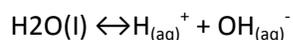


Phase equilibrium

Phase:-phase may be defined as any part of the system which is homogenous, physically distinct and mechanically separable part of the system e.g ; ice and water in equilibrium constitute a two phase system .Likewise two immiscible liquids (benzene and ethanol) constitute a two phase system as there exists an interface separating the two phases. However; two liquids that are completely miscible with each other (water and ethanol) form a single phase system since there is no physical boundary separating the two phases .Here one must keep in mind that definition of phase is not simply restricted to the states of matter as illustrated by the heterogeneous equilibrium below

$\text{CaCO}_{3(s)} \leftrightarrow \text{CaO}(s) + \text{CO}_{2(g)}$,the mixture contains two states of matter(solid and gas) but the number of phases are three. A gaseous mixture of nitrogen and hydrogen constitute a single phase system since it is homogenous as a whole and there is no interface separating the two phases.

Components:-components refers to the minimum number of independently variable chemical entities by means of which the composition of each phase/system can be described completely. Consider the Autopyrolysis of water



The number of chemical entities present in the system here are three($\text{H}_2\text{O}, \text{H}^+, \text{OH}^-$) but it is a one component system. It can be seen that if the concentration of any two species is arbitrarily set, the concentration of third is fixed and can be calculated from equilibrium constant. The equilibrium expression for this process is $K_w = [\text{H}^+][\text{OH}^-]$. Therefore, if the concentration of H^+ is known the concentration of OH^- is set .Analogously if the concentration of OH^- is known ,the concentration of H^+ is set .Hence, it is a one component system.

It can be computed using the formula

$C = S - R$ where S refers to the number of chemical constituents present in the system and R refers to the number of restrictions imposed on the independent variation of these constituents.

Consider the decomposition of MgCO_3 .

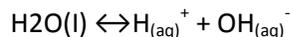
$\text{MgCO}_3(s) \leftrightarrow \text{MgO}(s) + \text{CO}_2(g)$, the number of chemical entities present, S is three i.e. $\text{MgCO}_3, \text{MgO}, \text{CO}_2$ and the number of equilibrium restrictions ,R is one that is the eqm. restricts the independent variation of these constituents .So the number of components is 2.

Let us take the example of acetic acid and ethanol. At the first sight we might predict two components because there are two constituents HoAc and EtOH , however these constituents react to give ethyl acetate and water. Therefore ethyl acetate and water are also present at equilibrium along with the reactants ,this raises the number of components to four .But because of equilibrium condition and since at equilibrium $[\text{EtOH}] = [\text{HoH}]$,the number of components is reduced back to two .If we consider the decomposition of PCl_5

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$\text{PCl}_5 \leftrightarrow \text{PCl}_3 + \text{Cl}_2$, three chemical species are present but the number of components is reduced to one .This is because of equilibrium condition and the relation $[\text{PCl}_3] = [\text{Cl}_2]$.

Degrees of freedom (F) :-refers to the number of intensive variables such as temperature, pressure, concentration which can be varied independently without disturbing the number of phases in equilibrium. Consider the Ice water equilibrium, the two phase exist in eqm. at a particular temperature of zero degree centigrade and a pressure of one atmosphere. If temperature is arbitrarily varied the two phases no longer remain in equilibrium as such the system has just one degree of freedom or we can say the system is uni -variant .that is we must change the pressure accordingly in order for the two phases to exist in equilibrium simultaneously. On the same note, if ice water and vapor are in equilibrium no variable that describe that equilibrium. can be varied independently without disturbing the number of phases in equilibrium , as such the degree of freedom for such a system is zero and the system is said to be non variant.For a system containing a single water phase only ,we can arbitrarily vary both temperature and pressure within the limits specified by phase diagram without affecting the nature of phase under consideration .as such the degrees of freedom available for such a system are two and the system is said to be bi -variant.

Phase rule:-

The phase rule establishes the relationship between the number of phases,the number of components and the number of degrees of freedom of a system at equilibrium at a given pressure and temperature.The rule is $F=C-P+2$,where 2 stands for the intensive variable pressure and temperature.

Derivation of phase rule:-

Let us consider a system of P phases and C components existing in equilibrium at constant temperature and pressure.The number of degrees of freedom is equal to the the number of intensive variables required to describe the system minus the number that can not be independently varied which inturn is given by the number of equations connecting the variables. Let us assume that all the C components are presents in P phases .Suppose a phase contains two components. Then if the mole fraction of one component is known, that of other can be calculated.. Hence in general, if a phase contains C components ,then to define it completely C-1 concentration variables are required and to define all the P phases P(C-1) variables are required .Besides these concentration variables temperature and pressure which are same for all phases are the required variables.

Total number of variables required= $P(C-1) +2$

Number of equations connecting the variables can be computed from chemical potential.

According to thermodynamics The chemical potential of component is same in all the phases when the system is at equilibrium.Thus if there are three phases,A,B,,then for a particular component I, $(\mu_i)_A = (\mu_i)_B = (\mu_i)_C$

Thus ,there are two equations for each component if there are three phases,So for P phases,the number of such relations = $P-1$ for each component

For C components = $C(P-1)$

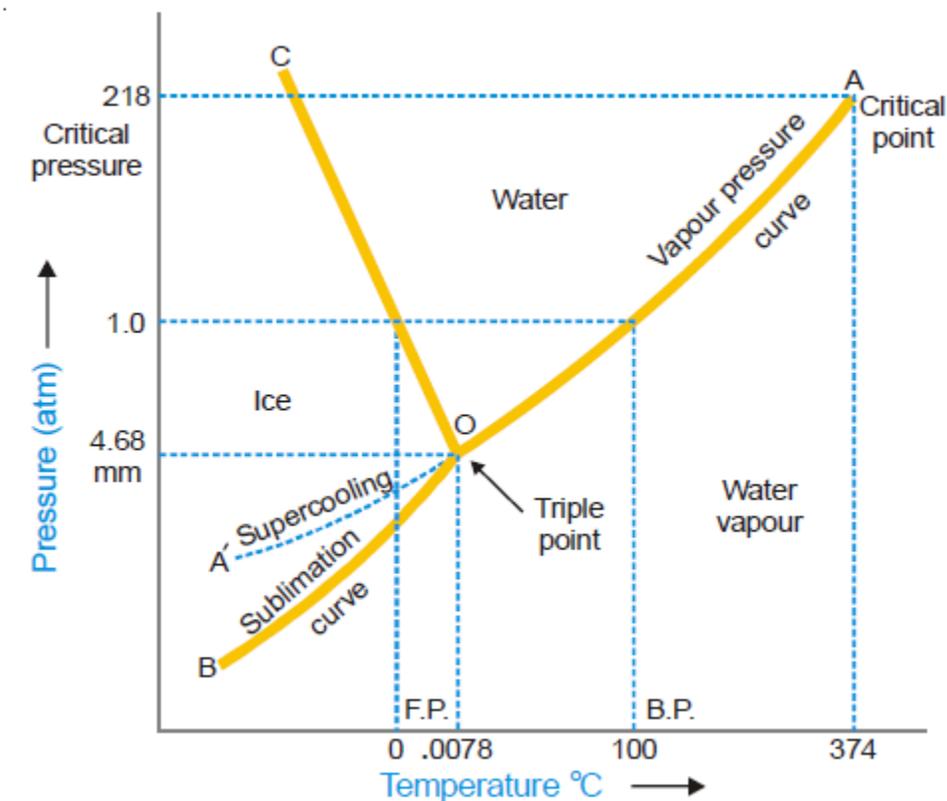
Hence the degrees of freedom of the system will be, $F = \text{total variables} - \text{number of equations}$

$F = P(C-1) + C(P-1) = C - P + 2$ which is Gibbs phase rule

One component system

Water system presents an excellent example of three phase, one component system since all the three phases can be represented by one chemical entity H_2O . Since water exists in three phases, there are three forms of equilibrium i.e.;

$\text{Solid} \leftrightarrow \text{liquid}$, $\text{solid} \leftrightarrow \text{gas}$, $\text{liquid} \leftrightarrow \text{gas}$. Each equilibrium is characterized by particular set of conditions of temperature and pressure which not only describe the number of phases existing in equilibrium but also reflect the stability of the phases in equilibrium under these particular set of conditions which is best represented by plotting the phase diagram in which pressure is plotted along y axis and the temperature is plotted along x axis as shown below.



The phase diagram of water consists of three curves OA, OB and OC which divide the diagram into three areas. At any point along each curve two phases are in equilibrium e.g; along curve OC solid and liquid phase are in equilibrium hence represents the melting curve of ice. This curve also depicts the effect of pressure on the melting point of ice. The fact that curve OC slopes towards left indicates that the melting point of ice falls as the pressure is increased in accordance to the Lechatlier's principle; along curve OA liquid and vapor phases are in equilibrium hence represents the vaporization curve while along OB solid and vapor are in equilibrium hence represents the sublimation curve of ice. On top of that, the three curves meet at point "O" which is what we call as triple point. At the triple point all the three phases co-exist in equilibrium. The triple marks the lowest temperature at which a liquid phase can exist under normal circumstances. Any point that lies within the area enclosed by the AOB, AOC, BOC represents a single phase. In addition to the three stable curves mentioned so far, another curve OD represents the metastable equilibrium in which supercooled water and vapour exist in equilibrium.

Applying phase rule to the phase diagram shown above in order to find out the number of degrees of freedom. Since water system is one component system, along each curve two phases are in equilibrium so the number of degrees of freedom along each curve (OA, OB, OC) are

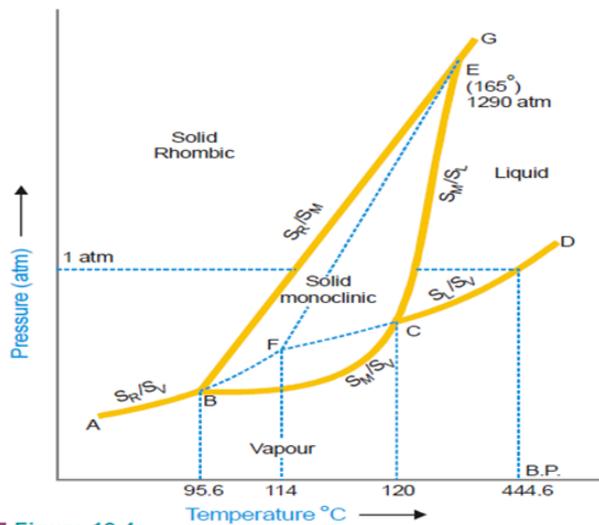
$F=C-P+2 > 1-2+2=1$, thus each point on any curve is uni-variant. Each area contains one phase only so the degrees of freedom are

$F=C-P+2 > 1-1+2=2$, area is bi-variant. At the triple point three phases are in equilibrium so the number of degrees of freedom are

$F=C-P+2 > 1-3+2=0$, hence the triple point is invariant.

THE SULPHUR SYSTEM

It is a four phase but one component system. The four phase phases that exist in equilibrium are two solid polymorphic phases Rhombic (Sr) and monoclinic sulphur (Sm), liquid sulphur and sulphur vapor. Since all the four phases can be represented by single chemical entity Sulphur, hence it is a one component system. The phase diagram for sulphur contains six curves which divide the diagram into four areas. These areas are labeled as rhombic, monoclinic, liquid sulphur and vapor. Since area represents single phase system it is bivariant ($F=2$)



SS

Figure 10.4

The curve AB is the vapor pressure curve of rhombic sulphur. Along this curve two phases rhombic and sulphur vapor are in equilibrium. It has one degree of freedom and is thus mono variant. The curve BC, is the vapor pressure curve of monoclinic sulphur. Monoclinic and sulphur vapor coexist in equilibrium along this curve. The curve is mono variant. The curve CD depicts the variation of vapor pressure of liquid sulphur with temperature. The two phases in equilibrium along this curve are liquid sulphur and vapor. Since the one atmospheric line intersects this curve at a temperature of 444.6 C, it represents the boiling point of sulphur.

The curve BE is the transition curve which reflects the effect of pressure on the transition temperature of rhombic and monoclinic sulphur. Below the transition temperature of 95.6°C S_R is stable and above this temperature monoclinic sulphur is stable. At the transition point each form can be gradually transformed into other form and the two forms are in equilibrium. The transformation of S_R and S_M is accompanied by increase of volume (density of $S_R=2.04, S_M=1.9$)

Thus the increase of pressure will shift the equilibrium to the left and the transition temperature will rise. That is the reason why the line BE slopes away from pressure axis showing thereby that the

transition temperature is raised with increase of pressure. The curve CE is the fusion curve of S_M . The phases in equilibrium along this curve are S_M and S_L . Since the curve slopes away from pressure axis the melting point of monoclinic sulphur is raised with pressure. The curve terminates at E because monoclinic sulphur ceases to exist beyond this point.

The curve EG is the fusion curve for S_R . Here the two phases in equilibrium are S_R and S_L . The number of phases being two, the system is mono variant.

There are three triple points in this phase diagram labeled as B,C,E. At all the triple points degrees of freedom is zero. The three phases in equilibrium at point marked as E are S_R, S_M, S_L . At point B rhombic changes to monoclinic reversibly and represents the transition point. At the triple point C, monoclinic liquid and vapor phase are in equilibrium. The temperature corresponding to point C is 120 and represents the melting temperature of monoclinic sulphur. The triple point E gives the conditions for the coexistence of S_R, S_M, S_L .

The change of rhombic to monoclinic sulphur takes place slowly, however if the process is carried out rapidly it is possible to get well above the transition point without getting monoclinic. In that case the phase diagram for sulphur will resemble water system.

Metastable Equilibria

The change of S_R to S_M takes place very slowly. If enough time for the change is not allowed and S_R is heated rapidly, it is possible to pass well above the transition point without getting S_M . In that case, there being three phases (S_R, S_L, S_V) only and one component, the phase diagram, like that of water system, will consist of three curves, one triple point and three areas.

The dashed curve BF, the Vapour Pressure curve of metastable S_R . This is a continuation of the vapour pressure curve AB of stable S_R . The metastable phases S_R and S_V are in equilibrium along this curve. It is a monovariant system.

The dashed curve CF, the Vapour Pressure curve of supercooled S_L . On supercooling liquid sulphur, the dashed curve CF is obtained. It is, in fact, the back prolongation of DC. The curve CF represents the metastable equilibrium between supercooled S_L and S_V . Thus it may be designated as the vapour pressure curve of supercooled SL. It meets the dashed curve BF at F.

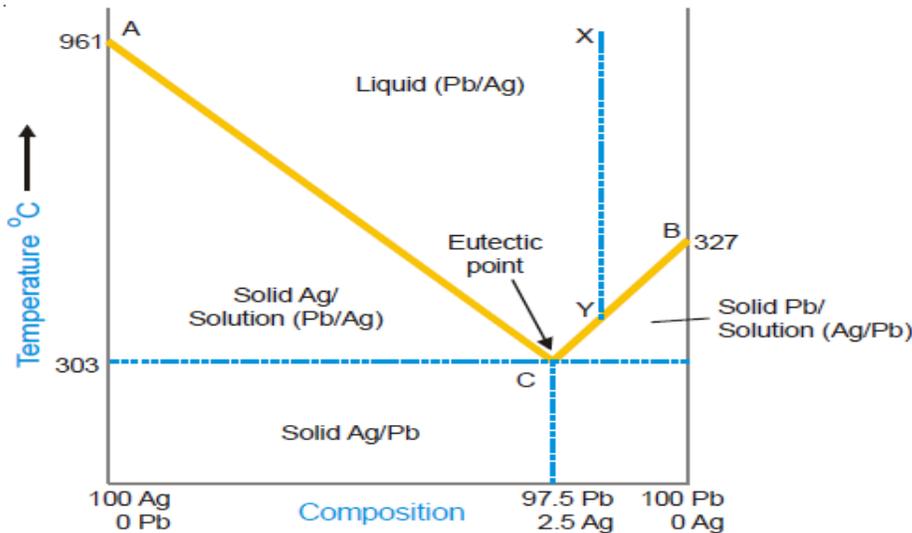
The dashed curve FE, the Fusion curve of metastable S_R . The two metastable phases S_R and S_L are in equilibrium along this curve and the system is monovariant. This shows that the melting point of metastable S_R is increased with pressure. Beyond E, this curve depicts the conditions for the

stable equilibrium S_R/S_L as the metastable S_R disappears.

The metastable Triple point F. At this point, three metastable phases S_R , S_L and S_V are in equilibrium. The system is a metastable triple point with no degree of freedom. The corresponding temperature is the melting point of metastable

Two component system (lead silver system)

This system has two components and four phases which include solid silver, solid lead, solution of molten silver and lead and the vapour. However, the melting point of silver and lead being considerably high the vapour phase is practically absent. Therefore Pb and Ag silver system is a condensed system and confirms to reduced phase rule equation and we just need two variables temperature and concentration for the complete description of the system. The phase diagram of such a simple eutectic mixture as shown below has two curves, AC and BC, Eutectic point C and three areas, Above ACB, below AC and below BC.



The curve AC is the freezing /melting curve of Ag and shows that the melting point of Ag(961) falls as lead is added to it. The phases in equilibrium along the curve are solid Ag and the melt of silver and lead. Applying reduced phase rule, the curve comes out to be mono variant.

The curve BC is the melting /freezing curve of Pb and shows the melting point is lowered by the addition of Ag. The phases in equilibrium along this curve are Pb and the melt of Ag and Pb. The system is mono variant.

Eutectic point. The curve AC and BC meet at point C ,which is called the eutectic point. Here three phases are in equilibrium solid Ag ,solid Pb and the melt. Applying reduced phase rule equation

$$F=C-P+1=2-3+1=0$$

The system of Ag/Pb/Melt is invariant at point C and both the variables, temperature and composition is fixed.(97.5Pb and 2.5Ag. Invariance of the eutectic point also reveals If we raise the temperature above eutectic temperature, solid phase of Ag and Pb will disappear .Cooling of the eutectic mixture below eutectic temperature results in the non existence of solution phase and we land into the solid Ag/Pb area.

The area above AOC represents single phase system ,the solution of molten silver and lead ,here single phase is present so the system is bi variant (F=2) and the area below AC represents Ag + solution while that below BC the phases Pb +solution and the area below eutectic point all contain two phases and are thus mono variant. F=1)

Pattinson's process for the desilverization of argentiferous lead

Pattinsons process involves the recovery of silver from argentiferous lead.The argentiferous lead containing small amount of silver (0.1%) is melted well above the melting point of pure lead so that the system contains only the liquid phase represented by point X in the phase diagram. It is then allowed to cool gradually along the line xy without any change in concentration till point Y on the curve is reached .As soon as this point is reached ,Lead starts to crystallize out and the solution would contain relatively large amount of silver .On further cooling ,more of lead separates and we travel along the curve BC until the eutectic point is reached. .At C an alloy containing 2.5% silver and 97.5 lead is obtained.

Two Component system(Magnesium-zinc system)

It is a typical two component system which involves the formation of an intermetallic compound $MgZn_2$.It has four phases solid magnesium, solid zinc solid $MgZn_2$, and the liquid solution of magnesium and zinc. The phase diagram appears to be made of two simple eutectic diagrams. The one towards the left represents the eutectic system Mg-MgZn₂ while the one to the right the system of Zn and MgZn₂.

The curve AC in the phase diagram shows that the melting point of magnesium is lowered on the addition of zinc .This continues till point C is reached. .Here a new phase appears .The curve CD shows the increase of concentration of zinc in the melt with the rise of temperature .At the maximum point D ,the composition of the melt and the solid compound becomes the same i.e; $MgZn_2$.The point D therefore represents the melting point of $MgZn_2$.The curve DE now shows the lowering of melting point

of Zinc until the lowest point is attained. Here solid zinc appears. The curve BE exhibits that the melting point of zinc falls with the addition of magnesium until point E is reached.

Along the freezing point curves AC, CDE and BE, there are two phases in equilibrium viz; one solid phase (Mg, Zn, MgZn₂) and the other liquid phase, hence

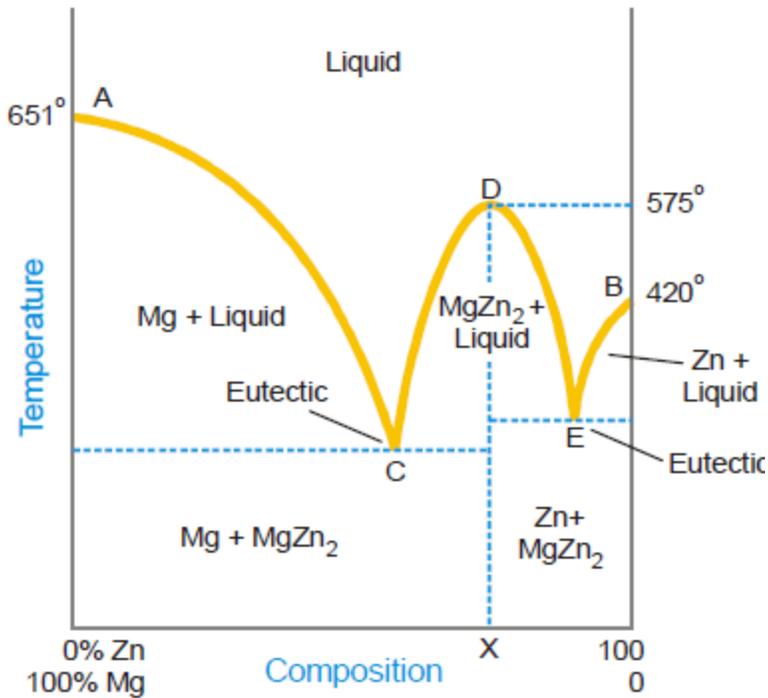
$$F = C - P + 1 = 2 - 2 + 1 = 1 \quad (\text{all are monovariant})$$

At the eutectic points C and E, there are two components and three phases in equilibrium, these systems are therefore non-variant, $F = C - P + 1 = 2 - 3 + 1 = 0$.

As already stated the composition of the compound MgZn₂ and the melt at D is identical, the corresponding temperature is the congruent melting point of the compound. Here the system has two phases, solid compound and the melt but just one component because both the phases can be represented by MgZn₂. Therefore the system at D is non-variant.

$$F = C - P + 1 = 1 - 2 + 1 = 0$$

The area above curve AC, CDE and BE represents a single phase which is bi-variant.



Freezing mixture

A combination of substances that when mixed lower the temperature of the mixture by absorbing the heat of solution of the systems components. To attain the lowest possible temperature, the components of the freezing mixture are used in quantities that will form a cryohydrate. A good freezing mixture is one that has low cryohydric point, the heat of solution of the salt should be high and the material should be cheap. The common freezing mixture is made from ice and common salt. For

attaining very low temperatures (-50°C to -70°C), acetone dry ice mixture is often used. Acetone is taken in a Dewar or insulating flask and dry ice is added to it till the lowest temperature is attained.

Nernst Distribution law

Nernst distribution law states that 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 the molecular solvents then

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

$C_1/C_2 = K_d$, where C_1 is the concentration of solute X in A and C_2 is the concentration of solute solvent X in solvent B. The constant K_d is called distribution coefficient or partition coefficient

Explanation:- This is an equilibrium law when the distribution of solute has reached dynamic equilibrium the rate at which molecules of X passes from solvent A to B is proportional to its concentration in A and the rate at which molecules of X pass from B to A is proportional to its concentration in B. Also at equilibrium the rate of migration of solute from one solvent to other is equal thus we have

$$R_1 \propto C_1 \quad \rightarrow R_1 = k_1 C_1, \text{ where } k_1 \text{ is constant}$$

$$R_2 \propto C_2 \quad \rightarrow R_2 = k_2 C_2, k_2 \text{ is constant}$$

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 distribution law equation. Since k_1 and k_2 are constants at constant temperature, the distribution coefficient K_d is also constant if temperature is fixed.

Applications:- Deducing the formula of a complex ion (I_3^-)

Some iodine is added to the solution of KI and the reaction mixture is shaken with benzene. The iodine $[I_2]$ in water layer can be found by knowing the value of K_d and the concentration of iodine in benzene is determined by titrating against thiosulphate

The total concentration of iodine $[I_2 + I_3^-]$ is found by titration against thiosulphate knowing I_2, I_3^- can be calculated.

The initial concentration of KI is represented by the equilibrium concentration $I^- + I_3^-$, knowing I_3^- I^- can be found

-]Substituting the above concentration values 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 is I_3^- as assumed.

Desilverization of lead.

When molten zinc is added to molten lead containing silver, 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 the silver passes into the zinc layer.on cooling the zinc layer ,an alloy of silver and zinc separates. The Ag-Zn alloy is distilled when zinc passes over leaving silver behind.

Solvent extraction:-

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

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 over simple extraction.

Determination of dissociation

Suppose a substance X dissociates in aqueous layer and remains intact in ether. If x is the degree of dissociation ,the distribution law is modified as

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

C₁ is concentration of X in benzene .

C₂ is concentration in aqueous layer

The value of x can be determined from conductivity measurements. While C₁ and C₂ are found experimentally. The value of K can thus be calculated. Using this value of K ,the value of x for any other concentration of X can be determined,

Roalts law:

Roalt's law states that the partial vapour pressure of a substance in a binary mixture is proportional to its mole fraction in the solution and its vapour pressure when pure.

$P_j = X_j \cdot P_j^0$, where P_j is the vapour pressure of pure substance in the mixture, P_j^0 is vapor pressure in pure state and X_j is the mole fraction of substance(solvent) in solution

Above equation can be written in the form

$$P_j/P_o = X_j = n_j/n_j+n_k$$

Subtracting each side of above equation from 1, we get

$$1 - P_j/P_o = 1 - n_j/n_j+n_k \quad P_o - p_j/P_o = n_k/n_j+n_k \dots\dots\dots$$

The left hand side of the above equation is relative lowering of vapour pressure and the right side is the mole fraction of the solute.

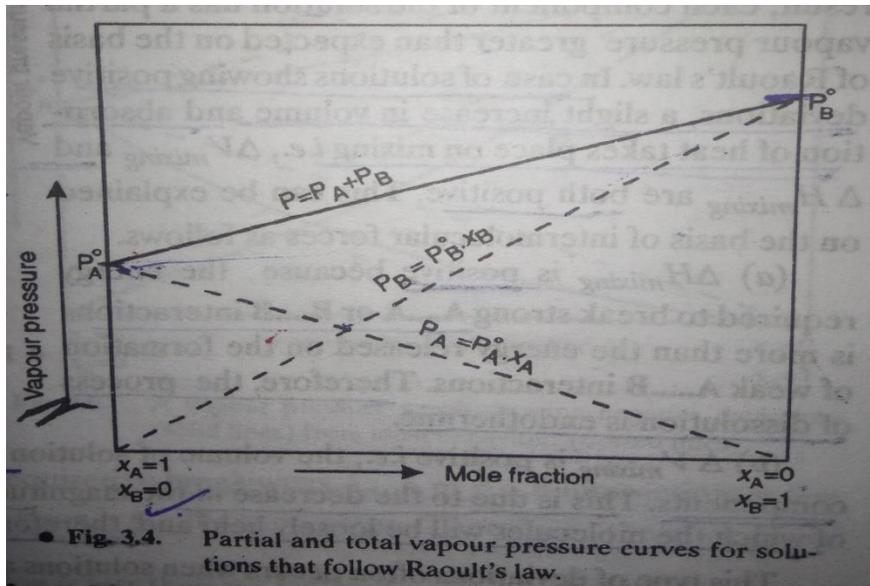
Thus the relative lowering of vapour pressure of a solution containing a non volatile solute is equal to the mole fraction of solute in the solution. Any solution whose vapour pressure depends on concentration as given by Raoult's law is called an ideal solution.

The molecular origin of the Raoult's law is the effect of solute on the entropy of the solution. In the pure solvent molecules have certain disorder and corresponding entropy. However when a solute is present the solution has higher entropy and hence lower tendency to escape into the vapor phase resulting in reduced vapour pressure in the solution phase.

IDEAL SOLUTION

A solution is said to be ideal if it obeys Raoult's law over an entire range of composition and temperature. Liquids with almost identical polarities tend to form an ideal solution. In such solutions, the magnitude of the interactions between the molecules remain almost of same type before and after mixing, therefore such solutions are not accompanied by any enthalpy and volume change i.e. ΔH_{mix} and ΔV_{mix} is equal to zero. Though there is no solution which strictly behaves as ideal solution yet they may behave as ideal when the concentration of solute is low.

Graphical representation of behavior of ideal solution:-



For a binary mixture of two volatile liquids(A and B) that obey Raoult's law, the total vapour pressure is given by

$$P = P_A + P_B \text{ where}$$

$$P_A = X_A \cdot P_A^0 \text{ and } P_B = X_B \cdot P_B^0$$

$$P = X_A \cdot P_A^0 + X_B \cdot P_B^0$$

$$P = (1 - X_B)P_A^0 + X_B P_B^0$$

$$P = P_A^0 + (P_B^0 - P_A^0)X_B$$

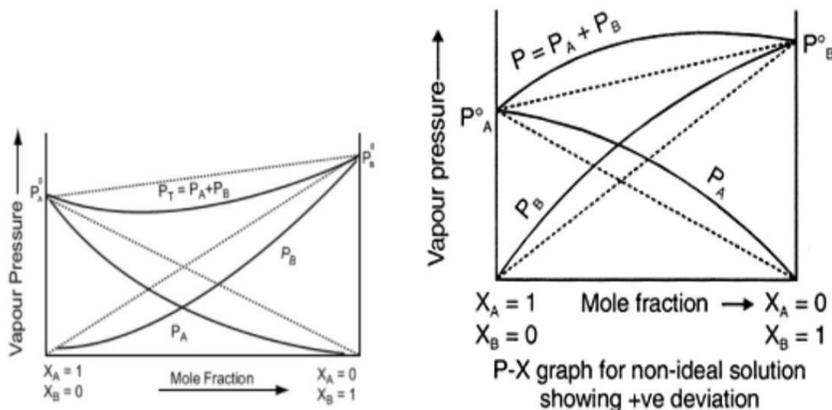
From the Above equation, it is evident that, total pressure is a linear function of mole fraction and thus when P is plotted against X_B , a straight line is obtained. From the graph plotted below, it is clear that the vapour pressure of solution of different composition in case of an ideal solution lies between vapour pressure of the pure components.

Non ideal mixture:-

A mixture is said to be non ideal if it does not follow Raoult's law. In such a mixture the molecular interactions between the solute and solvent molecules are different from that in the pure state. As such, such solutions are accompanied both by change in enthalpy and volume and the graph between the partial pressure and composition is not a straight line as expected for a solution obeying Raoult's law. Depending upon the nature of interaction the solution can have positive or a negative deviation from Raoult's law.

In non ideal solutions showing the negative deviation from Raoult's law, the molecular structure of the components is such that there are stronger attractive forces between unlike molecules than between

like molecules of the same kind. As a result, the mixing of such components is accompanied by evolution of heat ($\Delta H_{mix} = -ve$). Since the evolution of heat is an indication that the molecules in solution are in a lower energy state, the vapour pressure of each component is lower than would be predicted by Raoult's law. e.g; chloroform and acetone display such kind of behavior. On the contrary, in the solutions showing positive deviation, the attractive force between the unlike molecules are weaker than those between molecules of same kind. As a result, the mixing of such liquids is accompanied by absorption of energy ($\Delta H_{mix} = +ve$) and the molecules are thus in a state of higher energy and thus have increased tendency to escape and that the vapour pressure of each of the components is higher than that predicted by Raoult's law as shown in the graph below. e.g; acetone carbon disulphide, water and ethanol display such type of behavior. Carbon disulphide is a linear molecule and hence non polar while acetone has dipole moment, when the two are mixed, the vapour pressure of both the components exceeds the predictions of Raoult's law.



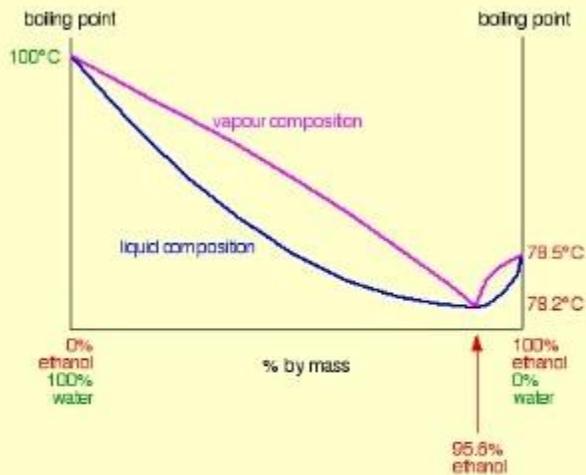
Azeotropic mixture :- Azeotropes are defined as mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in the liquid as well as in the vapour state. Thus, these are constant boiling mixtures because whole of the azeotrope changes into vapour state at a constant temperature and their components can not be separated by fractional distillation.

Minimum boiling azeotropes:- These azeotropes are formed by liquid pairs which show positive deviation from Raoult's law. A large positive deviation from Raoult's law produces a mixture with highest vapour pressure. The implication of this is that the boiling point/composition curve will have a boiling point lower than the boiling point of either of the pure liquids as shown below.

Suppose we are distilling a mixture of ethanol and water with composition C1, it will boil at a temperature given by the liquid curve and produce a vapour with composition C2. When the vapours

with composition C2 are condensed it will produce a new vapour with composition C3. If we carry on the process of boiling and condensing we will eventually end up with a vapour with a composition of 95.6% ethanol. If we condense that we will get a liquid with the same composition because the liquid curve and the vapour curve meet at that point. Thus it is impossible to get pure ethanol by distilling any mixture of ethanol and water containing less than 95.6% ethanol. Thus such a constant boiling mixture is called azeotropic mixture.

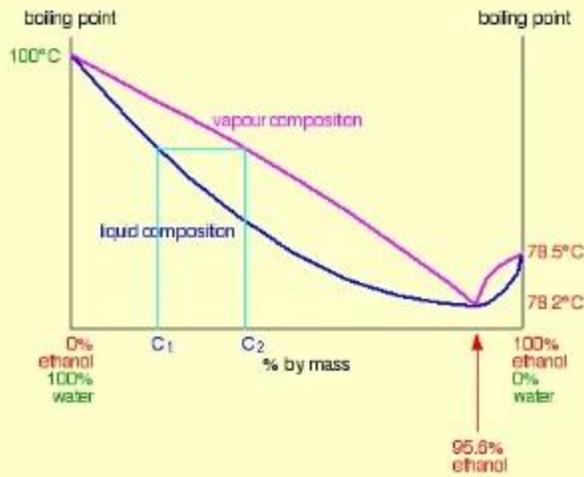
Maximum boiling azeotrope:- These azeotropes are formed by liquid mixtures which show negative deviation from Raoult's law. If the negative deviation is very large then there will be a minimum in the total vapour pressure at some particular composition for a given temperature. This implies that the boiling point curve will display a maximum because it needs extra heat to break the stronger attractions in the mixture. Nitric acid and water, HCl and water display such kind of behavior.



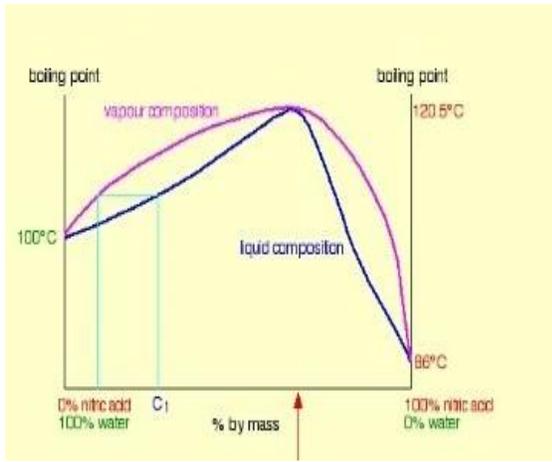
Note: This diagram is drawn grossly distorted. Look, for example, at the temperature scale and the position of the 95.6% value on the composition scale. The shapes of the two separate areas between the curves are also exaggerated. This is to make it easier to see what is going on in what comes next. It doesn't affect the argument in any way.

Using the diagram:

Suppose you are going to distil a mixture of ethanol and water with composition C_1 as shown on the next diagram. It will boil at a temperature given by the liquid curve and produce a vapour with composition C_2 .



When that vapour condenses it will, of course, still have the composition C_2 . If you reboil that, it will produce a new vapour with composition C_3 .



Henry's law:-

Raoult's law gives a good description of vapour pressure of solvent in a very dilute solution however it can not be expected to be a good description of vapour pressure of solute because a solute in a dilute solution is far from being pure because in dilute solution it is surrounded by nearly pure solvent molecules and hence it is unlikely that its vapour pressure will be related to the pure solute. However it is observed experimentally that in dilute solution is in fact proportional to its mole fraction, just as for solvent. Unlike the solvent the constant of proportionality is not the vapour pressure of solute. This linear but different dependence is summarized as Henry's law.

The vapour pressure of a volatile solute, B is proportional to its mole fraction in a solution.

$P_b = X_b K_h$, Where K_h is called Henry constant and is characteristic of the solute.

Henry's law also deals with the effect of pressure on the solubility of gases in a liquid at a particular temperature and can be stated as

The mass of gas dissolved in a given volume of liquid at a constant temperature is directly proportional to the pressure of gas present in equilibrium with the liquid. Mathematically

$m \propto P$, $m = K_h P$ where m = mass of gas dissolved in unit volume of solvent, P is pressure of gas in equilibrium with solvent

Partially miscible liquids:-

Liquid pairs which do not mix together in all proportions are called partly miscible liquids. The phenomenon is more or less akin to a sparingly soluble solid in a liquid e.g; if phenol is added to water, the substance at first dissolves completely but if the addition is continued, a stage is reached when no further dissolution takes place and the two liquid layers separate out. The two layers in equilibrium are called conjugate solutions. Each layer is a saturated solution of one in the other. Because the two solubilities vary with temperature the composition and proportions of the two liquid phases change as the temperature is changed. The temperature at which the two liquids which are otherwise partly miscible become completely miscible is called critical consolute temperature (CST)

Type 1:- systems with upper consolute temperature

If the phenol and water are mixed in roughly equal proportions the two layers are produced, one of solution of phenol in water and the other of solution of water in phenol. If the system is warmed, the amount of water in phenol layer increases as well as the amount of phenol in water. Ultimately at a particular temperature, the composition of both the layers becomes the same and thus the two become completely miscible. The minimum temperature at which the phenol and water become completely miscible is 66°C and the composition is 34% of phenol by weight.

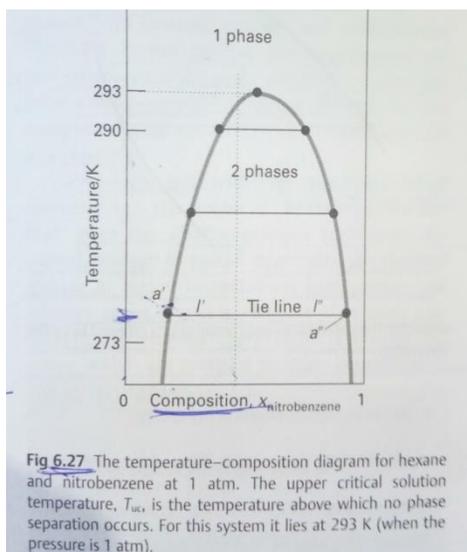
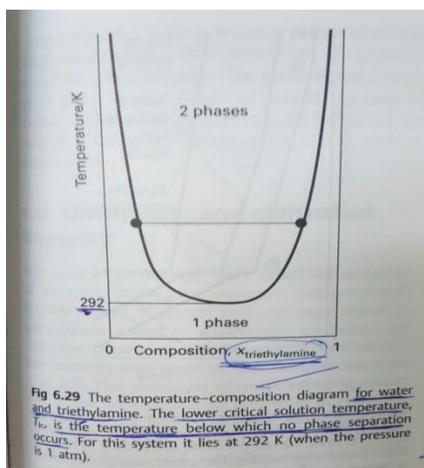


Fig 6.27 The temperature-composition diagram for hexane and nitrobenzene at 1 atm. The upper critical solution temperature, T_{uc} , is the temperature above which no phase separation occurs. For this system it lies at 293 K (when the pressure is 1 atm).

Type:-Systems with lower consolute temperature:-

In such systems the mutual solubility of the two liquids increase with decrease in temperature. Thus on cooling such a system ultimately a stage is reached when the two liquids become completely miscible. The temperature is called lower consolute temperature and is 18.5°C for triethylamine water system. For temperature and composition corresponding to any point within the curve there are two layers and outside it there is just one layer.



Type3:-system with both upper and lower consolute temperature:-

These are very unusual systems in which the mutual solubility of the two liquids increase both with increase as well as with decrease in temperature. Thus in such systems the two liquids become completely miscible above a particular temperature as well as below a particular temperature. In other words such systems have both upper critical consolute temperature as well as lower critical consolute temperature which in case of Nicotine water system are 208°C and 60.8°C respectively.

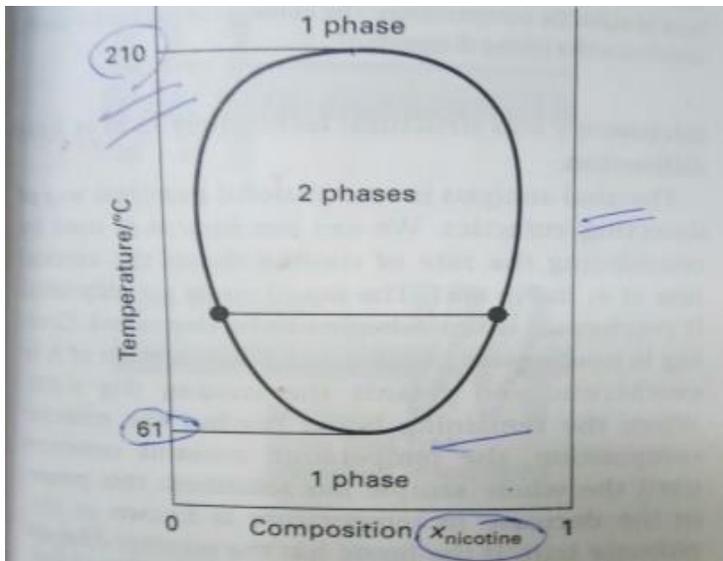


Fig 6.30 The temperature-composition diagram for water and nicotine, which has both upper and lower critical solution temperatures. Note the high temperatures on the graph: the diagram corresponds to a sample under pressure.

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.

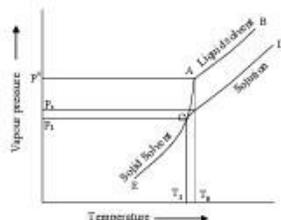


Fig. 4

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° 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.

$$\begin{aligned}\ln \frac{p_0}{p_1} &= -\frac{\Delta H_{sub}}{R} \left[\frac{1}{T_0} - \frac{1}{T_1} \right] \\ &= \frac{\Delta H_{sub}}{R} \left[\frac{T_0 - T_1}{T_1 T_0} \right]\end{aligned}\quad \dots\dots\dots(29)$$

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

$$\begin{aligned}\ln \frac{p_s}{p_1} &= -\frac{\Delta H_{vap}}{R} \left[\frac{1}{T_0} - \frac{1}{T_1} \right] \\ &= \frac{\Delta H_{vap}}{R} \left[\frac{T_0 - T_1}{T_1 T_0} \right]\end{aligned}\quad \dots\dots\dots(30)$$

Now subtracting equation (30) from equation (29)

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

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

$$\ln \frac{p_0}{p_s} = \frac{\Delta H_{fus}}{R} \left[\frac{T_0 - T_1}{T_1 T_0} \right]\quad \dots\dots\dots(32)$$

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

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

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

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

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

equation (34) reduces to

$$\begin{aligned} \Delta T_f &= \frac{RT_0^2 m M_1}{\Delta H_{fus} 1000} \\ &= \frac{RT_0^2 m}{\Delta H_{fus} n_1} \\ &= K_f m \dots\dots\dots(35) \end{aligned}$$

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

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.

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 boil 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.

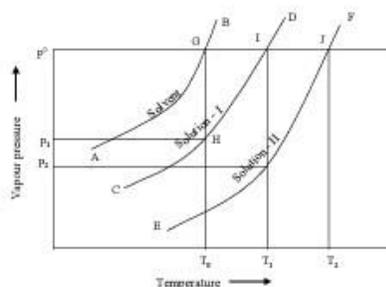


Fig. 3

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 $(T_1 - T_0) = \Delta T_b$ 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

$$p^0 - p_1 = \Delta p = GH$$

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

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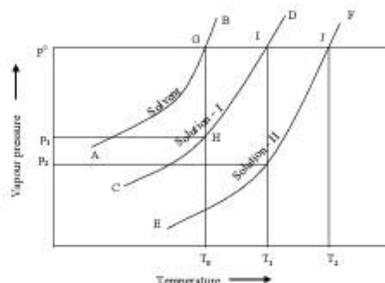


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$$\ln \frac{p^o}{p_1} = \frac{\Delta H_{vap}}{R} \left[\frac{1}{T^o} - \frac{1}{T_1} \right] \quad \dots\dots\dots(19)$$

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 $T_0 T_1 \approx T_0^2$ and the equation now becomes

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

$$\Rightarrow \frac{\Delta H_{vap}}{R} \left[\frac{\Delta T_b}{T^o{}^2} \right] \quad \dots\dots\dots(20)$$

Further according to Raoult's law

$$\frac{p_1}{p^o} = (1 - x_2) \quad \dots\dots\dots(21)$$

From equation (20) and (21) we get

$$\ln(1 - x_2) = - \frac{\Delta H_{vap}}{R} \left[\frac{\Delta T_b}{T^o{}^2} \right] \quad \dots\dots\dots(22)$$

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

as the solution is dilute

$$\ln(1 - x_2) \text{ may be approximated to } \approx -x_2$$

and the equation now becomes

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

$$\text{or } \Delta T_b = \frac{RT^o{}^2 x_2}{\Delta H_{vap}} \quad \dots\dots\dots(23)$$

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)

$$\Delta T_b = \frac{RT^{\circ 2}}{\Delta H_{vap}} \cdot \frac{w_2 M_1}{w_1 M_2} \quad \dots\dots\dots(24)$$

Molality of the solution may be given by

$$m = \frac{1000 w_2}{w_1 M_2} \quad \dots\dots\dots(25)$$

Combining equation (24) and (25)

$$\Delta T_b = \frac{RT^{\circ 2}}{\Delta H_{vap}} \cdot \frac{m}{n_1} \quad \dots\dots\dots(26)$$

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

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

$$\Delta T_b = K_b \cdot m \quad \dots\dots\dots(27)$$

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.

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

$$K_b = 1000 W_2 / W_1 M_2$$

$$M_2 = 1000 W_2 K_b / T_b W_1$$

$$\ln \frac{p^s}{p_1} = \frac{\Delta H_{vap}}{R} \left[\frac{1}{T^o} - \frac{1}{T_1} \right] \quad \dots\dots\dots(19)$$

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

$$\rightarrow K_b 1000 W_2 / W_1 M_2$$

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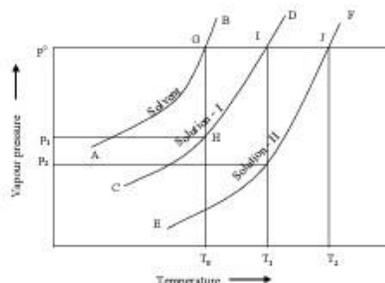


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Activity and Activity coefficient

The activity of any substance taking part in a chemical reaction is a measure of its effective concentration in the equilibrium system.

The effective concentration is defined differently in different cases:-

Activity of an ideal gas is defined to be exactly equal to its partial pressure and the activity of an ideally behaving solute is proportional to its concentration

The activity of a volatile liquid may be visualized as its escaping tendency into the vapor phase. In an ideal solution it is the ratio of partial pressure of liquid in a solution to the vapor pressure of pure liquid at the same temperature

Mathematically $a = p_A / p_A^\circ$

The above activity relation holds true provided the vapors behave ideally. In case vapor doesn't behave ideally another term called fugacity which has the dimensions of pressure has been introduced by Lewis to cater the non ideal behavior.

Where $f = \gamma \cdot P$

Where γ = activity coefficient of gas and may be defined as the ratio of fugacity of the gas in the given state to the pressure of gas in the given state. Obviously for real gas $\gamma = 1$

For a real gas $\gamma < 1$, greater the departure in the value of γ , greater is the non ideal behavior.

Mathematically, activity of a substance may be defined as the ratio of fugacity in a given state to that in its standard state i.e; $a = f / f^\circ$

The standard state may be defined as the state at which activity is equal to one.

In a non ideal solution, the concentration is corrected by multiplying it by γ to get the value of activity $A = \gamma \cdot c$.

The activity coefficient of any component in a solution is defined as the ratio of the activity of any component in the solution to the concentration of that component in the solution

For ideal solution $\gamma = 1$ and $a = c$

CLAYPERON AND CLAUSIS CLAYPERON EQUATION

The variation of free energy with temperature and pressure is given by the differential equation

$$dG = VdP - SdT \dots \dots \text{eq. 1}$$

Now, consider two phases 1 for instance the liquid phase and 2 the vapour phase. At certain temperature and pressure the two phases are in equilibrium and the molar Gibbs energy of the two phases is identical i.e; $G_m(1) = G_m(2)$. Once we change the pressure by an infinitesimal amount, dP and temperature by dT , the molar Gibbs energy of each phase changes as follows

$dG_m(1) = V_m(1)dP - S_m(1)dT$ $dG_m(2) = V_m(2)dP - S_m(2)dT$ where $V_m(1)$ and $S_m(1)$ are the molar volume and molar entropy of phase 1 and $V_m(2)$ and $S_m(2)$ those of phase 2. The two phases were in eqm before the change and their molar Gibbs energies were equal. They are still in eqm after the change so the two changes in molar Gibbs energies must be equal and we can write

This equation can be rearranged to $S_m(2) - S_m(1) dT = V_m(2) - V_m(1) dP$,

$\Delta S \times dT = \Delta V \times dP$, where ΔS is entropy of transition, the difference between the two molar entropies and ΔV is the difference between the molar volumes of the two phases.

On rearranging we get clayperon equation.

$$dP/dT = \Delta S / \Delta V,$$

The clayperon equation tells us the slope of any phase boundary in terms of the entropy and volume of transition.

Since for liquid vapour phase boundary, the entropy of vaporization is related to the enthalpy of vaporization, above equation can be written as

$dP/dT = \Delta_{vap}H / T \Delta_{vap}V$, because the molar volume of gas is much larger than molar volume of liquid, volume of vaporization is approximately equal to the volume of gas itself, therefore

$dP/dT = \Delta_{vap}H / T V_m(g)$. To a good approximation we can treat the gas as ideal and write its molar volume as $V_m = RT/P$, then

$$dP/dT = \Delta H / T(RT/P) \quad \Rightarrow \quad dP/dT = P \Delta H / RT^2$$

$$d \ln P / dT = \Delta H / RT^2 \quad \dots \dots \text{CLAUSIS clayperon}$$

After dividing both sides by P and using the mathematical relation in calculus $dP/P = d \ln P$, we obtain clausis clayperon equation

The Clausius-Clapeyron equation gives the slope of plot of the logarithm of the vapor pressure against the temperature and can be used in the integrated form as well as shown below

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

1. Applications:

This equation can be used to calculate the vapor pressure at one temperature provided we know it at another temperature.

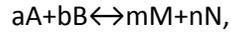
2. This equation tells us that for a change in temperature, the larger the enthalpy of vaporization, the greater the change in vapor pressure.

3. If the boiling point of liquid at one pressure is known, its boiling point at any other pressure can be computed.

4. Latent heat of vaporization of liquid can be computed if we know the boiling point of liquid at different temperatures.

Thermodynamic derivation of law of mass action

For a general reversible reaction as shown below



the total free energy change accompanying the reaction at constant temperature and pressure is

$$\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}}$$

Total free energy of reactants = $a\mu_A + b\mu_B + \dots$ and total free energy of products = $m\mu_M + n\mu_N + \dots$, where μ_A and μ_B represent the chemical potential of A and B and μ_M , μ_N represent the chemical potential of M and N respectively.

Thus eq 1 can be written as

$\Delta G = (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$, however when the system is at equilibrium overall free energy change is zero, thus

$$m\mu_M + n\mu_N - a\mu_A - b\mu_B = 0$$

$$m\mu_M + n\mu_N = a\mu_A + b\mu_B.$$

If all the reactants and product are considered ideal gases, the chemical potential of any component in the ideal gas mixture is

$\mu = \mu^\circ + RT \ln P$, where P is the partial pressure of gas in the mixture and μ° is chemical potential in the standard state whose value depends on temperature only

Substituting, $\mu_A = \mu_A^\circ + RT \ln P_A$,

$\mu_B = \mu_B^\circ + RT \ln P_B \dots \dots$

Above equation can thus be written as

$$m(\mu_M^\circ + RT \ln P_M) + n(\mu_N^\circ + RT \ln P_N) = b(\mu_B^\circ + RT \ln P_B) + a(\mu_A^\circ + RT \ln P_A)$$

$$RT(m \ln P_M + n \ln P_N) + (m\mu_M^\circ + n\mu_N^\circ) = RT(a \ln P_A + b \ln P_B) + (a\mu_A^\circ + b\mu_B^\circ)$$

$$RT(\ln P_M^m + \ln P_N^n) - (\ln P_A^a + \ln P_B^b) = a\mu_A^\circ + b\mu_B^\circ - (m\mu_M^\circ + n\mu_N^\circ)$$

$$RT \ln P_M^m P_N^n / P_A^a P_B^b = G^\circ_{\text{reactants}} - G^\circ_{\text{products}} = -(G^\circ_{\text{products}} - G^\circ_{\text{reactants}}) = -\Delta G^\circ_{\text{reaction}}$$

$$\ln P_M^m P_N^n / P_A^a P_B^b = -\Delta G^\circ / RT$$

$$P_M^m P_N^n / P_A^a P_B^b = e^{-\Delta G^\circ / RT}$$

As standard free energy change depends upon temperature only, hence at constant temperature right hand side of above equation is constant at constant temperature. This implies that for an ideal gas system at constant temperature

$$P_M^m P_N^n / P_A^a P_B^b = \text{constant}(K_p)$$

As we know that

$$\Delta G = -RT \ln P_M^m P_N^n / P_A^a P_B^b$$

$$\Delta G^\circ = -RT \ln K_p$$

Thus knowing ΔG° of reaction, equilibrium constant can be determined

Vant hoff reaction