Deg II Chem. Hons Paper- III

Phase Rule (Two Component system)

The Phase rule equation

$$F = C - P + 2 \quad \text{—— (I)}$$

For a two component system reduces to

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

$$\therefore \boxed{F = 4 - P} \quad \text{—— (II)}$$

since the minimum number of Phases in any system is one, it is evident from equation (II) that the maximum degree of freedom in a two component system will be 3.

$$\boxed{F = 4 - 1 = 3} \quad \text{—— (III)}$$

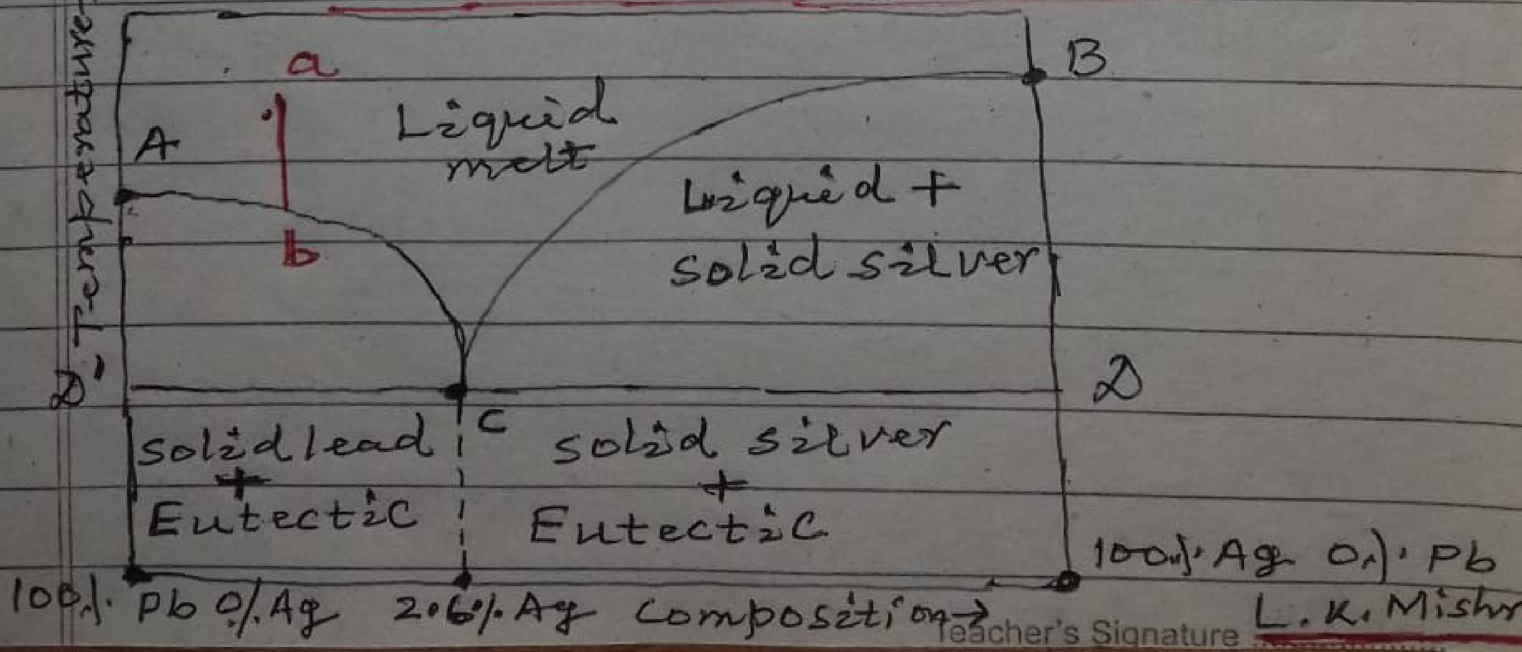
In addition to temperature and Pressure, therefore, a third variable composition has also to be taken into account. In order to represent the conditions of equilibrium graphically it is necessary to have three co-ordinate axes at right angles to one another. This will be three dimensional figures which which cannot be conveniently represented on Paper. It is therefore customary for graphic representation, assuming the third to remain constant. In the case of solid - liquid equilibria measurements are generally made at constant pressure. Therefore, one of the variables get fixed. This reduces the degree of freedom of the system by one. The phase rule equation for two component system is then written as

$$F = C - P + 1$$
$$= 2 - P + 1$$
$$\therefore \boxed{F = 3 - P} \quad \text{(IV)}$$

This expression is known as Reduced phase rule or Condensed Phase rule.

Solid - Liquid Equilibria :-

Lead - silver system



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As the experiment is being carried out at constant Pressure, the vapour phase is not considered and the condensed Phase rule is applied

$$F = C - P + 1$$

Curve AC :- A is the melting Point of Lead (327°C) when increasing quantity of pure silver are added to Lead metal, the freezing Point of Lead Lowers along the curve AC. Therefore, AC is the freezing Point curve of Lead.

Along the curve AC, the solid Lead is in equilibrium with the liquid melt. Thus the number of phases along this curve is two. As all measurements are made at atmospheric Pressure on applying condensed Phase Rule

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

Therefore the System is univariant. It means only composition varies along the curve AC

Curve BC :- Point B represents the melting Point of Pure silver (961°C) when increasing quantities of Pure Pb

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are added, the freezing Point of Ag lowers along the curve BC. Therefore, this curve is called freezing point curve of Ag. Again the solid Ag is in equilibrium with the liquid melt along along the curve BC. Thus there are two phases.

Applying the condensed phase rule equation we obtain

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

Again the curve BC like AC is univariant and only composition varies along this.

Eutectic Point C :—

The two curves AC and BC intersect each other at the eutectic point C. This point being common to both the curves represent the condition under which three phases solid silver, solid lead and liquid melt coexist. The degree of freedom here is zero, which is also supported by the reduced phase rule

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

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Thus the Point C is invariant. This Point C (300°c) lies at a temperature which is lower than the melting Point of silver as well as Lead metal.

The composition of an alloy of Lead (97.4%) and silver (2.6%) corresponding to the Point C is also fixed. Therefore, the Point C is called the eutectic Point i.e the lowest temperature at which liquid melt can exist.

The temperature corresponding to this Point is known as eutectic temperature and composition to this Point is known as eutectic composition.

Significance of Lead-silver system

The Phase diagram is utilised in the separation of silver from Lead in Pattinson's Process for desilverisation of Lead.

Suppose "a" represents the molten Argentiferous Lead containing a small amount of silver in it. Allow it to cool only temperature of the liquid melt falls.

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and there occurs no change in concentration till the Point "b" on the curve AC is reached.

On further cooling Lead begins to crystallise out the solution becomes richer in silver. Further cooling Lead begins to crystallise out and the solution becomes richer in silver on further cooling Lead begins to crystallise out, the solution becomes richer in silver. Cooling will continue along bc. Lead begins to crystallise and is constantly removed by means of Ladels

The liquid melt will be reacher in silver till the Point c is reached where an alloy containing 2.6% of Ag is obtained.

The above Process of decreasing the concentration of silver in "Argentiferrous Lead" is known as Pattinson's Process.

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