

UNIT – III ALLOYS AND PHASE RULE

3.1) ALLOYS – PROPERTIES - SIGNIFICANCE:

Alloy is a homogeneous solid solution of two or more elements and metals. If they contain mercury, they are called amalgams.

(eg) Brass, Bronze, stainless steel, nichrome.

Properties of alloys:

1. Alloys are harder than their component metals.
2. Alloys are less malleable than their component metals.
3. Alloys are possessing lower melting points than their component metals.
4. Alloys possess low electrical conductivity.
5. Alloys show higher corrosion resistivity.

Need for alloys (or) Significance of alloys:

S.No	Purpose	Example
1	To increase hardness	Generally pure metals are soft, but their alloys are hard. 1. Arsenic is added (0.5%) to lead to increase the hardness of gun bullets. 2. Carbon is added (2%) to iron to increase hardness of steel.
2	To decrease melting point	Alloying makes the metal easily fusible. Wood's metal (Pb + Bi + Cd + Sn) is having reduced melting point around 60.5°C
3	To resist corrosion	Cr, Ni are added to Fe to make stainless steel which is having increased corrosion resistivity.
4	Better castability	The addition of metals produce alloys which are hard, fusible and expand on solidification and thus give good casting. 5 % Tin and 2 % antimony are added to lead for better castability to make printing type faces.
5	Modify colour	The dull coloured metals are improved by alloying with metals. Copper (red) + Zinc (White) → Brass (Bright white)
6	To modify chemical activity	Aluminium amalgam is more reactive than aluminium. Sodium amalgam is less reactive than sodium.

Functions and Effects of Alloying various elements:

S.No	Element	Effect on properties	Uses of alloys
1	Nickel	Fine grains are produced. Corrosion resistance is increased. Expansion coefficient is decreased.	Balance wheel making
2	Chromium	Corrosion resistance is increased. Tensile strength is improved. Hardness is increased.	Surgical instruments, Cutlery, Connecting rods.
3	Manganese	Abrasion resistance is increased. Thermal shocks are minimized.	Grinding wheels, Steering spindles.
4	Vanadium	Tensile strength is improved. Abrasion resistance is increased. Stress withstanding capacity is improved.	Axle, crank pins, Automobile forgings, Piston rods.
5	Molybdenum	Thermal shocks are minimized. Hardness is increased.	High speed tools
6	Tungsten	Fine grains are produced. Hardness is increased. Magnetic stability is increased.	Cutting tools, Permanent magnets

3.2) HEAT TREATMENT OF STEEL

The process of heating and cooling the alloys under controlled condition is known as Heat treatment. It alters certain physical properties of the alloys without changing the chemical composition.

Objectives / Purpose / Uses of heat treatment:

- a) Removal of imprisoned gases.
- b) Removal of internal stress and strain
- c) Refinement of grain structure.
- d) Improves magnetic and electrical properties.
- e) Improves corrosion resistance.

Types of heat treatment:

1. Annealing	2. Hardening	3. Tempering	4. Normalizing
5. Case hardening	6. Carburising	7. Nitriding	8. cyaniding

1. Annealing:

The meaning of annealing is softening. Heating the metal to high temperature and cooled slowly is called annealing.

Types of annealing:

a) Low temperature annealing (or) Process annealing: Heating the steel below its lower critical temperature is known as low temperature annealing or process annealing.

b) High temperature annealing (or) Full annealing: Heating the steel 50°C above the higher critical point is known as full or high temperature annealing. High carbon steel is annealed at 775°C, medium steel at 800°C and low carbon steel at 850°C.

Purpose of annealing:

Annealing increases machinability, ductility, shock resistance and softness.

Drawback:

Annealing process takes more time.

2. Hardening (quenching):

Heating the steel beyond critical temperature and cooling suddenly by immersing in oil or brine solution or water is hardening or quenching. The faster the rate of cooling harder will be the steel. High carbon steel and medium carbon steel can be quenched, but low carbon steel cannot be quenched.

Purpose of hardening:

- i) It increases strength and wear resistance.
- ii) It increases abrasion resistance. So, the steel can be used in cutting tools.

Drawbacks:

After hardening process, the alloy becomes more brittle.

3. Tempering:

Heating the already hardened steel below its hardening temperature and cooling it slowly is called tempering. For increasing the hardness, the hardened steel is reheated by 400 – 600°C. For decreasing the brittleness, the reheating temperature should be below 400° C.

Purpose of Tempering:

- i) Tempering process decreases brittleness and also used making for blades, clusters etc.,
- ii) It removes the stress and strain of the alloys produced during quenching process.

4. Normalising:

It is the quick high annealing process. Here the steel is heated above its critical temperature and cooled slowly in air. But, it will be harder than the annealed steel.

Purpose of Normalising:

- i) Normalized steel is suitable for the use in engineering works.
- ii) It recovers the homogeneity of the steel structure.
- iii) It removes the stress and strain.
- iv) It is faster than the annealing process.
- v) The normalized steel will be harder than the annealed steel.

5. Case hardening:

The process of obtaining a hard and wear resistance surface (case) is known as case hardening. Carburising, Nitriding and cyaniding are collectively known as case hardening.

6. Carburizing:

Mild steel + Charcoal (In a cast iron box) $\xrightarrow{950^{\circ}\text{C}}$ High carbon steel

Conversion of low carbon steel into high carbon steel by reacting it with charcoal at 950°C in a cast iron box is known as carburizing. At high temperature the carbon is absorbed to required depth of the alloy. The article is then cooled slowly within the iron box itself.

7. Nitriding:

Nitriding is the process of heating the metal alloy in presence of ammonia at 550°C . The ammonia dissociates to produce nitrogen. The nitrogen then combines with the surface of the alloy to form hard nitride alloy. This results in super hard surface.

Soft metal alloy + NH_3 $\xrightarrow{550^{\circ}\text{C}}$ Nitride alloy (Hard surface)

8. Cyaniding:

Here, the preheated steel is dipped into cyanide bath containing sodium cyanide, sodium carbonate and sodium chloride. To this bath, some carbon and nitrogen atoms are diffused. Its poisonous nature makes this method less common. Anyhow, the cyanide layer makes the alloy stronger and corrosion resistance.

3.3) FERROUS ALLOYS

Alloy is a homogeneous solid solution of two or more elements and metals. Alloys containing Fe as the main component are ferrous alloys. They also contain various alloying elements like Cr, Ni, Mn, Co and C. (eg) *Stainless steel, Nichrome*.

Properties of Ferrous alloys:

1. Ferrous alloys have high corrosion resistance
2. Ferrous alloys have high abrasion resistance
3. The distortion and cracking in their structure is less.
4. They show good formability and weldability.
5. They have high yield point and high strength.
6. They can withstand higher temperature.

Example -1) STAINLESS STEEL

Stainless steel is an alloy of Iron, chromium, nickel, molybdenum and carbon. The superior quality stainless steel contains more than 16% of chromium and 0.3 to 1.5% of carbon. The chromium forms dense, non-porous, tough film of chromium oxide at the surface of metal. This layer resists corrosion by atmospheric gases. So, this is otherwise known as corrosion resistant steel. Even if the layer cracks, it gets automatically healed-up by atmospheric oxygen.

Types of stainless steel:

- a) Heat treatable stainless steel
- b) Non heat treatable (Magnetic, Non magnetic)

a) Heat treatable steel:

Composition:

If Carbon % is high, it is heat treatable stainless steel. These steels contain upto 1.2% of carbon and 12-16% of chromium.

Properties:

1. They possess magnetic properties.
2. They can be used in cold condition.
3. They are tough.

Uses:

1. They withstand up to 800°C.
2. They have good water resistance.
3. Used for surgery instruments, blades and scissors.

b) Non - Heat treatable steel:

If Carbon percentage is less, it is non-heat treatable steel. There are two types of non-heat treatable steel.

i) Magnetic type

Composition: It contains 22% chromium and 0.35% carbon .

Properties:

1. It can be forged, rolled and machined.
2. It has high corrosion resistivity.

Uses: It is used in automobile parts, chemical equipment.

ii) Non- magnetic type

Composition:

Non magnetic type stainless steel contains 18 – 26 % chromium, 8 to 21% nickel and 0.15% carbon. But the total percentage of Cr and Ni should always be more than 23.

18 / 8 steel is the most widely used non-magnetic type stainless steel. It contains 18% chromium and 8% steel.

Properties:

1. It shows very high resistance to corrosion.
2. Its corrosion resistivity is further enhanced by adding small quantity of Molybdenum.

Uses:

1. 18/8 steel is used in house hold utensils.
2. It is used in sinks.
3. It is used in dental and surgical instruments.

Example -2) NICHROME

Nichrome is a Ferrous alloy with Nickel and Chromium.

Composition	Percentage
Nickel	60%
Chromium	12%
Iron	26%
Manganese	2%

Properties:

1. When the Chromium content is high (16 – 20%) with lower carbon content (less than 0.15%) such Nichrome variants are having good heat resistance up to 900⁰ C.
2. It is having high corrosion resistance.
3. It is having very high melting point.
4. It possesses high electrical resistance.

Uses:

1. Nichrome is used for making heating elements in stoves.
2. They are used in resistance coils in electrical appliances.
3. Nichrome is used in boiler parts, steam lines, gas turbines, annealing boxes.
4. Nichrome is used to prepare machineries working at high temperatures.

3.4) INTRODUCTION – PHASE RULE – TERMS & DEFINITIONS:

1.PHASE RULE :

If a system in an equilibrium is not affected by gravitational , electrical and magnetic forces and is dependent on temperature , pressure and concentration , then the phase rule for such system is given by, $F = C - P + 2$,

where F = degree of freedom , C = component , P = Phase

2 indicates the variables pressure and temperature.

2. PHASE (P):

Phase is defined as “ the homogeneous, physically distinct , mechanically separable portion of a system, which is separated by definite boundaries from other portions” .

There are three phases: Solid , liquid , gaseous. Solids are completely immiscible. Liquids may or may not be miscible. Gases are completely miscible.

E.g) i) Sugar solution, salt solution , Water and alcohol – single phase

ii) Saw dust solution – two phase

iii) $\text{Ice}_{(s)} \leftrightarrow \text{water}_{(l)} \leftrightarrow \text{vapour}_{(g)}$ Three phases.

iv) $\text{CaCO}_{3(s)} \leftrightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$ Three phases.

3. COMPONENT (C):

It is the smallest number of independently variable constituents by means of which the composition of each phase can be expressed in the form of a chemical equation.

One component systems:

1. $\text{Ice}_{(s)} \leftrightarrow \text{water}_{(l)} \leftrightarrow \text{vapour}_{(g)}$, there are three phases. But they can be expressed by a single formula H_2O . So, it is an one component system.

2. Monoclinic sulphur_(s) ↔ orthorhombic sulphur_(s) ↔ liquid sulphur_(l) ↔ gaseous sulphur_(g)

There are four phases, but all of them are represented by same formula S.

3. (Special case) $\text{NH}_4\text{Cl}_{(s)} \leftrightarrow \text{NH}_{3(g)} + \text{HCl}_{(g)}$,

two phases , but when NH_3 and HCl are in equal quantity, then it is equal to NH_4Cl . So, all the phases are expressed by a single formula NH_4Cl .

Two component system:

1. $\text{CaCO}_{3(s)} \leftrightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$ Three phases.

This thermal decomposition of CaCO_3 can be expressed in terms of any two of the three components present.

Using CaCO ₃ & CaO		Using CaCO ₃ & CO ₂		Using CaO & CO ₂	
CaCO ₃	CaCO ₃ + 0 CaO	CaCO ₃	CaCO ₃ + 0 CO ₂	CaCO ₃	CaO + CO ₂
CaO	0 CaCO ₃ + CaO	CaO	CaCO ₃ - CO ₂	CaO	CaO + 0 CO ₂
CO ₂	CaCO ₃ - CaO	CO ₂	0 CaCO ₃ + CO ₂	CO ₂	0 CaO + CO ₂

So, it is a two component system.

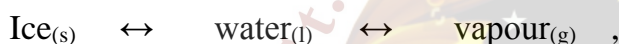


4. DEGREE OF FREEDOM:

The minimum number of independently variable factors (P,T,C) that must be fixed in order to define the system completely is known as degree of freedom.

$$F = C - P + 2, \text{ where } F = \text{degree of freedom}, C = \text{component}, P = \text{Phase}$$

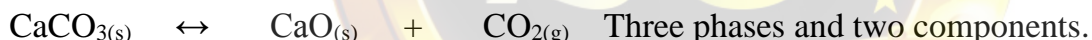
a) If $F=0$, it is **non variant** system.



There are three phases. But they can be expressed by a single formula H₂O. So, it is one component system.

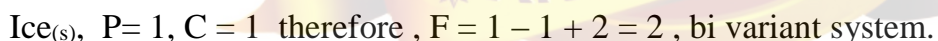
$$F = C - P + 2, F = 1 - 3 + 2 = 0, \text{ non variant system.}$$

b) If $F = 1$, it is **uni variant** system.



$$F = C - P + 2, F = 2 - 3 + 2 = 1, \text{ uni variant system.}$$

c) If $F = 2$, it is **bi variant** system.



5a. MERITS OF PHASE RULE:

1. Applicable to any kind of equilibrium.
2. We can classify the equilibrium system as uni, bi, non variant systems based on F.
3. Based on C, we can classify the system as one component, two component systems.
4. Used to know about whether the systems are in equilibrium or not.
5. It suggests that different systems with same F value will behave similarly.
6. As it deals with macroscopic systems, molecular level details are not needed.

5b. DEMERITS OF PHASE RULE:

1. Applicable only to equilibrium systems.
2. Not applicable for finely divided solids and liquids.
3. No allowances for gravity, magnetic force, electrical force and time.

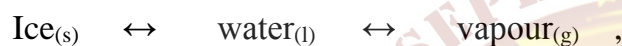
3.5) PHASE DIAGRAM – FOR ONE COMPONENT SYSTEM (WATER)

If any two degrees of freedom are plotted against each other, it is called as a **phase diagram**. For one component system it is plotted between Pressure Vs Temperature (P-T), For two component system it is between Temp and Concentration (T-C).

Uses of Phase diagram:

- a) We can understand the properties of materials in the equilibrium by phase diagram.
- b) Using phase diagram, study of Soldering materials can be done.
- c) Study of phase separation, solidification of metals, and change of structure during heat treatment.

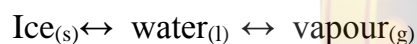
One component system – Eg. Water system:



There are three phases. But they can be expressed by a single formula H_2O . So, it is an one component system.

Explanation of Water system Phase diagram:

1. Triple point (O): The point at which all the three phases, solid , liquid and gases are co existing is known as triple point.



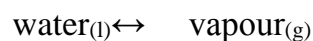
$$F = C - P + 2$$

$$F = 1 - 3 + 2 = 0,$$

Non variant,

For water system, triple point conditions are 0.0075°C temperature and 4.58mm of Hg pressure.

2. Vapourisation curve (OA): Along this curve water and its vapour are in equilibrium. The point A corresponds to critical temperature (374°C) and critical pressure (218 atm). Beyond this point only vapour will exist.

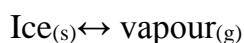


$$F = C - P + 2$$

$$F = 1 - 2 + 2 = 1,$$

Uni variant,

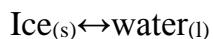
3. Sublimation curve (OB): Along this curve ice and its vapour are in equilibrium. Point B corresponds to absolute temperature (-273°C) below which only ice will be present.



$$F = C - P + 2$$

$$F = 1 - 2 + 2 = 1, \text{ Uni variant,}$$

4. Melting curve (OC) : Along this curve, water and ice are in equilibrium. This curve is slightly inclined towards pressure axis. This shows the melting point of ice decreases with increase in pressure.



$$F = C - P + 2$$

$$F = 1 - 2 + 2 = 1, \text{ Uni variant,}$$

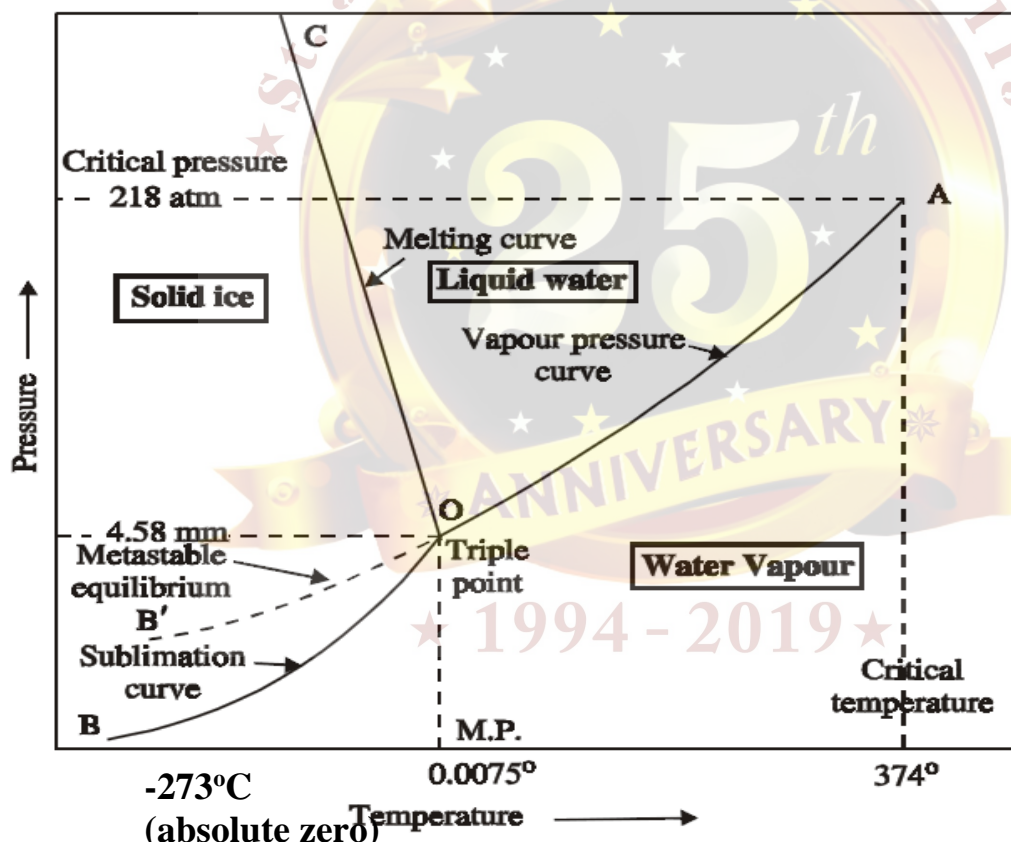
5. Metastable equilibrium (OB'): If Water is cooled below 0°C without ice formation; Such water is known as super cooled liquid. This state is highly unstable. Even a slight disturbance will cause ice formation. Along this curve super cooled water and its vapour are in equilibrium.



$$F = C - P + 2$$

$$F = 1 - 2 + 2 = 1, \text{ Uni variant,}$$

Phase diagram:



6. In Area AOC only liquid water exists.

Water

$$F = C - P + 2$$

$$F = 1 - 1 + 2 = 2,$$

Bi variant,

7. In area AOB only water vapour exists.

Vapour

$$F = C - P + 2$$

$$F = 1 - 1 + 2 = 2,$$

Bi variant,

8. In area BOC only solid ice exists.

Ice

$$F = C - P + 2$$

$$F = 1 - 1 + 2 = 2, \text{ Bi variant,}$$

Conclusion:

1. Point O is non variant.
2. Curves OA, OB, OC, OB' are uni variant.
3. Areas AOB, AOC, BOC are bi variant.

3.6) BINARY / TWO COMPONENT SYSTEMS –TYPES

There are three types of two component system.

- i) Solid solutions
- ii) Congruent and Incongruent system
- iii) Eutectic system

i) Solid solutions:

If the two components are miscible in solid and liquid phases, it is solid solution.

Eg. Cu – Ni system

ii) Congruent and Incongruent system:

On melting if the compound retains its original composition, it is called congruent compound.

Eg. Zn – Mg system.

If they do not retain their original composition it is incongruent system. eg. Au-Sb system

iii) Eutectic system:

If the two components are immiscible in solid state and miscible in liquid state, chemically non reactive with each other such system is known as eutectic system.

Eg. Pb – Ag system , Bi – Cd system

REDUCED PHASE RULE (CONDENSED PHASE RULE)

For a two component system with a single phase, the phase rule is

$$F = C - P + 2$$

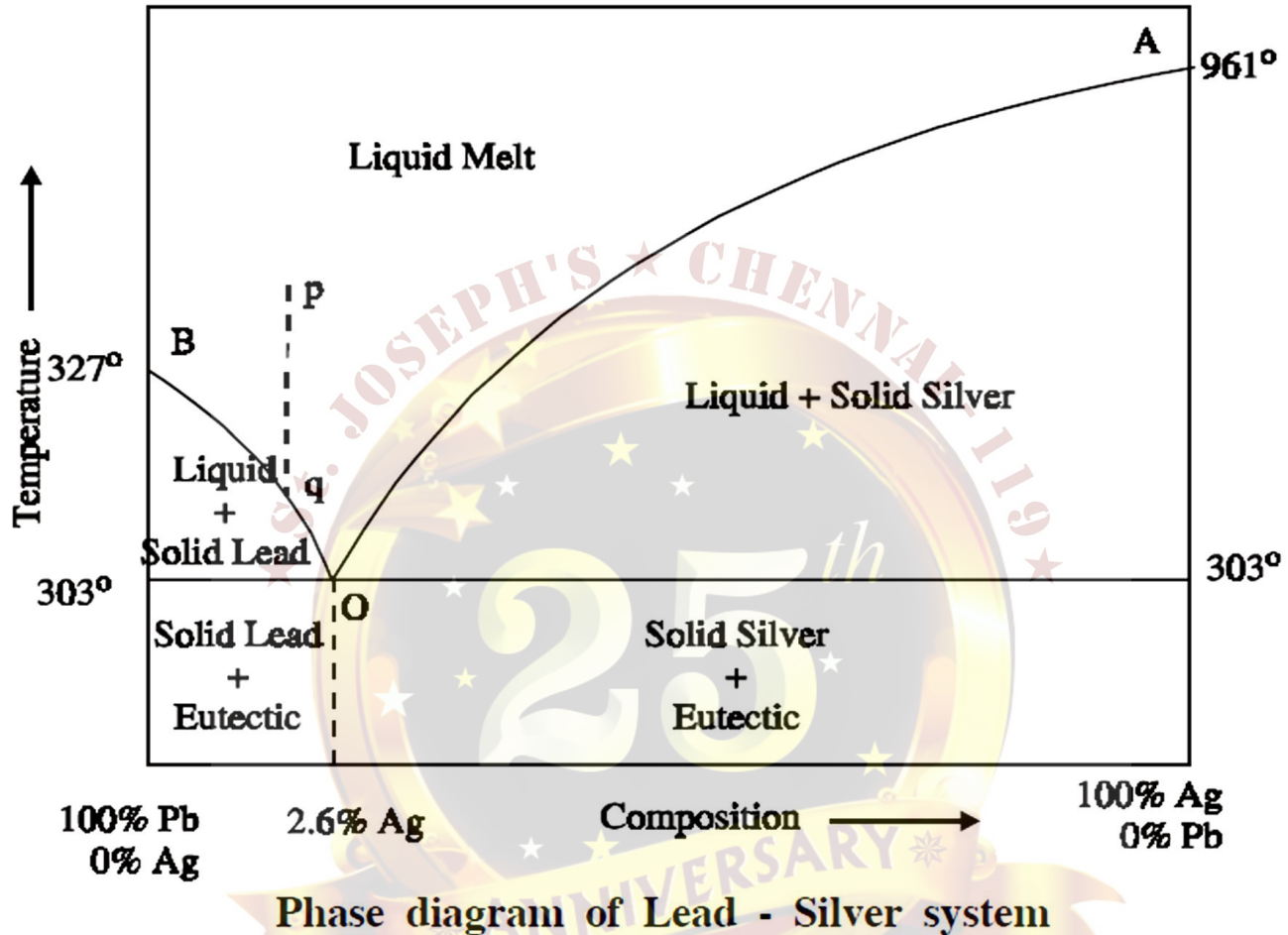
$$= 2 - 1 + 2 = 3$$

Then, the phase diagram will be complicated and three dimensional. To avoid this complication, we are assuming the system contains only solid and liquid. So, the effect of pressure is excluded. Then, the phase rule is reduced to, $F' = C - P + 1$, This is known as condensed phase rule or reduced phase rule, which is applicable for all two component systems.

3.7) PHASE DIAGRAM FOR TWO COMPONENTS SYSTEM – EUTECTIC SYSTEM (LEAD – SILVER (Pb / Ag) ALLOY SYSTEM)

If the two components are immiscible in solid state and miscible in liquid state, chemically non reactive with each other, such system is known as eutectic system.

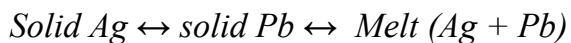
Eg. Pb – Ag system , Bi – Cd system



Explanation of Lead silver system Phase diagram:

1. Eutectic point (O):

The temperature at which solid A and solid B are in equilibrium with their melt is known as eutectic point.



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

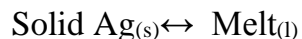
$$F' = 2 - 3 + 1 = 0$$

Non variant,

For Pb- Ag system, Eutectic point conditions are 303°C temperature and Composition of 97.4% Pb and 2.6% Ag.

2. Melting point curve (OA) for silver:

Along this curve Solid Ag and its melt are in equilibrium. Melting point of Ag is 961°C.

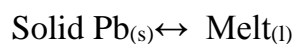


$$F' = C - P + 1$$

$$F' = 2 - 2 + 1 = 1 \text{ Uni variant,}$$

3. Melting point curve (OB) for Lead:

Along this curve Solid Pb and its melt are in equilibrium. Melting point of Pb is 327°C.



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

$$F' = 2 - 2 + 1 = 1 \text{ Uni variant,}$$

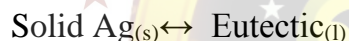
4. In Area AOB only Melt exists.

Melt

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

$$F' = 2 - 1 + 1 = 2 \text{ Bi variant,}$$

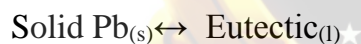
5. In area under OA curve, Solid Ag and Eutectic are in equilibrium.



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

$$F' = 2 - 2 + 1 = 1 \text{ Uni variant,}$$

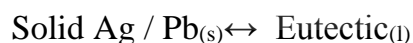
6. In area under OB curve, Solid Pb and Eutectic are in equilibrium.



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

$$F' = 2 - 2 + 1 = 1 \text{ Uni variant,}$$

7. In area under Point O, Solid Ag/Pb and Eutectic are in equilibrium.



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

$$F' = 2 - 2 + 1 = 1 \text{ Uni variant.}$$

Conclusion:

1. If the two components are immiscible in solid state and miscible in liquid state, chemically non reactive with each other, such system is known as eutectic system. Out of the various compositions, the mixture with the lowest melting point is known as eutectic mixture. (Eg. Composition of 97.4% Pb and 2.6% Ag)

2. Point O is Non variant.

3. Curves OA, OB, Areas Under OA, OB and Point O are Univariant.

4. Area AOB is bi variant.

Applications of Eutectic systems:

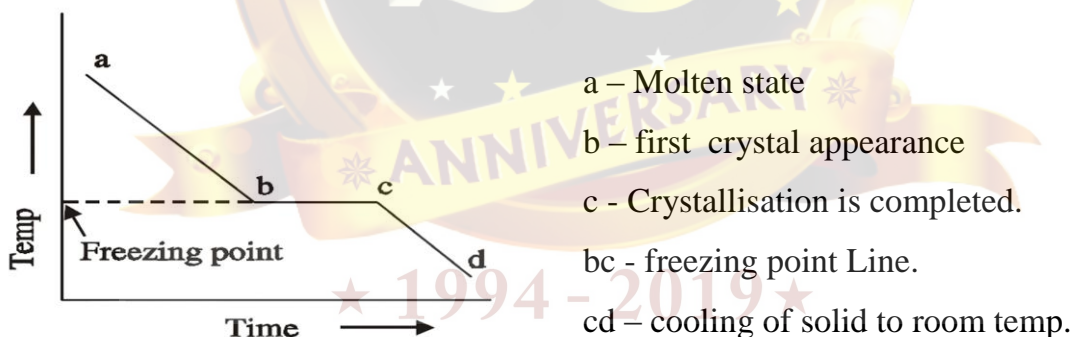
1. Used in solder manufacturing. Solders are used in joining metal parts.
2. It is used in Pattinson's process. If the mixture contains 99.9% Pb and 0.1% Ag, it is not considered as eutectic mixture. For this Pb is heated above its melting point 327°C (point p). Then it is cooled along pq line. The molten lead solidifies and separates out. So, proportion of Ag increases. The process is repeated until we get the required eutectic composition i.e 2.6%. Thus the process of raising the relative proportion of Ag in the alloy is known as Pattinson's process.

3.8) CONSTRUCTION OF PHASE DIAGRAM BY THERMAL ANALYSIS AND COOLING CURVE METHOD:

Thermal analysis is the study of the cooling curves of various compositions of a system during solidification. The cooling curves are plotted between temperature and time.

Case (i) :

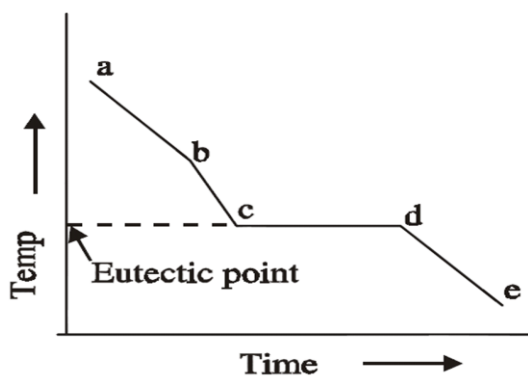
- 1) A pure substance M is taken and fused at very high temperature. This is denoted as A.
- 2) Then it is allowed to cool. Initially the rate of cooling is continuous and fast. When it reaches B, solid begins to appear.
- 3) Now temperature remains constant up to C.
- 4) At this line BC, Solid \leftrightarrow melt. This is called Freezing point line.
- 5) After C, the temperature begins to decrease along CD.



Cooling curve of pure solid

Case (ii) :

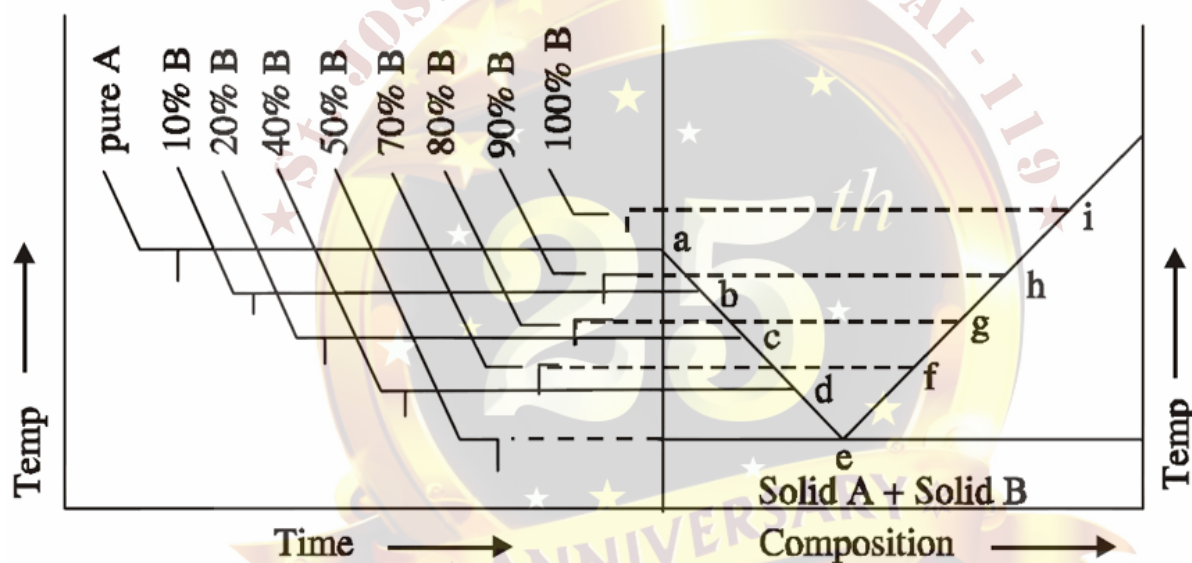
- 1) Mixture of metals A+B are taken and heated.
- 2) At point a, they are in molten state.
- 3) At point b, metal A crystallizes first.
- 4) At point c, metal B also crystallizes. Then the temperature remains constant up to d.
- 5) Along this line cd, Solid A \leftrightarrow solid B \leftrightarrow Melt (l).
- 6) This is called eutectic point line. After D, the temperature begins to decrease along DE. **61**



- Molten state of A and B
- first crystal of A appears
- first crystal of B appears
- Crystallisation of A and B over.
- cd - Eutectic point Line.
- de – cooling of solids to room temp.

Cooling curve of a mixture A+B

The experiment is repeated by varying the % of A and % of B and a plot of Temp (Vs) composition is drawn as shown below. This is called construction of phase diagram.



Cooling curve of various compositions of two solids

Uses of cooling curves:

- i) For constructing a phase diagram.
- ii) For determining freezing point, melting point and eutectic point.
- iii) For determining the % purity of compounds.
- iv) For studying the behaviour of various metals and their alloys.