Assignment No. : 2

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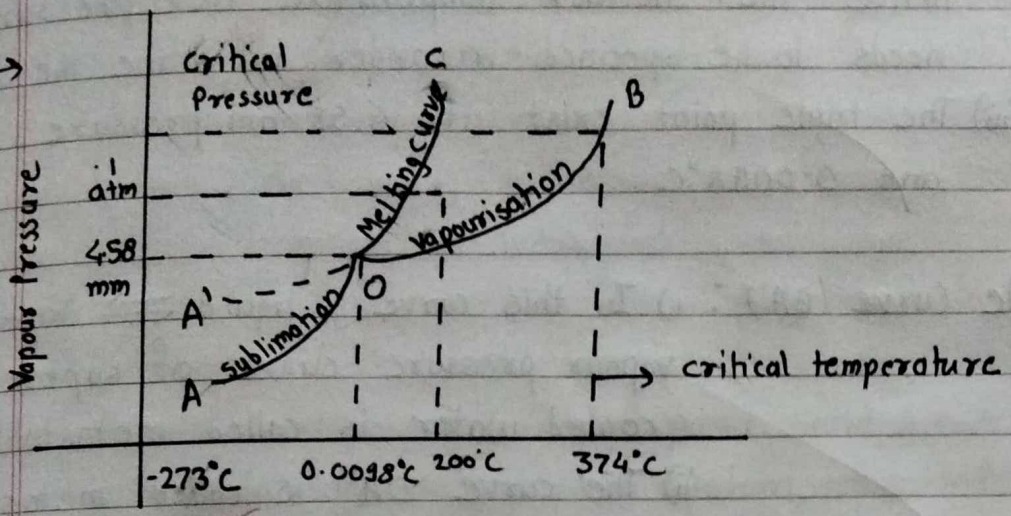
1) Draw phase diagram of one component water system and explain curves, triple point, areas of the phase diagram.



* One component Water System *

I) Area : i) AOB (Vapour) ii) AOC (solid) iii) COB (liquid).
- Contain only one phase and hence the degree of freedom are two i.e. both parameters temperature & pressure.

II) Curves : i) Curve OA (solid, gas) ii) Curve OC (solid, liquid)
iii) Curve OB (liquid, gas)
- It has two phases.
- $F = 3 - P$
  $= 3 - 2 = 1$

III) Triple Point : i) The curve OC, OA & OB meet at point 'O'. called triple point of water.

ii) At triple point, all the three phases i.e. solid, liquid and gases co-exist in equilibrium hence i.e. neither temperature nor pressure needs to be specified in order to define the system.

iii) The triple point exist at 4.58 mm pressure and 0.0098°C.

IV) Metastable Curve (OA') : i) In this curve, liquid $\rightleftharpoons$ Vapour, vapour pressure curve of super cooled water is called metastable

ii) The curve OA' is called metastable curve which is the extension of curve OA

iii) At freezing point, water would normally freeze and form ice but by careful removal of solid particles which promotes this crystallisation, water may be cooled below it freezing point.

iv) Thus, by preventing water to freeze at its freezing point, it is possible to exist the vapour pressure.

2) Reduced Phase Rule Equation - Describe it.

→ i) For two components system when $C = 2$ substituting the value in Gibbs phase rule equation, we get,

$$F = C - P + 2$$
$$= 2 - P + 2$$
$$= 4 - P$$

ii) Minimum one phase is required to define the system at equilibrium i.e. when $p = 1$ and $f = 3$.
Thus for two component system, the max no. of degree of freedom is 3.

iii) The phase diagram for 2 component system can be represented by 3-D graph of temperature, pressure, composition.

iv) In practice, one of the three variables is kept constant and graph of 2 variable is considered. Hence, in such cases no. of degree of freedom get reduced by 1.
Thus, phase rule become.

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

This equation is called as Reduced Phase Rule equation.

v) When pressure is kept constant, the system is called condensed system. Hence, in such case reduced phase rule is also called as Condensed System.

3) What is Phase Rule? Explain the term phase and degree of freedom with example.

→ Phase Rule: i) The Phase Rule, given by Willard Gibbs, is defined as, in heterogeneous system, if equilibrium between phases are not influenced by gravity, magnetic & electrical forces, but are influenced only by pressure, temperature and concentration.

ii) Then the number of degree of freedom (F) of the system is related to number of components (C) and number of phases (P) by the following phase rule equation.

$$F = C - P + 2$$

a) Phase: i) It is defined as "any homogenous, physically distinct and mechanically separable portion of the system, which is separated from other such parts of the system by definite boundary surfaces".

ii) Examples: ① A heterogeneous mixture like $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$, consists of three phases

② A solution of a substance in a solvent consists of one phase only i.e. Sugar solution in water.

b) Degree of Freedom : i) The degrees of freedom in a particular situation is the number of independent co-ordinates required to completely specify the state of a system.

ii) The number of degrees of freedom is the number of independent intensive variables, i.e. the largest no. of properties such as temperature or pressure that can be varied simultaneously and arbitrarily without affecting one another.

iii) An example of one-component system is a system involving one pure chemical, while two component systems, such as mixture of water and ethanol, have two chemically independent components.

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4) State phase rule equation and explain the term component of phase with example.

→ Phase Rule : i) The phase rule, given by willard gibbs, is defined as, in heterogeneous system, if equilibrium between phases are not influenced by gravity, magnetic & electrical forces, but are influenced only by pressure, temperature and concentration.

ii) Then the number of degree of freedom (F) of the system is related to number of components (C) and number of phases (P) by the following phase rule equation.

$$F = C - P + 2$$

Component : i) It is defined as the smallest no. of independent variable constituent taking part in the state of equilibrium by means of which the composition of each phase can be expressed in the form of chemical equation.

ii) For a system, in equilibrium obeying phase rule the no. of component can't be negative or zero.

iii) Example, In water system, irrespective of the no. of phases, the composition of each phase is expressed by single constituent 'H_2O'. Hence, water system has one component.

iv) In sulfer system, irrespective of the phases, the composition of each phase is expressed by single constituent 'S'.

$$\text{Monoclinic Sulphur}_{(s)} \rightleftharpoons \text{Rhombic Sulphur}_{(s)} \rightleftharpoons \text{Vapour Sulphur}_{(s)}$$

v) In the thermal decomposition of solid $CaCO_3$ as -

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

5) Explain in detail, phase diagram of sulphur system.

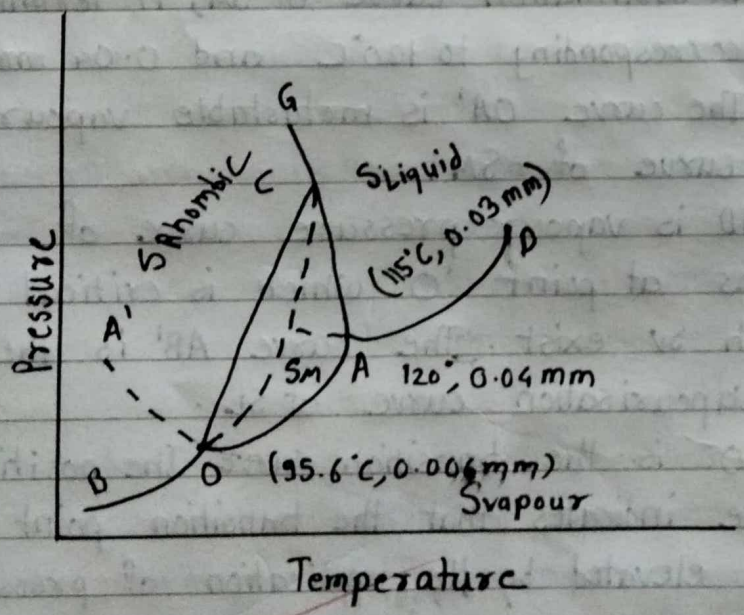
→ i) Rhombic Sulphur (S_R) $\rightleftharpoons$ Monoclinic Sulphur (S_M) $\rightleftharpoons$ Liquid Sulphur (S_L) $\rightleftharpoons$ Vapour Sulphur (S_V)

If P=1 then F=2 (Bivarient) : Need of 2 variable Pressure & Temp
If P=2 then F=1 (Monovarient) : Need of any 1 variable i.e Pressure/Temp

ii) For any system, degree of freedom is not negative, due to this reason, in sulphur system, the four phases are not in equilibrium & hence 3 phases are in equilibrium at a time.

iii) A system which exist 2 or more than 2 phases are in solid state, then it is called polymorphic system.

iv) In case of sulphur, rhomic sulphur and monoclinic sulphur exist in solid phase.



I) Area : i) BOAD (S_V), GCAD (S_L), GCOB (S_R), COA (S_M)
All these areas include only one phase hence, the degree of freedom are two i.e. temp & pressure needs to be specified in order to define the system.

II) Curves : i) The curves BO, OA, AD, OC, AC & CG comprise two phases in equilibrium and degree of freedom is one i.e. either temp or pressure needs to specified in order to define the system.

ii) The curve BO is the sublimation curve of S_R, it terminate at point B corresponding to 50°C which is the lowest limit, below which vapour pressure of S_R can't be measured.

iii) The point 'O' corresponding to 95.6C is a transition point where S_R and S_M are stable. In S_R, is heated rapidly, its transition into S_M doesn't occur and the curve extend upto B' which is the melting point of S_R.

iv) Hence, the curve OB' is the metastable vapour pressure curve of S_R.

v) AO curve is sublimation curve of S_M, it terminates at point A corresponding to 120°C and 0.04 mm pressure. The curve OA' is metastable vapour pressure curve of S_M.

vi) The curve AD is vapour pressure curve of , it terminates at point 'O' which is critical temperature below which Sv exist. The curve AB' is the metastable vapourisation curve of S_L.

vii) The curve OC is the transition curve. The positive slope of the curve indicates that the transition point bet^n S_R & S_L is elevated by the application of pressure. It also indicates that S_R is heavier than S_M. The curve terminate point C below which disappears.

viii) The curve AC is the melting point the curve S_M. The positive curve of slope indicate that the melting point of S_M is elevated by the increase of pressure and it also indicates S_M is heavier than S_L.

ix) The curve CG is melting point or freezing point curve of S_R. The curve CB' is the metastable vapourisation curve of S_R.

III) Triple Point: i) Triple point 'O' represents equilibrium S_R, S_M, S_V corresponding 95.6°C temperature and 0.006 mm pressure.

ii) Triple point 'A' represents the equilibrium bet^n S_M, S_L, S_V corresponding to 120°C temperature 0.04 mm pressure.

iii) Triple point 'C' represents the equilibrium bet^n S_M, S_L, S_R corresponding to 120°C temperature and 1288 atm pressure.

iv) Metastable triple point B' represents the equilibrium between S_R, S_M, S_V corresponding to 115°C and 0.03 mm pressure.

v) At triple point, since three phases are in equilibrium, degree of freedom is zero.

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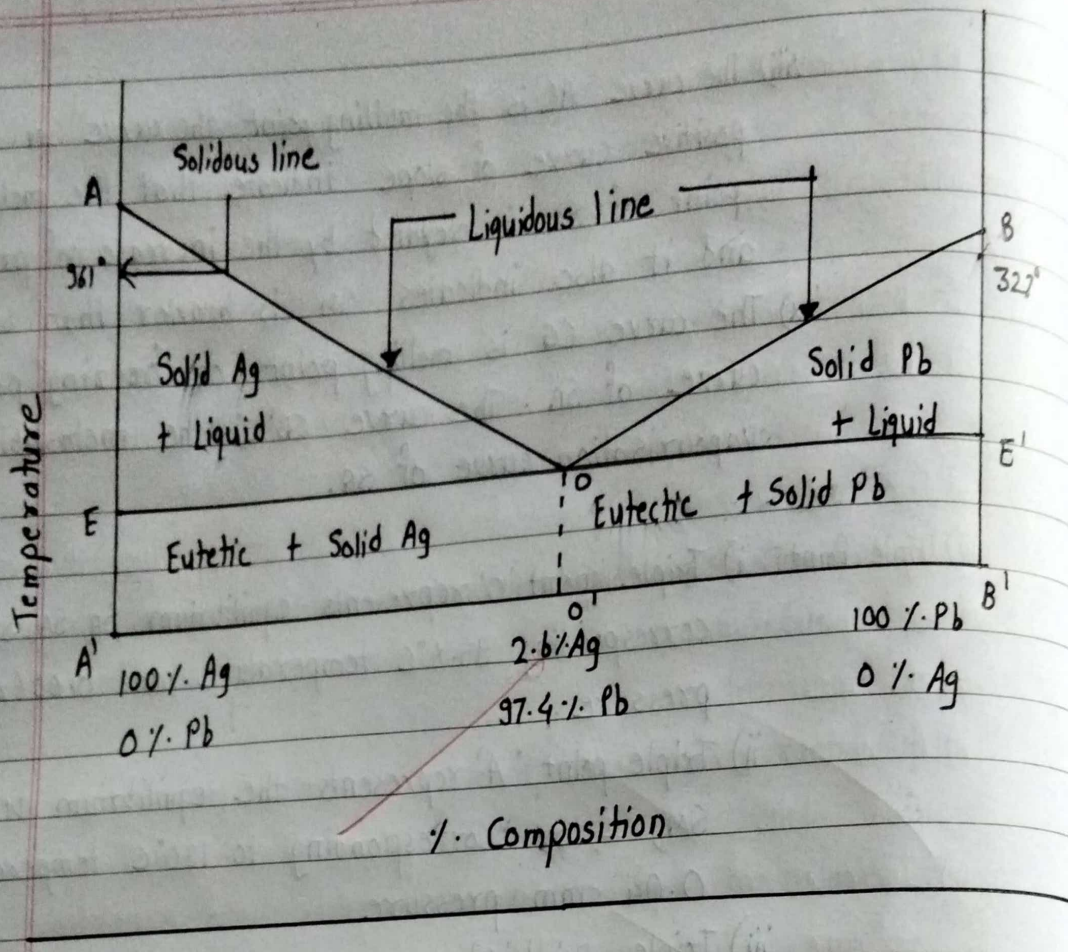
6) Describe phase diagram of 2 component system : Silver - Lead alloy.

→ i) It consist of two component system and 4 possible phases. Practically, gaseous phase is absent and effect of pressure is negligible. hence reduced phase rule is applicable : $F = 3 - P$

ii) Minimum 1 phase is required to define the system at equilibrium i.e. $p = 1$, $f = 2$. Thus Ag-Pb system, the degree of freedom is 2, they are temperature and percentage composition.



I) Area : i) Area AOB :

It consists of a single phase of liquid of Ag and Pb and degree of freedom are 2 i.e. both parameters composition and temperature needs to specify in order to define the system.

II) Curve : i) Curve AO :

It is freezing point of silver the curve starts from point A and 961°C which is melting point of Ag. It indicates that addition Pb to Ag, the melting point decreases gradually till point 'O' reach. At point 'O', no more lead can go in solution and if it is added its separate out as Solid Pb.

ii) Curve BO : It is freezzing point of Pb. The curve start from point B at 327°C which is melting point of Pb. It indicates that addition of Ag to Pb. The melting point of Pb decreases gradually along BO till point 'O' reach. At point 'O', no more Ag can go in solution and if it is added to separate out as solid Ag Along curve AO, solid Ag and liquid are in equilibrium while along curve, solid Pb and liquid are in equilibrium. Hence both curves has two phases. Degree of freedom is one i.e. either composition nor temperature needs to specified it in order to define the system.

Eutectic Point : i) The curve OA and OB meet at point 'O' called eutectic point of the system. At eutectic point all three phases that is, solid Ag, Pb and liquid co-exist in equilibrium. Hence, degree of freedom is zero. i.e. neither composition nor temperature needs to be specified in order to define the system.

ii) At eutectic point, the composition is 2.6 %. Ag and 97.4 %. Pb called eutectic composition where as temperature 303°C called eutectic temperatur