MODULE -III

PHASE RULE AND COMPOSITES

3.3 Reduced Phase rule

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3.4.1 Thermal Analysis

3.4.2 Cooling curves

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3.6 Lead-silver system

3.3 REDUCED PHASE RULE (or) CONDENSED PHASE RULE

In a two component system, if the number of phase is 1, the maximum degree of freedom will be,

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

$F=3$ (Trivarient system)

To represent the conditions of equilibrium graphically, it requires 3 co-ordinates namely P, T and concentration. This requires 3-D diagram which cannot be represented on a paper. Hence any two of these 3 variables must be chosen for graphical representation. Thus for a Two Component alloy system, the experiments are always carried out under constant pressure.

Condensed Phase rule

The system in which only solid and liquid phase are considered and gas phase is neglected is called condensed system and the phase rule reduces to,

$F'=C-P+1$

3.4 Thermal Analysis and Cooling curves

3.4.1 Thermal Analysis

Thermal analysis is a branch of material science where the properties of materials are studied as they change with temperature.Thermal Analysis is a classical method of determining phase diagrams. By melting and cooling an alloy of known composition and plotting temperature-time curves, the final phase change temperature can be determined.

3.4.2 Cooling curves

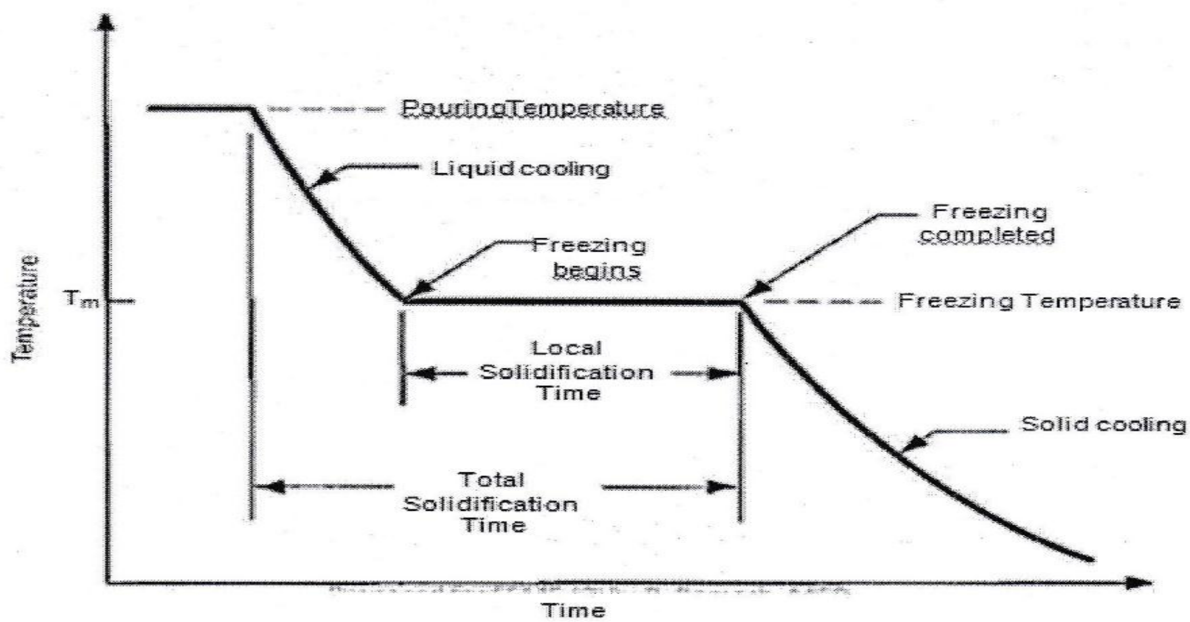
A cooling curve is a graphical plot of the changes in temperature with time for a material over the entire temperature range through which it cools.

It is one of the oldest and simplest methods to determine the phase diagram and phase transition. The freezing point, Eutectic point of a mixture can be deterinined easily.

Cooling Curve of Pure Metal

A pure substance in the fused state is allowed to cool slowly and the temperature is noted at regular intervals.The rate of cooling is continuous until the freezing point is reached.

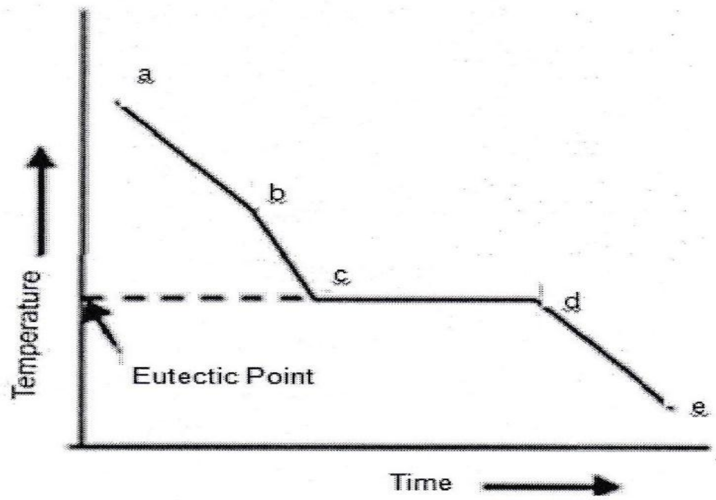
Formation of solid occurs and there is a break in the continuity of the cooling curve and the temperature remains constant until the liquid is fully solidified .When complete solidification occurs there will be a continuous fall in temperature.



Source: physical chemistry by Baul & Tuli

Cooling Curve of Mixture

When a mixture of two solids in the fused state is allowed to cool slowly and temperature is noted at different intervals.Initially the rate of cooling will be continuous.At point' b' when a solid phase begins to form, the rate of cooling curveexhibits a break and the temperature does not remain constant.The temperature decreases continuously until the eutectic point 'c' is reached .Now the temperature remams constant until complete solidification occurs. Thereafter, at the point 'd' the fall of temperature becomes uniform .



Source: physical chemistry by Baul & Tuli

Applications:

The melting point and eutectic temperature can be determined

The percentage of the compounds and its behaaviour can be found out.

The behaviour of the compound can be understood from the cooling curve.

To derive the phase diagram of any two component system.

3.5 Types of two component system

a).Simple Eutectic (Easy Melting) System

The two components are completely miscible in liquid state but completely immiscible in solid stateis called simple Eutectic system.

They do not react chemically. Of the two, the mixture having the lowest melting point is Eutectic mixture.(eg)Lead - Silver system

b). i) Formation of compound with congruent melting point

A compound is said to posses congruent melting point, if it melts exactly at a constant temperature into liquid having the same composition as that of the solid.(eg) Zn- Mg system

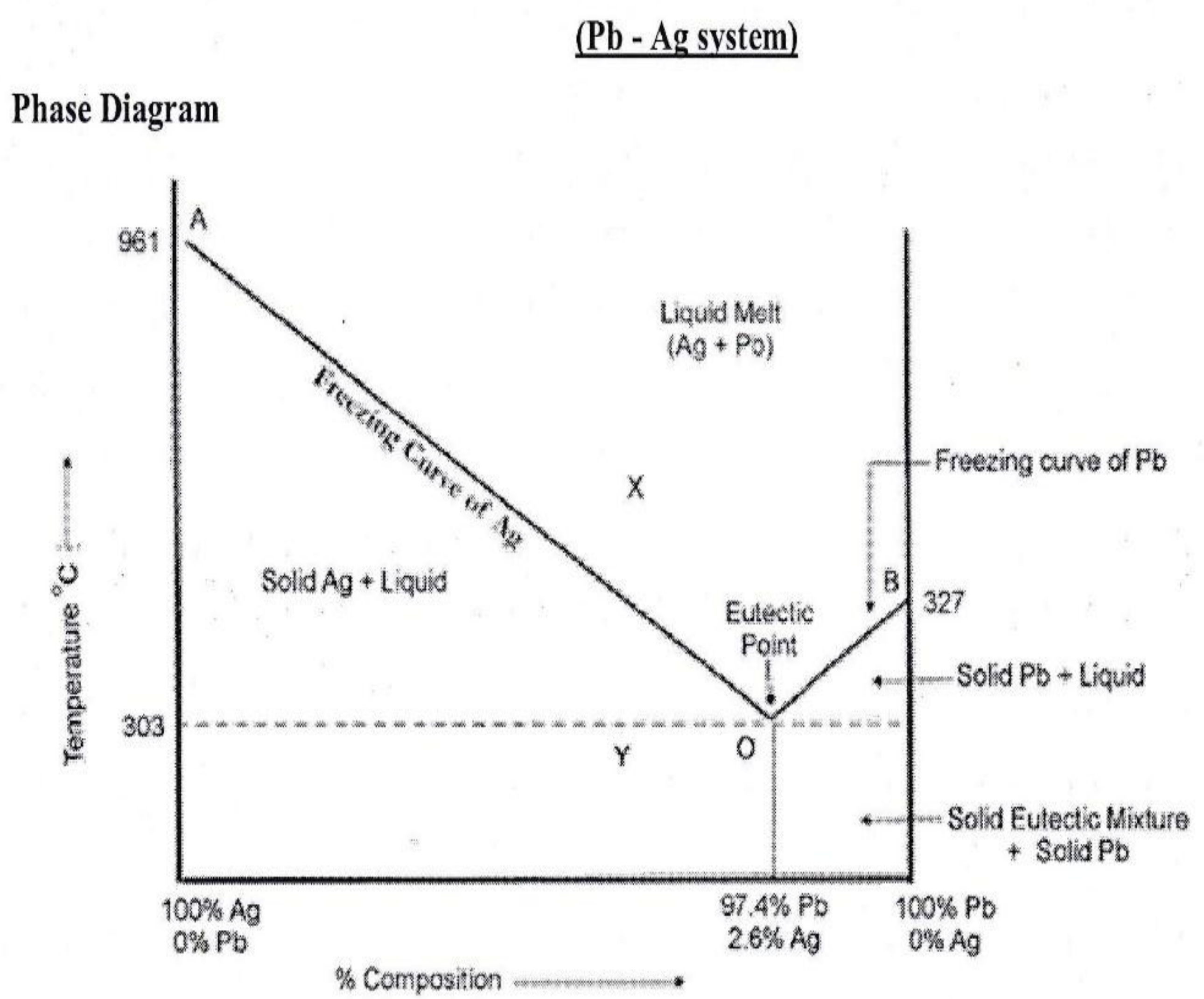
(ii) **Formation of compound with incongruent melting point**

A compound is said to posses' incongruent melting point, if it decomposes completely at a temperature below its melting point yielding a new solid phase with the composition different from that of the original. (eg) K- Na system

Formation of solid solution

In this type, when two substances especially metals are completely misible in both solid and liquid states, they form solid solution where mixing takes place in the atomic level.(eg) Cu – Ni system

3.6 LEAD-SILVER SYSTEM



Source: physical chemistry by Baul & Tuli

Curve AO	Curve BO	Point O
1) It is called Freezing point curve of silver.	It is called Freezing point curve of Lead.	The point 'O' is called Eutectic point.
2)' A' is the melting point of pure Silver(9610C)	'B' is the melting point of pure Pb (327.C)	Curve AO and BO meet at O at a temperature of 303^0c.
3)The melting point of silver decreases by the successive addition of Pb to silver.	The melting point of lead decreases by the successive addition of silver to lead.	Three phases (solid Ag, Solid Pb & liquid) are in equilibrium.
4)The equilibrium existing is, Liquid <-> Solid Ag Applying reduced phase rule, F'=C -P+l F' = 2-2 + 1 F' = l(univarient)	The equilibrium existing is,Liquid <-> solid Pb Applying reduced phase rule, F'=C-P+l F' = 2-2 + 1 F' = l(univarient)	The eutectic temperature at point O is 303c and eutectic co is 97.4% Pb and 2.6% Ag. solid Ag <->Solid Pb Applying reduced phase rule, F' = C-P+ 1 F' = 2-3 + 1=0 F' = 0 (nonvarient)

The system is studied under constant pressure, vapour phase is ignored and condensed phase rule is used.

Areas

AboveAOB	Area below AO, BO and 0
Area above AOB has single phase (liquid). Applying reduced phase rule, F' =C -P+ 1 F' = 2-1 + 1 F' = 2 (bivarient)	Area below AO, BO and 0 has two phases. Applying reduced phase rule, F' = C - P+ 1 F' = 2-2 + 1 F' = 1(univarient)

Application of Pb - Ag system

<u>Pattinson's process of desilverisation oflead</u>

Argentiferous lead (lead with small amount Ag) is heated to a temperature above its melting point (32TC) represented by point 'p' in the phase diagram.It is then cooled .The temperature falls down along 'pq'.As soon as 'q' is reached Pd crystallizes out. On further cooling, more and more Ph separates along BO. The melt become richer and richer in Ag until the point '0' is reached where the% of Ag rises to 2.6%.

Thus, raising the percentage of Ag in the alloy or removing Ag from lead is Pattinson's process.

<u>Difference between eutectic point and triple point</u>

Eutectic point	**Triple point**
It is the minimum temperature at which two solids and a liquid phase are in equilibrium. Solid A+ Solid B <-> Liquid	It is the temperature at which three phases are in equilibrium . Solid <-> Liquid <-> Vapour