Module III

PHASE RULE

3.2 Introduction

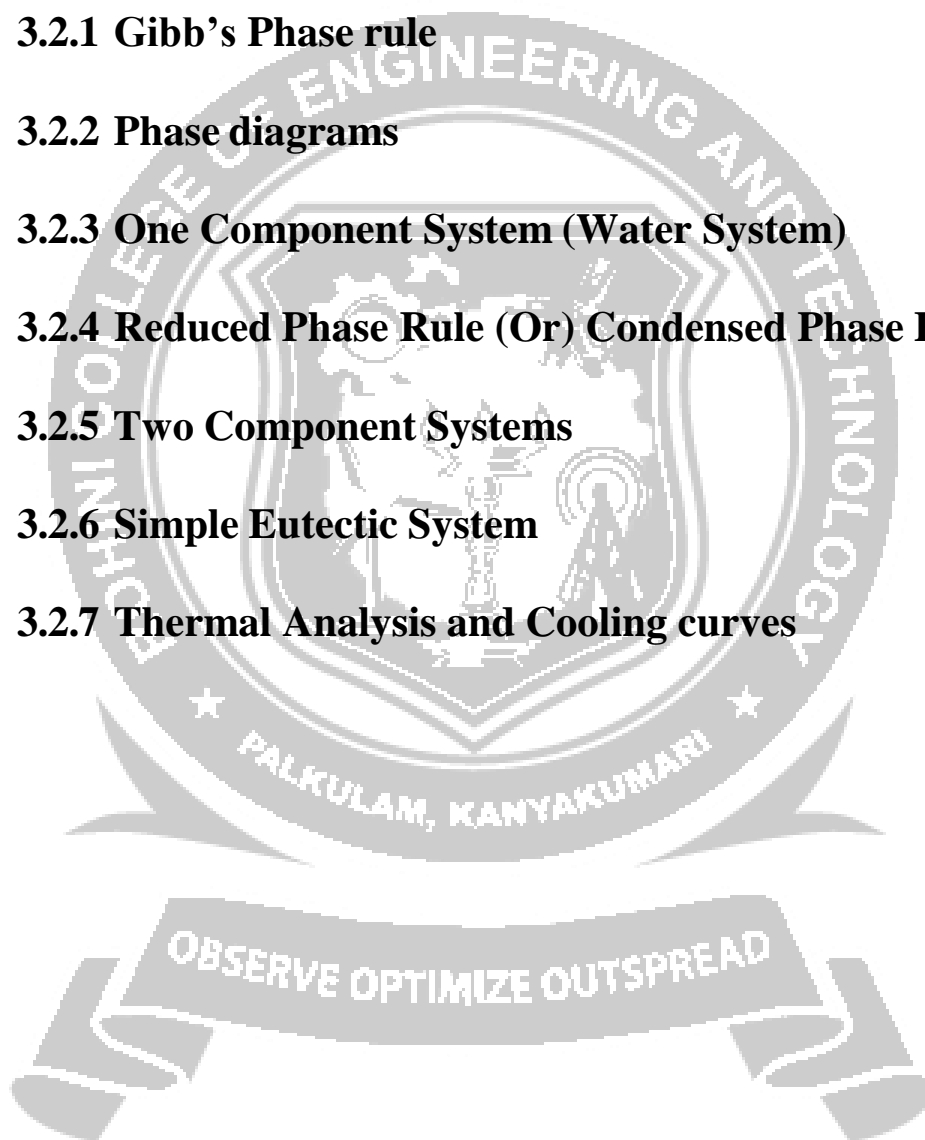**3.2.1 Gibb's Phase rule**

3.2.2 Phase diagrams

3.2.3 One Component System (Water System)

3.2.4 Reduced Phase Rule (Or) Condensed Phase Rule

3.2.5 Two Component Systems

3.2.6 Simple Eutectic System

3.2.7 Thermal Analysis and Cooling curves

3.2 Introduction

Generally, the reactions are classified into reversible and irreversible reactions. Further the reversible reactions are classified into two types based on the nature of the reactants and products. They are homogeneous reversible reactions and heterogeneous reversible reactions.

Homogeneous reversible reactions – reactants and products exist in same phase.

Heterogeneous reversible reactions - reactants and products exists in different phases.

The homogeneous reversible reactions can be explained by the Law of mass action and the behavior of heterogeneous reversible reactions can be studied by the Phase rule, which was proposed by Josiah Willard Gibbs in 1874.

3.2.1 Gibb's Phase rule

The heterogeneous system in equilibrium that is not influenced by gravity or electrical or magnetic forces, but is influenced by pressure, temperature and concentration, then the degree of freedom of the system is related to number of components(C) and number of phases (P) by the phase rule equation,

$$F = C - P + 2$$

Phase (P)

Any homogeneous, physically distinct and mechanically separable portion of a system which is separated from other parts of a system by a definite boundary is known as a phase.

It is classified into (a) gaseous phase, (b) liquid phase, (c) solid phase.

(a) Gaseous phase

All gases are completely miscible – so mixture of gases forms a single phase.

(b) Liquid phase

It depends on the number of liquids present and their miscibility.

Two miscible liquids – then 1 liquid phase and 1 vapour phase (Alcohol – water).

Two immiscible liquids – hen 2 liquid phases and 1 vapour phase (Benzene – water)

(c) Solid phase

Each solid contributes to a separate phase.

Examples of phases

S.No.	Examples of reactions	Number of phases
1.	Ice(s) $\rightleftharpoons$ water(l) $\rightleftharpoons$ vapour(g)	3
2.	Rhombic sulphur(s) $\rightleftharpoons$ monoclinic sulphur(s)	2
3.	$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$	3
4.	$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	3
5.	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	1

Component(c)

The smallest number of independently variable constituents by means of which the composition of each phase in taking part in a chemical equilibrium can be expressed in the form of a chemical equation is known as a component.

Examples of components

S.No.	Reactions	Number of components
1.	Ice(s) ⇌ water(l) ⇌ vapour(g)	1
2.	Rhombic sulphur(s) ⇌ monoclinic sulphur(s)	1

Degree of freedom (F)

The minimum number of independently variable factors such as temperature, pressure and composition of phases which must be fixed to define the system completely is known as degree of freedom. It is given by the expression, **F = C – P + 2.**

Examples of degree of freedom

S.No.	Examples of reactions	P	C	F = C – P + 2	F
1.	Ice(s) ⇌ water(l) ⇌ vapour(g)	3	1	F = 1 – 3 + 2	0
2.	Rhombic sulphur(s) ⇌ monoclinic sulphur(s)	2	1	F = 1 – 2 + 2	1
3.	$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$	3	2	F = 2 – 3 + 2	1
4.	$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	3	2	F = 2 – 3 + 2	1
5.	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	1	2	F = 2 – 1 + 2	3

If,

F = 1 (Univarient system)

F = 2 (Bivarient system)

F = 3 (Trivarient system)

F = 0 (Invarient system)

Uses (or) merits of phase rule

1. It is applicable both physical and chemical equilibria.
2. It is a convenient method of classifying the equilibrium states in terms of phases, components and degree of freedom.
3. It helps in deciding whether the given number of substances remains in equilibrium or not.

Limitations of phase rule

1. Phase rule can be applied only for systems in equilibrium.
2. Only three variables like P, T, & C are considered, but not electrical, magnetic and gravitational forces.
3. All the phases of the system must be present under the same conditions of pressure and temperature.
4. Solid and liquid phases must not be in finely divided state, otherwise deviations occur.

3.2.2 Phase diagrams

Phase diagram is a graph obtained by plotting one degree of freedom against another.

Types

1. **P – T diagram**

   If the phase diagram is plotted between **temperature against pressure**, then the diagram is called **P – T diagram**. (eg) One component system.

2. **T – C diagram**

   If the phase diagram is plotted between **temperature against composition**, then the diagram is called **T – C diagram**. (eg) Two component system.
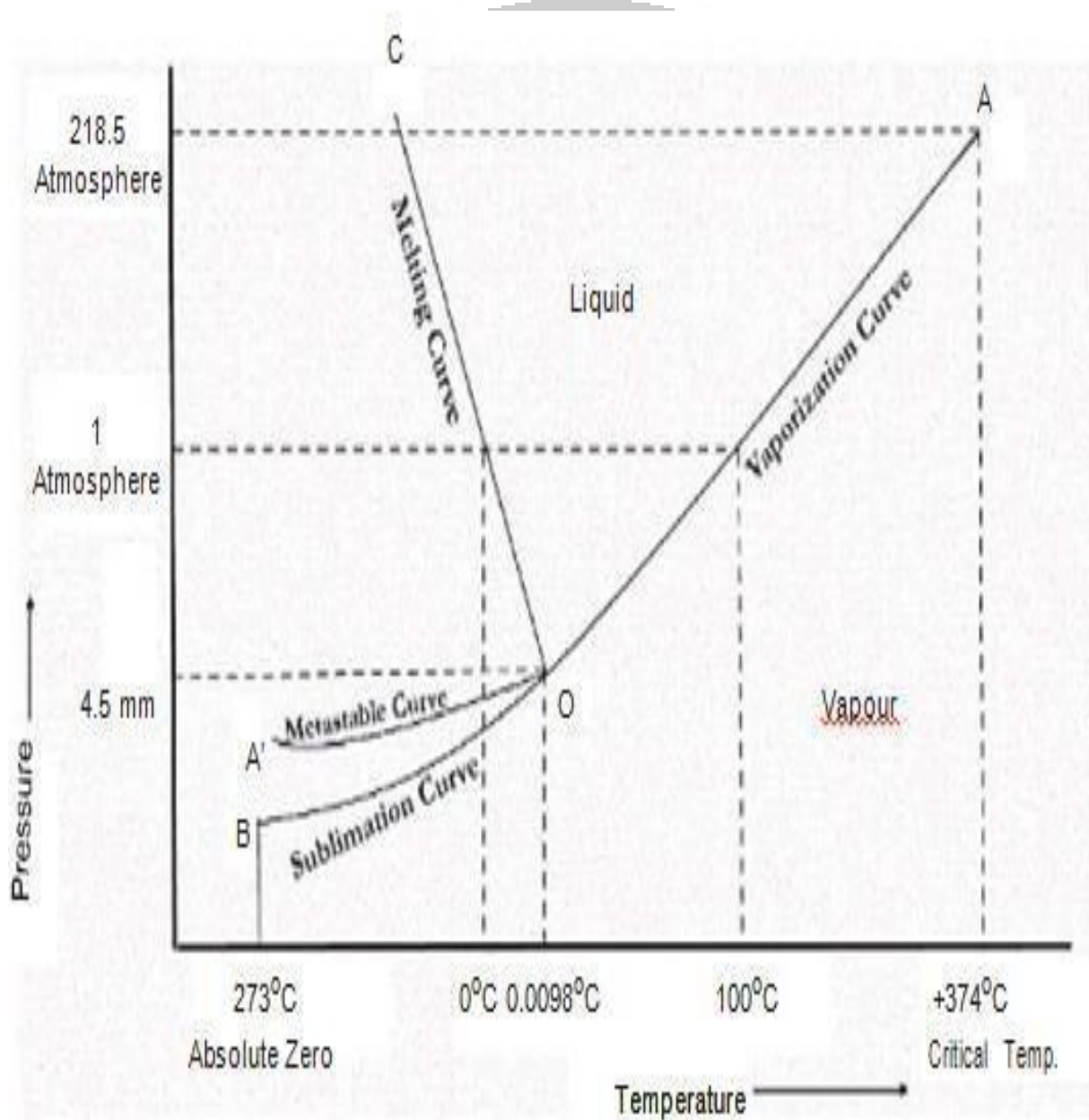
Uses of Phase Diagram

- Helps to understand the properties of materials.
- To study about the low melting alloys.

3.2.3 ONE COMPONENT SYSTEM (WATER SYSTEM)

Water exist in three possible phases namely **Solid, Liquid and Vapour.**

The phase diagram contains curves, areas & triple point.

Curve OA	Curve OB	Curve OC	Curve OA'
Curve OA is called **Vapourisation curve.** The equilibrium existing is, **Water ⇌ Vapour** P = 2 & C = 1 Applying phase rule equation, F = C – P + 2 F = 1 – 2 + 2 F = 1(**univarient**) This equilibrium will extend up to **374˚C.** Above this temperature, the equilibrium will disappear and **only vapour will exist.**	Curve OB is called **Sublimation curve.** The equilibrium existing is, **Ice ⇌ vapour** P = 2 & C = 1 Applying phase rule equation, F = C – P + 2 F = 1 – 2 + 2 F = 1 (**univarient**) This equilibrium will extend upto -**273˚C.** Below is temperature vapour cannot be present, **only ice exists**.	The curve OC is called **melting curve.** The equilibrium existing is, **Ice ⇌ water** P = 2 & C = 1 Applying phase rule equation, F = C – P + 2 F = 1 – 2 + 2 F = 1(**univarient**) The curve OC is slightly **inclined towards pressure axis.** This shows that melting point of ice decreases with increase of pressure.	Curve OA' is called **vapour pressure curve of super cooled water.** The equilibrium existing is, **super cool water ⇌ vapour** This equilibrium is called **meta stable equilibrium.** Super cool water is unstable and it can be converted into solid ice by slight disturbance or seeding.

Areas

- Phase diagram has 3 Areas, **Area AOC, Area BOC and Area AOB**
- **Area AOC** has - **water**, **Area BOC** has - **ice**, **Area AOB has** - **vapour**. In all these areas,

    P = 1, C = 1

    Applying phase rule equation, F = C – P + 2

    F = 1 – 1 + 2

    F = 2 (**bivarient**)

- At any point in this area, both temperature and pressure are different. All the three areas are bivarient.

Point

- The curve **OA, OB** and **OC** meet at a point "**O**" called **Triple point.**
- The equilibrium existing is, **Ice ⇌ Water ⇌ Vapour**

    Here, P = 3 & C = 1 Applying phase

rule equation, $F = C – P + 2$

$$F = 1 – 3 + 2$$
$$F = 0 \text{ (nonvariant)}$$

- Temperature and pressure are fixed at this point. **(0.0075° C and 4.58 mm)**

In water system,

> Curves – Univarient
> Areas – Bivarient
> Point – Invarient

3.2.4 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 C. 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 is stated as,

The system in which only solid and liquid phase are considered and gas phase is neglectedis called condensed system and the phase rule reduces to, **F'= C – P + 1.**

3.2.5 TWO COMPONENT SYSTEMS

Types of two component system

1. **Simple Eutectic (Easy Melting) System**

    - **The two components are completely miscible in liquid state but completely immiscible in solid state**is 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

2. **(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.

    (e.g.) 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. (e.g.) K – Na system
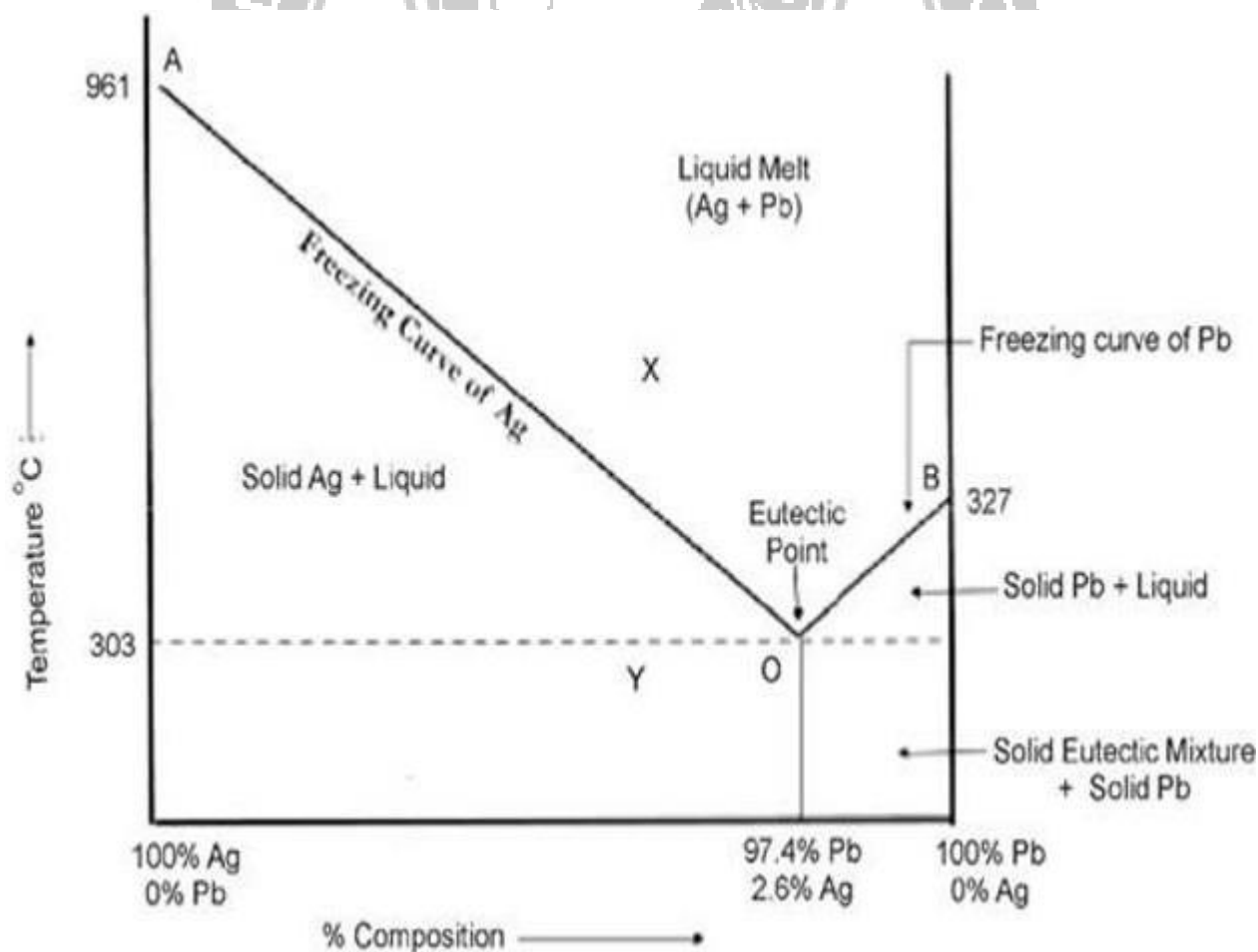
3. **Formation of solid solution**

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. (e.g.) Cu – Ni system

3.2.6 SIMPLE EUTECTIC SYSTEM

LEAD –SILVER SYSTEM

Phase Diagram

➤ The system is studied under constant pressure, vapour phase is ignored and

condensed phase rule **F' = C – P + 1** is used.

➢ The phase diagram contains **curves, areas and point.**

Curves

Curve AO	Curve BO	Point O
It is called **Freezing point curve of silver.**	It is called **Freezing point curve of Lead.**	Curve AO and BO meet at point **'O'** at a temperature of **303°C** where the three phases (**solid Ag, Solid Pb andliquid**) are in equilibrium.
' A' is the *melting point ofpure Silver*(**961°C**)	**'B'** is the *melting point ofpure Pb* (**327°C**)	
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.	The point **'O'** is called **Eutectic point.**
The equilibrium existing is,	The equilibrium existing is,	The eutectic temperature at eutectic point is **303°C** and eutectic composition is **97.4% Pb and 2.6% Ag.**
Liquid ⇌ Solid A	**Liquid ⇌ solid Pb**	**Solid Ag ⇌ Solid Pb ⇌ Liquid**
Applying reduced phase rule,	Applying reduced phase rule,	Applying reduced phase rule,
F' = C – P + 1	F' = C – P + 1	F' = C – P + 1
F' = 2 – 2 + 1	F' = 2 – 2 + 1	F' = 2 – 3 + 1
F' = 1(**univarient**)	F' = 1(**univarient**)	F' = 0 (**nonvarient**)

Areas

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

Application of Pb – Ag system

Pattinson's process of desilverisation of lead

- Argentiferous lead (lead with small amount Ag) is heated to a temperature above its

melting point (327°C) represented by point 'p' in the phase diagram.

- It is then cooled.
- The temperature falls down along 'pq'.
  - As soon as 'q' is reached Pb crystallizes out.
  - On further cooling, more and more Pb separates along BO. The melt become richer andricher in Ag until the point 'O' is reached where the % of Ag rises to 2.6%.

3.2.7 Thermal Analysis and Cooling curves

Thermal analysis

- Thermal analysis is a branch of material science where the properties of materials arestudied 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, thefinal phase change temperature can be determined.
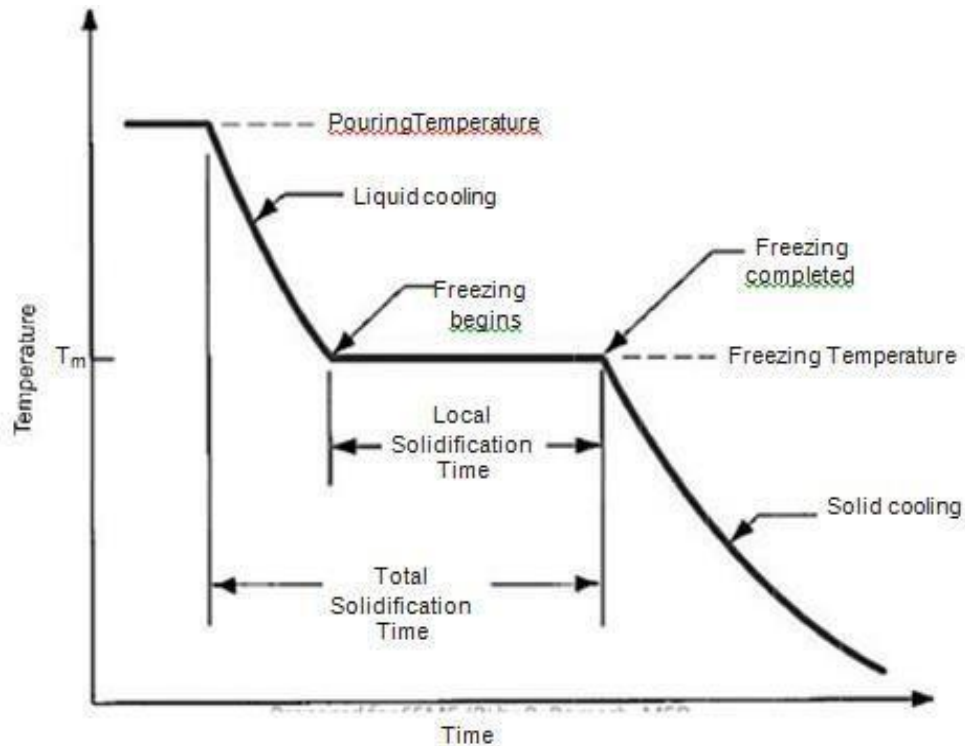
Cooling curves

- A cooling curve is a graphical plot of the changes in temperature with time for amaterial over the entire temperature range through which it cools.
- It is one of the oldest and simplest methods to determine the phase diagram and phasetransition. The freezing point, Eutectic point of a mixture can be determined easily.

a. Cooling curve of pure metal

- A pure substance in the fused state is allowed to cool slowly and thetemperature 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.

b. Cooling curve of mixture of solids

- 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 curve exhibits a break and the temperature does not remain constant.
- The temperature decreases continuously until the eutectic point 'c' is reached.
- Now the temperature remains constant until complete solidification occurs. Thereafter, at the point'd' the fall of temperature becomes uniform.
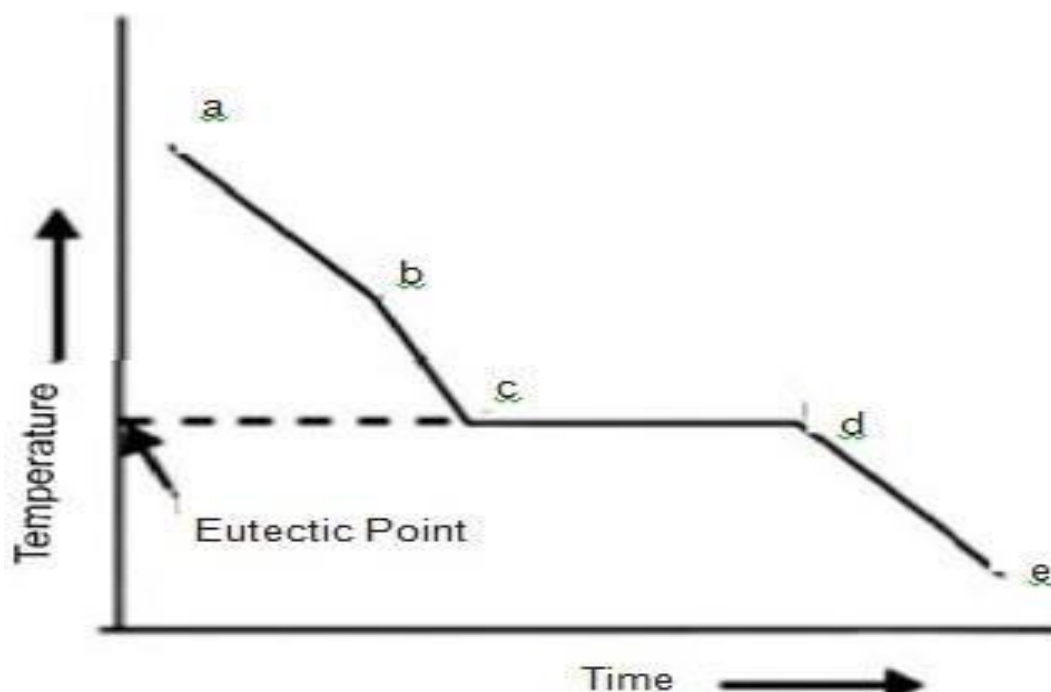
Applications

1. The melting point and eutectic temperature can be determined.
2. The percentage of the compounds and its behaviour can be found out.
3. The behavior of the compound can be understood from the cooling curve.
4. To derive the phase diagram of any two-component system.