can be used to determine molecular wt of unknown solute

Since molality is defined as "The number of moles of solute per kg of solvent" therefore

$$m = \frac{\text{moles of solute}}{\text{wt. of solvent in kg}}$$

$$m = \frac{w_2 / M_2}{w_1 / 1000}$$

$$m = \frac{w_2 \times 1000}{w_1 \times M_2}$$

Putting value of "m" in eq (1)

$$\Delta T_b = K_b \frac{w_2}{w_1 \times M_2} \times 1000$$

$$M_2 = \frac{K_b}{\Delta T_b} \frac{w_2 \times 1000}{w_1} \quad \text{--- (2)}$$

15
EXPERIMENTAL
DETERMINATION OF ELEVATION OF BOILING
POINT OF SOLUTION

15

LANDSBERGER'S METHOD

The elevation of boiling point can be determined experimentally by Landsberger method. The apparatus used for this purpose is shown below.

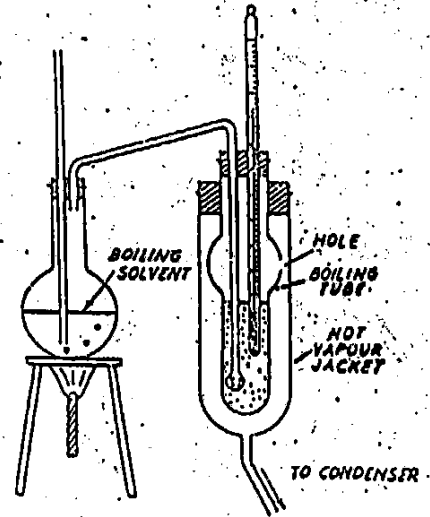


Fig. 13. Landsberger's Apparatus

The vapours of boiling solvent in round bottom flask are passed through pure solvent present in boiling tube fitted with a thermometer. These vapours cause the solvent in the tube to boil by latent heat of condensation. When solvent starts boiling, temperature becomes constant. This is boiling point of pure solvent.

A known supply of pure solvent vapours is cut off temporarily. A weighed amount of solute "w₂" whose boiling point is to be determined is dropped into solvent in the boiling tube. The solute is dissolved and boiling point of solution is determined in the same manner. The elevation of B.P. ($\Delta T_b = T - T_0$) is determined. By determining wt of solute and subtracting wt of solute, the wt of solvent can be determined "w₁".

$$M_2 = \frac{K_b}{\Delta T_b} \frac{w_2}{w_1} \times 1000$$

DEPRESSION OF FREEZING POINT CRYOSCOPIC CONSTANT

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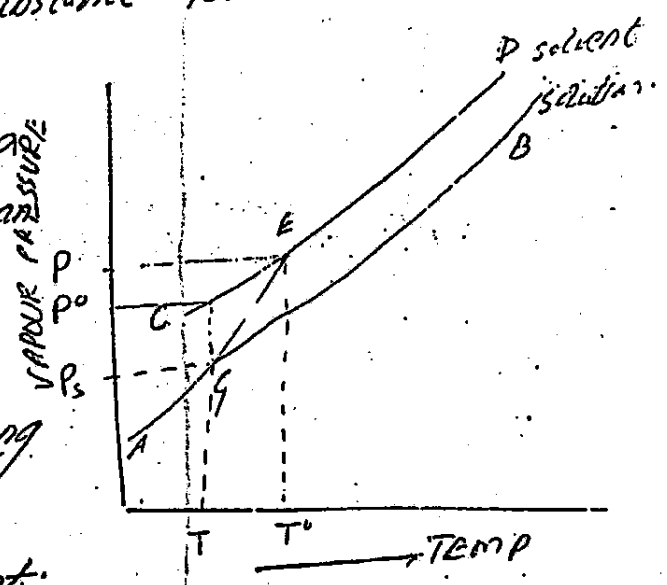
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$$\Delta T_f = K_f m$$

The cryoscopic constant is defined as "Lowering of freezing point produced by dissolving 1 mole of non volatile non electrolyte solute in a volatile solvent, provided solution obeys Raoult's law."

When a dilute solution is cooled a temperature is finally reached at which solid solvent begins to separate from solution. This is called freezing point of solution. Freezing point of solution may also be defined as temperature at which solution is in equilibrium with solid solvent. At freezing point solid and liquid forms of a substance have same vapour pressure.

The freezing point of a solution is always lower than freezing point of pure solvent. This is due to lowering of v.p. by dissolving non volatile non electrolyte solute in a volatile solvent.



The "vapour pressure - Temperature" diagram is shown above.

CURVES IN DIAGRAM :-

(i) "C.D" CURVE :- It is vapour pressure curve of solvent, indicates that vapour pressure increases on heating.

AE CURVE It is sublimation curve of ice. (3)

GB CURVE It is vapour pressure curve of solution.

CE CURVE vapour pressure curve of super cooled water.

The point of intersection of "ED" and "AE" curve is "E" which represent freezing point of pure solvent. At this point pure solvent and solid solvent has same v.p. This temperature is represented by T° in diagram.

The point of intersection of v.p. curve of solution and reverse sublimation curve is "G" at which solid solvent and solution have same v.p. This point is freezing point of solution which is obviously less than pure solvent. It is represented by T° .

$T^{\circ} - T = \Delta T_f$ is called lowering of freezing point. ΔT_f depends upon nature of solvent and concentration of solution. For dilute solution, " ΔT_f " varies linearly with concentration irrespective of its nature.

Depression of freezing point is directly proportional to molality of solution. $\Delta T_f \propto m$

where "m" is called MOLALITY of solution. K_f is called CRYOSCOPIC CONSTANT. It is defined as depression of freezing point for 1 molal solution of non volatile non electrolyte solute in a volatile solvent.

$$\Delta T_f = K_f \times 1 \quad (m = 1 \text{ molal sol})$$

CALCULATION OF MOLECULAR WT / Equation (1) can be used to determine M.Wt. of unknown solute

$$\Delta T_f = K_f \frac{w_2 / m_2}{w_1 / 1000}$$

$$\Delta T_f = K_f \frac{w_2 \times 1000}{w_1 \times M_2}$$

$$\therefore M_2 = \frac{K_f}{\Delta T_f} \frac{w_2 \times 1000}{w_1}$$

DESCRIPTION OF APPARATUS.

(i) FREEZING POINT TUBE:- It is a glass tube having a side arm. A definite amount of solvent is taken in F.P. tube. It is fitted with Beckmann's thermometer and a stirrer.

(ii) JACKET TUBE: It is a thickwalled tube placed in freezing mixture. In this tube freezing point tube is fixed by a proper rubber stopper. It ensures homogeneous cooling of solvent taken in F.P. tube.

FREEZING MIXTURE:- For ordinary purposes (for aqueous solutions) this mixture is (ice + salt). This mixture is continuously stirred for homogeneous cooling.

WORKING:- In actual practice 15-20 g of solvent is taken in freezing point tube. The tube is fixed in jacket tube and placed in freezing mixture. The temp. of solvent decreases as indicated by thermometer. After sometime temp becomes constant. The solvent is stirred vigorously the temperature increases a few degrees due to fusion of frozen solvent. Then again temperature begins to fall and becomes ~~once~~ constant at a definite temp. This is Freezing point of solvent.

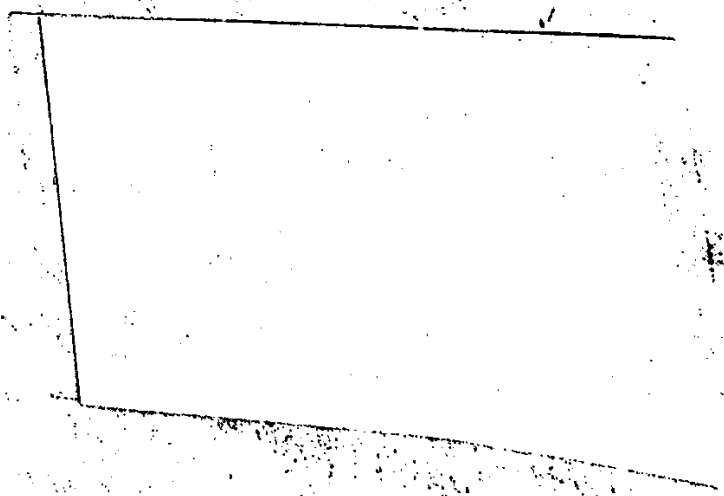
The freezing tube is removed from jacket tube. A weighed amount of solute is added from side arm and well shaken to dissolve all the solute.

The freezing point of solution is determined in the same manner as for solvent.

The depression in freezing point is determined as $\Delta T_f = T_0 - T_1$
From ΔT_f we can determine M.Wt of Solute $\left\{ \Delta T_f = K_{fp} \cdot \frac{w}{M} \right.$

APPLICATIONS OF ΔT_b AND ΔT_f

- Elevation of boiling point and depression of freezing point can be used to determine m.wts of unknown solutes
- The presence of solute increases liquid range of liquid by elevation of boiling point and depression of freezing point. For example by addition of solute water can exist as liquid even below 0°C and also above 100°C . An important application is use of ethylene glycol in radiator of Automobile. It is non volatile and miscible with water. It prevents water from freezing in winter and in hot summer, it prevents boiling.
- NaCl and KNO_3 are added to lower melting point of ice. Thus a mixture of ice and salt is used in ice cream.



Q.1:- WHAT IS HEAT OF SOLUTION? EXPLAIN? (2)

ANS:- The heat of solution is defined as "Enthalpy change which takes place when 1 mole of substance is dissolved in a specified number of moles of solvent at a given temperature. Heat of solution is actually energy difference between energy of components and energy of solution."

$$\Delta H_{\text{solution}} = H_{\text{solution}} - \sum H_{\text{components}}$$

However it is not possible to measure absolute values of "H" components and "H" of solution. We are mostly interested in measuring " ΔH ".

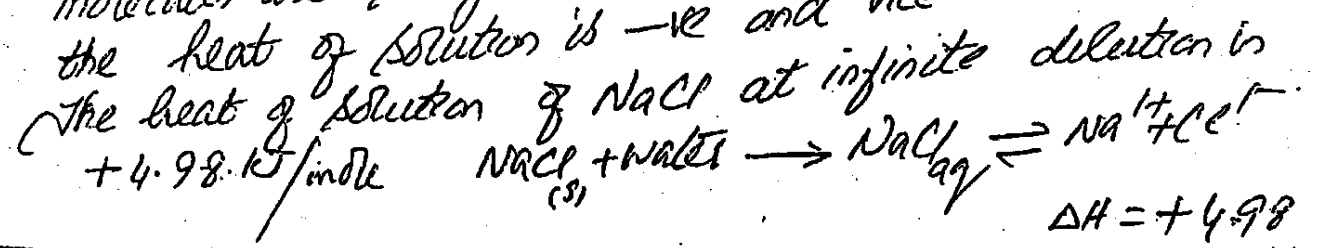
NEGATIVE HEAT OF SOLUTION | If solution has lesser energy as compared to energy of components the heat is evolved during solution formation. Thus dissolution process is exothermic.

POSITIVE ΔH_{sol} | It is an endothermic process. The energy of solution is greater than that of pure components.

For example when Lithium Chloride is dissolved in water, heat is evolved and temperature of solution increases. While dissolution of KNO_3 in water is ~~exothermic~~ endothermic process and temperature of solution falls during solution formation.

HOW TO ACCOUNT FOR HEAT OF SOLUTION | The heat of solution depends upon the relative strength of intermolecular forces between solute-solute, solvent-solvent and solute-solvent molecules.

If forces of attraction between solute and solvent molecules are stronger than that between pure components the heat of solution is -ve and vice versa.

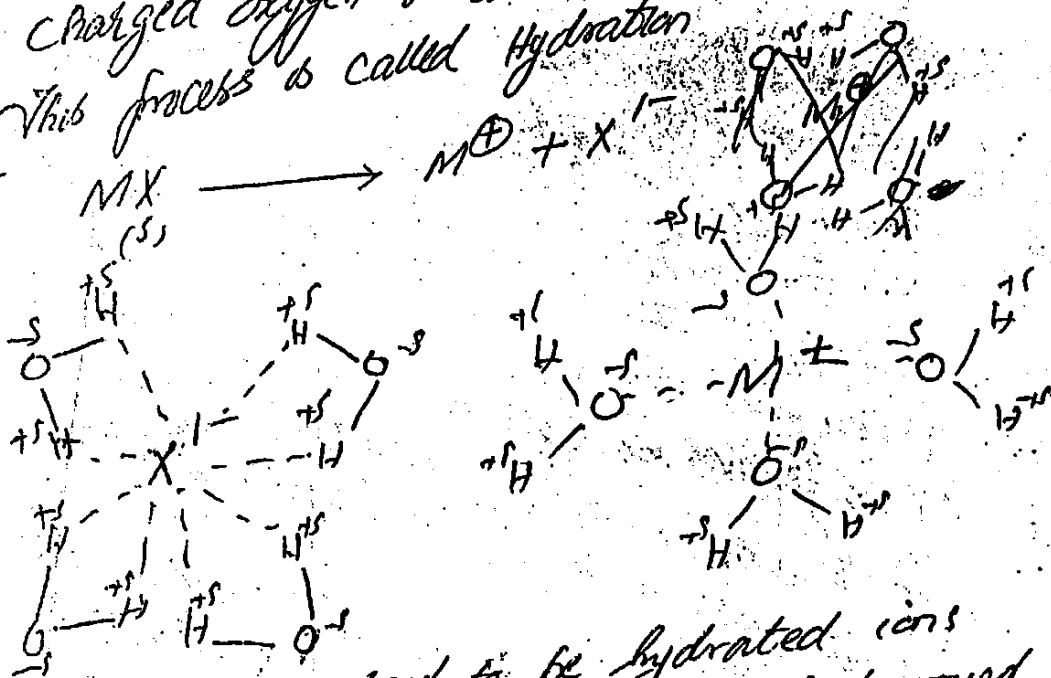


HYDRATION AND HYDRATES

HYDRATION:- The process in which solvent molecules surround and interact with solute ions or molecules is called HYDRATION.

When an ionic compound is dissolved in water, it splits up into positive and negative ions. The partial positively charged hydrogens of charged oxygen is attracted towards +ve ions and partial negatively charged oxygen is attracted towards -ve ions.

This process is called Hydration



The ions are said to be hydrated ions. The number of water molecules which surround a given ion depend upon charge density = $\frac{\text{charge}}{\text{volume}}$.

The positive ion has high charge density due to smaller size while -ve ion has lower charge density. Thus more number of solvent molecules are attached with +ve ion than -ve ion.

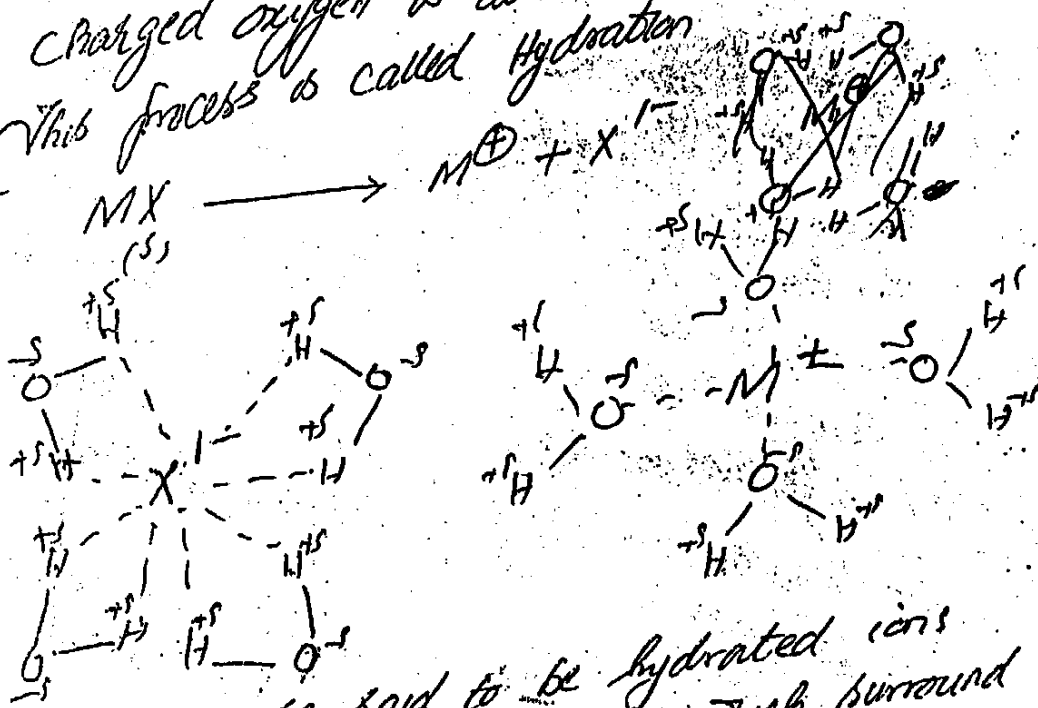
HYDRATES The crystalline substances which contain chemically combined water in definite proportion is called HYDRATE. Hydrates are mostly formed when aqueous solⁿ of soluble salts is evaporated. Acids, Bases, elements and salts exist in hydrated form. For example in $CuSO_4 \cdot 5H_2O$, four water molecules are attached

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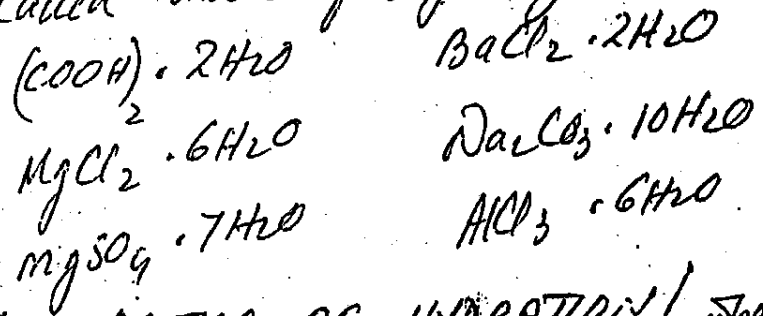
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with Cu^{2+} and ~~the~~ ^{one} water molecule is attached with SO_4^{2-} ion. It is due to high charge density of Cu^{2+} .

WATER OF CRYSTALLIZATION

The number of water molecules which are combined with compound in crystalline form is called water of crystallization or water of hydration



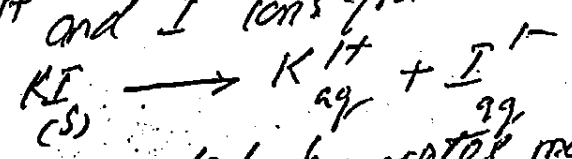
ENERGETICS OF HYDRATION

When a crystal is added to the solvent, two opposite processes take place. One is endothermic and other is exothermic

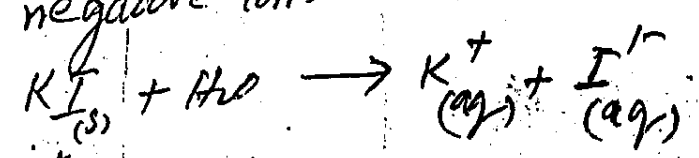
ENDOTHERMIC | The crystal lattice breaks up into constituent particles. This requires energy called lattice energy.

EXOTHERMIC | The attraction between solvent molecules and solute particles releases energy called heat of solvation. The energy of solvation must be greater than lattice energy.

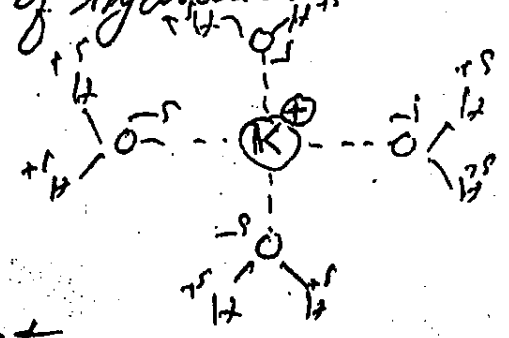
For example when $KI_{(s)}$ is dissolved in water the first step is sep. of K^+ and I^- ions from solid. This is endothermic process.



In second step ions are surrounded by water molecules releasing hydration energy (solvation energy). The positive ions have high heat of hydration than negative ions. Net reaction is



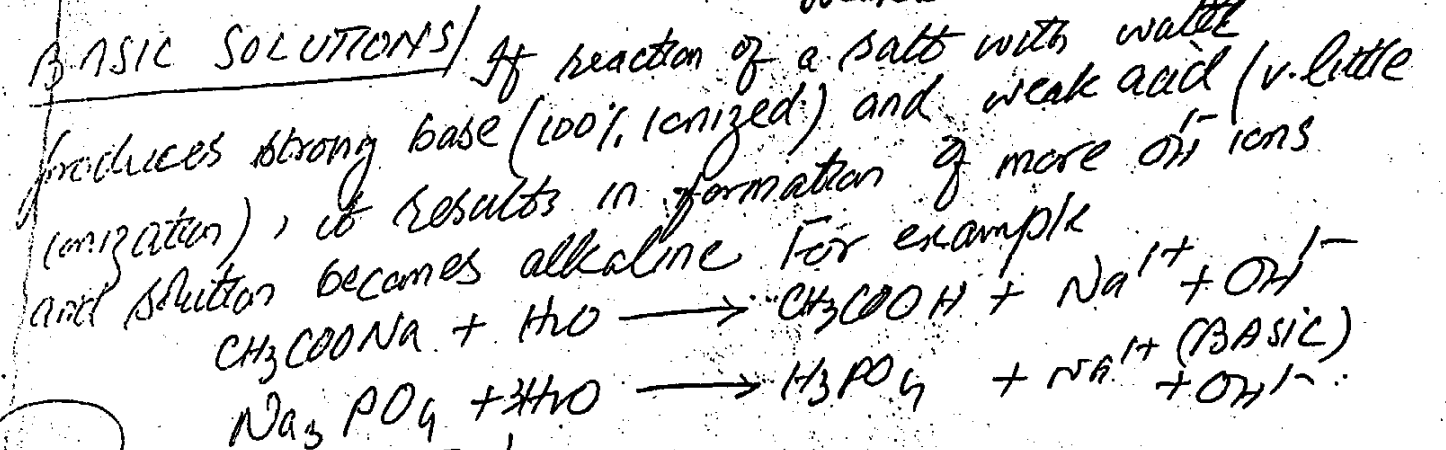
with increase in size of ion heat of hydration decreases.



HYDROLYSIS :: The reaction of salt and water to produce acidic basic or neutral solution is called HYDROLYTIC REACTION and process is called Hydrolysis.

In water conc. of H^+ ions and OH^- ions is equal. Thus water is perfectly neutral. However when a salt is added to water, the salts react with water to produce acid and base. The resulting sol. may become acidic basic or neutral depending upon degree of ionization of acid and base formed.

ACIDIC SOLUTION | If reaction of salt with water produces strong acid, it is almost 100% ionized and conc. of H^+ ions in water is increased, thus acidic sol. is formed.



BASIC SOLUTIONS | If reaction of a salt with water produces strong base (100% ionized) and weak acid (v. little ionization), it results in formation of more OH^- ions and solution becomes alkaline. For example

$CH_3COONa + H_2O$	\longrightarrow	$CH_3COOH + Na^+ + OH^-$
$Na_3PO_4 + 3H_2O$	\longrightarrow	$H_3PO_4 + 3Na^+ + 3OH^-$

(BASIC)

NEUTRAL SALTS | The salts of strong acids and strong bases are not hydrolyzed and produce neutral solution. For example $KCl, NaCl, KBr, Na_2SO_4$ produce neutral solution. Their positive and -ve ions are not hydrolyzed by water.

SOLUBILITY AND SOLUBILITY CURVES

Solubility is defined as, "The concentration of solute in the solution when it is in equilibrium with the solid substance is called solubility at that temp."

UNITS OF SOLUBILITY | Solubility is generally expressed in terms of number of grams of solute in 100g of solvent. For example at 0°C saturated sol. of NaCl contains 37.5g NaCl in 100g of water. The solubility of $CuSO_4$ at 0°C is 14.3g/100g of water.

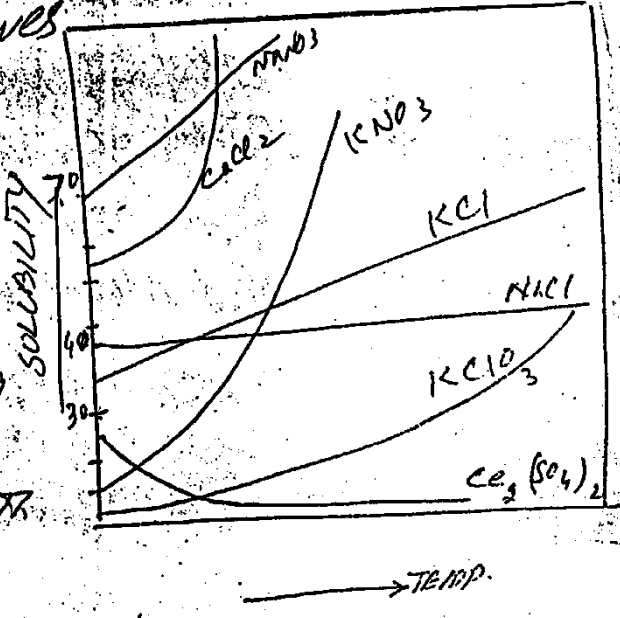
DETERMINATION | A saturated solution of solid is prepared at a definite temp. The solution is filtered. A known volume of solution is evaporated in a china dish. The mass of residue (salt) is ~~then~~ calculated. Hence solubility can be calculated.

SOLUBILITY CURVES | A curve drawn between solubility of a salt and temperature is called solubility curve. It shows effect of temperature on solubility of salt. There are two types of solubility curves.

- 1) Continuous Solubility Curve
- 2) Discontinuous Solubility Curve

Continuous solubility curves do not show sharp breaks anywhere.

Solubility curves of NaCl, $NaNO_3$, KCl show a straight line indicating that there is a little increase in solubility with increase of temp.

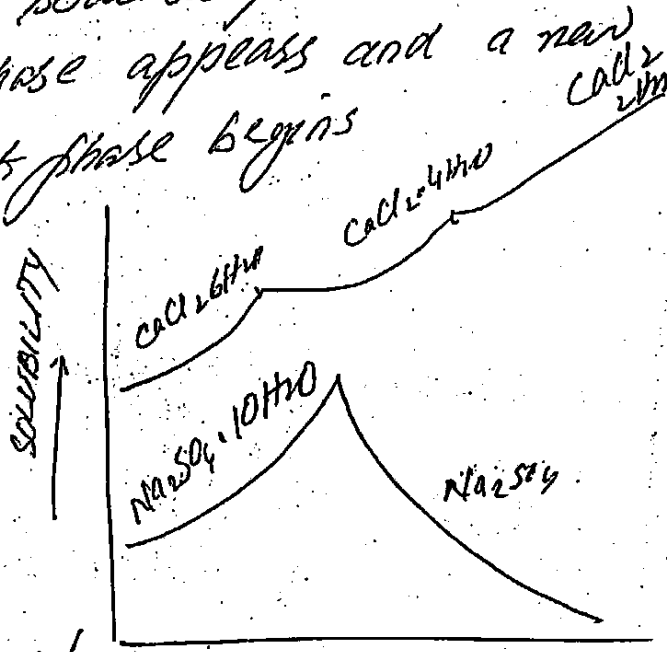


Na_2SO_4 shows abnormal behaviour. Its solubility decreases with increase in temperature. At 40°C it becomes constant.

DISCONTINUOUS SOLUBILITY CURVE

The solubility curves with sudden changes of solubility with increase in temp are called discontinuous solubility curves. Actually these solubility curves are combination of two or more solubility curve. At each break a new solid phase appears and a new solubility curve of that phase begins.

The best examples are $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Na_2SO_4 , $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.



FRACTIONAL CRYSTALLIZATION

The effect of temperature on solubility of salts is different for different substances. This difference can be used in fractional crystallization. By this technique different impurities are removed from chemical products. Procedure:- The impure solute is dissolved in a hot solvent in which solute is less soluble than impurities. The hot saturated sol. is cooled slowly. The solute being less soluble separates out first leaving impurities in the mother liquid. The pure crystals of desired product are obtained in this way.