

PHYSICAL CHEMISTRY

Unit-I Solutions

1.1 Solutions of liquids in liquids - Raoult's law – Vapour pressure of ideal solutions – Activity of a component in an ideal solution – Gibbs-Duhem-Margules equation – Thermodynamics of Ideal Solutions.

1.2 Vapour pressure of Non-ideal solutions – Fractional distillation of Binary liquid solutions – Azeotropic mixtures - Distillation of immiscible liquids - Partially miscible liquids - Phenol - Water, Triethylamine – Water and Nicotine – Water systems.

1.3 Nernst distribution law – Definition - Thermodynamic derivation – Applications.

SOLUTIONS OF LIQUID IN LIQUID

Binary liquid solutions or mixtures

It is a solution containing two liquids.

Classification of binary liquid mixtures

Depending on the relative solubility of one liquid in another liquid there are three types of binary mixtures.

1. Completely miscible liquids

In this type the two liquids are miscible in each other in all proportions.

e.g. Benzene in toluene and ethyl alcohol in water.

2. Partially miscible liquids

In this type a liquid is soluble in another to a partial extent.

e.g. Phenol in water and nicotine in water.

3. Immiscible liquids

In this type the two liquids do not dissolve in each other and remain separated.

e.g. Benzene and water, carbon tetra chloride and water.

Vapour pressure of liquids

When a solute (of any physical state - solid, liquid or gas) is dissolved in a liquid solvent the resultant solution is called a liquid solution. The solution which contains only two components (one solvent and one solute) is called a binary solution. We have already discussed the solution of a gaseous solute in liquid solvent under Henry's law.

Vapour pressure of binary solution of liquid in liquids

Now, let us consider a binary liquid solution formed by dissolving a liquid solute 'A' in a pure solvent 'B' in a closed vessel. Both the components A and B present in the solution would evaporate and an equilibrium will be established between the liquid and vapour phases of the components A and B.

The French chemist Raoult, proposed a quantitative relationship between the partial pressures and the mole fractions of two components A & B, which is known as Raoult's Law. This

law states that “in the case of a solution of volatile liquids, the partial vapour pressure of each component (A & B) of the solution is directly proportional to its mole fraction”. According to Raoult’s law,

$$p_A \propto x_A \quad (1)$$

$$p_A = k x_A$$

when $x_A = 1$, $k = p_A^\circ$ where p_A° is the vapour pressure of pure component ‘A’ at the same temperature. Therefore,

$$p_A = p_A^\circ x_A \quad (2)$$

Similarly, for component ‘B’

$$p_B = p_B^\circ x_B \quad (3)$$

x_A and x_B are the mole fraction of the components A and B respectively.

According to Dalton’s law of partial pressure the total pressure in a closed vessel will be equal to the sum of the partial pressures of the individual components.

Hence,

$$P_{\text{total}} = p_A + p_B \quad (4)$$

Substituting the values of p_A and p_B from equations (2) and (3) in the above equation,

$$P_{\text{total}} = x_A p_A^\circ + x_B p_B^\circ \quad (5)$$

We know that $x_A + x_B = 1$ or $x_A = 1 - x_B$

Therefore,

$$P_{\text{total}} = (1 - x_B) p_A^\circ + x_B p_B^\circ \quad (6)$$

$$P_{\text{total}} = p_A^\circ + x_B (p_B^\circ - p_A^\circ) \quad (7)$$

The above equation is of the straight-line equation form $y = mx + c$. The plot of P_{total} versus x_B will give a straight line with $(p_B^\circ - p_A^\circ)$ as slope and p_A° as the y intercept.

Let us consider the liquid solution containing toluene (solute) in benzene (solvent).

The variation of vapour pressure of pure benzene and toluene with its mole fraction is given in

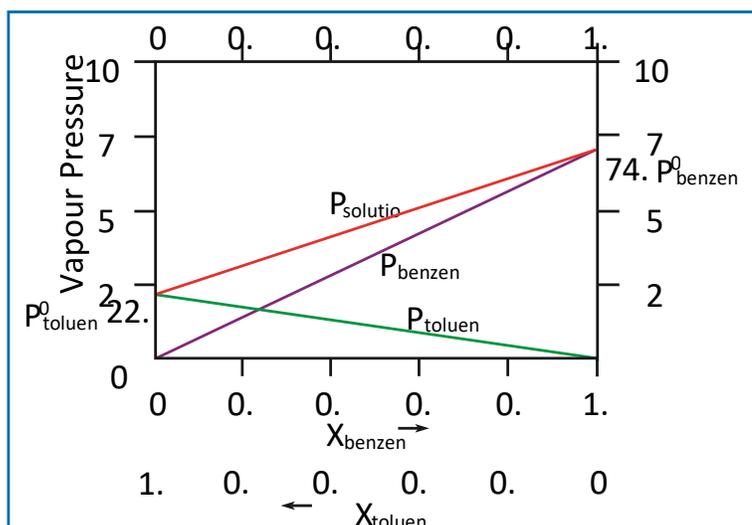


Figure1.1.1 Solution of benzene in toluene obeying Raoult's law.

The vapour pressures of pure toluene and pure benzene are 22.3 and 74.7 mmHg, respectively. The above graph shows, the partial vapour pressure of the pure components increases linearly with the increase in the mole fraction of the respective components. The total pressure at any composition of the solute and solvent is given by the following straight line (represented as red line) equation.

$$P_{\text{solution}} = p^{\circ} \text{toluene} + x_{\text{benzene}}(p^{\circ} \text{benzene} - p^{\circ} \text{toluene}) \quad (8)$$

Ideal and non-ideal solutions

Ideal Solutions:

An ideal solution is a solution in which each component i.e. the solute as well as the solvent obeys the Raoult's law over the entire range of concentration. Practically no solution is ideal over the entire range of concentration. However, when the concentration of solute is very low, the dilute solution behaves ideally. If the two Components present in the solution (A and B) are identical in size, structure, and having almost similar intermolecular attractive forces between them (i.e. between A-A, B-B and B-A) and then the solution tends to behave like an ideal solution.

For an ideal solution

- i) there is no change in the volume on mixing the two components (solute & solvents).

$$(\Delta V_{\text{mixing}} = 0)$$

ii) there is no exchange of heat when the solute is dissolved in solvent

$$(\Delta H_{\text{mixing}} = 0).$$

iii) Escaping tendency of the solute and the solvent present in it should be same as in pure liquids.

Examples for ideal solutions: benzene & toluene; n-hexane & n-heptane; ethyl bromide & ethyl iodide; chlorobenzene & bromobenzene.

Non-ideal solutions

The solutions which do not obey Raoult's law over the entire range of concentration, are called non-ideal solutions. For a non-ideal solution, there is a change in the volume and enthalpy upon mixing. i.e. $\Delta H_{\text{mixing}} \neq 0$ & $\Delta V_{\text{mixing}} \neq 0$. The deviation of the non-ideal solutions from the Raoult's law can either be positive or negative.

Non-ideal solutions - positive deviation from Raoult's Law:

The nature of the deviation from the Raoult's law can be explained in terms of the intermolecular interactions between solute (A) and solvent (B). Consider a case in which the intermolecular attractive forces between A and B are weaker than those between the molecules of A (A-A) and molecules of B (B-B). The molecules present in such a solution have a greater tendency to escape from the solution when compared to the ideal solution formed by A and B, in which the intermolecular attractive forces (A-A, B-B, A-B) are almost similar. Consequently, the vapour pressure of such non-ideal solution increases and it is greater than the sum of the vapour pressure of A and B as predicted by the Raoult's law. This type of deviation is called positive deviation.

$$\text{Here, } p_A > p_A^\circ x_A \text{ and } p_B > p_B^\circ x_B.$$

$$\text{Hence } p_{\text{total}} > p_A^\circ x_A + p_B^\circ x_B \quad (9.19)$$

Let us understand the positive deviation by considering a solution of ethyl alcohol and water. In this solution the hydrogen bonding interaction between ethanol and water is weaker than those hydrogen bonding interactions amongst themselves (ethyl alcohol-ethyl alcohol and water-water interactions). This results in the increased evaporation of both components from the aqueous solution of ethanol. Consequently, the vapour pressure of the solution is greater than the vapour pressure predicted by Raoult's law. Here, the mixing process is endothermic i.e. $\Delta H_{\text{mixing}} > 0$ and there will be a slight increase in volume ($\Delta V_{\text{mixing}} > 0$).

Examples for non-ideal solutions showing positive deviations: Ethyl alcohol & cyclohexane, Benzene & acetone, Carbon tetrachloride & chloroform, Acetone & ethyl

alcohol, Ethyl alcohol & water.

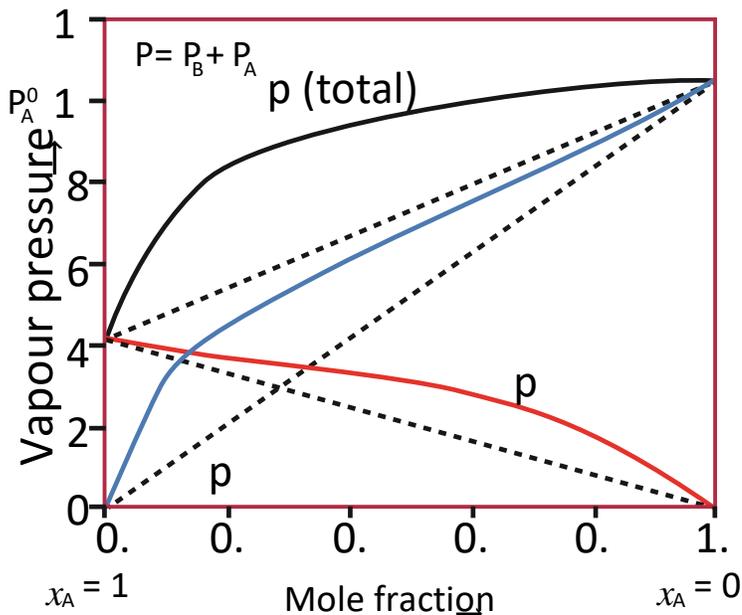


Fig.1.1.2 Vapour pressure diagram showing positive deviation

Figure 1.1.2 Positive deviations from Raoult's law. The dotted line (-----) is ideal behavior and the solid lines (____) is actual behavior

Non-ideal solutions - negative deviation from Raoult's Law:

Let us consider a case where the attractive forces between solute (A) and solvent (B) are stronger than the intermolecular attractive forces between the individual components (A-A & B-B). Here, the escaping tendency of A and B will be lower when compared with an ideal solution formed by A and B. Hence, the vapour pressure of such solutions will be lower than the sum of the vapour pressure of A and B. This type of deviation is called negative deviation. For the negative deviation $p_A < p_A^0 x_A$ and $p_B < p_B^0 x_B$.

Let us consider a solution of phenol and aniline. Both phenol and aniline form hydrogen bonding interactions amongst themselves. However, when mixed with aniline, the phenol molecule forms hydrogen bonding interactions with aniline, which are stronger than the hydrogen bonds formed amongst themselves. Formation of new hydrogen bonds considerably reduce the escaping tendency of phenol and aniline from the solution. As a result, the vapour pressure of the solution is less and there is a slight decrease in volume ($\Delta V_{\text{mixing}} < 0$) on mixing.

During this process evolution of heat takes place i.e. $\Delta H_{\text{mixing}} < 0$ (exothermic)

Examples for non-ideal solutions showing negative deviation: Acetone + chloroform, Chloroform + diethyl ether, Acetone + aniline, Chloroform + Benzene.

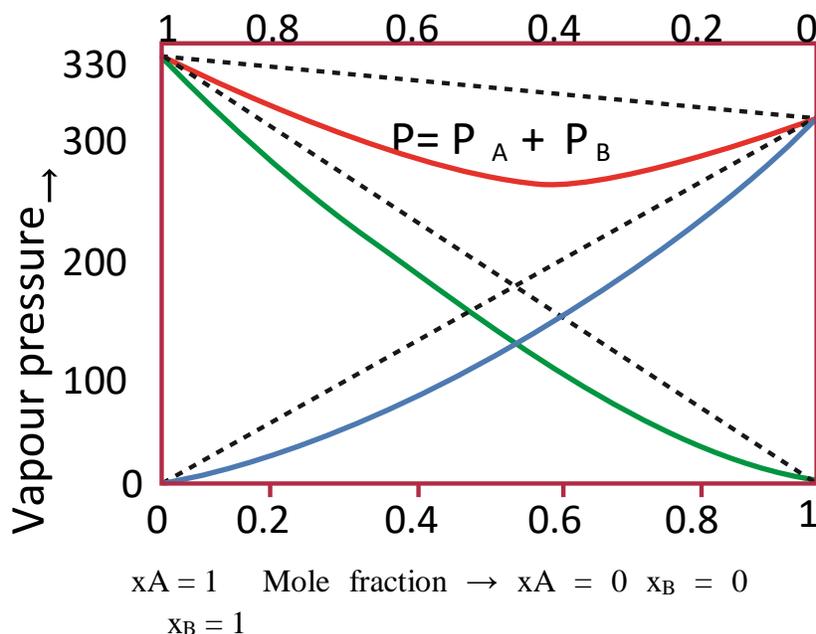


fig. 1.1.3 Vapour pressure diagram showing negative deviation

Figure Negative deviation from Raoult's law. The dotted line (-----) is ideal behavior and the solid lines (____) is actual behaviour

Factors responsible for deviation from Raoult's law

The deviation of solution from ideal behavior is attributed to the following factors.

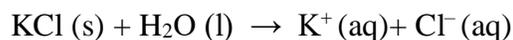
i) Solute-solvent interactions

For an ideal solution, the interaction between the solvent molecules (A-A), the solute molecules (B-B) and between the solvent & solute molecules (A-B) are expected to be similar. If these interactions are dissimilar, then there will be a deviation from ideal behavior.

ii) Dissociation of solute

When a solute present in a solution dissociates to give its constituent ions, the resultant ions interact strongly with the solvent and cause deviation from Raoult's law.

For example, a solution of potassium chloride in water deviates from ideal behavior because the solute dissociates to give K^+ and Cl^- ion which form strong ion-dipole interaction with water molecules.



iii) Association of solute

Association of solute molecules can also cause deviation from ideal behaviour. For example, in solution, acetic acid exists as a dimer by forming intermolecular hydrogen bonds, and hence deviates from Raoult's law.

iv) Temperature

An increase in temperature of the solution increases the average kinetic energy of the molecules present in the solution which causes decrease in the attractive force between them. As a result, the solution deviates from ideal behaviour.

v) Pressure

At high pressure the molecules tend to stay close to each other and therefore there will be an increase in their intermolecular attraction. Thus, a solution deviates from Raoult's law at high pressure.

vi) Concentration

If a solution is sufficiently dilute there is no pronounced solvent-solute interaction because the number of solute molecules are very low compared to the solvent. When the concentration is increased by adding solute, the solvent-solute interaction becomes significant. This causes deviation from the Raoult's law.

Activity of a component in an ideal solution

Consider a binary solution of component A and B forming an ideal solution. Let X_A and X_B be the mole fraction and a_A and a_B be the activities of the component A and B respectively.

Then according to Raoult's law, the partial vapour P of the component A is given by

$$P_A = X_A P_A^\circ$$

$$P_A / P_A^\circ = X_A$$

Since vapour P of liquid component of a solution at ordinary T are usually low (less than 1 atm) lying well within the range in which the fugacity (f) may be taken as equal to P , hence,

$$P_A / P_A^\circ = f_A / f_A^\circ = X_A$$

$$f_A / f_A^\circ = a_A$$

where f_A is the fugacity of component A in the solution, f_A° is the fugacity of pure component A and a_A is the activity of the component A in the solution. Hence $x_A = a_A$ and $x_B = a_B$ where a_B is the activity of the component B in the solution.

An ideal solution is defined as the one in which the activity of each component is equal to its mole fraction under all conditions of T, P and concentration. If the x_i is the mole fraction of a component i, then its activity a_i , is given by $a_i = x_i$.

Gibbs Duhem – Margules equation

The Duhem–Margules equation, named for Pierre Duhem and Max Margules, is a thermodynamic statement of the relationship between the two components of a single liquid where the vapour mixture is regarded as an ideal gas:

$$(d \ln P_A / d \ln X_A)_{T,P} = (d \ln P_B / d \ln X_B)_{T,P}$$

Where P_A and P_B are the partial vapour pressures of the two constituents and x_A and x_B are the mole fractions of the liquid.

Derivation

Duhem - Margulus equation give the relation between changes of mole fraction with partial pressure of a component in a liquid mixture.

Let consider a binary liquid mixture of two component in equilibrium with their vapour at constant temperature and pressure. Then from Gibbs - Duhem equation is

$$n_A d\mu_A + n_B d\mu_B = 0 \text{ -----1}$$

Where n_A and n_B are number of moles of the component A and B while μ_A and μ_B is their chemical potential.

Dividing equation (1) by $n_A + n_B$, then

$$(n_A / n_A + n_B) d\mu_A + (n_B / n_A + n_B) d\mu_B = 0$$

Or
$$X_A d\mu_A + X_B d\mu_B = 0 \text{ -----2}$$

Now the chemical potential of any component in mixture is depend upon temperature, pressure and composition of mixture. Hence if temperature and pressure taking constant then chemical potential

$$d\mu_A = (d\mu_A / dX_A)_{T,P} dX_A \text{ -----3}$$

$$d\mu_B = (d\mu_B / d X_B)_{T,P} dX_B \text{ -----4}$$

Putting these values in equation (2), then

$$d\mu_A (d\mu_A / dX_A)_{T,P} dX_A + d\mu_B (d\mu_B / d X_B)_{T,P} dX_B = 0 \text{ -----5}$$

Because the sum of mole fraction of all component in the mixture is unity i.e.,

$$X_A + X_B = 1$$

Hence $dX_A + d X_B = 0$

so equation (5) can be re-written:

$$d\mu_A (d\mu_A / dX_A)_{T,P} dX_A = d\mu_B (d\mu_B / d X_B)_{T,P} dX_B \text{ -----6}$$

Now the chemical potential of any component in mixture is such that

$$\mu = \mu^\circ + RT \ln P$$

where P is partial pressure of component. By differentiating this equation with respect to the mole fraction of a component:

$$d\mu / dx = RT \ln P / d X$$

So we have for components A and B

$$d\mu_A / dX_A = RT d \ln P / dx \text{ -----7}$$

$$d\mu_B / d X_B = RT d \ln P / dx \text{ -----8}$$

Substituting these value in equation (6), then

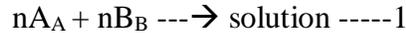
$$X_A d \ln P_A / d X_A = X_B d \ln P_B / d X_B \text{ (or)}$$

$$(d \ln P_A / d \ln X_A)_{T,P} = (d \ln P_B / d \ln X_B)_{T,P}$$

This is the final equation of Duhem- Margules equation.

Thermodynamics of an ideal solution

Gibbs free energy change of mixing (ΔG_{mix}) for an ideal solution. Suppose a solution is formed by mixing n_A moles of a liquid A and n_B moles of a liquid B. i.e



According to thermodynamics, the free energy (G) of the solution at a given temperature and pressure is given by

$$G = n_A \check{G}_A + n_B \check{G}_B \quad \text{-----2}$$

Where \check{G}_A and \check{G}_B are the partial molar free energy (i.e chemical potential) of the constituents A and B respectively.

If \check{G}_A and \check{G}_B are the partial molar free energy of the constituents A and B respectively. Then, change in the free energy of the system on mixing, called the free energy change of mixing, (ΔG_{mix}) is given by the expression.

$$(\Delta G_{\text{mix}}) = (\text{free energy of solution}) - (\text{sum of free energies of the pure constituents})$$

$$(\Delta G_{\text{mix}}) = G - n_A G_A^\circ + n_B G_B^\circ \quad \text{-----3}$$

Sub the value of G from eq. 2, we have

$$(\Delta G_{\text{mix}}) = (n_A \check{G}_A + n_B \check{G}_B) - (n_A G_A^\circ + n_B G_B^\circ)$$

$$(\Delta G_{\text{mix}}) = n_A (\check{G}_A - G_A^\circ) + (n_B \check{G}_B - G_B^\circ) \quad \text{-----4}$$

Where $(\check{G}_A - G_A^\circ)$ and $(\check{G}_B - G_B^\circ)$ are change in the partial molar energies of component A and B respectively.

$$\mu = \mu^\circ + RT \ln a_i \quad \text{-----5}$$

$$\check{G}_A = G_A^\circ + RT \ln a_A \quad (\text{or}) \quad \check{G}_A - G_A^\circ = RT \ln a_A \quad \text{-----6}$$

$$\check{G}_B = G_B^\circ + RT \ln a_B \quad (\text{or}) \quad \check{G}_B - G_B^\circ = RT \ln a_B \quad \text{-----7}$$

Including eq. 6,7 in eq.4, we have

$$\Delta G_{\text{mix}} = n_A RT \ln a_A + n_B RT \ln a_B \quad \text{-----8}$$

If the solution is ideal, the activity of each component should be equal to its mole fraction. $a_A = x_A$ and $a_B = x_B$. Hence free energy of mixing of an ideal solution may be expressed as,

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B \text{ -----9}$$

If there are more than two components of the solution, the above eq. becomes,

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B + \dots = RT \sum \ln x_i \text{ -----10}$$

Dividing both sides of eq. 9 by $n_A + n_B$, we get

$$\Delta G_{\text{mix}} / (n_A + n_B) = n_A / (n_A + n_B) RT \ln x_A + n_B / (n_A + n_B) RT \ln x_B = x_A RT \ln x_A + x_B RT \ln x_B \text{ --11}$$

If the total amount of two components is one mole i.e. $n_A + n_B = 1$ then 10

$$\Delta G_{\text{mix}} = RT(x_A \ln x_A + x_B \ln x_B) \text{ -----12}$$

If there are more than two components of the solution, then

$$\Delta G_{\text{mix}} = RT(x_A \ln x_A + x_B \ln x_B + \dots) = RT \sum \ln x_i \text{ -----13}$$

Since x_i the mole fraction, is always less than unity, ΔG_{mix} is always a negative quantity.

Volume change and enthalpy change of mixing for an ideal solution. Before the changes we may recall the following thermodynamic eq.

$$(\partial(\Delta G) / \partial T)_P = -\Delta S \text{ -----14}$$

$$(\partial(\Delta G) / \partial P)_T = -\Delta V \text{ -----15}$$

For free energy of mixing, we may write the above expression as

$$(\partial(\Delta G_{\text{mix}}) / \partial T)_P = -\Delta S_{\text{mix}} \text{ -----16}$$

$$(\partial(\Delta G_{\text{mix}}) / \partial P)_T = -\Delta V_{\text{mix}} \text{ -----17}$$

Refer to eq. 10 for free energy change of mixing for an ideal binary solution. We find that the expression on the right side is independent of pressure as it contains no pressure term, differentiation of eq. 10 with respect to pressure, at a constant T, yields

$$(\partial(\Delta G_{\text{mix}}) / \partial P)_T = 0 \text{ -----18}$$

Combining eq. 17 and 18, we have

$$\Delta V_{\text{mix}} = 0 \text{ -----19}$$

Thus, if two pure liquid constituents are mixed together in any proportion to give an ideal solution, there is no change in volume.

For a binary solution eq. 9 may also be written as

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B \text{ ----- 20}$$

Since the expression on the right side of the above eq. is independent of T as it contains no T term, differentiation of eq. 20 with respect to T yields

$$(\partial(\Delta G_{\text{mix}}) / \partial T)_P = 0 \text{ -----21}$$

An alternative expression by differentiating $(\Delta G_{\text{mix}}) / T$ with respect to T, at constant P can also be obtained. Thus,

$$(\partial(\Delta G_{\text{mix}}) / \partial T)_P = T (\partial(\Delta G_{\text{mix}}) / \partial T)_P - \Delta G_{\text{mix}} / T^2 \text{ -----22}$$

Applying the well known gibbs Helmholtz eq.

$$\Delta G - \Delta H = T \{ (\partial(\Delta G_{\text{mix}}) / \partial T)_P \} \text{ -----23}$$

We may write eq. 22

$$(\partial(\Delta G_{\text{mix}}) / \partial T)_P = \Delta G_{\text{mix}} - \Delta H_{\text{mix}} - \Delta G_{\text{mix}} / T^2 = -\Delta H_{\text{mix}} / T^2 \text{ -----24}$$

We have eq. 21 and 24

$$-\Delta H_{\text{mix}} / T^2 = 0 \text{ i.e } \Delta H_{\text{mix}} = 0 \text{ -----25}$$

Thus if two pure liquids are mixed together in any proportion to give an ideal solution, there is no change in enthalpy.

Entropy change of mixing for an ideal solution. Finally, let us consider entropy change of mixing in the case of an ideal solution. The well known eq.

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$

Since for an ideal solution $\Delta H_{\text{mix}} = 0$, we have

$$\Delta G_{\text{mix}} = - T\Delta S_{\text{mix}} \text{ -----26}$$

According to eq.9

$$\Delta G_{\text{mix}} = n_A RT \ln x_A + n_B RT \ln x_B$$

$$\Delta S_{\text{mix}} = n_A R \ln x_A + n_B R \ln x_B \text{ -----27}$$

If there are more than two components of the solution, then

$$\Delta S_{\text{mix}} = (n_A R \ln x_A + n_B R \ln x_B + n_C R \ln x_C \dots)$$

$$\Delta S_{\text{mix}} = - R \sum n_i \ln x_i \text{ -----28}$$

Since x_i is always less than unity, ΔS_{mix} is a positive quantity.

Fractional distillation of binary liquid mixtures principle

Distillation of solution of Type-I: Ideal system obeying Raoult's law e.g. Benzene and Toluene

The boiling temperature-composition diagram for a solution of this type involving the liquids A(Toluene), less volatile, and B(Benzene), more volatile, is as given.

Suppose we have a solution corresponding to composition a. No boiling will start until temperature T_a is reached.

The composition of the vapour phase at this stage will be a' i.e., it is richer in the component B (because $a' > a$). The residue, therefore, must become richer in A i.e., the composition of the residue shifts towards A, say it becomes equal to b. Now if the liquid mixture is heated, it will boil only when the temperature becomes equal to T_b .

The vapour will have composition corresponding to b' i.e., again it is richer in B and consequently the composition of the residue will be further enriched in A.

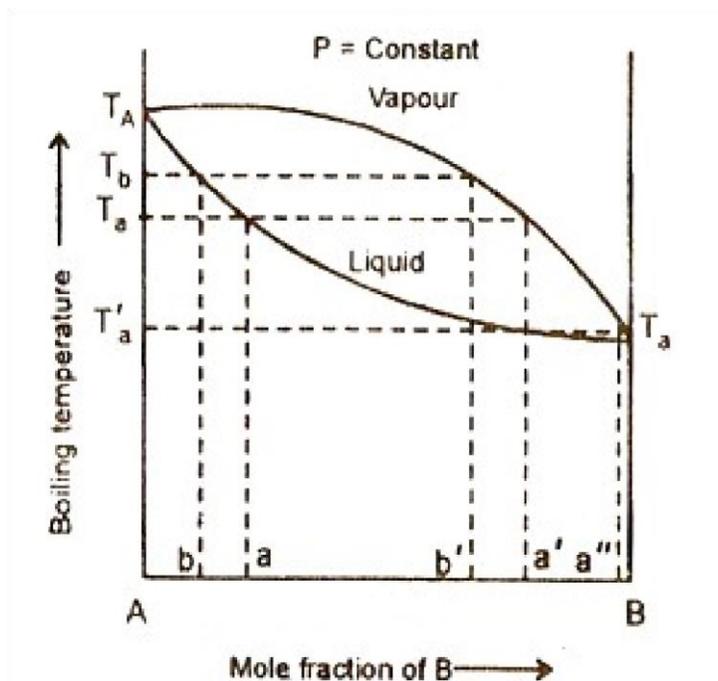


Fig. 1.2.1 Distillation of solution of Type-I: Ideal system obeying Raoult's law e.g. Benzene and Toluene

Thus if the process of heating the residue is continued, the boiling point of the solution will rise from the initial boiling point T_a towards the boiling point T_A of the pure liquid A. Moreover, every time the residue becomes richer in A than the original solution. This means that if the process is continued sufficiently long time, a final residue of pure A can be obtained.

Further, the vapour obtained in the first stage are condensed, a liquid mixture corresponding to a' is obtained. Now if this liquid mixture is distilled, it will boil when the temperature becomes T_a' . The composition of the vapours coming off will correspond to the point a'' i.e. the vapours have become richer in B than the original solution. This means that if the process of condensing the vapour and redistilling the liquid mixture is continued, until a distillate of pure B is obtained.

Thus a liquid mixture of Type-I can be separated completely by fractional distillation.

Distillation of solution of Type-II: Non-ideal system showing positive deviation from Raoult's law. e.g. Ethyl alcohol and water

The boiling temperature-composition diagram for the solutions of this type involving the liquids A(Water),less-volatile, and B(Ethyl alcohol),more volatile, is as shown. The boiling point-composition curves of the liquid and vapour meet at the minimum point C. At the point C, both liquid and vapour have the same composition. The liquid mixture represented by the point C will

boil at constant temperature and will distill completely without change of composition. This mixture is known as azeotropic mixture. It is not possible to separate the components from such a mixture by distillation. Considering the distillation of a mixture of composition a.

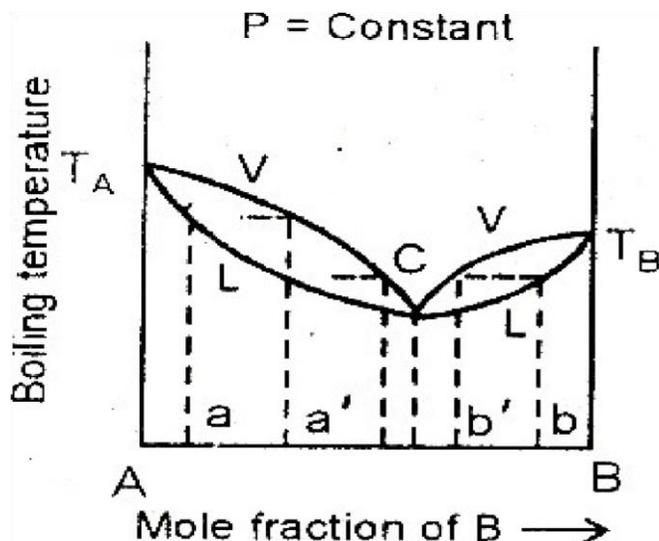


Fig. 1.2.2 Distillation of solution of Type-II: Non-ideal system showing positive deviation from Raoult's law. e.g. Ethyl alcohol and water

Then the first fraction obtained will have a composition shown by a' . The mixture is richer in the constant boiling mixture. The composition of the residual liquid, therefore, will shift towards A. As the distillation proceeds, the composition of the distillate changes towards C and that of the residual solution towards A. Ultimately by repeated fractional distillation, the mixture of the minimum point of composition C will be obtained as distillate and the pure liquid A will be left as residue in the distillation flask.

If, on the other hand, a mixture of composition b is distilled, the composition of the first fraction will be represented by b' . Evidently, it will be richer in the constant boiling mixture. Therefore, the composition of the residual liquid will be richer in B. As the distillation proceeds, the successive fractional distillates will become increasingly rich in the constant boiling mixture while the residual liquid will increasingly rich in the pure component B. Ultimately by repeated fractional distillation, the mixture of the minimum point of composition C will be obtained as distillate and the pure liquid B will be left as residue in the distillation flask.

Thus a liquid mixture of Type-II can be separated into azeotropic mixture, pure A and pure B, by fractional distillation.

Distillation of solution of Type-III: Non-ideal system showing negative deviation from Raoult's law. e.g. Water and hydrochloric acid

The boiling temperature-composition diagram for the solutions of this type involving the liquids A(Water),less-volatile, and B(hydrochloric acid),more volatile, is as shown.

The boiling point- composition curves of the liquid and vapour meet at the maximum point D. At the point D, both liquid and vapour have the same composition. The liquid mixture represented by the point D will boil at constant temperature and will distils completely without change of composition. This mixture is known as azeotropic mixture. It is not possible to separate the components from such a mixture by distillation.

Considering the distillation of a mixture of composition a. Then the first fraction obtained will have a composition shown by a'. The mixture is richer in the constant boiling mixture.

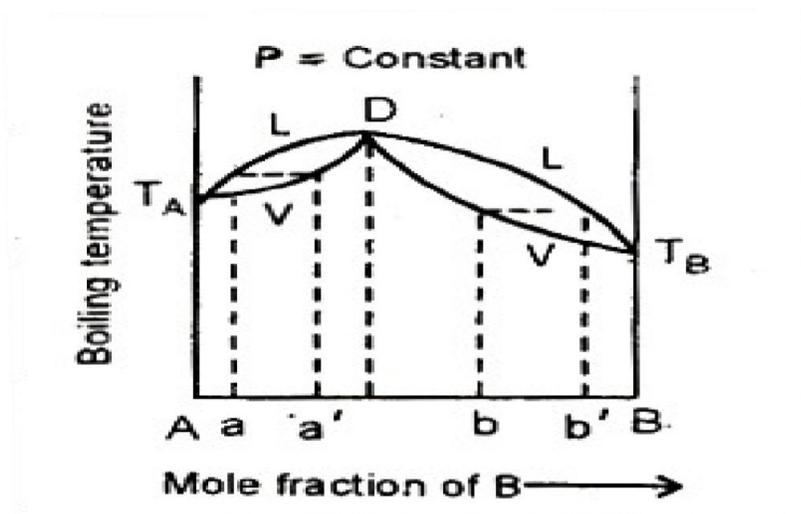


Fig.1.2.3 Distillation of solution of Type-III: Non-ideal system showing negative deviation from Raoult's law. e.g. Water and hydrochloric acid

The composition of the residual liquid, therefore, will shifts towards A. As the distillation proceeds, the composition of the distillate changes towards D and that of the residual solution towards A. Ultimately by repeated fractional distillation, the mixture of the maximum point of composition D will be obtained as distillate and the pure liquid A will be left as residue in the distillation flask.

If, on the other hand, a mixture of composition b is distilled, the composition of the first fraction will be represented by b'. Evidently, it will be richer in the constant boiling mixture. Therefore, the composition of the residual liquid will be richer in B. As the distillation proceeds, the successive fractional distillates will become increasingly rich in the constant boiling mixture while the residual liquid will increasingly rich in the pure component B. Ultimately by repeated fractional distillation, the mixture of the maximum point of composition D will be obtained as distillate and the pure liquid B will be left as residue in the distillation flask. Thus a liquid mixture of Type-III can be separated into azeotropic mixture, pure A and pure B, by fractional distillation.

Azeotropic mixtures

Mixtures of liquids which boil at constant temperature like a pure liquid such that the distillate has the same composition as the liquid mixture are called constant boiling mixtures or azeotropic mixtures or simply azeotropes.

These azeotropes are of two types:

1. Minimum boiling point azeotropes:

These azeotropes are formed by those liquid pairs, which show positive deviation from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the highest and hence the boiling point is the lowest. Such azeotropes have boiling points lower than that of the pure components.

e.g. Ethyl alcohol (B.P. = 78.3°C) and water (B.P. = 100°C) combine in a composition of 95.57% and 4.43% respectively to form an azeotropic mixture with a constant boiling point of 78.15°C.

2. Maximum boiling point azeotropes:

These azeotropes are formed by those liquid pairs, which show negative deviation from ideal behaviour. Such an azeotrope corresponds to an intermediate composition for which the total vapour pressure is the minimum and hence the boiling point is the maximum. Such azeotropes have boiling points lower than that of the pure components.

e.g. Hydrochloric acid (B.P. = -85°C) and water (B.P. = 100°C) combine in a composition of 20.3% and 79.7% respectively to form an azeotropic mixture with a constant boiling point of 110°C.

Distillation of immiscible liquids

In the case of immiscible liquids, the addition of one liquid to the other does not alter the properties of either liquid. Each liquid, therefore, exerts its own vapour pressure independent of the presence of the other. Hence, the total vapour pressure above the mixture containing two immiscible liquids in any proportion will be the sum of the vapour pressure of the pure liquids at that T. Thus, $P = P_A^0 + P_B^0$ where P_A^0 and P_B^0 are the vapour pressure of the pure liquids A and B are respectively, at the prevailing T.

Since the boiling point of any system is the T at which its total vapour pressure becomes equal to the prevailing pressure, the mixture will boil at the T at which

$$P_A^0 + P_B^0 = \text{atmospheric pressure}$$

Evidently, this T will be lower than the normal boiling point of either of the liquids, alone. In other words, any mixture of two immiscible liquids will boil at a T lower than that at which any pure constituent of the mixture boils. Again, since the total vapour pressure is constant and independent of the amounts of the components. It follows that the boiling point of the mixture will remain constant as long as the two liquids are present together.

The relative proportions of the two liquids in the distillate can be calculated remembering that the number of moles of each component present in the vapour phase is proportional to its vapour pressure. If n_A and n_B are the no. of moles of the component A and B in the vapour phase at the boiling point, then

$$n_A/n_B = P^0_A / P^0_B$$

If w_A and w_B represent the actual masses of the two components in the distillate and M_A and M_B are their respective molar masses, then above eq. may be written as

$$w_A / w_B = n_A M_A / n_B M_B = P^0_A M_A / P^0_B M_B$$

Thus, the masses of the liquids in the distillate will be in the ratio of their vapour pressure and molar masses.

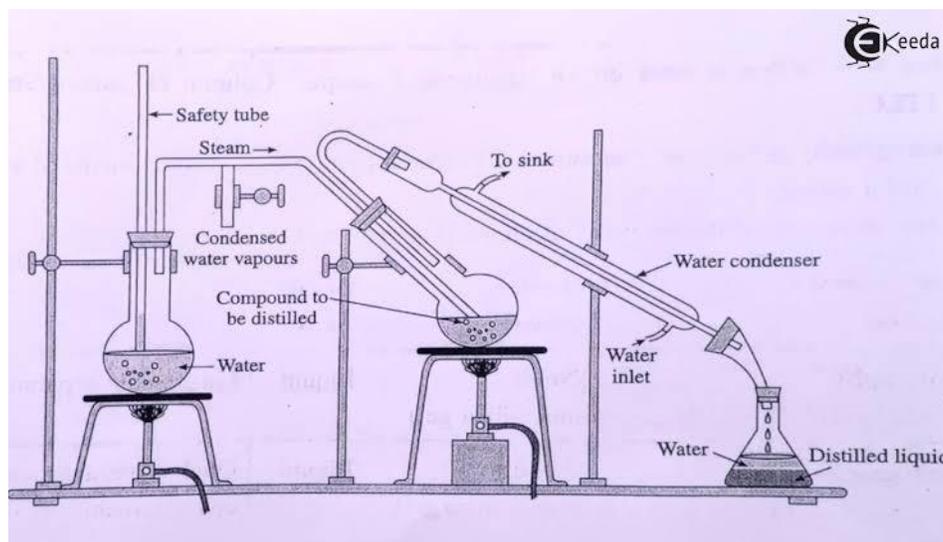


Fig.1.2.4 distillation of immiscible liquids

The above principle is made use of in the process of steam distillation. It is used in the purification of organic compounds which have high boiling points. The compounds must be immiscible or nearly so in water. A common example is that of aniline. Its normal boiling point is 180°C . But it can be made to boil and distil over at a much lower temperature by passing steam through it. The apparatus is shown in figure. The steam is generated in a metal can. The solution to be distilled is placed in the round bottom flask. Clamped at an angle so as to prevent the solution

from being splashed into the condenser. The tube carrying the steam from the can dips below the liquid in the flask. The distillation flask is kept heated gently on a sand bath in order to avoid too much condensation of water into it. The vapours of the organic compound mixed with steam pass over and are condensed in the receiver, as shown. The boiling in this manner takes place at about 98.5 C which is lower than the boiling point of either water or aniline.

$$\text{Mass of H}_2\text{O} / \text{mass of aniline} = 18\text{g mol}^{-1} \times 717 \text{ torr} / 93\text{g mol}^{-1} \times 43 \text{ torr} = 3.23$$

It will be seen that although the partial vapour pressure of aniline at the boiling temperature is only 43 torr out of a total of 760 torr (i.e., less than 6% of the total), its relative proportion by mass in the distillate is about 30%. Evidently, its higher molar mass, relative to that of water, compensates to some extent for the lower vapour pressure.

Solubility of partially miscible liquids

Four types of partially miscible liquids – liquids system. These are

1. Those in which the partial miscibility increases on increasing the T. examples phenol-water, aniline-water, aniline-hexane, methanol-carbondisulphide and cyclohexane-methanol system. At and above a certain T, the liquids becomes completely miscible.
2. Those in which the partial miscibility increases on lowering the T. examples $(\text{C}_2\text{H}_5)_2\text{NH}-\text{H}_2\text{O}$, $(\text{C}_2\text{H}_5)_3\text{N}-\text{H}_2\text{O}$ system. At and below the certain T, the liquids becomes completely miscible.
3. Those in which the partial miscibility increases on both raising as well as lowering the T in certain range. Examples are H_2O -nicotine and H_2O - β -picoline system. These liquids become complete miscibility both above and below certain T.
4. Those in which complete miscibility T cannot be obtained. Example ether-water system.

The T above or below which a pair of partially miscible liquids becomes miscible in all proportions, is called critical solution temperature (CST) or consolute temperature for the pair. Some liquid pairs attain complete miscibility above a certain temperature in which case they are said to have the upper critical solution temperature (UCST) while some liquid pairs show complete miscibility below a certain temperature when they said to have lower critical solution temperature (LCST).

On the other hand some liquid pairs show both UCST and LCST. All partially miscible liquid pair have, in general, an UCST or LCST. However the UCST cannot realized if one or both the component freeze out before it is reached and the LCST may not be observed if one or both the components freeze out before it is reached. Thus, under atmospheric conditions none of the CSTs is observed for ether-water system.

The CSTs for a few PMS are in table

Component A	Component B	UCST	LCST
Water	Phenol	68.1	-
Cyclohexane	Methanol	49	-
Methanol	CS ₂	49.5	-
Aniline	Hexane	59.6	-
Water	(C ₂ H ₅) ₂ NH	-	43
Water	(C ₂ H ₅) ₃ N	-	18.5
Water	Nicotine	208	60.8
Water	β-picoline	153	49.1
Glycerine	m-toluidine	120	7.1

The two phases having dissimilar composition in equilibrium with each other as a given T constitute a pair of conjugate phases. The composition points of the conjugate phases are joined by tie lines. Any composition – temp coordinates placing a point in the area of parallel miscibility represent a system of two liquid phases and a vapour phase. We can determine the mass ratio of the liquid phases by locating the overall composition point on the tie line for the specified T. the boiling point mole fraction diagram for a mixture of partially miscible liquids with an UCST, we see that

$$\text{Mass of phase a} / \text{mass of phase b} = bc / ac$$

The above proportionality is called the lever rule as mentioned above.

It may be mentioned here that the presence of another substances dissolved in one or both phases has a marked effect on the CST as well as the liquid phase composition at the CST, a substance soluble in only one of the original liquids raise the UCST and lowers the LCS, however, a substance soluble in the both the original liquids tends to lower the UCST and raise the Lower CS. As a matter of fact, substances taken in sufficiently large amounts. May convert partial miscibility of a liquid pair into complete miscibility.

Small amount of impurities may produce larger changes in the CST. This observation forms the basis of the crismar band which can detect and measure minute quantities of impurities. It is found that the change in the CST value is a linear function of the concentrations of the impurities. Thus, 1% of sodium chloride present in water raise its UCST with phenol by 12°C. Traces of water in alcohols can be estimated by measuring their CSTs with cyclohexane. Sodium oleate is soluble in both phenol and water. Addition of 0.98% sodium oleate to the phenol water system. Lowers the CST by 43.7°C.

Phenol-water system

Phenol and water are only partially miscible at ordinary T. therefore, on shaking these two liquids with each other, two saturated solutions of different composition one of phenol in water and other of water in phenol are obtained. As already mentioned these solutions of different compositions coexisting with one another are termed conjugate solutions.

The mutual solubility of phenol and water increases with rise in T and therefore, the conc. Of phenol in water as well as that of water in phenol goes on increases with raise in T and ultimately at a certain T the two conjugate solutions change into one homogeneous solution the consolute T for phenol water system is found to be 68.1°C.

The composition of the solution then is 36.10% phenol and 63.90% water. Above the consolute T, the two liquids becomes miscible with each other in all proportions. The variation of mutual solubility of water and phenol with T is represented by graphically.

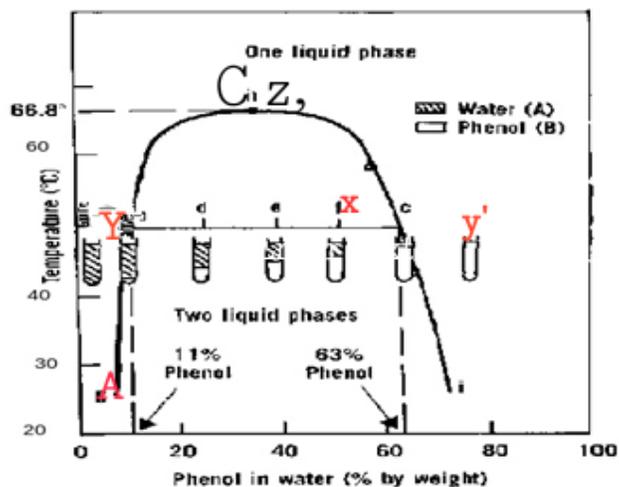


Fig.1.2.5 phenol – water system

When T and composition of a mixture of water and phenol is represented by a point say x within the curve ABC the system consists of two layers of compositions represented by the point a and b. if the T and composition represented by a point on the left of curve AC or on the right side

of the curve CB. Say as at Y and y' , the mixture will consist only of one solution. At y it will be an unsaturated solution of phenol in water and as y' it will be an unsaturated solution of water in phenol. Further addition of phenol y or of water y' ultimately result in the separation of the two phases. Lastly if the T and composition as represented by a point say z. above the curves ACB the system will consist again of one homogeneous solution but now., since this point lies above the consolute T at which the two liquids are miscible in all proportions, further of phenol to water to phenol will meet lead in formation of two layers. The composition of such a solution thus can have any value.

Triethylamine-water system

A system in which the mutual solubility increases with decrease in T. i.e., it has a LCST or lower consolute temperature.

The mutual solubilities of the two liquids are plotted graphically. The CST is 18.5°C. Above this T, the liquid give rise to two distinct layers but below this T they are completely miscible in all proportions.

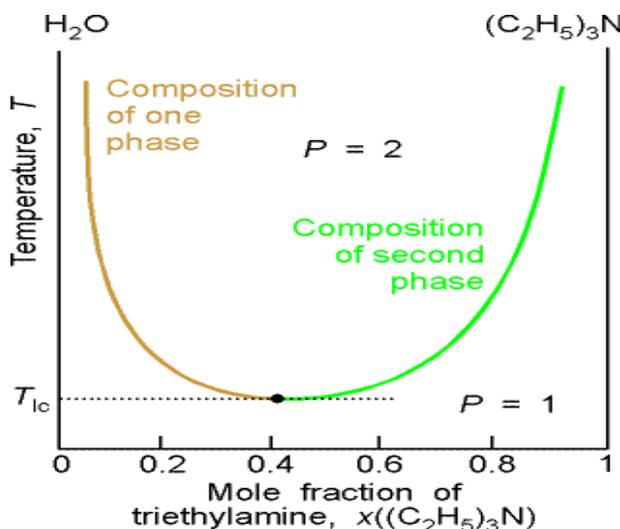


Fig.1.2.6 Triethylamine-water system

Nicotine-water system

Nicotine – water system show an UCST as well as LCST. In other words, these liquids are completely miscible above a certain critical temperature (UCST) and again below a certain critical temperature (LCST). Between these two limiting temperatures, they are partially miscible.

The solubilities of these liquids in one another at different temperatures are shown graphically. The UCST is 208.0°C and the LCST is 60.8°C. Between these two temperatures, mixtures of water and nicotine separate into two layers.

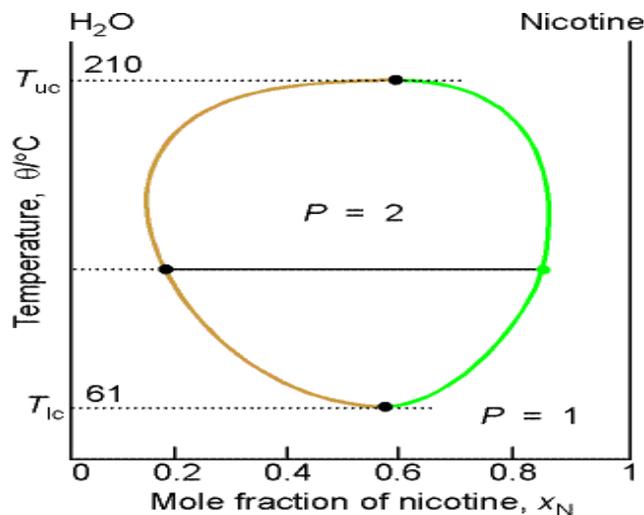


Fig.1.2.7 Nicotine-water system

STATEMENT OF NERNST DISTRIBUTION LAW

Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called Nernst's Distribution law (or Nernst's Partition law) or simply Distribution law or Partition 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,

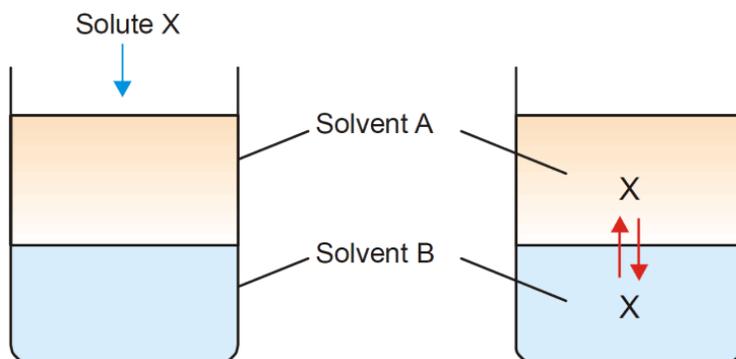


Fig. 1.3.1 Distribution of solute X between solvent A & B.

$$\text{Concentration of X in A} / \text{Concentration of X in B} = K_D$$

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B, Nernst's Distribution law can be expressed as

$$C_1 / C_2 = K_D$$

The constant K_D (or simply K) is called the Distribution coefficient or Partition coefficient or Distribution ratio.

Solubilities of Nernst Distribution Law

When a solute is shaken with two non-miscible solvents, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, we can write the distribution law as

$$C_1 / C_2 = S_1 / S_2 = K_D$$

Where S_1 and S_2 are the solubilities of the solute in the two solvents.

Hence knowing the value of the Distribution coefficient (K_D) and the solubility of solute in one of the solvents, the solubility of solute in the second solvent can be calculated.

Thermodynamic derivation of Nernst distribution law

This is an equilibrium law. When the distribution of the solute X has reached dynamic equilibrium, the rate (R_1) at which molecules of X pass from solvent A to B is proportional to its concentration (C_1) in A . The rate (R_2) at which molecules of X pass from solvent B to A is proportional to its concentration (C_2) in B . At equilibrium, the rate of migration of solute from one solvent to the other is equal. Thus we have

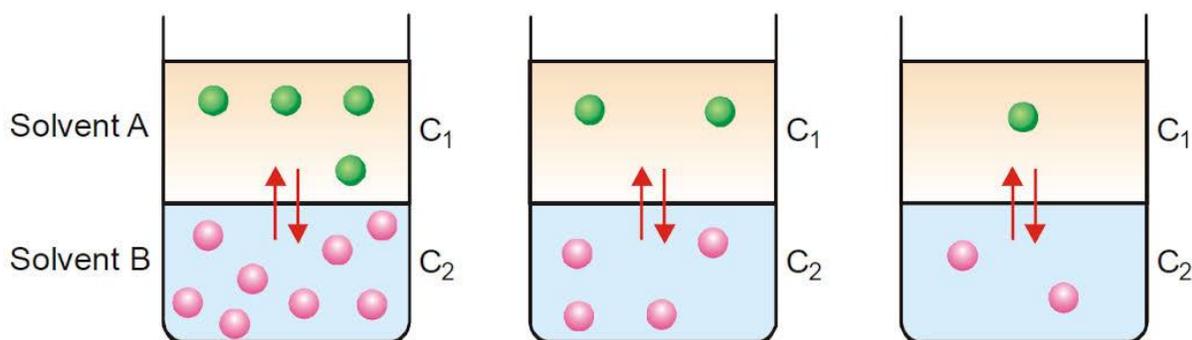


Fig. 1.3.2 At equilibrium, the no. of molecules of X passing from solvent A & B is proportional to its conc. in A and vice versa. Also, the rate of migration of solute molecules from A to B and B to A is equal.

$$R_1 \propto C_1$$

$$R_1 = K_1 \times C_1$$

$$R_2 \propto C_2$$

$$R_2 = K_2 \times C_2$$

Since, at equilibrium

$$R_1 = R_2$$

$$K_1 \times C_1 = K_2 \times C_2$$

$$C_1 / C_2 = K_2 / K_1 = K_D$$

$$C_1 / C_2 = K_D$$

This is the Nernst's Distribution law equation. Since k_1 and k_2 are constants at the same temperature, the distribution coefficient K_D is also constant if temperature is fixed

Limitations

The conditions to be satisfied for the application of the Nernst's Distribution law are :

- 1. Constant temperature.** The temperature is kept constant throughout the experiment.
- 2. Same molecular state.** The molecular state of the solute is the same in the two solvents. The law does not hold if there is association or dissociation of the solute in one of the solvents.
- 3. Equilibrium concentrations.** The concentrations of the solute are noted after the equilibrium has been established.
- 4. Dilute solutions.** The concentration of the solute in the two solvents is low. The law does not hold when the concentrations are high.
- 5. Non-miscibility of solvents.** The two solvents are non-miscible or only slightly soluble in each other. The extent of mutual solubility of the solvents remains unaltered by the addition of solute to them.

Factors affecting Nernst distribution law

1. Solute undergoes Association

It was pointed out by Nernst that C_1/C_2 is constant only if the solute exists as simple molecules in the two solvents. If the solute undergoes association or dissociation in one of the solvents, it is found that C_1/C_2 is not constant. In these cases, distribution law applies only to that part of the solute which is present as simple molecules.

Suppose the solute is present as simple molecules X in solvent A. In solvent B, n molecules of X associate to form X_n molecules. Assuming that a few single molecules X are also present in solvent B the equilibria that exist in the two solvents are shown in Fig. 1.3.3.

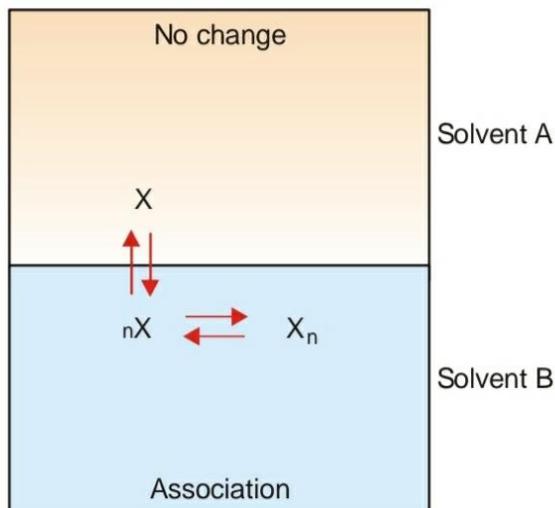


Fig. 1.3.3 distribution diagram when the solute is associated in one solvent.

Let C_1 be concentration of X in solvent A.

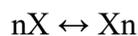
C_3 be concentration of X in solvent B

C_2 be concentration of X_n in solvent B. Applying distribution law to the equilibrium

X in solvent A \leftrightarrow X in solvent B

$$C_1 / C_2 = K_D$$

Applying mass law to the chemical equilibrium



$$[X]^n / [X_n] = K_C \text{ or } C_3^n / C_2 = K_C$$

Taking nth root on both side in equation

$$C_3 / \sqrt[n]{C_2} = \sqrt[n]{K_C}$$

$$C_1 / \sqrt[n]{C_2} = K_D / \sqrt[n]{K_C} = K \text{ (a constant)}$$

Thus when association occurs in one solvent, the distribution equation is modified as

$$C_1 / \sqrt[n]{C_2} = K_D$$

Since the solute exists largely as associated molecules, the total concentration of X determined experimentally in solvent B is taken as the concentration of the associated molecules X_n .

The constant value of partition coefficient now arrived at, suggests that benzoic acid is associated into double molecules in the benzene layer.

2. When Solute undergoes Dissociation

Suppose the solute is present as normal molecules X in solvent A and it dissociates into A + B in solvent B. The equilibria set up in the two solvents are shown in Fig.

Let C_1 be the concentration of X in solvent A and C_2 the total concentration of X (dissociated and undissociated) in solvent B.

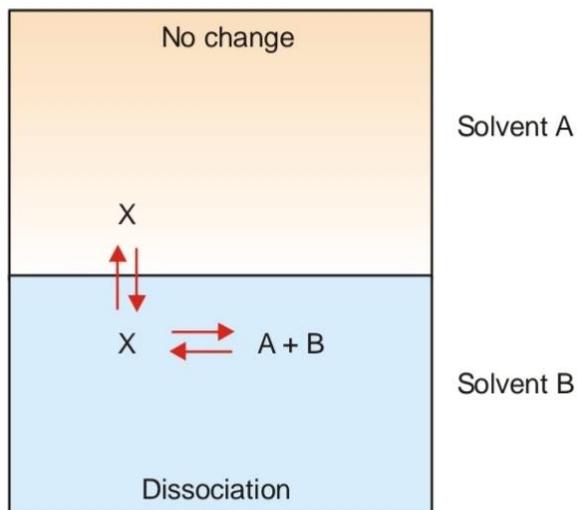
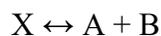


Fig. 1.3.4 distribution diagram when dissociation occurs in one solvent.

If the degree of dissociation in solvent B is x ,



Hence the concentration of the dissociated molecules in solvent B is $C_2 (1 - x)$.

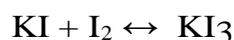
Applying distribution law

$$C_1 / C_2(1-x) = K_D$$

This is the modified distribution law equation when there is dissociation in one of the solvents. A case of this type arises in the distribution of a weak acid (*e.g.*, succinic acid or oxalic acid) between ether and water. C_1 and C_2 can be determined by direct titration of the two layers against standard alkali solution. The value of x can be found by measuring electrical conductance of solution in solvent B.

3. 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.



This reaction can be carried in water, while iodine is soluble in both water and benzene.

Procedure

(i) To find the distribution coefficient of I_2 .

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

$$\text{Conc. Of } \text{I}_2 \text{ in H}_2\text{O} / \text{Conc. Of } \text{I}_2 \text{ in benzene} = K_D$$

(ii) 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,

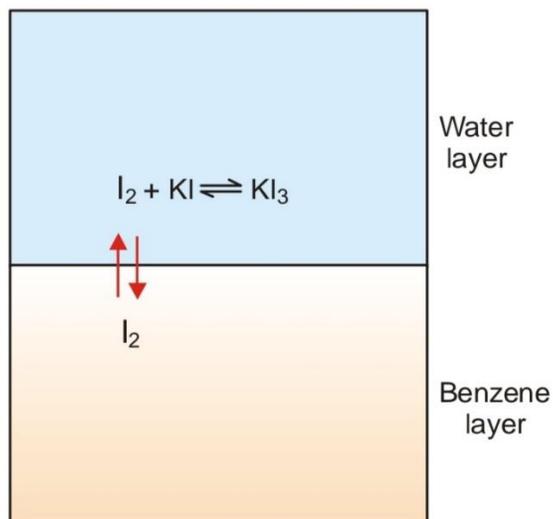


Fig. 1.3. 5 determination of equilibrium constant.

Conc. Of I_2 in H_2O / Conc. Of I_2 in benzene = K_D

Conc. Of I_2 in water layer = $K \times b$

Conc. KI_3 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



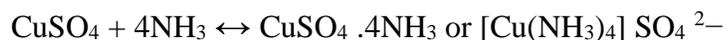
$$K_C = \frac{[KI_3]}{[KI][I_2]} = \frac{c - Kb}{(a - c + Kb) Kb}$$

The square brackets denote concentrations in water layer. Since all the quantities on the right-hand side are known, the equilibrium constant (K_C) can be Calculated.

4. Study of complex ion

If the value of K_C comes out to be constant by taking different concentrations of KI and I_2 to start with, it proves the existence of KI_3 or the complex ion – I_3^-

The distribution law is, therefore, helpful in the study of complex ions. Other examples of complex formation are :



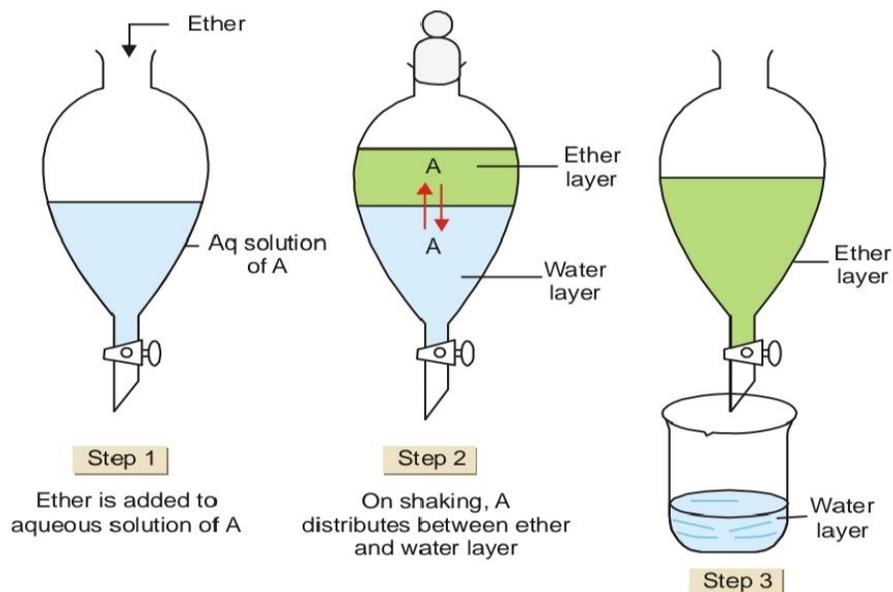


Fig. 1.3.6 extraction in a separatory funnel.

5. Extraction with 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.

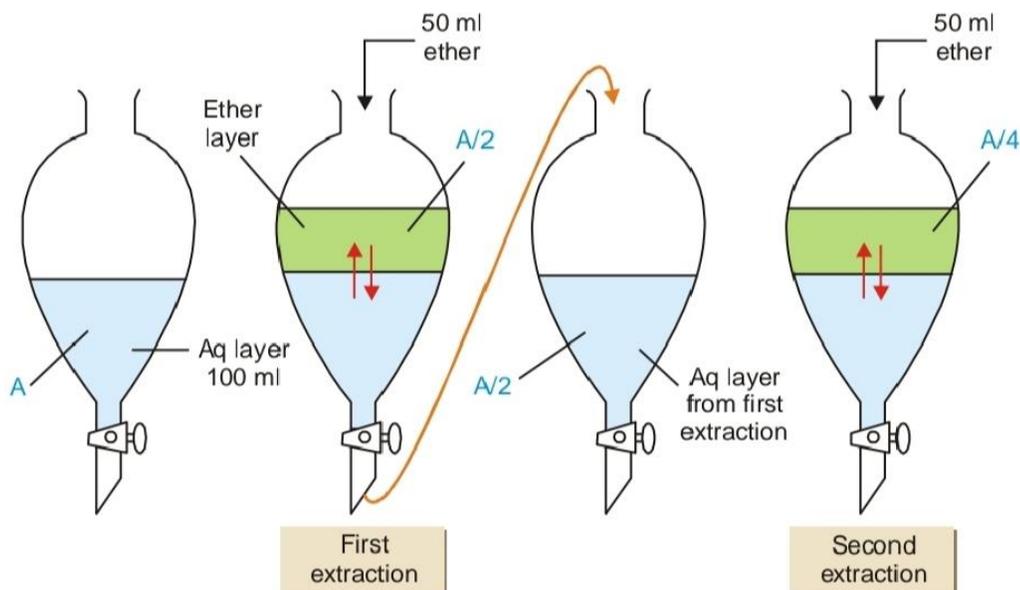


Fig. 1.3.7 illustration of multiple extraction. The given solvent (ether) is used in two successive portions of 50 ml each.

why multiple extraction is more efficient?

The fact that it is more efficient to use a specified volume of solvent in small portions rather than in one whole, may be illustrated in a simple way.

Suppose we have 100 ml of an aqueous solution containing A grams of an organic substance. We can extract the substance with ether (ethoxyethane), its distribution ratio being twice in favour of ether. We are provided with 100 ml of ether which may be used in one lot or in two portions of 50 ml each.

- (1) **Using all the ether in one lot. Let x grams be the weight of the substance extracted in the solvent layer**

Then the amount of substance left in the water layer = $A - x$ grams. Therefore,

$$\text{Concentration in ether layer} = x/100$$

Concentration in water layer = $(A - x)/100$

C ether / C water = K

$$(X / 100) / (A - x) / 100 = 2$$

Hence $X = 2/3A$

Thus 66 % of substance is extracted.

(2) Using two 50 ml portions of ether. Let x_1 grams of substance be extracted in the first operation with 50 ml ether. Thus,

Concentration in ether layer = $x_1/50$

Concentration in water layer = $(A - x_1)/100$

C ether / C water = 2

$$(X_1 / 50) / (A - X_1) / 100 = 2$$

Hence $X = 1/2A$

Thus 50 % of substance is extracted.

(3) The substance left in water layer is 1/ 2. A Let x_2 grams be the substance removed from the water layer when it is extracted with another 50 ml portion of ether. Hence,

Concentration in ether layer = $x_2/50$

Concentration in water layer = $1/2 A - x_2$

$$(X_2 / 50) / (1 / 2A - X_2) / 100 = 2$$

Hence $X_2 = 1/4 A$

Thus, 25% of substance is extracted.

Thus 75 per cent of substance is extracted by using two 50 ml portions of the solvent as against 66 per cent when 100 ml solvent is used in one lot. Similarly, it can be shown that by using four 25 ml portions of ether it is possible to extract 80.2% of substance.

Five 20 ml portions of ether would likewise remove 83.8%.

It is clear from above that it is more advantageous to use a given quantity of the solvent in as many portions as conveniently possible. It must be understood, however, that it is not possible to remove the whole of the dissolved substance, however large the number of extractions may be. Every time, the substance distributes itself between the two solvents and a quantity, however small, must always be left behind.

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.

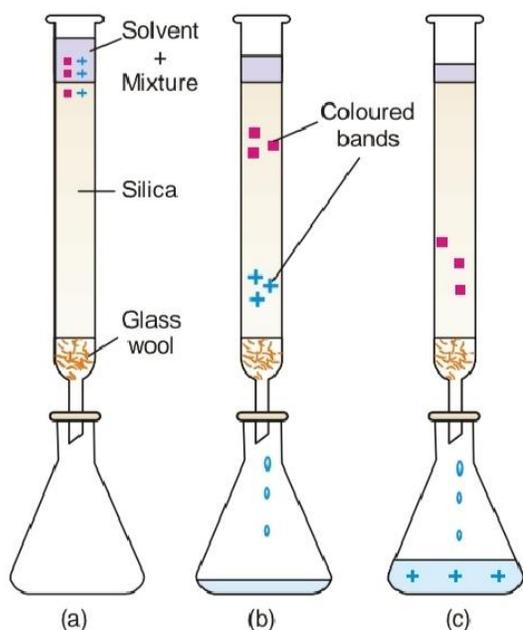


Fig. 1.3.8 chromatography column.

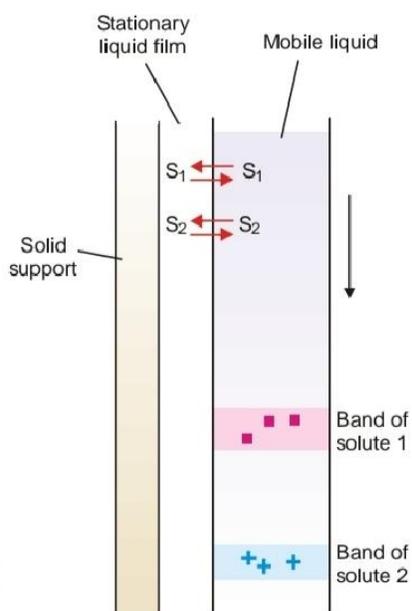


Fig.1.3.9 in partition chromatography.

The process of extraction is more efficient if the solvent is used in a number of small portions than in one whole lot. Thus multiple extraction is preferred to simple extraction.

The multiple extraction is also the basis of the industrial counter flow solvent extraction. A dilute solution of the substance enters at the top of a column or tower. At the same time the extracting

solvent enters at the bottom. As the aqueous solution and the solvent pass each other, the solute distributes itself in favour of the solvent. Since the process of extraction is repeated many times at different levels in the tower, maximum quantity of substance is removed in the solvent.

(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) Desilverization of Lead (Parke's Process)

When molten zinc is added to molten lead containing silver (argentiferous lead), zinc and lead form immiscible layers and silver is distributed between them. Since the distribution ratio is about 300 in favour of zinc at 800° C, most of silver passes into the zinc layer. On cooling the zinc layer, an alloy of silver and zinc separates. The Ag-Zn alloy is distilled in a retort when zinc passes over leaving silver behind.

The lead layer still contains unextracted silver. This is treated with fresh quantities of molten zinc to recover most of the silver.

(4) 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 tri chloro methane (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.

(5) Determination of Association

When a substance is associated (or polymerized) in solvent A and exists as simple molecules in solvent B, the Distribution law is modified as

$$\sqrt[n]{C_A / C_B} = K$$

when n is the number of molecules which combine to form an associated molecule. Suppose benzoic acid is associated to bimolecules, $(C_6H_5COOH)_2$, in benzene and is present as simple molecules in aqueous layer. Then equation (1) can be written as follows where $n = 2$.

$$\sqrt[2]{C_{\text{benzene}}} / C_{\text{aqueous}} = K$$

The concentrations in benzene and aqueous layer are determined experimentally. If the under root of the concentration in benzene divided by the concentration in aqueous layer gives a constant value benzoic acid exists as bimolecules (*dimer*) in benzene.

(6) Determination of Dissociation

Suppose a substance X is dissociated in aqueous layer and exists as single molecules in ether. If x is the degree of dissociation (or ionisation), the distribution law is modified as

$$C_1 / C_2 (1 - X) = K$$

C_1 conc. Of X in benzene

C_2 conc. Of X in aqueous layer

The value of x can be determined from conductivity measurements, while C_1 and C_2 are found experimentally. Thus the value of K can be calculated. Using this value of K , the value of x for any other concentrations of X can be determined.

(7) Determination of Solubility

Suppose the solubility of iodine in benzene is to be determined. Iodine is shaken with water and benzene. At equilibrium concentrations of iodine in benzene (C_b) and water (C_w) are found experimentally and the value of distribution coefficient calculated.

$$C_b / C_w = K_D$$

$$S_b / S_w = K_D$$

where S_b = solubility in benzene; and S_w = solubility in water

If the solubility of iodine in water (S_w) is known, the solubility in benzene can be calculated.

(8) Deducing the Formula of a Complex Ion (I_3^-)

Some iodine is added to a solution of KI and the reaction mixture shaken with benzene. (a) The $[I_2]$ in water layer can be found knowing the value of K_D (determined separately) and concentration of iodine in benzene (determined by titration against thiosulphate). (b) The total concentration of iodine, $[I_2] + [I_3^-]$ in water layer is found by titration against thiosulphate. Knowing $[I_2]$ from (a), $[I_3^-]$ can be calculated.

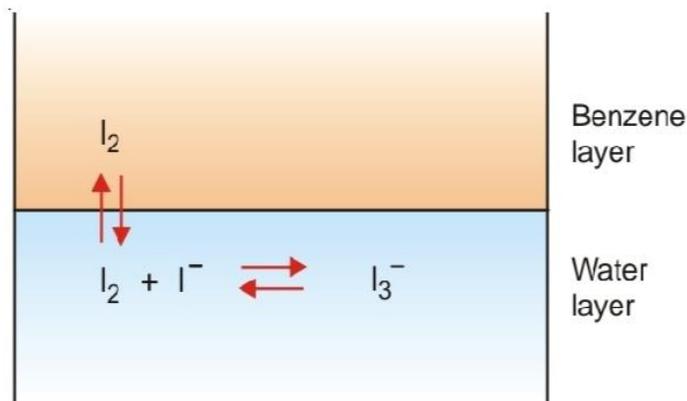


Fig.1.3.10 complex ion (I_3^-)

(c) The initial concentration of KI taken is represented by the equilibrium concentrations

$[I^-] + [I_3^-]$. Knowing $[I_3^-]$ from (b), $[I^-]$ can be found.

Substituting the above values of concentrations in the law of Mass Action equation of the reaction in water layer,

$$\frac{[I_3^-]}{[I_2] [I^-]} = K$$

The value of equilibrium constant K can be calculated. If it comes out to be constant for different concentrations of iodine, it stands confirmed that the formula of the complex I_3^- , which we assumed is correct.

(9) 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 carbon tetrachloride) is added to the solution. The bulk of any iodine present passes into the organic layer and imparts intense violet colour to it.

Reference

1. Principles of Physical Chemistry - B. R. Puri, Sharma and Madan S. Pathania, Vishnal Publishing Co., - 2013.
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Questions

Section – A

1. Define solution.
2. State Raoult's law.
3. Write the criteria for an ideal solution.
4. Define activity.
5. Distinguish between an ideal and non-ideal solutions.
6. What is meant by fractional distillation?
7. What is meant by azeotropic mixtures?
8. Define CST
9. State Nernst distribution law.

Section – B

1. Draw and explain the vapour pressure diagram for an ideal solution
2. Explain activity of a component of an ideal solution.
3. Explain the both +ve and -ve deviation from Raoult's law.
4. Derive the Gibbs-Duhem equation.
5. Explain phenol – water system.
6. Derive the thermodynamic expression for Nernst distribution law.
7. Detailed about solvent extractions.

Section – C

1. Derive the thermodynamic expression for an ideal solution.
2. Explain the fractional distillation of binary liquid solution.
3. Explain the distillation of immiscible liquids.
4. Write the Nernst distribution law and its applications?
5. Detailed about azeotropic mixtures.
6. Explain about steam distillation