

I. DRAW A NEAT ONE COMPONENT WITH SYSTEM AND EXPLAIN ONE COMPONENT SYSTEM.

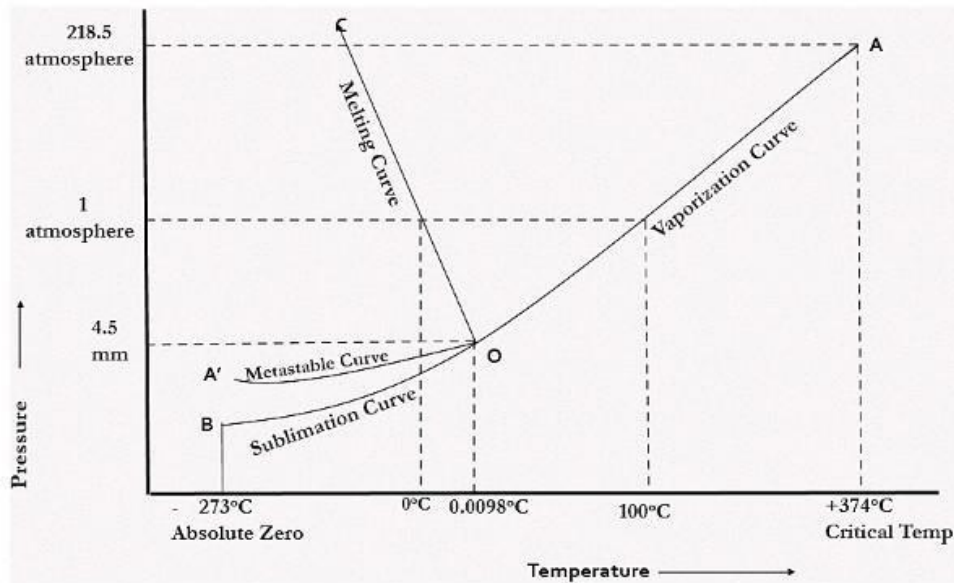
Water exists in three phases namely solid , liquid and vapor. Hence, there can be 3 forms in equilibria.

Solid \rightleftharpoons Liquid

Liquid \rightleftharpoons Vapour

Solid \rightleftharpoons Vapour

Each of the above equilibrium involves two phases. The phase diagram for the water systems is



1. Curve OA : [Vapourisation curve]

i) The curve OA is called Vapourisation curve

The equilibrium exist between water and vapour.

ii) At any point on the curve the following equilibrium will exist

Water \rightleftharpoons Water vapour (liq) (gas)

$$P=2 ; C=1 F$$

$$= C -P +2$$

$$F= 1 -2 +2$$

$$F = 1$$

a) The degree of freedom is one [univariant]

b) The equilibrium (line OA which extend upto the critical temperature (373⁰ C).

c) Beyond critical temperature the equilibrium will disappear only vapor exist.

2 . Curve OB ; [Sublimation curve]

The curve OB is called Sublimation curve of ice, it represents the equilibrium between solid (ice) and vapour

Ice \rightleftharpoons Vapour

a) The degree of freedom is one [univariant]

b) The equilibrium (line OB) will extend upto the absolute zero (-273⁰ C),

c) Where no vapour can be present and only ice will exist.

$$P=2 ; C=1$$

$$F= C -P+2$$

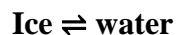
$$F = 1 -2 +2$$

$$F=1$$

3. Curve OC [Melting point curve] :

The curve OC is Melting point curve.

It represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.



- a) The degree of freedom is one [univariant]
- b) The curve Oc is slightly inclined towards y-axis (pressure). This, Shows that melting point of ice decreases with increase of pressure.

$$P = 2 \quad ; \quad C = 1$$

$$F = C - P + 2$$

$$F = 1 - 2 + 2$$

$$F = 1$$

4. Point 'O' (Triple Point)

The three curves OA , OB, OC meet at point 'O', where three phases namely solid, liquid and vapour are simultaneously at equilibrium.



- a) The degree of freedom is zero [non variant]
- b) Temperature = 0.0075°C
- c) Pressure = 4.58 mm at the point O.

$$P=2; C=1 .$$

$$F = C - P + 2$$

$$F = 1 - 3 + 2$$

$$F = 0$$

5. Curve OB' (Metastable equilibrium)

The curve OB' is vapour pressure curve of the super-cool or Metastable equilibrium
Where the following equilibrium will exist



- a) The degree of freedom is one [univariant]
- b) water cooled below 0°C without formation of ice that water is called super cooled water
- c) Super cooled water is unstable and can be converted to solid by seeding.

6. Areas (AOC , BOC , AOB)

AOC represents water ;

BOC represents Solid Ice;

AOC represents Vapour respectively.

- a) Only one phase exist at each area,
- b) So the degree of freedom is 2 , [Bivalent].

$$P=2; C=1.$$

$$F = C - P + 2$$

$$F = 1 - 1 + 2$$

$$F = 2$$

IV . DRAW THE PHASE - DIAGRAM OF LEAD - SILVER SYSTEM TWO COMPONENT SYSTEM AND EXPLAIN BRIEFLY WRITE ABOUT PATTISON'S PROCESS :

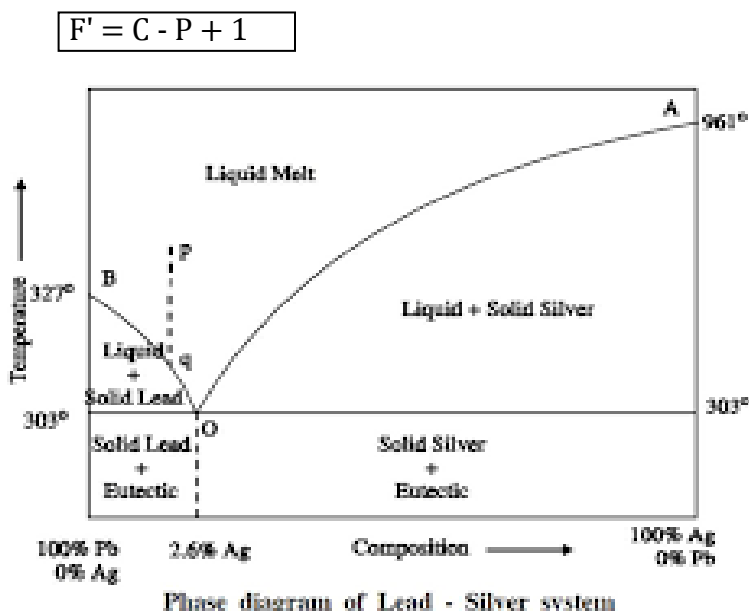
LEAD SILVER SYSTEM (Pb -Ag alloy):

This system has two components and four phases.

The phases are

- (i) Solid silver
- (ii) Solid lead
- lii)Solution of molten Ag &Pb and
- (iv) vapour.

The boiling points of Ag &Pb being considerably high, the vapour phase is practically absent. Thus Pb/Ag is condensed system with three phases. In such a case, pressure can have no effect on the system. Therefore we need only two variables, namely temperature (T) and composition (C).



1. Curve AO [Freezing Point curve of silver]

- A'' represents the melting point of pure Ag (961OC).
- The curve AC is the freezing point curve of Ag.
- Addition of Pb lowers the melting point of Ag along the curve AC.
- Along AC, solid Ag and liquid melt (solution of Ag &Pb) are in equilibrium.
- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 2 + 1 = 1$. Hence the system is univariant along the curve AC.
- **Solid Ag \rightleftharpoons Melt**

(S) (l)

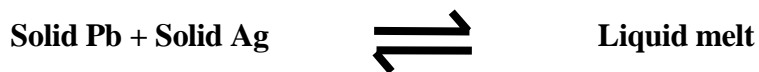
The degree of freedom is univariant [i.e. one]

2. Curve BO [Freezing Point curve of lead]

- B'' represents the melting point of pure lead ($\gamma\beta 70^\circ\text{C}$).
- The curve BC is the freezing point curve of Pb.
- Addition of Ag lowers the melting point of Pb along the curve BC.
- Along BC, the solid Pb and liquid melt (solution of Ag & Pb) are in equilibrium.
- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 2 + 1 = 1$. Hence the system is univariant along the curve BC.
- **Solid Pb \rightleftharpoons Melt**
- The degree of freedom is univariant [i.e. one]

3. Eutectic Point „C“:

- The curve AC and BC intersect at „C“ which is called eutectic point.
- Below the point „C“ both Pb & Ag exist in the solid state.
- At this point three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium.



- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 3 + 1 = 0$. Hence the system is nonvariant at point „C“.
- Eutectic point is the lowest possible temperature (303°C) in the system that corresponds to fixed composition (97.4% Pb & 2.6 % Ag), below which a liquid phase cannot exist and above which the solid phases disappear.
- The temperature and composition corresponding to the eutectic point „C“ are called eutectic Temperature and eutectic composition.
- A liquid mixture of two components – Ag & Pb, which has the lowest freezing point compared to all other liquid mixtures, is called eutectic mixture.

4.Areas:

- The area above ACB represents a single phase (solution of molten Pb & Ag).
- Applying reduced phase rule, $F'' = C - P + 1 = 2 - 1 + 1 = 2$. The system is bivariant.
- Area below AC represent the phases solid Ag + liquid melt, area below BC represents the phases solid Pb + liquid melt and area below .

DCE'' represents solid Pb + solid Ag.

All the three areas have two phases and hence the system is univariant.

$$(F'' = C - P + 1 = 2 - 2 + 1 = 1)$$

APPLICATIONS OF PATTINSONS PROCESS FOR THE DESILVERISATION OF ARGENTIFEROUS LEAD :

Pattinson's Process for the Desilverisation of Argentiferous Lead:

The process of recovery of silver from argentiferous lead is called as desilverisation. Argentiferous lead contain very small amount of silver (less than 0.1%). Desilverisation of lead is based on the formation of eutectic mixture.

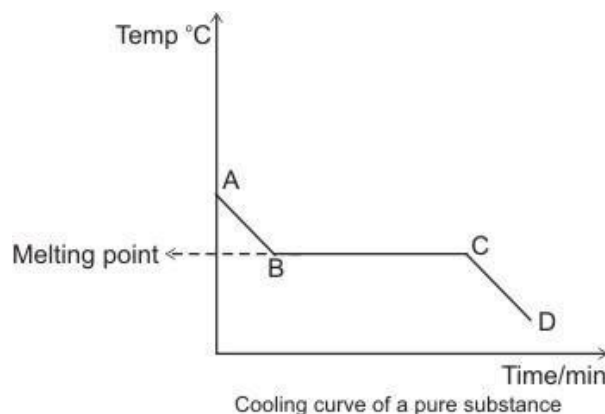
- Argentiferous lead is heated well above the melting point of pure lead (327°C) so that the system consists only of the liquid phase represented by the point "p" in the phase diagram.
- Then the liquid melt is allowed to cool gradually, the temperature of the melt falls along the dashed line "pq". As soon as the temperature corresponding to "q" is reached, solid lead begins to separate and the solution would contain relatively larger amount of silver.
- On further cooling, more and more of lead is separated along BO. At „O“, a eutectic mixture consisting of $\beta.6\%$ Ag and 97.4% Pb is obtained. The eutectic alloy is then treated for the recovery of silver profitably. The process of raising the relative proportion of Ag in the alloy is known as Pattinson's process.

V. WHAT IS THERMAL ANALYSIS ? DRAW THE COOLING CURVES OF PURE SUBSTANCES AND MIXTURE AND DISCUSS .

THERMAL ANALYSIS (OR) COOLING CURVE :-

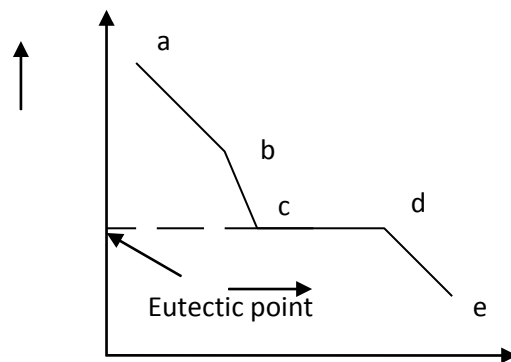
Thermal analysis is to method involving a study of the cooling curves of various compositions of a system during solidification.

Example 1 :- A pure substance in the fixed state is allowed to cool slowly and the temperature is noted at different intervals of time. The graph is plotted between temperature and time.



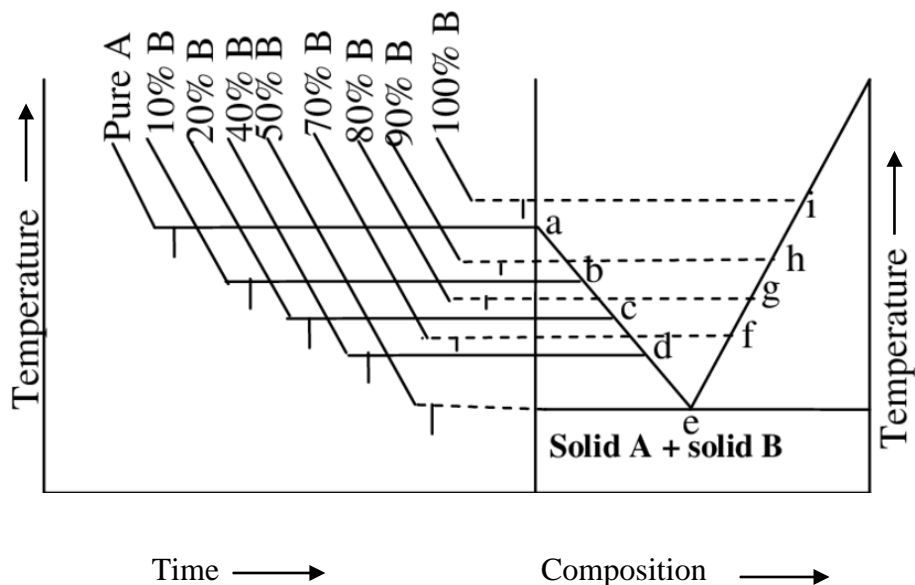
1. Initially the rate of cooling is continuous.
2. When it reaches the point 'b' Solid begins to appear , now the temperature remains constant untill the liquid melt is completely solidified.
3. At point 'C' solidification completes.
4. The lines ' bc ' represents equilibrium between the solid and liquid melt.
5. At point 'c' temperature of the solid begins to decrease along the curve 'cd'

Example 2:- If a mixture of two substances (A and B) in the fused state is allowed to cool slowly , the cooling curves is obtained in a similar manner.



- Initially the rate of cooling is continuous.
- When it reaches the point 'b' one substance (A or B) begins to solidify out of the melt, which is indicated by a break and rate of cooling is different.
- On further cooling at the break point 'c', the second compound also begins to solidify.
- Now the temperature remains constant, until the liquid melt is completely solidified, It forms Eutectic mixture (line cd)
- After the break point 'd' , cooling of solid mass begins .
- The temperature of horizontal line 'cd' gives eutectic temperature .

The experiment is repeated for different compositions of A and B the various cooling curves are recorded. From the cooling curves of various compositions, the main phase diagram can be drawn by taking composition in X-axis and the temperature in Y-axis.



USES OF COOLING CURVES

- Melting point and Eutectic point can be noted from cooling curve.
- The behavior of the compound can be clearly understood from the cooling curve.
- Percentage purity of the compounds can be noted from the cooling curve.
- The composition corresponding to its freezing point yields the composition of the alloy.
- The procedure of thermal analysis can be used to derive the phase diagram of any two component system.