PHYSICAL CHEMISTRY

Solutions

Prof. Saroj Aggarwal
School of Basic and Applied Sciences
Guru Gobind Singh Indraprastha University
Kashmere Gate
Delhi-110 006

(02.06.2006)

CONTENTS

Keywords
Phase, Solute, Solvent, Partial pressure, mole fraction, Colligative property, Vant Hoff factor, activity, fugacity, Chemical potential

What is a solution?

A solution may be described as a homogeneous mixture, constituting one phase only, of two or more components. A solution may be gaseous, liquid or solid. Binary solutions are composed of two constituents, ternary solutions three & quatnery four. There is no fundamental difference between the roles of these components, it is convenient to call the one present in the greatest amount as solvent, while those constituents – one or more – present in relatively small amounts are called the solutes. The distinction between solvent and solute is an arbitrary one, nothing fundamental distinguishes them. It is not possible to classify the two constituents of a binary solution into solute and solvent when both of them are present in equal amounts. Anyone may be treated as solute or the solvent.

A solution may exist in gaseous state, liquid state or solid state. Significant types of solutions are

1. Solid-in-liquid solutions
2. Liquid-in-liquid solutions
3. Gas-in-liquid solutions

Methods for expressing the concentration of a solution

There are many ways to express the concentration of a solution.

(i) Molarity
(ii) Molality
(iii) Normality
(iv) Mole fraction
(v) Mass percentage
(vi) Volume percentage
(vii) Mass of a solute in a definite mass of solvent
(viii) Mass of a solute per definite mass of solution
(ix) Mole percent
(x) Parts per million

In a two component (binary) solution, it is customary to denote the solvent by subscript 1 and solute by subscript 2.

Molarity:- The molarity (M_A) of a component A in solution is defined as the number of moles of the component present per litre (dm^3) of the solution. Thus,

M_A = Moles of A/Volume of solution
= n_A/V in litres.

Molality:- The molality, m_A, of a component A in solution is defined as the number of moles of the component present in one kilogram of the solvent. Thus,

m_A = Moles of A/Mass of solvent
= n_A/Kg of solvent.

Normality:- The normality (N_A) of component A in solution is defined as the number of gram equivalents of the component present in one litre of the solution.

N_A = gram equivalent of A/ Volume in litres

Mole fraction:- It is amount in moles of a given substance A divided by the total amount (in moles) of all constituents of a solution.

In solution containing n_1 moles of component 1, n_2 moles of component 2, n_3 moles of component 3 and so on, the mole fraction x_i of the i^{th} component is given by

$$x_i = \frac{n_i}{\sum n_i} = \frac{n_i}{n_1 + n_2 + n_3 + ...}$$

The sum of the mole fractions of the components of a solution is unity. i.e

$$\Sigma x_i = 1$$

The other concentration units are less frequently used:-

Ideal Solution: A solution of two or more constituents is said to be ideal if it obeys Raoult's law under all conditions of temperature and concentration. We are considering a solution composed of a volatile solvent and one or more involatile solutes.

An ideal gas is defined as that which behaves ideally at any pressure and temperature. In practice there is no gas which is perfectly ideal. The ideal gas law is an important example of a limiting law. We can arrive at a similar limiting law from observing the behaviour of solutions. For this we examine the equilibrium between the solution and the vapour. If a pure liquid is placed in a container which is initially evacuated, the liquid will evaporate till the space above is filled with vapour. The temperature of the system is kept constant. At equilibrium, the pressure established is the vapour pressure of the pure component (p^0). If an involatile material is dissolved, the equilibrium vapour pressure (p) over the solution is less than over the pure liquid i.e. there is a decrease in the vapour pressure

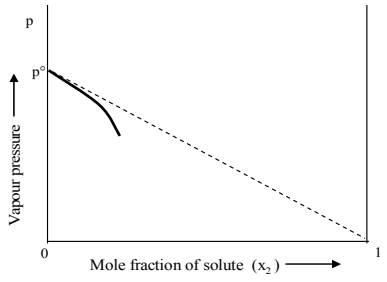


Fig. 1

Fig. (1) shows the variation of vapour pressure of the solution with respect to mole fraction of the solute. It can be seen that as x_2 increases p decreases, at $x_2 = 0$, $p = p^0$, i.e. vapour pressure of the pure liquid. The important feature of the figure is that the vapour pressure of the dilute solution (for very small values of x_2) approaches the dashed line connecting vapour

pressure p^0 and 1. Depending upon the solvent and solute considered, the experimental vapour pressure curve at higher concentration may fall below/above or even lie exactly on it. However for all solutions the experimental curve is tangent to the dashed line (at $x_2 = 0$) and approaches the dashed line closely as the solution under consideration is more and more dilute.
The equation for the dashed line (Ideal solution) may be written as

$$p = p^\circ - p^\circ x_2 = p^\circ(1 - x_2) \qquad \text{.....(1)}$$

x_2 is the mole fraction of the solute

If x_1 is the mole fraction of solvent in solution then above equation becomes

$$p = x_1 p^\circ \qquad \text{.....(2)}$$

Which is Raoult's law and may be stated as;

"The partial pressure of any volatile component of a solution at any temperature is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution".

Raoult's law is another example of a limiting law. The ideal solution is defined as one that follows Raoult's law over entire range of concentration.

Real solutions follow Raoult's law more closely as the solution becomes more dilute.
The lowering of vapour pressure is then;

$$p^\circ - p = p^\circ - x_1 p^\circ = (1 - x_1) p^\circ$$

$$\Rightarrow x_2 p^\circ \qquad \text{.....(3)}$$

The vapour pressure lowering is proportional to the mole fraction of the non volatile solute in solution. If more than one solute are present then it is still true that

$p = x_1 p^\circ$ but in this case

$(1 - x_1) = x_2 + x_3 + x_4 + ...$

where $x_2, x_3, ...$ represent the mole fraction of various solute present

$$\& \qquad (p^\circ - p) = (x_2 + x_3 + ...) p^\circ \qquad \text{.....(4)}$$

Thus we can say that in a solution containing several nonvolatile solutes, the lowering of vapour pressure depends on the sum of the mole fractions of the various solutes. The vapour pressure depends only on the relative number of solute molecules. Equation (3) can be written alternatively as

$$\frac{p^\circ - p}{p^\circ} = x_2 \qquad \text{.....(5)}$$

Where (p°-p) is the lowering of vapour pressure and $\frac{p^\circ - p}{p^\circ}$ is the relative vapour pressure lowering. The relative vapour pressure lowering is therefore a colligative property

$$\text{Mole fraction } x_2 = \frac{n_2}{n_1 + n_2} \qquad \text{…….(6)}$$

Where n_1 and n_2 are the number of moles of solute and solvent respectively.

For a dilute solution the value of n_2 can be neglected as compared to n_1. Hence

$$x_2 \approx \frac{n_2}{n_1} = \frac{w_2 / M_2}{w_1 / M_1} = \frac{w_2 M_1}{w_1 M_2} \qquad \text{…….(7)}$$

Where w_1 and w_2 are the amounts of the solvent and solute and M_1 and M_2 the molar mass of solvent and solute respectively. So equation (5) becomes

$$\frac{p^\circ - p}{p^\circ} = x_2 = \frac{w_2 M_1}{w_1 M_2} \qquad \text{…….(8)}$$

Equation (8) can be used to determine the molar mass of a solute.

Colligative properties of dilute solutions

A colligative property of a system is one which depends on the number of solute particles present in the solution. Solutions may be of two types.

1. Solutions of non electrolytes
2. Solutions of electrolytes

In solutions of non electrolytes the dissolved solute remains in the same form as it exists in the solid form i.e. it does not undergo any association or dissociation. In case of solutions of electrolytes the solute may either undergo association or dissociation in solution yielding lower or higher number of particles respectively. First let us consider the properties of solutions of non-volatile non-electrolyte solutes and it is also assumed that the solutions are dilute i.e. the interactions between solute-solvent particles are negligibly small and the solutions behave ideally. Apart from lowering the vapour pressure of the solvent, which we have already considered, a non volatile solute has three main effects.

1. Elevation of Boiling point
2. Depression in freezing point
3. Development of an osmotic pressure

These properties all stem from changes in disorder of the solvent, and the increase in disorder does not depend on the identity of the solute present in solution. It only depends on the number of solute particles present and not on their chemical identity. For this reason these are called colligative properties. Colligative properties have been extensively used for determining the molar masses of non volatile dissolved substances.

The freezing point and boiling point correspond to the temperature at which the graph of the molar Gibbs energy of the liquid intersects the graph of the molar Gibbs energy of the solid and gas phases respectively. Because we are dealing with mixtures we have to think about partial molar Gibbs energy (The Chemical potential) of the solvent. The presence of a solute lowers the chemical potential of the liquid. As a result we see that freezing point moves to lower values and the boiling point moves to higher values. Fig. 2(a) & 2(b) show the depression in freezing point and elevation in boiling point respectively.

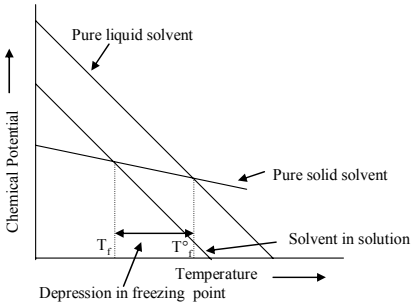


Fig. 2 (a)

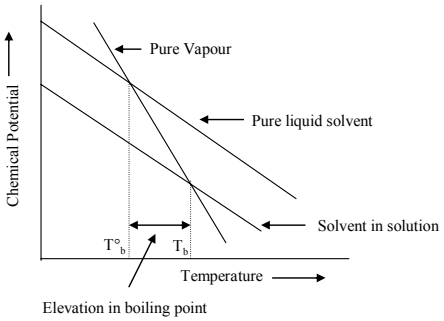


Fig. 2 (b)

We will be using clausius clapeyron equation for the thermodynamic derivation of elevation in boiling point and depression in freezing point.

Clapeyron equation:- Suppose a single substance exists in two phases A and B in equilibrium with each other at constant temperature and pressure. If one mole of substance is transferred from phase A to other phase B without making any change in temperature and pressure. In this case we can say that

$$dG = 0, \qquad dP = 0, \qquad dT = 0$$

i.e. $$G_A = G_B \qquad \text{…….(9)}$$

i.e. the molar free energy of a substance is the same in the two phase which are in equilibrium. In a phase change we have

$$dG = VdP - SdT \qquad \text{…….(10)}$$

So for phase A and phase B, it can be written as

$$dG_A = V_A dP - S_A dT \qquad \text{…….(11)}$$

$$dG_B = V_B dP - S_B dT \qquad \text{…….(12)}$$

from equation (11) and (12) we have

$$dG_B - dG_A = (V_B - V_A)dP - (S_B - S_A)dT$$

But $dG_B - dG_A = 0$ so

$$(V_B - V_A)dP = (S_B - S_A)dT$$

or $$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

But we know $\Delta S = \frac{\Delta H}{T}$

Therefore $$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} \qquad \text{…….(13)}$$

The above equation is applicable to various equilibria as solid $\Leftrightarrow$ liquid, liquid $\Leftrightarrow$ vapour and equilibria between two solid modifications.

For solid liquid equilibrium: Solid and liquid forms of a substance can exist together only at freezing point or melting point. So in equation (13) T will be the freezing point and P the external pressure

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

here

$$\Delta V = V_l - V_S$$

$$\Delta H = \Delta H_f$$

V_l and V_S represent the molar volume of the solid and the liquid phases and ΔH_f- molar enthalpy of fusion. So equation (13) can be rewritten as

$$\frac{dp}{dT} = \frac{\Delta H_f}{T(V_l - V_S)} \qquad \text{…….(14)}$$

For liquid vapour equilibrium:-

$$\Delta H = \Delta H_v \text{ (enthalpy of vaporization)}$$

$$\Delta V = V_v - V_l$$

So the main equation now is

$$\frac{dp}{dT} = \frac{\Delta H_v}{T(V_v - V_l)} \qquad \text{…….(15)}$$

Equation (15) represents rate of change of vapour pressure (p) of the liquid with temperature.

Clausius Clapeyron equation: If the temperature of the liquid is not too near the critical point then we can easily neglect the volume of the liquid i.e. V_l as compared to V_v
In such case equation (15) reduces to

$$\frac{dp}{dT} = \frac{\Delta H_V}{TV_v} \qquad \text{…….(16)}$$

Further, under such conditions the vapour pressure is very small, it may be assumed that the vapour behaves as an ideal gas to which the equation

$pV_v = RT$ is applicable

$$\frac{dp}{dT} = \frac{\Delta H_V}{T\dfrac{RT}{p}}$$

$$\frac{1}{p}\frac{dp}{dT} = \frac{\Delta H_V}{RT^2}$$

$$\frac{d}{dT}\ln p = \frac{\Delta H_V}{RT^2} \qquad \text{…….(17)}$$

Equation (17) is known as clausius – clapeyron equation and its integrated form is applied in thermodynamic derivations of elevation in boiling and depression in freezing point. It can be obtained as follows

Assumption is made that enthalpy of vaporization/fusion is independent of temperature. If equation (17) is integrated between the limits T_1 to T_2 and p_1 to p_2 we get

$$\int_{P_1}^{P_2} d\ln p = \frac{\Delta H_V}{R}\int_{T_1}^{T_2}\frac{1}{T^2}dT$$

$$\Rightarrow 2.303\log\frac{p_2}{p_1} = \frac{\Delta H_V}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\Rightarrow \log\frac{p_2}{p_1} = \frac{\Delta H_V}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \qquad \text{…….(18)}$$

For solid liquid equilibrium the integrated form of clausius Clapeyron equation will be

$$\log \frac{p_2}{p_1} = \frac{\Delta H_f}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Elevation of boiling point of a solution

Boiling point of a solvent is the temperature at which the vapour pressure of the solvent becomes equal to that of external pressure, normally the atmospheric pressure. The addition of a non volatile solute to the solvent lowers its vapour pressure and a higher temperature is required when the vapour pressure of the solution will equalize itself with the external pressure on it, i.e. we can say the liquid now will boils at a higher temperature. Thus an elevation in the boiling point of the liquid is caused due to the presence of the non volatile solute dissolved in it. The difference in the boiling point of solution and of pure solvent is known as the elevation in boiling point of the solution. Elevation in boiling point can readily be understood from the lowering in vapour pressure concept.

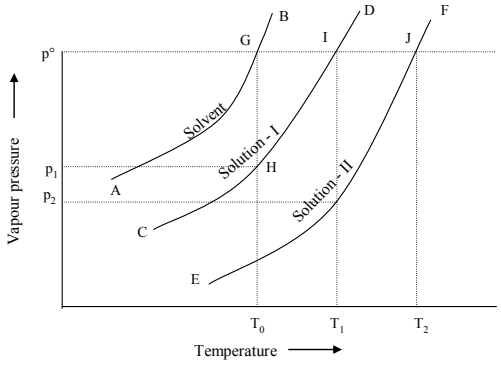


Fig. 3

Curve AB represents the variation of vapour pressure with temperature for a pure solvent while the curves CD and EF show the variation of vapour pressure with temperature for solution I and solution II respectively. Solution I is dilute as compared to solution II, although both contain the same nonvolatile solute.

T_0 is the boiling point of the pure solvent at one atmospheric pressure. At this temperature the solution has vapour pressure lower than one atmosphere and hence it does not boil. If the temperature is increased to T_1, the vapour pressure of the solution rises and now is equal to one atmosphere and the solution boils. This means solution has a higher boiling point than that of the pure solvent. Thus $(T_1\text{-}T_0) = \Delta T_b$ is the elevation in the boiling point of solution. The point G and H represent the vapour pressure of the pure solvent and solution I at temperature T_0. The lowering of vapour pressure thus is given by

$$p^0 - p_1 = \Delta p = \text{GH}$$

Since the points H and I lie on the vapour pressure curve of the solution I at temperatures T_0 and T_1. The clausius clapeyron equation can be applied

$$\ln \frac{p^\circ}{p_1} = \frac{\Delta Hvap}{R}\left[\frac{1}{T^\circ} - \frac{1}{T_1}\right] \qquad \text{…….(19)}$$

Where ΔH_{vap} is the enthalpy of vaporization per mole of the solvent. For a dilute solution T_0 and T_1 are not very much different so $T_0T_1 \approx T_0^2$ and the equation now becomes

$$\ln \frac{p^\circ}{p_1} = \frac{\Delta Hvap}{R}\left[\frac{T_1 - T^\circ}{T^{\circ 2}}\right]$$

$$\Rightarrow \frac{\Delta Hvap}{R}\left[\frac{\Delta T_b}{T^{\circ 2}}\right] \qquad \text{…….(20)}$$

Further according to Raoult's law

$$\frac{p_1}{p^\circ} = (1 - x_2) \qquad \text{…….(21)}$$

From equation (20) and (21) we get

$$\ln(1 - x_2) = -\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T^{\circ 2}}\right] \qquad \text{…….(22)}$$

$$\ln(1 - x_2) = -x_2 + \frac{x_2^2}{2} - \frac{x_2^3}{3} + ...$$

as the solution is dilute

$\ln(1 - x_2)$ may be approximated to $\approx -x_2$.

and the equation now becomes

$$-x_2 = -\frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T^{\circ 2}}\right]$$

$$or\ \Delta T_b = \frac{RT^{\circ 2}x_2}{\Delta H_{vap}} \qquad \text{…….(23)}$$

Now x_2 which is mole fraction of the solute is equal to

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1} \text{ (for a dilute solution)}$$

where n_1 and n_2 are representing the number of moles of solvent and solute respectively.

$$\frac{n_2}{n_1} = \frac{w_2 / M_2}{w_1 / M_1}$$

$$= \frac{w_2 M_1}{w_1 M_2}$$

Putting the value of x_2 in equation (23)

$$\Delta T_b = \frac{RT^{\circ 2}}{\Delta H_{vap}} . \frac{w_2 M_1}{w_1 M_2} \qquad \text{…….(24)}$$

Molality of the solution may be given by

$$m = \frac{1000 w_2}{w_1 M_2} \qquad \text{…….(25)}$$

Combining equation (24) and (25)

$$\Delta T_b = \frac{RT^{\circ 2}}{\Delta H_{vap}} . \frac{m}{n_1} \qquad \text{…….(26)}$$

Where $n_1 = \frac{1000}{M_1}$. is the number of moles of solvent in 1000 g of solvent

For any solvent the quantity $\left(\frac{RT^{\circ 2}}{\Delta H_{vap}} . \frac{M_1}{1000} \right)$ is constant and is equal to K_b which is known as molal elevation constant or ebullioscopic constant. So

$$\Delta T_b = K_b . m \qquad \text{…….(27)}$$

It is evident from equation (27) that elevation in boiling point of a solution is directly proportional to molality of the solution. If the molality of the solution is one, then $\Delta T_b = K_b$ so molal elevation constant is defined as the elevation in the boiling point of a solution whose molality is Unity.

Equation (27) can be used to calculate the molar mass of the solute.

$$\Delta T_b = K_b . m$$

$$\Rightarrow \mathrm{K_b}\ \frac{1000\, w_2}{w_1 M_2}$$

$$\text{or} \quad M_2 = \frac{1000\, w_2\, \mathrm{K_b}}{T_b w_1} \qquad \text{.....(28)}$$

Other factors known the value of M_2 can be calculated from equation (28).

Depression in Freezing point

The lowering of vapour pressure on dissolution of a solute causes the solution to freeze at a lower temperature, because at the freezing point of the liquid, its vapour pressure becomes equal to the vapour pressure of the solid which separates out and remains in equilibrium with the liquid phase. Fig. (4) shows the vapour pressure as a function of temperature for solution and the pure solvent.

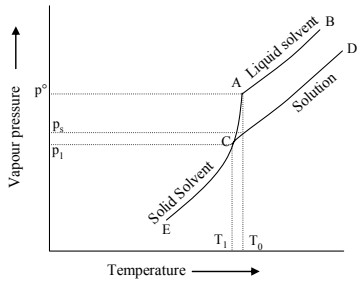


Fig. 4

AB represents the vapour pressure curve of pure liquid solvent. CD represents the vapour pressure curve for solution & EA is the sublimation curve. The sublimation curve EA and liquid solvent curve AB intersect at the point A, where the vapour pressure of the liquid solvent and the solid solvent are equal so the temperature corresponding to this vapour pressure p^0 is the freezing point of the pure solvent. This is represented by T_0.

The vapour pressure curve of a dilute solution of a non volatile solute is represented by CD & is lower than that of the pure solvent. The point of intersection of the curves EA and CD (i.e. point C) is thus the freezing point of the solution and is lower than T_0 and is represented by T_1 in the figure. The depression in freezing point (ΔT_f) is thus given by

$$\Delta T_f = (T_0 - T_1).$$

The magnitude of ΔT_f depends on the nature of the solvent and the concentration of the solution. If p° and p_1° are the vapour pressure corresponding to temperature T_0 and T_1, and as the point A & C lie on the same vapour pressure curve, they may be related by clausius – clapeyron equation. i.e.

$$\ln \frac{p_0}{p_1} = -\frac{\Delta H_{sub}}{R}\left[\frac{1}{T_0} - \frac{1}{T_1}\right]$$

$$= \frac{\Delta H_{sub}}{R}\left[\frac{T_0 - T_1}{T_1 T_0}\right] \qquad \text{…….(29)}$$

where ΔH_{sub} is enthalpy of sublimation

Again for solution p_s is the vapour pressure at temperature T_0 and p_1 is the vapour pressure at temperature T_1, therefore

$$\ln \frac{p_s}{p_1} = -\frac{\Delta H_{vap}}{R}\left[\frac{1}{T_0} - \frac{1}{T_1}\right]$$

$$= \frac{\Delta H_{vap}}{R}\left[\frac{T_0 - T_1}{T_1 T_0}\right] \qquad \text{…….(30)}$$

Now subtracting equation (30) from equation (29)

$$\ln \frac{p_0}{p_s} = \frac{(\Delta H_{sub} - \Delta H_{vap})}{R}\left[\frac{T_0 - T_1}{T_1 T_0}\right] \qquad \text{…….(31)}$$

But $\Delta H_{sub} - \Delta H_{vap} = \Delta H_{fus}$. So putting it in equation (31) we get

$$\ln \frac{p_0}{p_s} = \frac{\Delta H_{fus}}{R}\left[\frac{T_0 - T_1}{T_1 T_0}\right] \qquad \text{…….(32)}$$

since solution is dilute so $T_1 T_0 \approx T_0^2$ and also using Raoult's law

$$\frac{p_s}{p_0} = x_1 = (1 - x_2)$$

equation (32) becomes

$$-\ln(1 - x_2) = \frac{\Delta H_{fus}}{R}\left[\frac{T_0 - T_1}{T_0^2}\right] \qquad \text{…….(33)}$$

as $T_0 > T_1$ so $(T_0 - T_1)$ can be written as (ΔT_f) and the equation (33) becomes

$$-\ln(1-x_2) = \frac{\Delta H_{fus}}{R}\frac{\Delta T_f}{T_0^2} \qquad \text{.....(34)}$$

approximating $\ln(1-x_2) \approx -x_2$

we have

$$x_2 = \frac{\Delta H_{fus}\Delta T_f}{RT_0^2}$$

also

$$x_2 \approx \frac{n_2}{n_1} = \frac{w_2 M_1}{M_2 w_1}$$

and molality $m = \dfrac{1000 w_2}{w_1 M_2}$

equation (34) reduces to

$$\Delta T_f = \frac{RT_0^2 m M_1}{\Delta H_{fus} 1000}$$

$$= \frac{RT_0^2 m}{\Delta H_{fus} n_1}$$

$$= K_f m \qquad \text{.....(35)}$$

where $K_f = \dfrac{RT_0^2}{\Delta H_{fus} n_1}$ .....(36)

K_f is known as molal freezing point constant of a solvent.

When m = 1, $K_f = \Delta T_f$

Thus molal depression constant K_f can be defined as the depression in freezing point of a solution whose molality is one. Equation (35) can be used to calculate the molecular weight of the solute.

Osmotic Pressure

The fourth colligative property of dilute solution is osmotic pressure. Before going into the details of this property one must know about the chemical potential in ideal solutions.

Chemical Potential in ideal solutions: The ideal solution follows Raoult's law over the entire range of concentration. This concept about ideal solutions combined with general equilibrium condition leads to the analytical expression of chemical potential.

According to second law of thermodynamics if the solution is in equilibrium with its vapours, then the chemical potential of the solvent in solution and vapours has the same value.

$$\mu_{liq} = \mu_{Vap} \qquad \text{…….(37)}$$

Where μ_{liq} is the chemical potential of the solvent in liquid phase, μ_{Vap} the chemical potential of the solvent in the vapour phase.

Vapour is the pure solvent, and assuming that the vapour is an ideal gas

$$\mu_{Vap} = \mu^0{}_{Vap} + RT \ln p \qquad \text{…….(38)}$$

From equation (37) and (38) we get

$$\mu_{liq} = \mu_{Vap} = \mu^0{}_{Vap} + RT \ln p \qquad \text{…….(39)}$$

Making use of Raoults law ($p = xp^0$), equation (39) becomes

$$\mu_{liq} = \mu^0{}_{Vap} + RT \ln p^0 + RT \ln x \qquad \text{…….(40)}$$

If pure solvent were in equilibrium with vapour, the pressure would be p°; and the equilibrium condition is

$$\mu^0_{liq} = \mu^0{}_{Vap} + RT \ln p^0 \qquad \text{…….(41)}$$

Where $\mu^0{}_{liq}$ represents the chemical potential of the pure liquid solvent. From equation (40) and (41) we obtain.

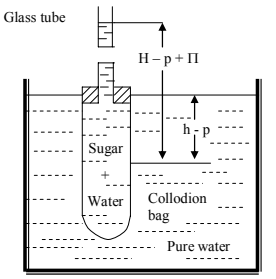
$$\mu_{liq} - \mu^0{}_{liq} = RT \ln x \qquad \text{……(42)}$$

This equation does not contain anything pertaining to vapour and dropping the subscript (liq) one gets.

$$\mu = \mu^0 + RT \ln x \qquad \text{…….(43)}$$

This equation is used in deriving the expression for Osmotic pressure.

The phenomenon of Osmotic pressure is illustrated by the apparatus shown in fig. (5)



Simple Osmotic Pressure experiment

Fig. 5

A collodion bag is tied to a rubber stopper and a piece of glass capillary tubing is inserted in it. The bag is filled with a dilute solution say of sugar in water. It is then immersed in beaker containing pure water. It is observed that the level of the solution in the tube rises till it reaches a definite height, which of course depends on concentration of the solution filled in the bag. The extra hydrostatic pressure resulting from the difference of levels of the sugar solution in the tube and that of pure water in beaker is the osmotic pressure of the solution.

Observing carefully we note that no sugar has escaped through membrane into pure water in the beaker. The increase in the volume of the solution in the tube is the result of passage of water through the membrane into the bag. Colldion works as a semipermeable membrane which allows the solvent to pass through it but not the solute particles (sugar in the present example). When the equilibrium condition is reached, the sugar solution at any depth below the level of pure water is under an excess of hydrostatic pressure due to extra height of sugar solution in the tubing.

The Osmotic pressure developed between a solvent and a solution depends only on the mole fractions of the components of solution and properties of the solvent. The equilibrium established between the solvent and solution requires that the chemical potential of the water must have the same value on each side of the membrane at every depth in the beaker. The equality of the chemical potential is achieved by a pressure difference across the two sides of the membrane. At any depth 'h' the solvent is under pressure 'P' while the solution is having a pressure of '$P+\pi$' Let $\mu(T,\ P+\pi,\ x_1)$ be the chemical potential of the solvent in the solution, and $\mu^0(T,P)$ that of the pure solvent, then equilibrium condition should be

$$\mu(T,P+\pi,x_1) \ = \ \mu^0(T,P) \qquad \text{.....(44)}$$

but according to equation (43)

$$\mu(T,P+\pi,x_1) \ = \ \mu^0(T,P+\pi)+RT\ln x_1$$

so

$$\mu^0(T, P+\pi) + RT \ln x_1 = \mu^0(T, P) \qquad \text{.....(45)}$$

Applying the fundamental equation $d\mu^0 = \overline{V^0} dP$, where $\overline{V^0}$ is the molar volume of pure solvent. We have

$$\mu^0(T, P+\pi) - \mu^0(T, P) = \int_P^{P+\pi} \overline{V^0} dP \qquad \text{.....(46)}$$

so equation (45) becomes,

$$\int_P^{P+\pi} \overline{V^0} dP + RT \ln x_1 = 0 \qquad \text{.....(47)}$$

If solvent is incompressible, then $\overline{V^0}$ is independent of pressure, so equation (47) gives

$$\overline{V^0}\pi + RT \ln x_1 = 0 \qquad \text{.....(48)}$$

This is the relation between Osmotic pressure π and the mole fraction of the solvent in solution.

To express it in the solute concentration, we can take

$\ln x_1 = \ln(1 - x_2)$ & as the solution is dilute

$\ln(1 - x_2) \approx -x_2$

Mole fraction of the solute in turn will be equal to

$$x_2 \Rightarrow \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

i.e. $\ln(1 - x_2) = -\frac{n_2}{n_1}$

Putting this in equation (48),

$$\overline{V^0}\pi - RT\frac{n_2}{n_1} = 0$$

$$\pi = \frac{RTn_2}{\overline{V^0} n_1} \qquad \text{.....(49)}$$

If solution is dilute n_2 is very small, so that $V \approx n_1 \overline{V^0}$. Equation (49) then reduces to

$$\pi = \frac{RTn_2}{V\ n_1} \Rightarrow \overline{C}RT \qquad \text{.....(50)}$$

Where $\overline{C}$ is the concentration of solute (mol/m^3) in the solution. Equation (50) is termed as Van't Hoff equation for osmotic pressure, and can be used in the calculation of molecular mass of the solute.

If w_2 is the mass of the solute dissolved in the volume V, then $\overline{C} = \frac{w_2}{M_2 V}$

& the equation (50) now becomes

$$\pi = \frac{w_2 RT}{M_2 V}$$

or $$M_2 = \frac{w_2 RT}{\pi V} \qquad \text{.....(51)}$$

Even if w_2 is small and M_2 is large, the value of Osmotic pressure is measurable and equation (51) may be used in calculating the value of Molar mass.

Colligative properties of strong and weak electrolytes

We know that colligative properties of a solution depend on the number of particles of the solute present. So the colligative properties of an electrolylic solution of a given concentration are higher than that of a nonelectrolytic solution of the same concentration. An electrolyte in solution dissociates into positive and negative ions but the condition of electro neutrality is maintained. The net effect is number of species is increased. The colligative properties of a dilute solution of a strong electrolyte are found to be approximately an integral multiple of the corresponding values for a non electrolyte solution of the same concentration. The strong electrolyte undergoes complete dissociation and the value of the integral multiple is equal to the number of ions produced by a molecule of the strong electrolyte.

For example: -the value of the colligative property of a solution of $BaCl_2$, NaCl and urea having the same concentration are in the ration of 3:2:1 as one molecule of Barium Chloride produces three ions and one molecule of sodium Chloride produces two ions.

Colligative properties of weak electrolytes:- Weak electrolytes do not dissociate completely in solution, rather an equilibrium is established between undissociated molecules and the dissociated molecules. So the values of colligative properties for weak electrolytes lie in between the values for non electrolytes and electrolytes of same concentration.

If we take solution of potassium chloride, acetic acid and urea, we can see that KCl dissociates as

$$KCl \rightarrow K^+ + Cl^-$$

In this case an almost complete dissociation takes place, whereas if we consider ethanoic acid we have the equilibrium,

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$. Dissociation is very small in this case.

No dissociation takes place in non-electrolytes like urea, glucose etc.

So the number of species (particles) in an acetic acid solution is more than those in the solution of urea but less than those in the solution of Potassium Chloride provided the concentration of all the three solutions is same.

A factor 'i' called the van't Hoff factor is used to express the colligative properties of an electrolytic solution vis-à-vis of a non electrolytic solution. Van't Hoff factor is defined as the ratio of the colligative effect produced by a given concentration of an electrolytic solution to that of the same solution, of same concentration considering that there is no dissociation,.

$$i = \frac{Colligative\ effect\ produced\ by\ a\ given\ concentration\ of\ an\ electrolyte\ solution}{Colligative\ effect\ produced\ by\ the\ same\ solution\ considering\ that\ there\ is\ no\ dissociation}$$

$$i = \frac{(Colligative\ property)}{(Colligative\ property)_0}$$

$$= \frac{-\Delta T_f}{(-\Delta T_f)_0} = \frac{\Delta T_b}{(\Delta T_b)_0} = \frac{\pi}{(\pi)_0} = \frac{\Delta p}{(\Delta p)_0}$$

the expression is relating all colligative properties of electrolytic solution to that of non electrolytic solution which is shown by a subscript.

We can also write

$$\Delta T_f = i(\Delta T_f)_0 = iK_f m$$

similarly for

$$\Delta T_b = i\ K_b m$$

The value of i can be calculated from the experimental data for each electrolyte at various concentrations.

Variation of i with dilution:-Strong electrolytes may be assumed to be completely dissociated in dilute solutions so the value of i approaches the limit of an integral number equal to the ions produced by a molecule of electrolyte. Sometimes variation in the colligative properties of strong

electrolytes is observed on dilution. It is not due to the increase in the number of species of the electrolyte on dilution but it can be explained on the basis of Debye-Huckel theory of inter-ionic attraction. According to it there exists an ionic atmosphere around each and every ion. The net charge on the ionic atmosphere is equal and opposite to the central ion. The properties of the electrolytes are determined by the interaction of the central ion with its ionic atmosphere. At a fixed temperature for a given solvent, the interaction between the ions depends only on the charges of the ions and their concentration and not on their nature.

Debye Huckel showed that the variation of Van't Hoff factor on dilution is due to the variation of the ionic strength of the solution on dilution. The agreement between the calculated values of i and the experimental values is good for very dilute solutions upto 0.01 mol dm^{-3}. Deviations creep in when molarity is more than this and are larger for electrolytes with higher values of Z_+Z_-.

But in case of weak electrolytes the variation of i is more wide in nature. Use of Arrhenius equation may be made in order to explain the behaviour of weak electrolytes. Consider an electrolyte A_xB_y which partly dissociates in solution yielding x ions of A^{y+} and y ions of B^{x-} and if α is the degree of dissociation and C is the initial concentration of the solute than the dissociation equilibrium in solution can be represented as

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$

Initial concentration	C	0	0
Concentration at Equilibrium	$C(1-\alpha)$	$Cx\alpha$	$Cy\alpha$

The number of moles at equilibrium = $Cx\alpha + Cy\alpha + C(1-\alpha)$

$$= C[1+\alpha(x+y-1)$$

$$\text{Hence } i = \frac{C[1+\alpha(x+y-1)]}{C}$$

or the degree of dissociation is given by

$$\alpha = \frac{i-1}{(x+y-1)}$$

The above equation is applicable to any colligative property and provides an important method for calculation of the degree of dissociation of an electrolyte.

If α is unity, dissociation is complete & i = x + y, i.e. the observed colligative property will be (x + y) times the calculated value.

Now a situation may be there when association of a solute A to (A)n takes place i.e.

$\rightleftharpoons$

nA (A)n

Where n is the number of molecules of solute which combine to form an associated species.

Let C be the concentration and α the degree of association of the solute,

$$nA \rightleftharpoons (A)n$$

At equilibrium the number of moles of the unassociated solute is C(1-α) and that of associated form is $\frac{C\alpha}{n}$, Total number of moles in solution is given by

$$C(1-\alpha)+\frac{C\alpha}{n}$$

$$C(1-\alpha+\frac{\alpha}{n})$$

Van't Hoff factor $i=\dfrac{C(1-\alpha+\frac{\alpha}{n})}{C}$

or $\alpha=\dfrac{i-1}{\frac{1}{n}-1}$

If α = 0, it means no association occurs.

Solution of liquid in liquid: When two liquids are mixed, they may be completely miscible, partly miscible or completely immiscible. If there are two components forming an ideal solution in which there is complete uniformity in cohesive forces, it must posses the following characteristics;

1. ΔH_{mixing} is zero
2. ΔV_{mixing} is zero
3. It must obey Raoult's Law over the whole range of concentration.

If we have an ideal solution containing volatile component A and B, the vapours present above the solution are in equilibrium and exert definite pressure. If p_A and p_B are the partial pressure of the component A and B, then total pressure $p = p_A + p_B$. The vapour pressure of the individual components of an ideal solution can be easily determined by Raoult's Law.

Let x_A and x_B be the mole fractions of a liquid pair A and B, which are volatile and completely miscible. Also let $p°_A$ and $p°_B$ be the vapour pressure of the pure liquids A and B.

The partial vapour pressure is given by

$$p_A = p_A^o x_A$$

$$p_B = p_B^o x_B \qquad \text{.....(52)}$$

The total vapour pressure of the solution is

$$p = p_A + p_B \qquad \text{.....(53)}$$

putting the values for p_A and p_B

$$p = p_A^0 x_A + p_B^0 x_B \qquad \text{.....(54)}$$

Since $x_A + x_B = 1$, so

$x_A = (1 - x_B)$

Eleminating x_A from equation (54)

$$p = p_A^0 (1 - x_B) + p_B^0 x_B$$

$$= p_A^0 + x_B (p_B^0 - p_A^0) \qquad \text{……(55)}$$

p_A, p_B and p are plotted against mole fraction of either component of the solution, say x_B at a given temperature, the plots obtained are as shown below.

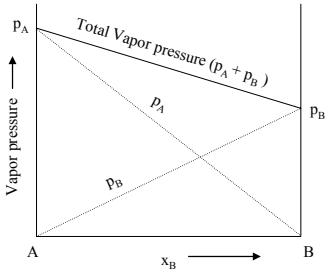


Fig. 6

Dotted lines represent the partial pressure of A and B. These lines pass through the origin indicating the ideal behaviour of both components. The solid line indicates the total vapour pressure of the ideal solution.

Vapour pressure composition diagram for ideal solution

Equation (55) gives the relationship between total pressure and the mole fraction of the components of the solution. A relation between the composition of vapour above a solution and the composition of the solution can be found. If y_B is the mole fraction of component B in the vapour phase and of course its mole fraction in solution is x_B then using Dalton's law of partial pressure.

$$y_B = \frac{p_B}{p} = \frac{p_B}{p_A + p_B}$$

$$= \frac{p_B^0 x_B}{p_A^0 x_A + p_B^0 x_B}$$

$$= \frac{p_B^0 x_B}{p_A^0(1 - x_B) + p_B^0 x_B}$$

$$= \frac{p_B^0 x_B}{p_A^0 + x_B(-p_A^0 + p_B^0)} \qquad \text{.....(56)}$$

As p_A^0 and p_B^0 are known at particular temperature y_B can be calculated for different values of x_B. x_B and y_B are not identical except when $p_A^0 = p_B^0$

From equation (56)

$$x_B = \frac{y_B p_A^0}{p_B^0 + y_B(p_A^0 - p_B^0)} \qquad \text{.....(57)}$$

Using the values of x_B in equation (55)

$$p = p_A^0 + \frac{y_B p_A^0}{p_B^0 + y_B(p_A^0 - p_B^0)} (p_B^0 - p_A^0) \qquad \text{.....(58)}$$

or rearranging we get

$$\frac{1}{p} = \frac{1}{p_A^0} + y_B\left[\frac{1}{p_B^0} - \frac{1}{p_A^0}\right]$$

$$= \frac{1}{p_A^0}(1 - y_B) + \frac{y_B}{p_B^0}$$

$$= \frac{y_A}{p_A^0} + \frac{y_B}{p_B^0} \qquad \text{.....(59)}$$

Equation (59) gives the dependence of the total pressure on the composition of the vapour phase. The ratio of mole fraction of B in vapour to its mole fraction in solution is obtained as,

$$y_B = \frac{p_B}{p_A + p_B}$$

$$= \frac{p_B^0 x_B}{p_A^0 x_A + p_B^0 x_B}$$

$$\frac{y_B}{x_B} = \frac{p_B^0}{p_A^0 x_A + p_B^0 x_B}$$

$$= \frac{1}{x_B + \frac{p_A^0}{p_B^0} x_A} \qquad \text{.....(60)}$$

It is clear from the above equation (60) that $p_B^0 > p_A^0$ i.e. component B is more volatile than component A. In other words the vapour is richer in more volatile component B than the solution. This is known as Konowaloff's rule.

Konowaloff's rule:- The vapour phase is richer in the component whose addition to the liquid mixture causes an increase in the total vapour pressure or the liquid phase is richer in the component whose addition to the liquid mixture results in a decrease in the total vapour pressure. A vapour pressure composition diagram can be constructed by plotting 'p' (Total pressure) v/s x_B or y_B for solutions obeying Raoults Law.

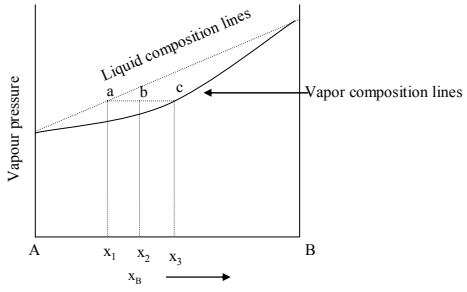


Fig. 7

The liquid composition curve lie above the vapour composition curve as liquid is stable at higher pressure while the vapour exist at lower pressure. Liquid can not be present alone below the liquid composition curve. The points lying between the curves represent the state where liquid and vapour coexist in equilibrium. For example the point 'b' in the diagram is made up of liquid

having composition x_1 and vapour having composition x_3. This is obtained by drawing a horizontal line abc_ known as the tie line, it is connecting the composition of the liquid and vapour phases in equilibrium.

The relative amounts of liquid and vapour required to yield an overall composition 'b' can be calculated. If n_v and n_l be the total number of moles of both the components A and B in vapour and liquid phases respectively the using material balance, we have

$$x_2\ (n_v + n_l) = x_1 n_l + x_3 n_v$$

$$\frac{n_l}{n_v} = \frac{x_2 - x_1}{x_3 - x_2} = \frac{ab}{bc}$$

This expression is known as Lever rule, point 'b' being the fulcrum of the lever. If b lies very close to 'c' then $n_l << n_v$ the system consists mainly of vapour and if b is very close to 'a' system consists mainly the liquid. Only a few pairs of liquids obey Raoult's Law over the entire range of concentration these are **benzene Toluene**, **n-hexane-n-heptane chlorobenzene-bromobenzene etc.**

Deviation from Raoult's Law (Non Ideal Solution)

Most of the mixtures of two miscible liquids do not obey Raoult's law over the entire range of concentrations. However as the solution is diluted i.e. $x_2 \rightarrow 0$, represents the limiting behaviour of Henry's Law as applicable to the solute and the behaviour of solvent as solution becomes more and more dilute approaches more closely to Raoult's Law.

The deviations from Raoult's law may be accounted due to the differences in the molecular structure of the two components. This results in the difference in intermolecular forces. If cohesive forces between A –B are smaller than A-A and B – B, the escaping tendency of the components in solution are higher than that in pure components. Thus the partial pressure of pure components are higher than that predicted from Raoult's Law. This leads to positive deviation than ideal value. This is shown in the vapour pressure v/s composition diagram (Fig. 8)

Systems showing this type behaviour are **ether-acetone, water-dioxane, acetone-carbon disulphide, Carbontetrachloride-heptane, ethyl alcohol-heptane etc.** For such systems $\Delta V_{mix} > 0$ and $\Delta H_{mixing} > 0$.

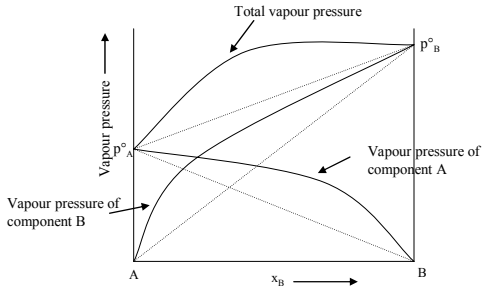


Fig. 8

The other situation may be that cohesive force between A-B is more than that of pure liquids i.e. A-A and B-B. Now the escaping tendency of a component from solution is less than that in a pure liquid. The partial pressures of both components is less than predicted from Raoult's Law. It can be shown in Fig. (9). The pairs of liquids showing negative deviations are **methanol-acetone, Pyridine-acetic acid/formic acid, Chloroform-acetone, ethylether-acetone. Mixture of chloroform and a ketone/ether/ester/amine.**

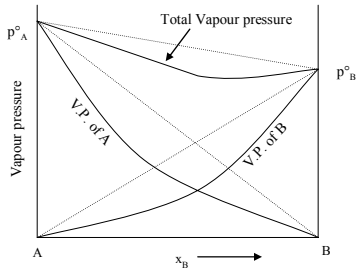


Fig. 9

For such systems $\Delta V_{mixing} < 0$ and $\Delta H_{mixing} < 0$.

A third category of non-ideal solution show small deviations from ideal behaviour. The vapour pressure of each component being only slightly higher than that predicted from Raoult's Law. Such type of behaviour is shown by the liquid pair cyclohexane-carbontetrachloride.

Suppose component 'A' and 'B' are completely miscible with each other. The solution will boil on heating under constant pressure (say atmospheric pressure) when its total vapour pressure becomes equal to atmospheric pressure.

i.e. $p = p_A + p_B$ where p_A and p_B represent the partial pressures of the two components. Fig. 10(a), represent vapour pressure/composition graph and fig. 10(b) represents boiling point/composition graph.

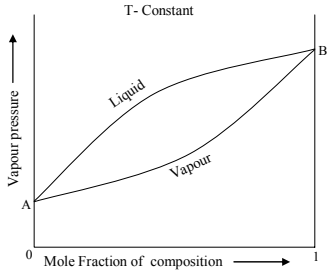


Fig. 10 (a)

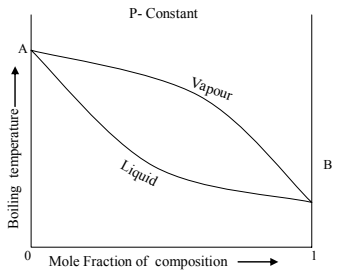


Fig. 10 (b)

Solution of gases in liquids:

Gases dissolve in liquids to form true solutions. Most of the gases are soluble in water as well as in some other liquids. Solubilities of gases can be expressed in terms of absorption coefficient (α), introduced by Bunsen.

This is defined as the volume of gas, reduced to STP (i.e. 0°C and one atmospheric pressure), that has been dissolved by unit volume of solvent under partial pressure of one atmosphere of the gas. If v_0 is the volume (reduced to S.T.P.) of the gas dissolved under partial pressure p of the gas, the absorption coefficient is given as,

$$\alpha = \frac{v_0 / p}{V}$$

The solubility of the gas may also be expressed in terms of coefficient of solubility (suggested by W. Ostwald). It is defined as the volume of gas measured under given conditions of temperature and pressure dissolved by a unit volume of the solvent. If v is the volume of the gas dissolved by volume V of the solvent, then coefficient of solubility is

$$\beta = \frac{v}{V}$$

- The solubility of a gas in a liquid depends on the nature of the gas, nature of the solvent, temperature and pressure.
- The gases which are capable of forming ions in aqueous solution are much more soluble in water than in other solvents.
- Gases which can be easily liquefied are more soluble in common solvents, gases like CO_2 and NH_3 are appreciably soluble in water.

Temperature effect:- It has been observed that at constant pressure, the solubility of a gas diminishes with increase of temperature. As most of the gases dissolve in a liquid with evolution of heat.

$$\frac{d}{dT} \ln S = \frac{\Delta H}{RT^2}$$

, where S is solubility of the gas in mol/dm^3.

Effect of Pressure:- The solubility of a solid in a liquid and liquid in a liquid are almost independent of pressure. But if one of the component is a gas the pressure has a marked effect. The quantitative relation connecting the solubility of a gas in a liquid with pressure was given by W. Henry and is known as Henry's Law.

"It states that at a given temperature the mass of the gas dissolved in a given volume of a solvent is proportional to the pressure of the gas with which it is in equilibrium." Let m be the mass of the gas dissolved by unit volume of the solvent at an equilibrium pressure p, then

$$m \propto p$$

according to Henry's Law.

$$\text{or } m = kp$$

Where k is constant of proportionality. Fig. (11) shows the graph of solubility and external pressure. It is a straight line.

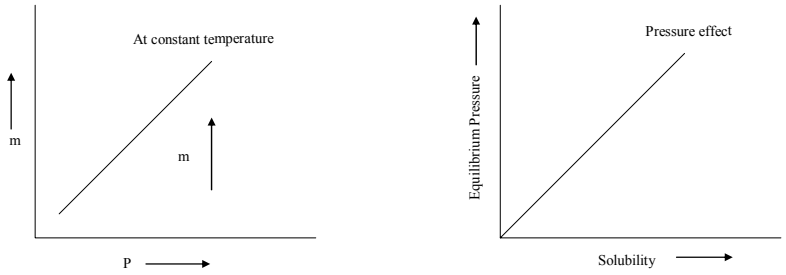


Fig. 11

It has been observed that most gases obey Henry's law, provided the pressure is not too high, the temperature is not too low and gas is not highly soluble, and the gas does not enter into a chemical combination with the solvent.

If we take two gases HCl and NH_3 then as per above conditions Henry's Law may not be applicable for the solubility study of these. The reason is that HCl dissociates ($HCl + H_2O \rightarrow H_3O^+ + Cl^-$) while NH_3 enters into chemical combination with water and resulting into NH_4^+ & OH^- ions. Henry's law may also be stated in an alternate form as;

The volume of a gas dissolved in a solvent at a given temperature is independent of pressure. The statement is valid keeping in mind the inverse relationship between volume and pressure of a gas at constant temperature as per Boyle's Law. This is illustrated by the data given below for solubility of CO_2 in water at 25°C under different pressures.

Pressure in mm of Hg	**mass of gas (in grams) dissolved per ml. of H_2O**	**Volume of gas (in C.C.) measured under experimental conditions**
271	0.270	0.825
495	0.492	0.825
755	0.751	0.826
927	0.922	0.826

If v is the volume of the gas dissolved at the experimental pressure p, in a given volume of the solvent at temperature T, then according to ideal gas law,

$$pv = nRT$$

$$= \frac{m}{M} RT$$

or $$v = \frac{m}{p}\left(\frac{RT}{M}\right)$$

According to Henry's Law definition $\frac{m}{p} = k$

so

$$v = k\frac{RT}{M}$$

Since the right hand side is constant for a given gas at a given temperature, the volume of the gas dissolved in a given volume of the solvent has a constant value.

Activity & activity coefficient:-

Activity:- It is accepted that each substance in a given state has a tendency to escape from that state. This escaping tendency of a substance was termed as fugacity by Lewis. Activity of a substance in any given state is defined as the fugacity of the substance in that state to the fugacity of the substance in the pure state. We can write

$$\mu_i^0 = \mu_i^* + RT \ln f_i^0 \qquad \text{.....(61)}$$

where μ_i^0 is the chemical potential of the substance in pure state. μ_i^* is the chemical potential of the substance when its fugacity is unity & f_i^0 is the fugacity of the substance in pure state & f_i its fugacity. Let μ_i be the chemical potential of the substance in some other state then,

$$\mu_i = \mu_i^* + RT \ln f_i \qquad \text{.....(62)}$$

subtracting we get

$$\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0}$$

$$\text{thus activity } a = \frac{f_i}{f_i^0} \qquad \text{.....(63)}$$

For an isothermal, reversible & infinitesimal change involving work of expansion only

$$dG = Vdp$$

$$= \frac{RT}{p} dp$$

$$= RT\, d \ln p \qquad \text{.....(64)}$$

For a gas which does not behave ideally the above equation will not hold good, but a function 'f' known as fugacity if introduced, the equation becomes.

$$dG = RT\, d \ln f$$

This relationship is always satisfied.

Activity Co-efficient:- Consider a solution of any electrolyte, there should be equilibrium between free ions and undissociated molecules; these may consist of true nonionised molecules or ion pairs.

The equilibrium can be written as,

$$MA \rightleftharpoons M^+ + A^- \qquad \text{.....(65)}$$

M^+ & A^- are free ions and MA undissociated portion of the electrolyte. If we apply Law of equilibrium, we can write

$$K = \frac{a_{m+} + a_{A-}}{a_{MA}} \qquad \text{.....(66)}$$

where a_{M+} & a_{A-} the activities of M^+ and A^- respectively and K is called the dissociation constant. Replacing the activities as the product of concentration in moles per litre 'C' and the activity coefficient γ, it becomes

$$K = \frac{C_{M+}\, C_{A-}}{C_{MA}} \frac{\gamma_{M+}\gamma_{A-}}{\gamma_{MA}} \qquad \text{.....(67)}$$

If α is the degree of dissociation of the electrolyte i.e. fraction of the electrolyte in the form of free ions, then C_{M+} & C_{A-} both are equal to Cα while C_{MA} is equal to C(1-α). Putting the values in equation (67) we get

$$K = \frac{\alpha^2 C}{(1-\alpha)} \frac{\gamma_{M+}\gamma_{A-}}{\gamma_{MA}} \qquad \text{.....(68)}$$

If the solution is sufficiently dilute the activity coefficients are approximately unity and so the equation (68) reduces to

$$K = \frac{\alpha^2 C}{(1-\alpha)} \qquad \text{.....(69)}$$

which is the expression for dilution Law. K in equation (69) is not really a constant, because of the neglect of the activity coefficient, while K (eqn. 68) is a true thermodynamic constant.

Mean ionic activity coefficient:- Any solution considered should be neutral so we can not determine activities or activity coefficient of individual ions and a new term mean ionic activity and mean ionic activity coefficient is introduced. Consider an equilibrium

$$MA \rightleftharpoons M^+ + A^-$$

and if we denote the activity of cation as a_+ and activity of anion as a_- then mean ionic activity is denoted by and

$$(a_+)(a_-) = (a\pm)^2$$

In general we may write for a solution of M_xA_y,

$$(a_+)^x (a_-)^y = (a\pm)^{x+y}$$

& $$\gamma_+ \gamma_- = (\gamma_\pm)^2$$

The values of activities are determined by E.M.F., Freezing point depression & vapour pressure methods.

Solved Numerical Problems

1. What is the molarity of sodium chloride solution, which is prepared by dissolving 50g. of sodium chloride in 2.0 litre of solution

Ans. Molecular mass of NaCl = 58.5

Number of moles of sodium chloride = $\frac{50}{58.5}$

= 0.9345

Total volume of the solution is 2 litres.

So number of moles of NaCl present/litre of solution

= $\frac{0.9345}{2}$

= 0.46725

hence molarity of solution is 0.46725

2. Calculate the molarity and molality of a 20% solution of sulphuric acid. (density = 1.10g/mol.

Ans. Molecular mass of H_2SO_4 = 98

100 ml of solution contains 20.0 g of H_2SO_4

1000 ml. Of solution contains = 200 g of H_2SO_4

Number of moles = $\frac{200}{98}$

Hence molarity of solution is = 2.0408

Calculation of molality

Mass of 1 litre of solution = 1000 x 1.1

= 1100g

Mass of the acid per litre = 200g

Mass of water = 1100-200

= 900g.

900g of water contains 2.0408 moles of H_2SO_4

1000g of water contains = $\frac{2.0408}{900}$ x 1000

= 2.2675

hence molality of the solution = 2.2675

3. 2.5 g of glucose (Molar mass 180) are dissolved in 40 g of water. Calculate mole fraction of glucose & water.

Number of moles of Glucose = $\frac{2.5}{180}$ = .0138

Number of moles of water = $\frac{40}{18}$ = 2.222

Total number of moles = .0138 + 2.222

= 2.236

Mole fraction of Glucose = $\frac{.0138}{2.236}$ = .00617

Mole fraction of Water = 1-.00617

= 0.99383

4. The vapour pressure of water at 293 K is 17.51 mm, Lowering of vapour pressure of sugar solution is 0.082mm. Calculate vapour pressure of the solution, relative lowering of vapour pressure and mole fraction of water.

Ans. Let the vapour pressure of the solution = p
Vapour pressure of solvent (water) = 17.51mm
Lowering of vapour pressure = $p^\circ - p$ = .082

Relative Lowering of vapour pressure = $\frac{p^\circ - p}{p^\circ}$

$= \frac{.082}{17.51}$

$= 4.683 \times 10^{-3}$

Vapour pressure of solution = 17.51 - .082
= 17.428 mm

Now according to Raoult's Law

$$\frac{p^\circ - p}{p^\circ} = x_2$$

$\therefore$ Mole fraction of water = 1- .004683
= 0.995317

5. Vapour pressure of water at 298 K is 23.75 mm of Hg. Calculate the vapour pressure at the same temperature for 7.0% solution of urea.

Molecular mass of urea = 60
Molar mass of water = 18
According to Raoult's Law

$$\frac{p^\circ - p}{p^\circ} = \frac{wM}{mW}$$

p° here is 23.75 mm.
w = 7.0 g
W = 93.0 g
Putting these values we get

$$\frac{23.75 - p}{23.75} = \frac{7 \times 18}{60 \times 93}$$

or p= 23.75 – 0.5362
= 23.2138 mm

6. The vapour pressure of a 5% aqueous solution of a non volatile solute at 373 K 752 mm. Calculate molar mass of the solute.

Weight of non volatile solute = 5.0 g
Weight of solvent (water) = 95.0 g
Vapour pressure of pure solvent = 760 mm.
Vapour pressure of solution = 752 mm

Using the expression $\frac{p^\circ - p}{p^\circ} = \frac{w}{m}\frac{M}{W}$

$$\frac{760 - 752}{760} = \frac{5}{m} \text{ x } \frac{18}{95}$$

$$m = \frac{5 \text{ x } 18 \text{ x } 760}{95 \text{ x } 8} = 90$$

7. An aqueous solution of sodium hydroxide contains 10g of Sodium hydroxide and 90 g of water. The solution has a density of 1.12 kg dm^{-3}. Calculate
   (a) Mass percent of sodium hydroxide
   (b) Molality of the solution
   (c) Mole fraction of sodium hydroxide
   (d) Molarity
   (e) & Normality of the solution.

Mass percent of NaOH $= \frac{Mass\ of\ NaOH}{Total\ mass}$ x 100

$$= \frac{10}{100} \text{ x } 100$$
$$= 10.0$$

(b) Number of moles of NaOH $= \frac{10}{40} = 0.25$

Number of moles of water $= \frac{90}{18} = 5.0$

Molality = Number of g. moles of solute per 1000 g of solvent

$$= \frac{0.25}{90} \text{ x } 1000 = 2.78 \text{ m}$$

(c) Mole fraction of sodium hydroxide $= \frac{0.25}{5 + 0.25} = .0476$

(d) Volume of solution corresponding to 100 x 10^{-3} *k*g of solution is;

$$V = \frac{100\ x\ 10^{-3}\ kg}{1.12\, kg dm^{-3}}$$

$= 89.3 \text{ x } 10^{-3} \text{ dm}^3$

hence Molarity = $\frac{0.25}{89.3 x 10^{-3}} \; x \; \frac{1}{dm^{-3}}$

= 2.8

(e) The normality of the solution is equal to its molarity

8. A solution contains 25% water, 25% ethanol and 50% acetic acid by mass. Calculate mole fractions of each component.
Let the total mass of solution be 100g
Mass of water 25 g

Number of moles of water $= \frac{25}{18} = 1.39$

Number of moles of ethanol $= \frac{25}{46} = 0.544$

Number of moles of acetic acid $= \frac{50}{60} = 0.833$

Total number of moles of all components = 1.39 + 0.544 + 0.833 = 2.767

Mole fraction of water $= \frac{1.39}{2.767} = 0.502$

Mole fraction of ethanol $= \frac{0.544}{2.767} = 0.196$

Mole fraction of acetic acid = 1-0.502 –0.196

= 0.302

(9) The vapour pressure of two pure liquids A and B are 15000 and 30,000 Nm^{-2} at 298 K. Calculate the mole fraction of A and B in the vapour phase when an equimolar solution of the liquids is made.

p_A° = 15000Nm^{-2}

p_B° = 30,000 Nm^{-2}

Mole fraction of A and B are equal to $X_A = X_B = 0.5$ in solution.
Applying Raoult's Law of ideal solution

$p_A^{\circ} = p_A^{\circ} X_A$

= 15000 x 0.5

= 7500 Nm^{-2}

$p_B = p_B^o X_B$

= 30000 x 0.5

= 15000 Nm^{-2}

Total pressure $p = p_A + p_B$

$= 7500 + 15000$

$= 22500\ Nm^{-2}$

In the vapour phase

$$\text{Mole fraction of A} = \frac{Partial\ pressure\ of\ A}{Total\ pressure}$$

$$= \frac{7500}{22500}$$

$$= 0.3333$$

Mole fraction of B = 1 – 0.3333

= 0.6666

10. Two hydrocarbons (A & B) having boiling points 353.1K and 383.6 K from a very nearly ideal solution. The vapour pressure of pure liquid hydrocarbons at 313 K and 160 mm of Hg and 60 mm of Hg respectively. The molecular wt. of two hydrocarbons are 78 and 92. Assuming an ideal solutions behaviour, Calculate the partial pressures of the two and the total pressure over the following solutions.

(i) One made by equal number of molecules of the two hydrocarbons.
(ii) One made by 4 moles of B and 1 mole of A
(iii)One made by combining equal masses of A and B.

(i) When the number of molecules of A and B are equal it means number of moles of the two liquids are also equal.

$$X_A = \frac{1}{2} = 0.5$$

$X_B = 0.5$

According to Raoult's Law

$p_A = p_A^{\circ}\ x\ A$

$=$ 160 x 0.5

$=$ 80 mm of Hg.

Partial pressure of B is

$p_B = p_B^{\circ}\ x\ B$

$= 60 \times 0.5$

$=$ 30.0 mm. of Hg.

Total vapour pressure = 80 + 30 = 110.0 mm of Hg.

(ii) Mole fractions of A,

$$X_A = \frac{1}{1+4} = \frac{1}{5} = 0.2$$

Mole fraction of A = 0.8

Partial pressure of A = 160 x 0.2
= 32.0 mm. of Hg.
Partial pressure of B = 60 x 0.8
= 48.0 mm of Hg.

Total vapour pressure = 32 + 48 = 80.0 mm of Hg.

(iv) Masses of the two liquids are the same, let it be m,g.

$$\text{Mole fraction of A} = \frac{m/78}{\frac{m}{78}+\frac{m}{92}} = 0.541$$

Mole fraction of B = 1 – 0.541 = 0.459
Partial pressure of A = 160 x 0.541 = 86.56 mm of Hg.
Partial pressure of B = 60 x 0.459 = 27.54 mm of Hg.
Hence total vapour pressure = 86.56 + 27.54
=114.1 mm of Hg.

11. A solution containing 6.0 g of benzoic acid in 50g. of ether has a vapour pressure 5.466 x 10^4 Nm^{-2} at 300 K. Given that vapour pressure of the at the same temperature is 5.893 x 10^4 Nm^{-2}, Calculate the molecular mass of benzoic acid.

Ans. Vapour pressure of pure solvent = p° = 5.893 x 10^4 Nm^{-2}
Vapour pressure of solution = p = 5.466 x 10^4 Nm^{-2}
Molecualr weight of solvent = 74
Let the molecular weight of solute be m
Applying the formula

$$\frac{p^\circ - p}{p^\circ} = \frac{w}{m}\frac{M}{W}$$

$$\frac{5.893 \text{ x } 10^4 - 5.466x10^4}{5.893 \text{ x } 10^4} = \frac{6 \text{ x } 74}{m \text{ x } 50}$$

$$m = \frac{6 \text{ x } 74 \text{ x } 5.893}{50 \text{ x } 0.427}$$

= 122.55

12. Calculate the amount of oxygen (0.20 atm.) dissolved in 1 dm^3 of water at 293 K. The Henry's constant for oxygen is 4.58 x 10^4 atmospheres at 293 K.

$$X_2 = \frac{p}{K_H}$$

$$= \frac{0.2}{4.58 x 10^4} = 4.35 \text{ x } 10^{-6}$$

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

$$= \frac{n_2}{18 \text{ x } 10^{-3} + n_2}$$

$$= 4.35 \text{ x } 10^{-6}$$

$$n_2 = 2.41 \text{ x} 10^{-4}$$

hence amount of oxygen dissolved = 2.41 x 10^{-4} x 32 x 10^{-3}
= 7.71 x 10^{-6} kg.

13. When 2.0 g. of a non volatile hydrocarbon is dissolved in 100g. of benzene, the vapour pressure of benzene at 20° C is lowered from 74.66 to 74.01 mm of Hg. Calculate the molecular mass of the

w_2 = 2.0 g
w_1 = 100g
M_1 = 78

$$p_1^\circ = 74.66 \text{ mm of Hg}$$

p1 = 74.01 mm. of Hg.

$$\frac{p_1^\circ - p_1}{p_1^\circ} = x_2 = \frac{n_2}{n_1} = \frac{w_2}{M_2} \frac{M_1}{w_1}$$

$$M_2 = \frac{w_2 M_1}{w_1} \frac{p_1^\circ}{p_1^\circ - p_1}$$

$$\frac{2 \text{ x } 78 \text{ x } 74.66}{100 \text{ x } (74.66 \ \ 74.01)}$$

= 179 g mol^{-1}

Empirical formula;

$$C = 94.4\% = \frac{94.4}{12} = 7.86$$

$$H = 5.6\% = \frac{5.6}{1} = 5.6$$

$$\frac{7.86}{5.6} = 1.4$$

$$\frac{5.6}{5.6} = 1$$

ratio 1.4 : 1 converted to whole number ratio is 7:5

$\therefore$ empirical formula is C_7H_5
Empirical formula weight = 89

$$\frac{\text{Molecular weight}}{\text{Empirical formula weight}} = \frac{179}{89} \approx 2$$

Molecular formula = $(C_7H_5)_2 = C_{14}H_{10}$.

14. The osmotic pressure of blood is 7.65 atm. at 37°C. How much glucose should be used per litre for an intraveinous injection that is to have the same osmotic pressure as blood.

$$\pi = C_2RT = \frac{n_2}{v}RT$$

$$n_2 = \frac{\pi V}{RT} = \frac{7.65 \text{ x } 1.00}{.0821 \text{ x } 310} = 0.301$$

$$n_2 = \frac{mass\ of\ solute}{Molar\ mass\ of\ solute}$$

$$0.301 = \frac{x}{80}$$ [where x may be taken as mass of solute]

x = 180 x 0.301
= 54.18 g

15. A 0.5% aqueous solution of potassium chloride was found to freeze at –0.24° C. Calculate the Vant Hoff factor and the degree of dissociation of the solute. K_f for water = [1.86 k kg mol^{-1}]

Molecular weight of potassium chloride = 74.5 $gmol^{-1}$

$$M_{obs.} = \frac{k_f w_2}{w_1 \Delta T} = \frac{1.86 \text{ x } .5 \text{ x } 10^{-3}}{100 \text{ x } 10^{-3} \text{ x } .24}$$

$$= 38.75 \text{ g mol}^{-1}$$

$$\text{Van't Hoff factor I} = \frac{\text{M normal}}{\text{M observed}}$$

Let α be the degree of dissociation for KCl

$$\frac{1+\alpha}{1} = \frac{\text{M normal}}{\text{M observed}}$$

$= 1.923$

or $\alpha = .923$

16. Calculate the osmotic pressure of a 0.010 molal aqueous solution of sodium bromide at 25°C assuming (a) an ideal solution (b) $\gamma \pm$ is the mean ionic activity.
as $NaBr \rightarrow Na^+ Br^-$

$\pi = iC_2 RT$
$= 2 \times .01 \times .0821 \times 298$
0.489 atm

(b) $\gamma \pm = .903$
$C_2 = .903 \times .01$
$= .0093$
$\pi = 2 \times .0093 \times .0821 \times 298$
$= .454$ atm.

Unsolved Problems

1. Calculate the molal boiling point elevation constant of benzene if its heat of vaporization at 80.1° C is 30.67 KJ mol^{-1}.

Ans. 2.63

2. The boiling point of chloroform was raised by 0.325 when 5.141×10^{-4} kg of a solute was dissolved in 35×10^{-3} kg. of chloroform. Calculate the molar mass of the solute . K_b for chloroform is 3.9.

Ans. 176.3 $gmol^{-1}$

3. A brass sample composed of 20.0% Zinc and 80.0% Copper by mass melts at 1268 K. Pure copper melts at 1357 K. What is the molal depression constant for copper.

Ans. 23.14

4. A sample solution contains 5.0 g of dissolved protein per 100 cm^3 of the solution at 25 mm of Hg at body temperature. Calculate the molar mass of the protein.

Ans. 38,661.96

5. 0.1M solution of a metal nitrate (MNO_3) has an osmotic pressure of 4.5 atmosphere at 300 K. Calculate the degree of dissociation of the salt.

Ans. 83.0%

6. 0.45 g of glucose is place inside a tube having an area of cross section of unity and closed at one end with a semi permeable membrane. The tube is kept in water. Calculate the height of the solution inside the tube, when equilibrium is attained, and the osmotic pressure of the solution. The density of the solution is 1.017 g cm^{-3} at 27° C, g = 980.67 cm s^{-2}

Ans. h = 249.96 cm

π = 0.246 atm.

7. Assume that ΔH_{fus} is independent of temperature and that the thermometer available can measure a freezing point depression to an accuracy of ± 0.01. The simple law for freezing point depression is based on the limiting condition that m = 0. At what molality will this approximation no longer predict the result within the experimental error in water?

Ans. -5.376×10^{-3} mol/Kg.

8. For CCl_4, K_b = 5.03 k kg/mol and K_f = 31.8 k kg/mol. If 3.0 g of a substance in 100 g of CCl_4 raises the boiling point by 0.6. Calculate (a) the freezing point depression. (b) The relative vapour pressure lowering, (c) The osmotic pressure at 25° C and (d) The molar mass of the substance. The density of CCl_4 is 1.59 g cm^{-3} and the molar mass is 153.823 g/mol.

Ans. (a) 3.8
(b) .018
(c) 4.7×10^5 Nm^{-2}
(d) 250 g mol^{-1}

9. Calculate the osmotic pressure of an aqueous solution containing 20.0 g of glucose per litre of the solutions.

Ans. 2.754×10^5 Nm^{-2}

10. A solution containing 0.1526 g of Naphthalene (Molecular mass 128 $gmol^{-1}$) in 50.0 g of carbontetrachloride yields a boiling point elevation of 0.402. If 0.6216 g of an unknown solute is dissolved in the same mass of the solvent a boiling point elevation of 0.647° is observed. Calculate the molar mass of unknown solute.

Ans. 96.7 g mol^{-1}

11. A solution contains 1.0% glycerol (Molecular Mass 92 $gmol^{-1}$) and 99% water by mass. The vapour pressure of pure water at 298 K is 23.756 mm Hg. Assuming glycerol to be nonvolatile and the solution has the same density as pure water, calculate (a) The vapour pressure of the solution at 298 k (b) Freezing point of the solution (c) The boiling point of the solution at 1 atmospheric Pressure (d) The osmotic pressure of the solution at 298 k.

Ans.
(a) 23.709
(b) -0.20
(c) 100.056

(d) 2.66 atm.

12. Which of the following aqueous solution will show the highest freezing and highest freezing point depression at 27°C.
    (a) 0.1 M glucose
    (b) 0.1M sodium hydroxide
    (c) 0.1M Aluminium sulphate

Ans. (a) & (c)

13. A solution containing 10.0 g of sodium chloride in 1.0 kg of water freezes at –0.604°C. Calculate the degree of dissociation of sodium chloride in water. $K_f = 1.85$ k *k*g mol^{-1}.

Ans. 91.0%

14. A 5.5 % solution of sucrose is isotonic with 0.96% solution of an unknown nonvolatile solute. Calculate the molar mass of the solute.

Ans. 60

15. The complex $K_3[Fe(CN)_6]$ is 45% dissociated in 0.1 M aqueous solution of the complex at 25° C. What is the osmotic pressure of the solution.

Ans. 5.74 atm.

16. The average osmotic pressure of the human blood is 7.8 atmosphere at 37°C. What is the concentration of an aqueous solution of sodium chloride that can be used in the blood stream.

Ans. 55.08 g/*l*