VIVEKANANDA COLLEGE, THAKURPUKUR

NAAC Accredited Grade—A

STUDY MATERIAL

Subject : Physical Chemistry

Course Title : Applications of Thermodynamics II

Topic : **Phase Equilibrium- Discussion on** Lever Rule, problems based on phenol- water system, Eutectic mixture, Congruent melting pt., Incongruent Melting point.

Paper : Physical Chemistry **– 3 (CODE: CEMA-CC-4-9-TH)**

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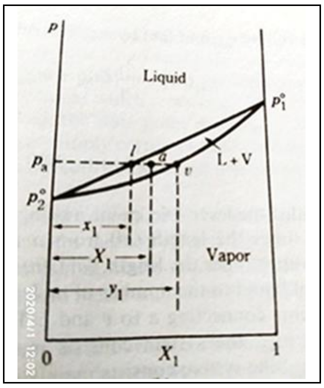
LEVER RULE:

In any two-phase region say L - V in the [Figure1], the composition of the entire system may vary between the limits x1 and y1, depending on the relative amounts of liquid and vapour present. If the state point ‘a’ is very near the liquid line, the system would consist of large amount of liquid and a relatively small amount of vapour. If ‘a’ is nearer to the vapour line, then the system would consist of large amount of vapour and a relatively small amount of the liquid. The relative amounts of the liquid and vapour present are calculated by Lever Rule. Let the length of the line segment between a and l in the [figure1] be $a\bar{l}$ and that between a and v be $a\bar{v}$. Then let n1(liq)and n1(vap) be the number of moles of component 1in the liquid and in the vapour respectively, then let n1 = n1(liq) + n1(vap). If n_{liq} and n_{vap} are the total number of moles of the liquid and vapour respectively and if $n = n_{liq} + n_{vap}$.



Figuer1

$a\bar{l}$ =X1 -x1 = n1/n - n1 (liq) /n_{liq} ------(1)

$l\bar{v}$ = y1- X1 = n1(vap) /n_{vap} – n1/n ------(2)

(n liq)* $a\bar{l}$ = n_{liq} [n1/n - n1 (liq) /n_{liq}] -------(3)

(n_{vap}.)* $l\bar{v}$ = n_{vap}.[n1(vap) /n_{vap} – n1/n]

Therefore, $n_{liq\,.}$ $a\bar{l}$ = n_{vap}. $l\bar{v}$

$n_{liq\,.}$/ n_{vap}. = $l\bar{v}$ / $a\bar{l}$

If $l\bar{v} > a\bar{l}$, then no. of moles of vapour will be greater than no. of moles of liquid. In contrast, $a\bar{l} > l\bar{v}$, then no. of moles of liquid will be greater than no. of moles of vapour.
This is called Lever Rule and ‘a’ being the point of fulcrum of the lever.

Thus, the ratio of the number of moles of the liquid to the number of moles of the vapour is applicable for calculating the relative amounts of two phases present in any two-phase region of a two-component system.

Math Problem:

At 30 ºC, a mixture of phenol and water is made up containing 60% by weight of H_2O. The mixture splits into two layers, the C_6H_5OH layer containing 70% by weight of C_6H_5OH and H_2O layer containing 92% by weight of H_2O. Calculate the relative weights of two layers.

Let total weight of two layers = 100g.
Let weight water rich layer = a, then weight of phenolic layer = (100-a) g.
Let the amount water present in the water rich layer = X g.
Therefore, % of water in water rich layer (X/a).100 = 92
% of water in phenol rich layer = (60 -X)/(100-a).100 = 30
Solving above equations, we get X =0.92a and a = 48.38g.

Therefore, weight of phenolic layer = 100-48.38= 51 .62g

Math Problem:

For the 50% phenol-water mixture, the composition of two liquid layers observed are 9.2% and 65% phenol. Calculate the weight ratio two layers.

Let the weight of the aqueous layer = a g.

Thus, the weight of the phenolic layer = (100-a) g.

By problem,

(9.2/100). a + (65/100). (100-a) = 50

∙: a = 26.8 g.

Wt. of aqueous layer = 26.8 g.

Wt. of phenolic layer = 73.2 g.

Ratio of aqueous layer to the phenolic layer = 26.8/73.2 = .3661

Gibbs phase rule when applied to a two-component system gives $F = C – P + 2 = (4 – P)$. Therefore, the maximum number of phases that can exist at invariant point are four ($P = 4$, $F = 0$) and the maximum number of degrees of freedom could be 3. In practice, one variable i.e. either the pressure or the temperature is kept constant and only two variables temperature and mole fraction or pressure and mole fraction are specified. Thus, in an isobaric T – X phase diagram or in an isothermal P – X phase diagram for two component system is usually constructed. Under this condition modified phase rule would be $F = 2-P+1$ or, $F+P = 3$. Hence maximum number of phases in equilibrium at invariant point ($F=0$) for a two-component system will b the following types:

I.(a) two solid phases are not miscible into each other and form a eutectic mixture.
(b) two solid phases form a stable compound with congruent melting point.
(c) two solid phases form association compound with in congruent melting point.
(d)two solids are miscible into each other and form solid solutions.
(e)two solids are only partially miscible.

II. The two components are only partially miscible in the liquid state and possibilities of existence of type - I (a) to (e) systems are also there.

Eutectic Systems: Since two solids are not miscible to each other, there would be two solid phases and one liquid phase for this system. The various possibilities depicted from phase rule are summarized below for a two-component system (A+B).

Two phase equilibria: (i) Solid A – liquid; (ii) Solid B – liquid; the degree of freedom is $F = 3-P = 1$, these are represented by the T -X diagram.

Three phase equilibria: solid A – solid B -liquid, the degree of freedom is $F = 3-3 = 0$. This will be represented by a point which will be invariant at constant pressure as $F = 0$. Thus, eutectic point is isobaric ally invariant point and is fixed for each system but is a function of pressure. The temperature and composition at which the three phase equilibria exist are known as eutectic temperature T_e and eutectic composition x_e respectively.

Thermal analysis and thaw-melt method are usually applied for constructing the phase diagram. However, for partially miscible liquid mixtures as well as for ternary mixtures, solubility measurements are resorted to.

Theoretical method:

When a liquid solution is cooled to a sufficiently low temperature, then one of the components which is in excess in solution separates as solid. This temperature is the freezing point of the solution. The variation of freezing point with composition can be expressed as:

$$d\ \ln x_A = (\Delta H_{A\ fus} / RT^2).\ dT \ \ldots\ldots\ldots\ldots..(1)$$

for the other component, $d\ \ln x_B = (\Delta H_{B\ fus} / RT^2).\ dT \ \ldots\ldots\ldots\ldots\ldots..(2)$

If T is plotted against x_A an x_B, the curves AEA' and BEB' are obtained. If these two curves are combined, a final curve AEB is obtained which will represent the complete set of equilibria of eutectic system.

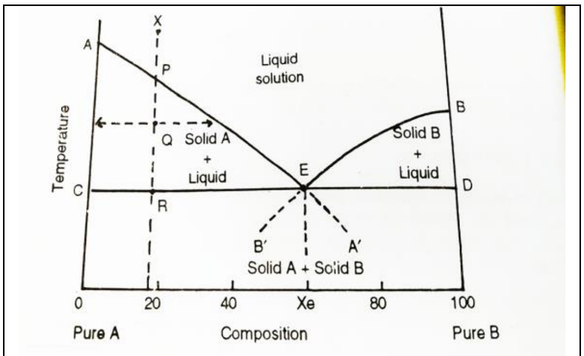
Calculation of eutectic point: If we take the approximation that the two components of the mixture obey the ideal law, then using the above equations (1) & (2) , we will able to find out the eutectic temperature, Te and eutectic composition xe. Assuming ΔH_{fus} is supposed to be independent of temperature and integrating of both equations for the limits T_0 and Te, we can calculate Te.

$-\ln x_A = (\Delta H_{A\ fus} /R\ [1/Te-1/T_{0A}]$ or $x_A = \exp -\Delta H_{A\ fus} /R[1/Te-1/T_{0A}]$…………(3)

$-\ln(1- x_A) = \Delta H_{B\ fus} / RT[1/Te - 1/T_{0B}]$ or $(1- x_A) = \exp\text{-}\Delta H_{B\ fus} / RT[1/Te - 1/T_{0B}]$….(4)

$(3) + (4) \rightarrow\ 1 = \Delta H_{A\ fus} / R[1/ T_{0A} - 1/Te] + \Delta H_{B\ fus} / R[1/T_{0B} -1/Te]$

The above equations help us to calculate Te and xe. Moreover, is a good guess that the more volatile component will have greater mole fraction in the eutectic mixture.



Phase diagram of a eutectic system. *E* is the eutectic point where the two curves *AEA′* and *BEB′* meet.

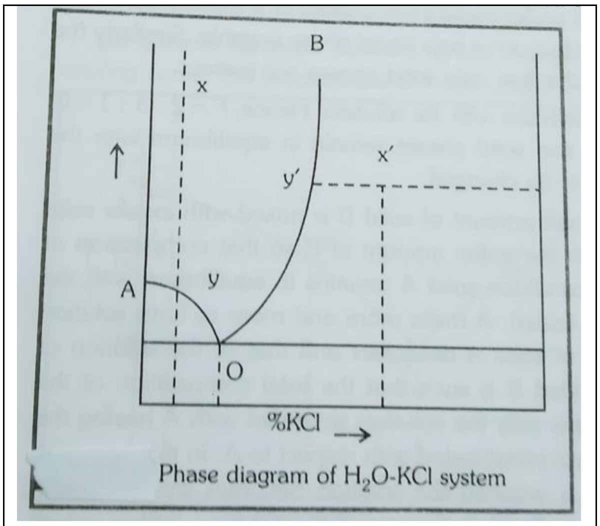
Figure2

Simple eutectic systems include:

1. Sb-Pb system where the eutectic composition is 80% lead and eutectic temperature is 246 ºC (m.pt.of Sb = 631 ºC, m.pt. of Pb = 327 ºC).
2. Chloroform – aniline.
3. KCl – water system.
4. KI – water system.

KCl -water system:

This system belongs to simple eutectic system where liquidus AO represents the variation of freezing point of water with the addition of KCl whereas OB presents the solubility curve of KCl in water. If a dilute solution is cooled from x, then ice does not separate until the temperature drops to a value (less than 0 ºC) corresponding to the point y. At y separation of ice starts. Hence at y, ice remains in equilibrium with KCl solution. Hence, F = 2-2+1 = 1 i.e. the system become univariant. With progressive cooling, more and more ice separates and freezing point changes along yO. At point O ice along with KCl separates in the weight ratio same as that of the solution. ‘O’ represents eutectic point also called Cryohydric point, therefore, $F = 2-3+1 = 0$; below Cryohydric point both ice and KCl crystals. If KCl – water system contains w% KCl, then at x′, the system contains saturated solution of KCl in water having composition corresponding to the point y′ and excess of solid KCl.



Phase diagram of H_2O-KCl system

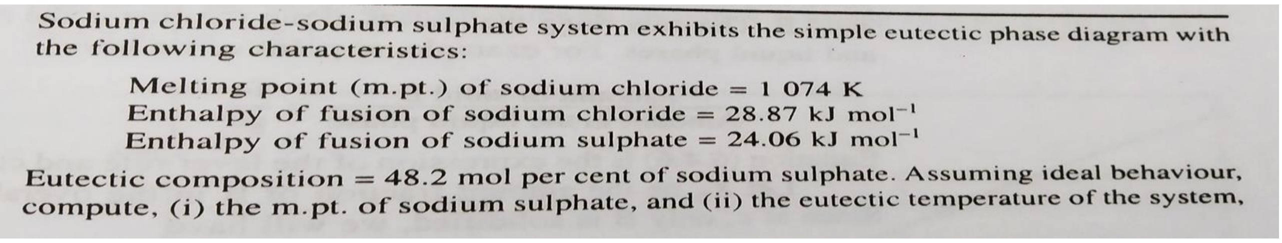
Figure 3

Type II (Components form compound):

In simple eutectic system, the components are miscible in liquid phase and immiscible in the solid phase. Sometimes it may happen that two components A and B form one or more compounds such as AB, AB_2 and A_2B etc. If the compounds are stable up to the normal melting point and melts without a change in composition, then the compounds said to have congruent melting points. E.g., Sn/Mg, phenol / aniline, and Mg / Zn system.

When the compounds are not stable upto the melting point and decompose to a liquid and a solid of different composition, the compounds are said to have incongruent melting point and the change is called peritectic change.

Compounc C = Compound C ′+ solution



Sodium chloride-sodium sulphate system exhibits the simple eutectic phase diagram with the following characteristics:

Melting point (m.pt.) of sodium chloride = 1 074 K
Enthalpy of fusion of sodium chloride = 28.87 kJ mol^{-1}
Enthalpy of fusion of sodium sulphate = 24.06 kJ mol^{-1}

Eutectic composition = 48.2 mol per cent of sodium sulphate. Assuming ideal behaviour, compute, (i) the m.pt. of sodium sulphate, and (ii) the eutectic temperature of the system.

Ans:
Identifying NaCl as component A and Sodium sulfate as component B, then by problem, we can write

$-\ln x_A = (\Delta H_A fus /R)[1/Te- 1/T_A]$……(1) here $x_A = 0.518$; $T_A = 1074$ K;
Or, $- \ln x_B = \ln(1-x_A) = (\Delta H_B fus /R)[1/Te- 1/T_B]$…..(2)

Therefore, $-\ln (.518). (8.314/28870) +1/1074 = 1/Te$
Or Te = 892.43 K (eutectic temperature)
Putting the value of Te in equation (2), we get

$-(1/T_B) = -\ln(.482).(8.314/24060) – (1/892.43)$
Or, $\mathbf{T_B = 1151.6}$ **K**.

Congruent Melting Point:

A compound is said to have congruent melting point if it melts completely at one temperature giving a liquid as the same composition of the solid. The examples of binary system forming solid compounds with congruent melting point are: Aniline + phenol (1:1); gold +tellurium (1:2); urea + phenol (1:1) etc. For a general case of binary system (A+B), which form a solid compound of general formula A_xB_y. If the compound A_xB_y is considered as a separate component, then this phase diagram may be imagined to be made up of two diagrams of the simple eutectic type ACD and DEB placed side by side. In this case in one diagram would be the A- A_xB_y diagram represented by ACD curve and the other diagram A_xB_y-B is represented by DEB curve. The concept of simple eutectic combination can now be applied to the two portions of the phase diagram. The regions above the curve ACDEB represents the existence of only liquid phase and the points A, B and D represents the freezing points of A, B and A_xB_y respectively.

Curve AC presents the equilibrium conditions of solid A and the solution; the liquidus curve CDE represents the equilibrium the solid compound A_xB_y and the liquid solution. The points on the curve BE give the temperature and composition for the equilibrium between the solid B and the liquid solution.

When B is added to A, the freezing point of A decreases along AC until the first eutectic point C is reached where A and A_xB_y separate out as eutectic mixture. Similarly, the melting point of B changes by the addition of A along BE. At the second eutectic point E, the solid compound A_xB_y and pure B separate out. Thus, the liquid having the composition corresponding to the points C, E or D will freeze at constant temperature.

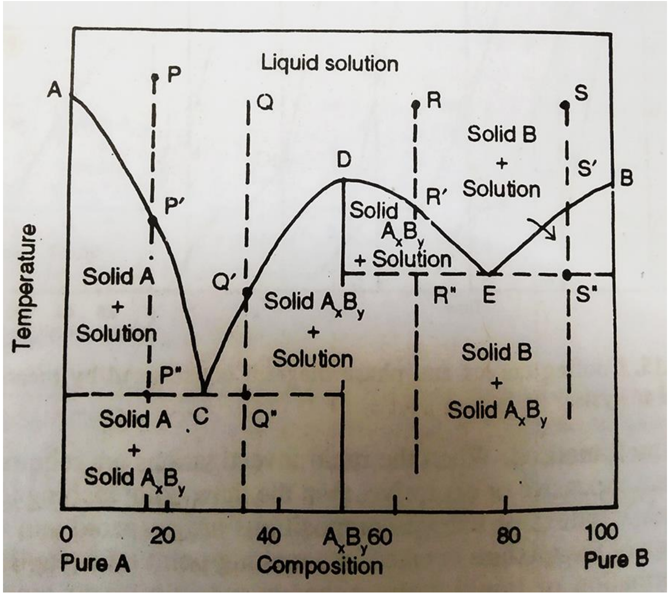


Figure 4

Conglomerates of A and A_xB_y coexist in contact with solution of definite composition indicated by point C. Conglomerates of B and A_xB_y coexist in equilibrium with solution of definite composition indicated by E.

Shape of the curve CDE will depend upon the stability of the compound formed. If the compound is stable in the liquid phase and the solid phase, the bend of the curve will be sharper. Greater the degree of dissociation, flatter the curve will be.

Key features of Cooling of Various mixtures in Figure 4:

1. Start with P. At P′, solid A will separate and the composition will move along P′C; at P′′, A_xB_y also separating out and temperature remains constant till the crystallization is complete.

2. Start with Q. At Q′, A_xB_y appears and the composition will move along Q′C; at Q′′, solid A will also start appearing and the freezing is complete at constant T and constant composition.

3. Start with S. At S′, solid B appears and the composition will move along S′E. At S′′, A_xB_y also separating out and temperature remains constant till the crystallization is complete.

4. Start with R. At R′, solid A_xB_y appears and the composition will move along R′E. At R′′, solid B will also start appearing and the freezing is complete at constant T and constant composition.

Examples:

(i) Sn-Mg system- The compound Mg_2Sn has the m.pt. 783 °C while the eutectic temperatures are 210 °C and 565 °C. Melting point of Sn and Mg are respectively 232 °C and 651 °C.

(ii) Mg-Zn system with congruent m.pt. 575 °C for the compound $MgZn_2$.

(iii) Systems containing organic compounds are- phenol / aniline, urea / phenol, ethyl alcohol/ acetaldehyde.

Compounds with Incongruent Melting Point:

A compound is said to incongruent melting point if it decomposes before it's melting temperature. The composition of the solid is therefore different than the liquid solution. The situation at the peritectic point may be represented by A_xB_y = solution +S1. Here S1 is the new solid phase which may itself a new compound $A'_xB'_y$ or the constituent A or B. **Figure5** shows the phase diagram of such a system where the dotted curve represents the metastable state of the compound and D is the hypothetical melting point. The compound AxBy undergoes dissociation at E, below the melting point and also the composition of the liquid does not have same composition like the solid. The point E is called **Incongruent Melting point**. This point represents the limit of existence of the compound, A_xB_y.it is an invariant point as there are three phases present at E.

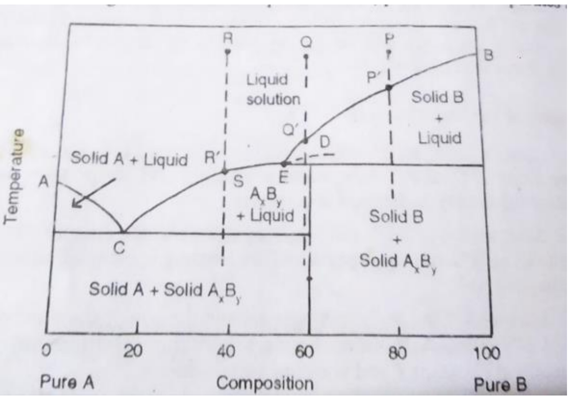


Figure 5

1. On cooling a mixture at P, pure solid B separates, temperature and composition moves further along BE. E is the maximum temperature at which stable compound A_xB_y exists. Thus, E is the true transition point. At a temperature corresponding to point E solid B reacts with the melt to form the new compound $A'_xB'_y$. The temperature remains constant till the solidification of B and $A'_xB'_y$ is completed.

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2. On cooling a mixture with the composition given by point Q, the separation of solid B starts when the temperature corresponds to Q′. The composition follows the path Q′ E, at point E, solid B reacts with the melt to form compound AxBy. The temperature remains constant till the whole of the solid is used to form A_xB_y. Some melt is still there, as the temperature decreases further along the vertical dotted line, solid A_xB_y start separating out and the composition moves along EC. At C, solid A starts separating and the temperature remains constant till the crystallization is completed.

3. Cooling of third mixture from R to R′. At R′, solid A_xB_y starts separating out till C when solid A also shows its appearance.

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