UTKALMANI GOPABANDHU INSTITUTE OF ENGINEERING, ROURKELA

LECTURE NOTES

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Liquid State

INTERMOLECULAR FORCES IN LIQUIDS

Intermolecular forces in liquids are collectively called van der Waals forces. These forces are essentially electrical in nature and result from the attraction of charges of opposite sign. The principal kinds of intermolecular attractions are:

(1) Dipole-dipole attractions

(2) London forces

(3) Hydrogen bonding.

DIPOLE–DIPOLE ATTRACTIONS

Dipole-dipole attractions exist between molecules that are polar

A polar molecule is a molecule in which one end of the molecule is slightly positive, while the other end is slightly negative. Example (H_2O, NH_3, H_2S)

The intermolecular force is weak compared to a covalent bond, but this dipole-dipole interaction is one of the stronger intermolecular attractions.

LONDON DISPERSION FORCES

London dispersion forces exist in nonpolar molecules.

These forces result from temporary charge imbalances.

The temporary charges exist because the electrons in a molecule or ion move randomly in the structure.

The nucleus of one atom attracts electrons form the neighbouring atom. At the same time, the electrons in one particle repel the electrons in the neighbour and create a short lived charge imbalance.

HYDROGEN BONDING

Hydrogen bonding is a unique type of intermolecular attraction. There are two requirements:

(1) Covalent bond between an H atom and either F, O, or N. These are the three most electronegative elements.

(2) Interaction of the H atom in this kind of polar bond with a lone pair of electrons on a nearby atom like F, O, or N.

VAPOUR PRESSURE

The pressure exerted by the vapour in equilibrium with the liquid at a fixed temperature.

The rate of evaporation exactly equals the rate of condensation. Thus a dynamic equilibrium is established between the liquid and the vapour at the given temperature.

If the temperature of the liquid is increased, the vapour pressure will increase. This is so because at higher temperature more molecules in the liquid will have larger kinetic energy and will break away from the liquid surface

SURFACE TENSION

This property of liquids arises from the intermolecular forces of attraction.

The surface tension (γ) is defined as : the force in dynes acting along the surface of a liquid at right angle to any line 1 cm in length.

In SI system, the unit is Newton per metre (Nm–1).

In in CGS system is dynes per centimetre (dyne cm–1).

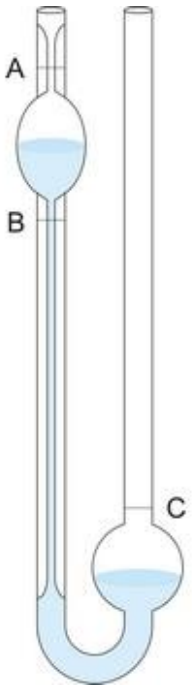
Surface tension decreases with increase in temperature.

VISCOSITY

Viscosity of a liquid is a measure of its frictional resistance. The SI unit of viscosity is poiseiulle (PI). Its other units are newton-second per square metre (N s m^{-2}) or pascal-second (Pa s.)

OSTWALD VISCOMETER

The apparatus commonly used for the determination of relative viscosity of a liquid is known as Ostwald viscometer or viscometer. A simple form of it is shown in Fig 11.24. The left-hand limb is essentially a pipette with two calibration marks A and B. A length of capillary tube joins the pipette to a bulb C in the right-hand limb.



A definite volume of liquid (say 25 ml) is poured into the bulb C with a pipette. The liquid is sucked up near to the top of the left-limb with the help of a rubber tubing attached to it. The liquid is then released to flow back into the bulb C. The time (t 1) from A to B is noted with a stopwatch. Then the

apparatus is cleaned and the experiment repeated with water, taking about the same volume. The time of flow of water (t 2) from A to B is recorded. The density of the liquid (d) and water (dw) are determined with the help of a pyknometer. The relative viscosity coefficient is calculated from the expression

$$\eta_1 / \eta_w = d\, t_1 / d_w t_2$$

Knowing the value of the viscosity coefficient of water (ηw) at the temperature of the experiment, the absolute viscosity coefficient (η) of the given liquid can be found.

In general, the viscosity decreases with increase in temperature

REFRACTIVE INDEX The refractive index (n) of a substance is defined as the ratio of the velocity of light in vacuum or air, to that in the substance :

n = Velocity of light in substance /Velocity of light in air

When a ray of light passes from air into a liquid, its direction is changed. This change of direction is called refraction.

The refractive index of the liquid with respect to air is given by Snelle's Law. According to it

where i is the angle of incidence and r the angle of refraction

SPECIFIC REFRACTION Lorenz and Lorenz (1880) purely from theoretical considerations derived the following relation for the refractive power of substance.

where Rs is the Specific Refraction, d the density and n the refractive index. The value of Rs was constant at all temperatures

MOLAR REFRACTION It is defined as the product of specific refraction and molecular mass. Thus molar refraction of a liquid (RM) is obtained by multiplying equation (1) by molecular mass

The value of molar refraction is characteristic of a substance and is temperature-independent. It can be determined by substituting the values of n, M and d in the equation

SOLVED PROBLEM. The refractive index of carbon tetrachloride for D-line of sodium has been found to be 1.4573. Calculate its molar refraction if the density is 1.595 g/cm3

Determination of Refractive Index

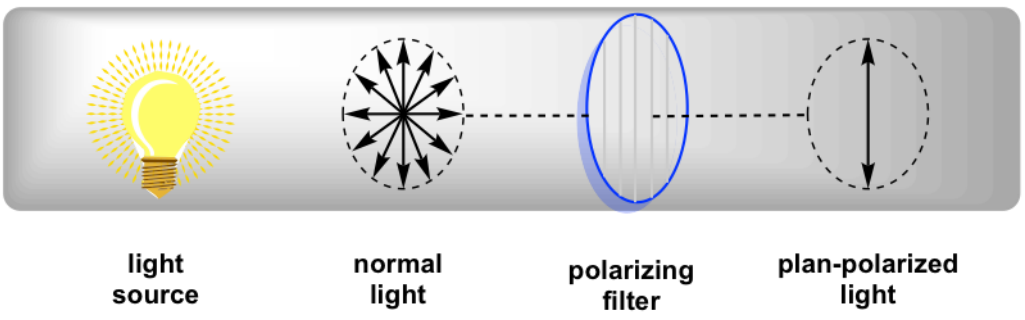
The refractive index of a liquid can be determined with the help of an instrument called Abbe Refractometer.A thin film of the liquid is placed between the two prisms. Light from a sodium lamp is made to fall on lower side of the lower prism with the help of a mirror. The hypotenuse surface of the lower prism is ground and, therefore, light enters the liquid at all angles of incidence. However, no ray can enter the upper prism with greater angle of refraction than the grazing incidence (i.e., at an angle) slightly less than 90ºC. Thus the view in the telescope appears to be divided into two bands, one bright and one dark. The prism assembly is rotated with the help of a side knob till the cross wire of the telescope coincides with the edge of the bright band. A pointer attached to the prism assembly indicates the refractive index on the scale calibrated to read refractive indices directly.



OPTICAL ACTIVITY

A compound that can rotate the plane of polarized light is called optically active. This property of a compound is called optical activity

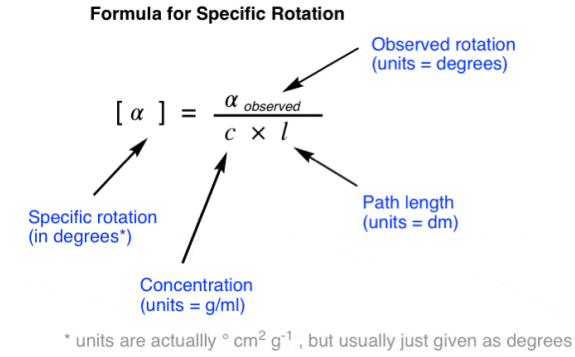
A beam of ordinary light consists of electromagnetic waves oscillating in many planes. When passed through a polarizer (e.g., a Polaroid lens), only waves oscillating in a single plane pass through. The emerging beam of light having oscillations in a single plane is said to be plane polarized.

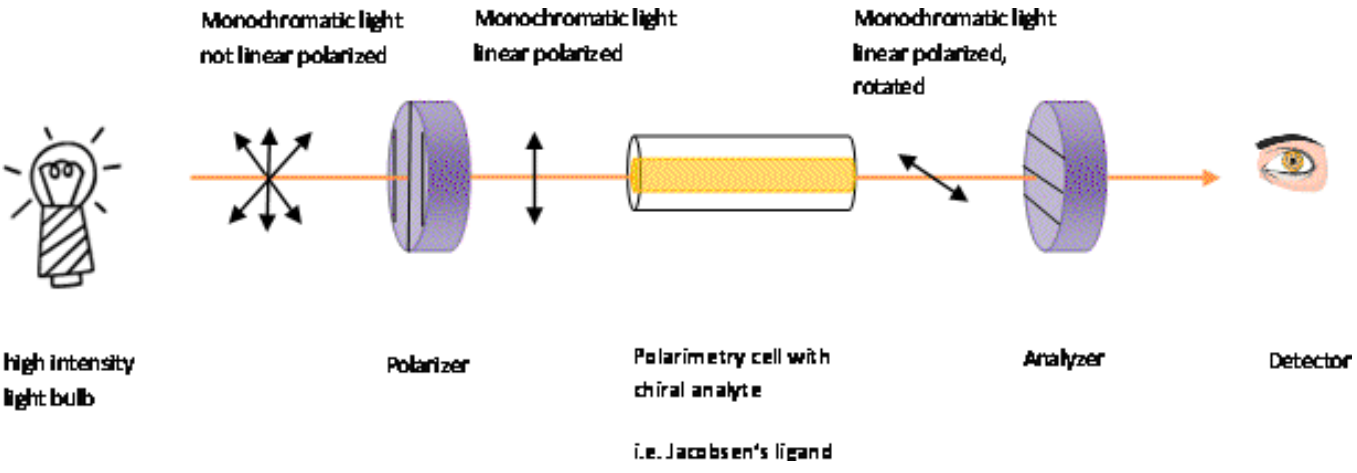


A compound which rotates the plane-polarized light to the left (anticlockwise), is said to be levorotatory. A compound that rotates the plane-polarized light to the right (clockwise), is said to be dextrorotatory.

Measurement of Optical Activity

Optical activity is measured with the help of an instrument known as polarimeter. This is basically a system of polarizers with a sample tube placed in between. First, an optically inactive medium (air or solvent) fills the sample tubes and polarized sodium light emerging from the polarizer passes through it. The analyzer is then turned to establish a dark field. This gives a zero reading on the circular scale around the analyzer. Then the solution of the given optically active compound is placed in the sample tube. The plane of polarized light passing through it is rotated. The analyzer is turned to re-establish the dark field. The angle of rotation (α) is then noted in degrees on the circular scale. The specific rotation is calculated using the expression

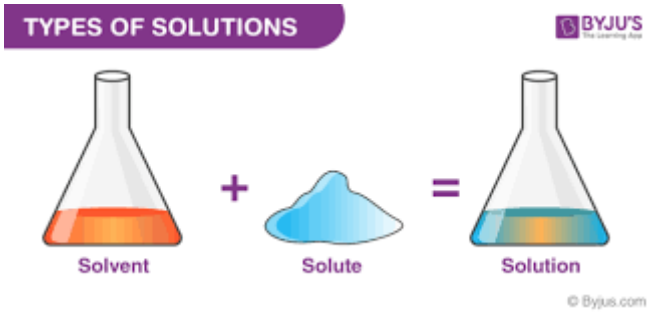




EXAMINATION QUESTIONS

1. Define or explain the following terms : (a) van der Waal's forces (b) Hydrogen bond (c) Vapour pressure (d) Boiling point (e) Surface tension (f) Viscosity (g) Ostwald's method (h) Refractive index (i) Specific Refraction (j) Molar Refraction (k) Optical activity (l) Specific rotation
2. Define viscosity and coefficient of viscosity. Describe one method of determining the viscosity of liquids.
3. Define coefficient of viscosity. How does it vary with temperature?
4. What is the effect of temperature on surface tension of a liquid?
5. Why do you use the same viscometer for the liquid and water during the experimental determination of viscosity by the Ostwald viscometer? Describe the experiment.
6. Describe the terms : Viscosity and coefficient of viscosity. Give their units.
7. (a) What is surface tension? Why rain drops are spherical? Write SI units of surface tension.
8. Water passes through a viscometer in 30 seconds. The same volume of oil required 2263.7 seconds. Calculate the viscosity of oil if its density is 1.1 × 103 kg m–3. Density of water is 0.998 × 103 kg m–3, viscosity of water is 0.00101 kg m–1 s–1. Answer. 0.8400 poise
9. The refractive index of a liquid of molar mass 72 is 1.34 and its density is 0.98 g cm–3. Find its molar refraction. Answer. 15.40 cm3 mol–1
10. The refractive index of a liquid at 25 ºC is 1.6 and its density is 0.87 g cm–3. Find the molar refraction. (Molar mass of the liquid is 78) Answer. 26.36 cm3 mol–1

SOLUTIONS



A solution is a homogeneous mixture of two or more substances on molecular level. The constituent of the mixture present in a smaller amount is called the Solute and the one present in a larger amount is called the Solvent.

CONCENTRATION OF A SOLUTION

The concentration of a solution is defined as : the amount of solute present in a given amount of solution.

$$Concentration = \frac{Amount\ of\ solute}{Amount\ of\ solvent}$$

or

$$Concentration = \frac{Amount\ of\ solute}{Amount\ of\ solution}$$

A solution containing a relatively low concentration of solute is called Dilute solution. A solution of high concentration is called Concentrated solution.

TYPES OF SOLUTIONS

The common solutions that we come across are those where the solute is a solid and the solvent is a liquid. In fact, substance in any three states of matter (solid, liquid, gas) can act as solute or solvent. Thus there are seven types of solutions

Table 9.1 Types of binary solutions

Solute	Solvent	Example
Solid solution		
Solid	Solid	Copper dissolved in gold (Alloys)
Liquid	Solid	Mercury with sodium (amalgam)
Liquid solution		
Solid	Liquid	Sodium chloride dissolved in water
Liquid	Liquid	Ethyl alcohol dissolved in water
Gas	Liquid	carbon-di-oxide dissolved in water (Soda water)
Gaseous solution		
Liquid	Gas	Water vapour in air (cloud)
Gas	Gas	Mixture of Helium-Oxygen gases,

WAYS OF EXPRESSING CONCENTRATION

There are several ways of expressing concentration of a solution :

(a) Per cent by weight

(b) Mole fraction

(c) Molarity

(d) Molality

(e) Normality

Per cent by Weight It is the weight of the solute as a per cent of the total weight of the solution.

% by weight of solute = (weight of solute/ Wt.of solution)* 100

Q. What is the per cent by weight of NaCl if 1.75 g of NaCl is dissolved in 5.85 g of water. Ans (23.0)

MOLE FRACTION

A simple solution is made of two substances : one is the solute and the other solvent. Mole fraction, X, of solute is defined as the ratio of the number of moles of solute and the total number of moles of solute and solvent.

Mole Fraction (*X*)

$$X_{Solute} = \frac{\text{Moles of solute}}{\text{Total moles of solution}}$$

$$X_{Solvent} = \frac{\text{Moles of solvent}}{\text{Total moles of solution}}$$

Where:

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

Q. Calculate the mole fraction of HCl in a solution of hydrochloric acid in water, containing 36 per cent HCl by weight. Ans(0.218)

MOLARITY

In current practice, concentration is most often expressed as molarity. Molarity (symbol M) is defined as the number of moles of solute per litre of solution. If n is the number of moles of solute

Molarity

$$\text{Molarity} = \frac{\text{No of Moles}}{\text{Liters of solution}}$$

or

$$\text{Molarity} = n/v = \frac{\text{No of Moles}}{\text{Volume}}$$

unit of molarity is mol litre–1.

Q. What is the molarity of a solution prepared by dissolving 75.5 g of pure KOH in 540 ml of solution.(2.50 M.)

MOLALITY

Molality of a solution (symbol m) is defined as the number of moles of solute per kilogram of solvent.

Notice the difference between molality and molarity. Molality is defined in terms of mass of solvent while molarity is defined in terms of volume of solution.

$$Molality = m = \frac{moles\ of\ solute}{kg\ of\ solvent}$$

$$m = \frac{mol}{kg}$$

Q. What is the molality of a solution prepared by dissolving 5.0 g of toluene (C7H8) in 225 g of benzene (C_6H_6) ? Ans(0.24 m)

NORMALITY

Normality of a solution (symbol N) is defined as number of equivalents of solute per litre of the solution

$$Normality\ (N) = \frac{number\ of\ gram\ equivalent\ of\ solute \times 1000}{volume\ of\ the\ solution\ in\ litre}$$

$$Gram\ equivalent\ mass = \frac{Mass\ of\ solute}{equivalent\ mass}$$

$$equivalent\ mass = \frac{molecular mass}{\begin{matrix}number\ of\ H^+\ and\ OH^-\ ion \\ (acidity\ or\ basicity)\end{matrix}}$$

Q. 5 g of NaCl is dissolved in 1000 g of water. If the density of the resulting solution is 0.997 g per ml, calculate the molality, molarity, normality and mole fraction of the solute, assuming volume of the solution is equal to that of solvent.

SOLUTIONS OF GASES IN GASES

When a gas is mixed with another gas a completely homogeneous solution results provided of course they do not react chemically. It is obvious that such gaseous solutions will have the following characteristic properties :

(1) Complete miscibility. According to the Kinetic Theory, a gas consists of tiny molecules moving about in vacant space and thus when one gas is dissolved in another gas they form a homogeneous solution quite readily. In such a gaseous mixture, the components can be present to an unlimited extent.

(**2) Dalton's law of Partial pressures**. Since in a gaseous mixture the constituent molecules exist separately, it is obvious that the properties of the mixture will be the sum of properties of the components. Thus Dalton (1842) was the first to show that the total pressure exerted by a gaseous mixture is the sum of the individual or partial pressures of the component gases. If p1, p2, p3... be

the partial pressures of the constituents, the total pressure P of the mixture is given the expression P = p1 + p2 + p3 + ... Like other gas laws, Dalton's law holds strictly only when the partial pressures are not too high. This law can be experimentally tested by comparing the total pressure of a gaseous mixture with the sum of the individual pressure of each gas before mixing.

HENRY'S LAW

It may be stated as : for a gas in contact with a solvent at constant temperature, concentration of the gas that dissolves in the solvent is directly proportional to the pressure of the gas.

Mathematically,

Henry's Law may be expressed

as $C \propto P$ or $C = k P$

where P = pressure of the gas; C = concentration of the gas in solution; and k = proportionality constant known as Henry's Law Constant. The value of k depends on the nature of the gas and solvent, and the units of P and C used

Limitations of Henry's Law

It applies closely to gases with nearly ideal behaviour.

(1) at moderate temperature and pressure.

(2) if the solubility of the gas in the solvent is low.

(3) the gas does not react with the solvent to form a new species.

Thus ammonia (or HCl) which react with water do not obey Henry's Law.

(4) the gas does not associate or dissociate on dissolving in the solvent.

Q. The solubility of pure oxygen in water at 20°C and 1.00 atmosphere pressure is 1.38×10^{-3} mole/litre. Calculate the concentration of oxygen at 20°C and partial pressure of 0.21 atmosphere

SOLUTIONS OF LIQUIDS IN LIQUIDS

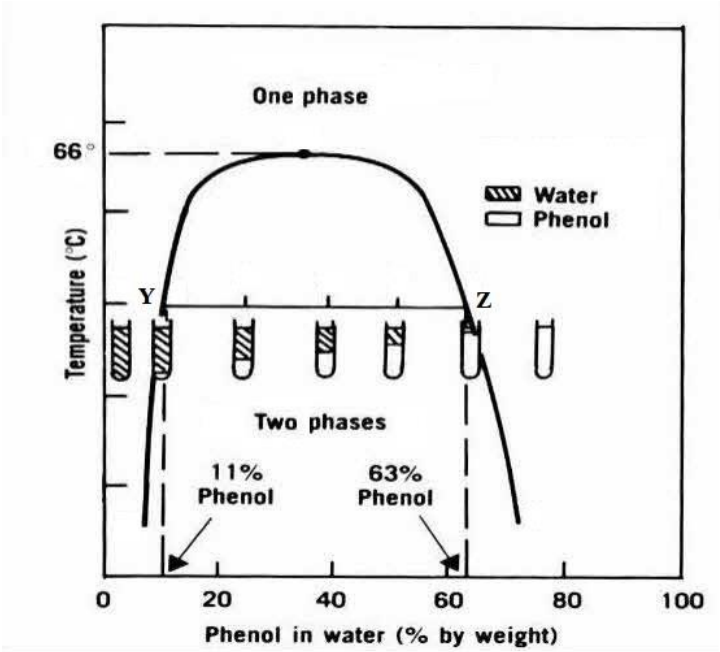
The solutions of liquids in liquids may be divided into three classes as follows : (1) Liquids that are completely miscible .EX alcohol and water (2) Liquids that are partially miscible EX ether and water (3) Liquids that are practically immiscible EX benzene and water

SOLUBILITY OF PARTIALLY MISCIBLE LIQUIDS

A large number of liquids are known which dissolve in one another only to a limited extent e.g., ether and water. These two solutions are referred to as conjugate solutions. The effect of temperature on the mutual solubility of these mixtures of conjugate solutions is of special interest. We will study the effect of temperature on the composition of such mixtures with reference to three typical systems : (1) Phenol-Water system (2) Triethylamine-Water system (3) Nicotine-Water system

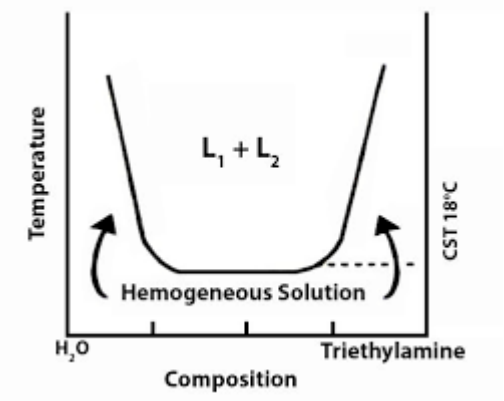
PHENOL–WATER SYSTEM

The curve in represents the miscibility of phenol and water. The left hand side of the parabolic curve represents one of the two conjugate solutions which depicts the percentage of phenol dissolved in water at various temperatures. The solubility of phenol increases with temperature. The right hand side of the curve represents the other conjugate solution layer that gives the percentage of water in phenol. The solubility of water in phenol also increase with increase of temperature. The two solution curves meet at the maxima on the temperature-composition curve of the system. This point here corresponds to temperature 66°C and composition of phenol as 33%. Thus at a certain maximum temperature the two conjugate solutions merge, become identical and only one layer results. The temperature at which the two conjugate solutions (or layers) merge into one another to from one layer, is called the Critical Solution Temperature (CST) or Upper Consulate Temperature. At any temperature above the critical solution temperature, phenol and water are miscible in all proportions. Outside the curve there is complete homogeneity of the system, i.e., one layer only exists; and under the curve there may be complete miscibility but it depends upon the composition of the mixture.



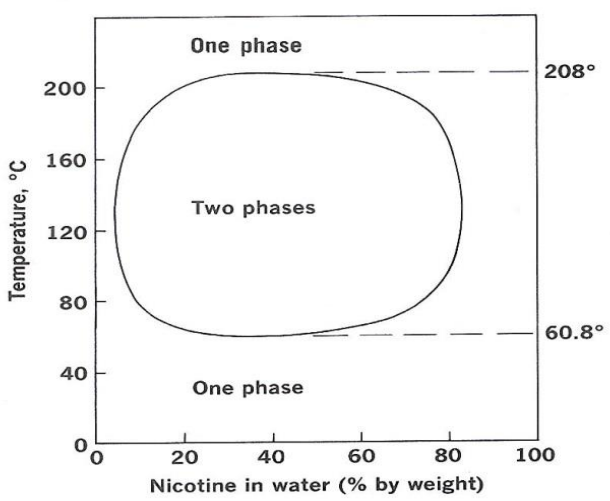
TRIETHYLAMINE–WATER SYSTEM

The temperature-composition curve of mutual solubilities of triethylamine and water is given.The left hand side of the curve indicates the solubility curve of triethylamine in water and the right hand side of that of water in triethylamine. Unlike phenol-water system, the solubilities decrease with the increase in temperature in this system. The two conjugate solutions mix up completely at or below 18.5°C. This temperature is also called the critical solution temperature or the lower consolate temperature. As in the above case, any point above the horizontal line corresponds to heterogeneity of the system (two layers) while below it is complete homogeneity (one layer). Thus an equi-component mixture (50–50) will be completely miscible at 10°C but at 50°C there will be separating out two layers having compositions corresponding to the points C and D.



NICOTINE–WATER SYSTEM

The behaviour of this type of system is as if it were a combination of the first two types. At ordinary temperature nicotine and water are completely miscible but at a higher temperature the mutual solubility decreases and as the temperature is raised further the two liquids again become miscible. In other words, the mutual solubility increases both on lowering as well as raising the temperature in certain ranges. Thus we have a closed solubility curve and the system has two critical-solution-temperatures, the upper 208°C and the lower 61°C. The effect of pressure on this system is that the lower critical temperature is raised while the upper critical temperature is lowered gradually until finally they become one. At this point the liquids are miscible at all the temperatures.



ROULTS LOW

It states that the partial pressure of each component of an ideal mixture of liquids is equal to the vapor pressure of the pure component multiplied by its mole fraction in the mixture.

IDEAL SOLUTION

An ideal solution is a mixture in which the molecules of different species are distinguishable, however, unlike the ideal gas, the molecules in ideal solution exert forces on one another. When those forces are the same for all molecules independent of species then a solution is said to be ideal

Some examples include;

- Toluene and Benzene.
- Ethyl Iodide and Ethyl Bromide.
- Bromobenzene and Chlorobenzene.
- N-heptane and n-hexane.

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OSMOSIS AND OSMOTIC PRESSURE

WHAT IS OSMOSIS?

Let us consider a pure solvent and solution separated by a membrane which permits the passage to solvent molecules but not to solute molecules. Only the solvent will diffuse through the membrane into solution. A membrane which is permeable to solvent and not to solute, is called a semipermeable membrane. The flow of the solvent through a semipermeable membrane from pure solvent to solution, or from a dilute solution to concentrated solution, is termed Osmosis.

Examples of Osmosis: Examples of osmosis include red blood cells swelling up when exposed to fresh water and plant root hairs taking up water.

WHAT IS OSMOTIC PRESSURE?

The hydrostatic pressure built up on the solution which just stops the osmosis of pure solvent into the solution through a semipermeable membrane, is called Osmotic Pressure.

SEMIPERMEABLE MEMBRANES

Animal and vegetable membranes are not completely semipermeable. Cupric ferrocyanide, Cu2Fe(CN)6, membrane deposited in the walls of a porous pot is perfectly semipermeable and is used for accurate experimental work. All semipermeable membranes have fine holes or capillaries in their structure. These allow passage to solvent molecules but not to larger solute molecules

ISOTONIC SOLUTIONS

When two solutions are separated by a semipermeable membrane and there is no flow of water across the membrane, the solutions are said to be Isotonic. If the membrane is completely semipermeable, isotonic solutions are also iso-osmotic i.e., have the same osmotic pressure since osmotic pressure depends on the number of molecules. The isotonic solutions have equimolar concentrations.

Of the two solutions separated by a semipermeable membrane if one is of lower osmotic pressure, it is said to be hypotonic relative to the second solution. If it has a higher osmotic pressure than the second solution, it is said to be hypertonic relative to the second solution.

THEORIES OF OSMOSIS

(1) The Molecular Sieve Theory According to this theory, the membrane contains lots of fine pores and acts as a sort of 'molecular sieve'. Smaller solvent molecules can pass through the pores but the larger molecules cannot. Solvent molecules flow from a region of higher solute concentration to one of lower concentration across such a membrane. But since some membranes can act as sieves even though the solute molecules are smaller than the solvent molecules, this theory remains in doubt.

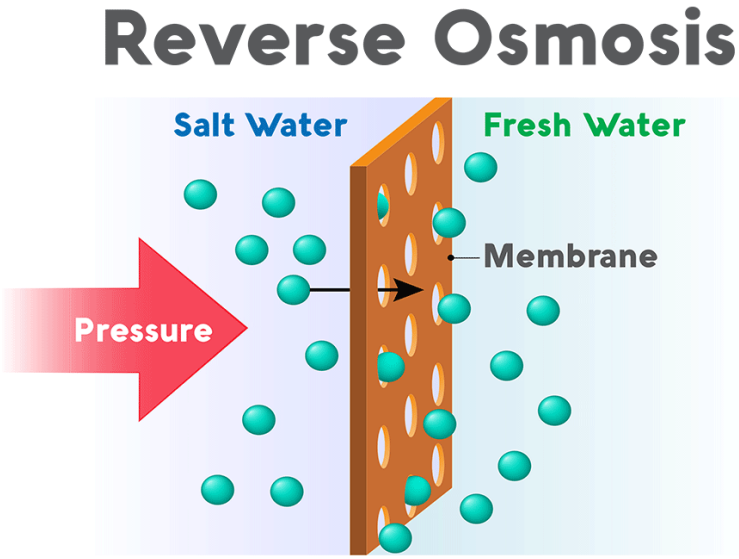
(2) Membrane Solution Theory Membrane proteins bearing functional groups such as – COOH, – OH, – NH2, etc., dissolve water molecules by hydrogen bonding or chemical interaction. Thus membrane dissolves water from the pure water (solvent) forming what may be called 'membrane solution'. The dissolved water flows into the solution across the membrane in a bid to equalise concentrations. In this way water molecules pass through the membrane while solute molecules being insoluble in the membrane do not.

(3) Vapour Pressure Theory It suggests that a semipermeable membrane has many fine holes or capillaries. The walls of these capillaries are not wetted by water (solvent) or solution. Thus

neither solution nor water can enter the capillaries. Therefore each capillary will have in it solution at one end and water at the other, separated by a small gap. Since the vapour pressure of a solution is lower than that of the pure solvent, the diffusion of vapour will occur across the gap from water side to solution side. This will result in the transfer of water into the solution. The vapour theory offers a satisfactory explanation of the mechanism of osmosis in most cases

(4) Membrane Bombardment Theory This theory suggests that osmosis results from an unequal bombardment pressure caused by solvent molecules on the two sides of the semipermeable membrane. On one side we have only solvent molecules while on the other side there are solute molecules occupying some of the surface area. Thus there are fewer bombardments per unit area of surface on the solution side than on the solvent side. Hence the solvent molecules will diffuse more slowly through the membrane on the solution side than on the solvent side. The net result causes a flow of the solvent from the pure solvent to the solution across the membrane.

REVERSE OSMOSIS



The osmosis taking place from solution to pure water by application of pressure greater than osmotic pressure, on the solution, is termed Reverse Osmosis.

LAWS OF OSMOTIC PRESSURE

From a study of the experimental results obtained by Pfeffer, van't Hoff showed that for dilute solutions :

(a) The osmotic pressure of a solution at a given temperature is directly proportional to its concentration.

(b) The osmotic pressure of a solution of a given concentration is directly proportional to the absolute temperature. From the above findings, van't Hoff (1877) established the laws of osmotic pressure and pointed out that these were closely related to the gas laws.

Q. Calculate the osmotic pressure of a 5% solution of glucose (mol wt = 180) at 18°C.

Q.Find the osmotic pressure in millimetres of mercury at 15°C of a solution of naphthalene ($C_{10}H_8$) in benzene containing 14 g of naphthalene per litre of solution.

RELATION BETWEEN VAPOUR PRESSURE AND OSMOTIC PRESSURE

Consider an aqueous solution contained in a tube closed at the lower end by a semipermeable membrane and immersed in pure water. The whole apparatus is enclosed under a bell-jar which is evacuated. When the osmotic equilibrium is reached, the bell jar is saturated with water vapour. Let the height of solution in the tube be h cm. If the solution is sufficiently dilute, the density of the solution will be approximately the same as that of the pure solvent, d. Since at equilibrium, the osmotic pressure of solution (π) is exactly balanced by hydrostatic pressure due to h cm column of solution of density d, we can write,

$\pi = h \times d$……..1

If p is the vapour pressure of the solvent at the given temperature and p, the vapour pressure of the solution, the pressure at all points on a level with A will be p and at all points on a level with B will be Ps . Now, the pressure at A is greater than at B due to the weight of the column of solvent vapour of height h.

Thus,

$P - Ps = Hd$……..2 where D = density of solvent vapour at pressure p.

Dividing (1) by (2), we have

$\pi/(P-P_S)=hd/Hd=d/D$

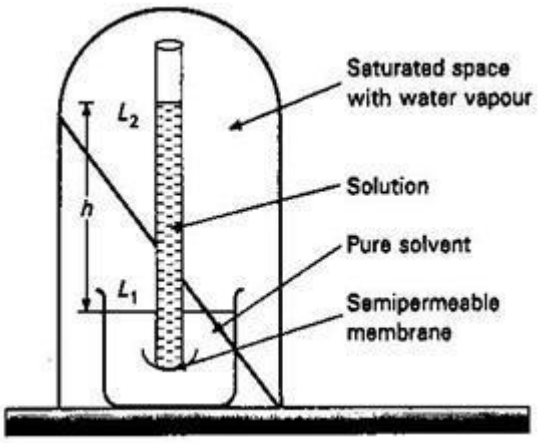
At a given temperature, d and D are constant. That is

$\pi/(P-P_S)$= Constant

π = constant × (p – ps)

$\pi \propto (p - ps)$

This shows that osmotic pressure is directly proportional to the lowering of vapour pressure.



EXAMINATION QUESTIONS

1.Define or explain the following terms : (a) Osmosis (b) Osmotic pressure (c) van't Hoff equation (d) Raoult's law (e) Isotonic solutions.

2.(a) State the laws of osmotic pressure. Explain how osmotic pressure is analogous to gas pressure. How can the molecular mass of a substance in solution be determined from its osmotic pressure?

3. What is osmosis? Derive a relationship between osmotic pressure and concentration of a dissolved solute. Calculate osmotic pressure of solutions at 25°C containing (i) 5.85 g of NaCl, and (ii) 5.0 g of urea per litre of solutions.

4. How is relative lowering of vapour pressure of solutions of non-volatile solute and volatile solvent is related to osmotic pressure? Deduce the relationship.

5. What is the difference between osmosis and diffusion?

6. Derive the relationship between lowering of vapour pressure and osmotic pressure of a solvent.

7. An aqueous solution contains 20 g of glucose in one litre of the solution. Assuming the solution to be ideal, calculate its osmotic pressure at 25 o C (2.718)

DISTRIBUTION LAW

NERNST'S DISTRIBUTION LAW

If a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,

Concentration of X in A / Concentration of in X in B = K_D

DETERMINATION OF EQUILIBRIUM CONSTANT FROM DISTRIBUTION COEFFICIENT

Distribution law helps in determining the equilibrium constant of a reaction when one of the reactants is soluble in two non-miscible solvents.

Let us illustrate by taking example of the reaction when potassium iodide reacts with iodine to form potassium triiodide.

$$KI + I_2 \rightleftharpoons K^{\oplus} I_3^{\ominus}$$

This reaction can be carried in water, while iodine is soluble in both water and benzene. Procedure (1) To find the distribution coefficient of I2. Iodine is shaken with water and benzene in a bottle.

The concentration of iodine in the two layers is then determined by titration against standard thiosulphate solution. Thus,

Concentration of I_2 in water / Concentration of I_2 in benzene= K (Distribution coefficient)

(2) To find the equilibrium constant using the value of K. A solution of KI of concentration a is shaken with iodine in a bottle. To this is added some benzene and shaken. On standing, the mixture separates into two layers. The equilibria that are set up are shown in Fig. The concentration of iodine is determined in the two layers by titration against standard thiosulphate solution. Let b be the concentration of I_2 in benzene layer, c be the concentration of I_2 in water layer which is really the total of the concentration of free I_2 and KI_3. K is the value of distribution coefficient of iodine between water and iodine as determined earlier. Thus,

Concentration of I_2 in water / Concentration of I_2 in benzene= K (Distribution coefficient)

∴ Conc of I2 (free) in water layer = K × b

Hence conc of KI3 in water layer = c – Kb

∴ Conc of KI in water layer = a – (c – Kb)

= a – c + Kb

We can now say that the equilibrium constant of the reaction

$$KI + I_2 \rightleftharpoons K^{\oplus} I_3^{\ominus}$$

$K_C = (KI_3)/(KI)(I_2)$

$=(c-Kb)/(a-c-Kb)Kb$

The square brackets denote concentrations in water layer.

Since all the quantities on the right-hand side are known, the equilibrium constant (Kc) can be calculated.

EXTRACTION WITH A SOLVENT

The extraction (removal by a solvent) of an organic substance from an aqueous solution is probably the most important application of Distribution law. The process is carried by shaking the aqueous solution with a immiscible organic solvent, say ether (ethoxyethane), in a separatory funnel. The distribution ratio being in favour of ether, most of the organic substance passes into ether layer. On standing, the aqueous and ether layers separate in the funnel. The lower aqueous layer is run out, leaving the ether layer behind. This is then transferred to a distillation flask. Ether is distilled over while the organic substance is left as residue in the flask. If desired, the process may be repeated with aqueous layer left after the first extraction with a fresh quantity of the solvent. The other common solvents used for extraction are hexane, benzene, chloroform, acetone, carbon disulphide, etc. The greater the distribution ratio is in favour of the organic solvent, the greater will be the amount extracted in any one operation.

MULTIPLE EXTRACTION The process of extraction when carried with the total amount of the given solvent in a single operation, is referred to as simple extraction. To recover the maximum amount of the substance from aqueous solution, the extraction is made in two or more successive operations using small portions of the solvent provided. This is called multiple extraction or multi-step extraction. In such a process the aqueous solution is first extracted with a portion of the solvent in a separatory funnel. The aqueous layer from which some substance has been removed is then transferred to another funnel. This is shaken with a second portion of the solvent. Similarly, the aqueous layer from the second extraction is treated with a third portion of solvent, and so on

LIQUID–LIQUID CHROMATOGRAPHY (Partition Chromatography) This is a versatile and wide-spread technique for separation of a mixture of small amounts of organic substances. The operation is carried in a glass tube packed with an inert solid material (silica) soaked in a solvent 1 (water). The mixture paste is applied to the column top. Then a layer of another immiscible solvent 2 (hexane) is allowed to flow down the column (Fig. 18.10). A film of solvent 1 held by the silica forms the stationary liquid phase, while the running solvent 2 the mobile liquid phase. Each component of the mixture distributes itself between the stationary liquid phase and the mobile liquid phase. Thus,

$C_S/C_M = K_D$

where Cs = concentration in stationary liquid phase and Cm = concentration in the mobile liquid phase. Different components in the mixture have different distribution coefficient. They pass into the mobile phase in order of their distribution coefficients. The component (say S2) with higher distribution coefficient is extracted (eluted) first and is the first to move down the column. The location of the components is easy if these are coloured. Otherwise they are visualised with the help of a locating agent. The portion of the solvent (or band) containing each component is received in a separate vessel and the solute recovered from it by distillation.

APPLICATIONS OF DISTRIBUTION LAW

There are numerous applications of distribution law in the laboratory as well as in industry. Here we will discuss some more important ones by way of recapitulation.

(1) Solvent Extraction This is the process used for the separation of organic substances from aqueous solutions. The aqueous solution is shaken with an immiscible organic solvent such as ether (or benzene) in a separatory funnel. The distribution ratio being in favour of ether, most of the organic substance passes into the ethereal layer. The ethereal layer is separated and ether distilled off. Organic substance is left behind

(2) Partition Chromatography This is a modern technique of separating a mixture of small amounts of organic materials. A paste of the mixture is applied at the top of a column of silica soaked in water. Another immiscible solvent, say hexane, is allowed to flow down the column. Each component of the mixture is partitioned between the stationary liquid phase (water) and the mobile liquid phase (hexane). The various components of the mixture are extracted by hexane in order of their distribution coefficients. Thus the component with the highest distribution coefficient is first to move down in the flowing hexane which is collected separately. Similarly, a component with a lower distribution ratio comes down later and is received in another vessel.

(3) Confirmatory Test for Bromide and Iodide The salt solution is treated with chlorine water. Small quantity of bromine or iodine is thus liberated. The solution is then shaken with trichloromethane (chloroform). On standing chloroform forms the lower layer. The free bromine or iodine being more soluble in chloroform concentrates into the lower layer, making it red for bromine and violet for iodine.

(4) Distribution Indicators In iodine titrations, the end point is indicated by adding starch suspension which turns blue. A greater sensitivity can be obtained by using what we may call 'Distribution Indicator'. A few drops of an immiscible organic solvent such as chloroform (or carbons tetrachloride) is added to the solution. The bulk of any iodine present passes into the organic layer and imparts intense violet colour to it.

EXAMINATION QUESTIONS

1.State Nernst distribution law. What are its important applications?

2. At 25°C the iodine solution in water which contains 0.0516 g lit–1 is in equilibrium with CCl_4 solution containing 4.1280 g lit–1 of iodine. If at 25°C iodine solution contains 0.410 g lit–1 of iodine, find out the solubility of iodine in CCl_4 solution. Answer. 32.8 g litre–1

3. State Distribution law and give the conditions under which the law is applicable.

4. If the distribution coefficient of benzoic acid between water and benzene is 3.304 at 20°C, calculate the number of molecules of benzoic acid which may be extracted from 100 ml of 0.2 molar aqueous solution by 10 ml of benzene. Answer. 0.046 mole

COLLOIDS

WHAT ARE COLLOIDS ?

The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions.

When the diameter of the particles of a substance dispersed in a solvent ranges from about 10 Å to 2,000 Å, the system is termed a colloidal solution, colloidal dispersion, or simply a colloid.

TYPES OF COLLOIDAL SYSTEMS

As we have seen above, a colloidal system is made of two phases. The substance distributed as the colloidal particles is called the Dispersed phase. The second continuous phase in which the colloidal particles are dispersed is called the Dispersion medium.

Dispersed phase	Dispersion medium	Type of colloid	Example
Solid	Solid	Solid sol	Some coloured glasses, and gem stones
Solid	Liquid	Sol	Paints, cell fluids
Solid	Gas	Aerosol	Smoke, dust
Liquid	Solid	Gel	Cheese butter, jellies
Liquid	Liquid	Emulsion	Milk, hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud, insecticide sprays
Gas	Solid	Solid sol	Pumice stone, foam rubber
Gas	Liquid	Foam	Froth, whipped cream, soap-lather