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CHAPTER-6

PHASE RULE

6.1 Introduction

A phase is defined as any homogeneous and physically distinct part of a system bounded by a surface and is mechanically separable from other parts of the system.

A phase may be gaseous, liquid or solid. It is perfectly homogeneous and distinct from every other phase that is present in the system. There must be a definite boundary between any two phases. This boundary is known as the interface.

Air constitutes a single phase only as it contains a mixture of nitrogen, oxygen, carbon dioxide, water vapour etc.. A system consisting of only one phase is said to be **homogeneous**.

A mixture of two immiscible liquids such as water and benzene, will exist in two distinct liquid phases and in addition there will be a vapour phase. Thus there will be three phases each separated from the other by a well-defined bounding surface.

A system consisting of more than one phase is said to be heterogeneous. When various phases are in equilibrium with one another in a heterogeneous system, there can be no transfer of energy or mass from one phase to another. This means that at equilibrium, the various phases must have the same temperature and pressure and their respective compositions must remain constant all along.

The homogeneous reversible reactions can be studied using the law of mass action. For heterogeneous reversible reactions, the phase rule given by Williard Gibbs is used.

6.2 Phase Rule

Statement

Phase rule states that “ *If the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action but are influenced only by temperature, pressure and concentration , then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) by the following phase rule equation :*

$$F = C - P + 2$$

6.3 Explanation of terms

I) Phase (P)

A **phase** is defined as “ *an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces*”

Example :

1. Liquid phase :

The number of liquid phase depends on the number of liquids present and their miscibility.

i) If two liquids are **immiscible**, they will form **two separate liquid phases**.

Example : benzene and water

ii) If two liquids are **miscible** they will form **one liquid phase** only.

Example : alcohol and water

2. Solid phase

Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it.

Example : Many forms of sulphur can exist together, but these are all separate phases.

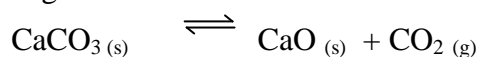
3. Gaseous phase

Since a gaseous mixture are thoroughly miscible in all proportions, it will form one phase only.

Example : a mixture of N_2 and H_2 forms one phase only.

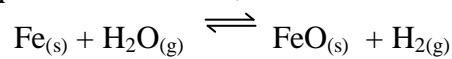
4. A solution of a substance in a solvent consists of one phase only, e.g. glucose solution.

5. A heterogeneous mixture like:



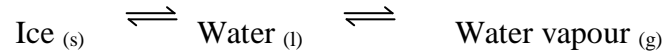
consists of three phases (i.e., two solids and one gaseous).

In the equilibrium reaction,



There are two solid phases, Fe and FeO and one gaseous phase consisting of $H_2O_{(g)}$ and $H_{2(g)}$. Thus **three phases** exists in equilibrium.

6. At freezing point, water consists of three phases:



7. A **homogeneous solid solution** of a salt forms a **single phase**.

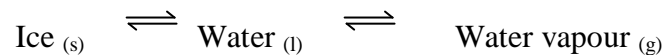
Example : Mohr's salt [$\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$] solution has a **single phase**.

II) Component (C)

Component is defined as “ *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* ”.

Example :

i) In the water system,

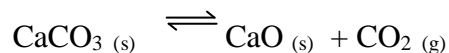


The chemical component of all the three phases is H_2O and therefore it is **one component system**.

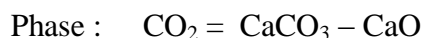
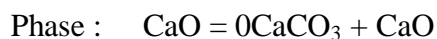
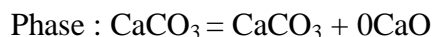
ii) Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is S. Thus is an one component system.

iii) A system of saturated solution of NaCl consists of solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H_2O . Therefore it is a **two component** system.

iv) In the thermal decomposition of CaCO_3 ,



The composition of each of the three phases can be expressed in terms of at least any two of the independent variable constituents, CaCO_3 , CaO and CO_2 . Suppose CaCO_3 and CaO are chosen as the two components, then the composition of different phases is represented as follows:



Thus, it is a two component system..

v) In the equilibrium, $\text{Fe}_{(s)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{FeO}_{(s)} + \text{H}_2_{(g)}$, the minimum components required to express the composition of each phase is three. Thus it is a **three component** system.

vi) In the dissociation of NH_4Cl , the following equilibrium occurs:



The system consists of two phases namely solid NH_4Cl and the gaseous mixture containing $\text{NH}_3 + \text{HCl}$.

When NH_3 and HCl are present in equivalent quantities the composition of both the phases can be represented by the same chemical compound NH_4Cl and hence the system will be a one component system.

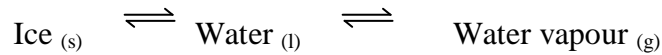
III) Degree of freedom

Degree of freedom is defined as *the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.*

A system having 1,2,3 or 0 degrees of freedom is called univariant, bivariant, trivariant and nonvariant respectively.

Example :

i) Consider the water system,

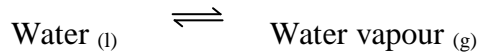


The three phases can be in equilibrium only at particular temperature and pressure.

Therefore, when all the three phases are present in equilibrium, then no condition need to be specified. The system is therefore zero variant or invariant or has no degree of freedom.

In this system if pressure or temperature is altered, three phases will not remain in equilibrium and one of the phases disappears.

ii) Consider a system consisting of water in contact with its vapour,



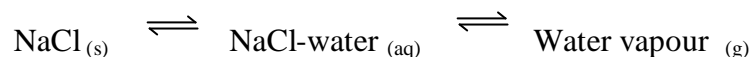
To define this system completely, we must state either the temperature or pressure. Thus degree of freedom is one and the system is univariant.

iii) For a system consisting of water vapour phase only, we must state the values of both the temperature and pressure in order to

define the system completely. Hence the system is bivariant or has two degrees of freedom.

iv) For a gaseous mixture of N_2 and H_2 , we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degrees of freedom or bivariant system.

v) Consider a system consisting of



we must state either the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence the system is univariant.

Merits of the Phase rule:

1. It is applicable to both physical and chemical equilibria.
2. It requires no information regarding molecular/micro-structure, since it is applicable to macroscopic systems.
3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.
4. It helps us to predict the behaviour of a system, under different sets of variables.
5. It indicates that different systems with same degree of freedom behave similarly.
6. It helps in deciding whether under a given set of conditions :
 - a) various substances would exist together in equilibrium(or)

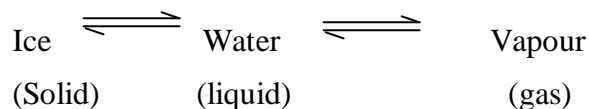
b) some of the substances present would be interconverted or (c) some of the substances present would be eliminated.

Limitations of Phase rule:

1. It can be applied only for system in equilibrium. Consequently, it is of little value in case of very slow equilibrium state attaining system.
2. It applies only to a single equilibrium system; and provide no information regarding any other possible equilibria in the system.
3. It requires at most care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus even if a trace of phase is present, it accounts towards the total number of phases.
4. It conditions that all phases of the system must be present simultaneously under the identical conditions of temperature and pressure.
5. It conditions that solid and liquid phases must not be in finely-divided state; otherwise deviations occurs.

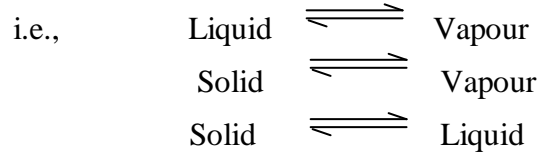
6.4 Applications of Phase rule to one component system (water system)

The water system is a one component system



Since water exists in three possible phases such as solid, liquid and vapour, there are three forms of equilibria :

Liquid – vapour , solid vapour and solid liquid



Each equilibrium involves two phases. The nature of these phases which exist in equilibrium at any time depends on the conditions of temperature and pressure. These conditions have been determined and summarized in the pressure-temperature diagram in which pressure is treated as independent variable and is plotted along y – axis whereas temperature is plotted along x-axis.

The phase diagram for the water system is shown in Fig 6.1.

The phase diagram consists of

1. Curves : There are three curves OA, OB and OC.

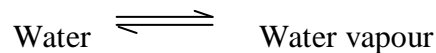
2. Areas : Three curves OA , OB and OC divide the diagram into three areas AOB, AOC and BOC.

3. Triple point : The above three curves meet at the point O and is known as triple point.

4. Metastable equilibrium : The curve OA represents the metastable equilibrium.

1) Curve OA

The curve OA is called **vapourisation curve**, it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.



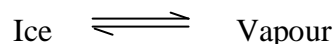
The degree of freedom of the system is one, i.e, univariant. Thus applying phase rule equation,

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

This equilibrium (i.e, line OA) will extend upto the critical temperature (374°C). Beyond the critical temperature the equilibrium will disappear only water vapour will exist.

2)Curve OB

The curve OB is called **sublimation curve** of ice, it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.



The degree of freedom of the system is one, i.e., univariant.

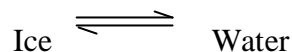
This is predicted by the phase rule.

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

This equilibrium line will extend upto the absolute zero(-273°C) where no vapour can be present and only ice will exist.

3) Curve OC

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.



The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

The degree of freedom of the system is one. i.e., univariant.

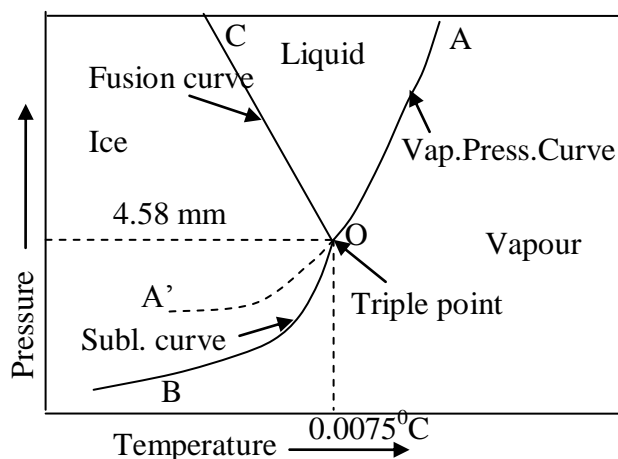


Fig 6.1 Water System

iv) Triple point (Point 'O')

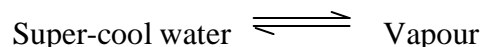
At triple point all the three phases namely ice, water and vapour coexist. Thus the value of P is 3. Applying phase rule equation, the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are 0.0075°C and 4.58 mm respectively.

At this triple point, neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases. The triple point is not the same as the ordinary melting point of ice (i.e, 0°C). It's value has been increased due to the fact that 0°C is the melting point of ice at 760mm of mercury and a decrease of 4.58 mm will rise the melting point to 0.0075°C .

v) Curve OB (Metastable equilibrium)

The curve OB is called vapour pressure curve of the super-cool water or metastable equilibrium.

Where the following equilibrium will exist.



Sometimes water can be cooled below 0°C without the formation of ice, this water is called super-cooled water. Supercooled water is unstable and it can be converted into solid by 'seeding' or by slight disturbance.

vi) Areas

Area AOC, BOC , AOB represents water ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure. The degree of freedom of the system is two. i.e., Bivariant.

This is predicted by the phase rule

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

6.5 Phase Diagram

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

If the phase diagram is plotted between temperature against pressure, the diagram is called P-T diagram. P-T diagram is used for one component system.

If the phase diagram is drawn between temperature against composition, the diagram is called T-C diagram. T-C diagram is used for two component system.

Uses of Phase diagram

1. From the phase diagram, it is possible to predict whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.
2. The phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.
3. The study of low melting eutectic alloys, used in soldering, can be carried out using phase diagrams.

6.5 Two component system**Reduced phase rule or condensed phase rule.**

We know the phase-rule equation,

$$F = C - P + 2 \quad \dots\dots\dots (1)$$

For a two component system, $C = 2$ and hence the above equation becomes,

$$F = 2 - P + 2 = 4 - P \quad \dots\dots\dots (2)$$

The minimum number of phases in any system at equilibrium is one. It is clear from the equation (2), the maximum number of degree of freedom is three.

Thus, three variables – pressure, temperature and composition of one of the components must be specified to describe the system. This will lead to three dimensional figures which cannot be conveniently represented on a paper. To make this simple, one of the three variables is kept constant.

In solid-liquid equilibrium of an alloy, practically there is no gaseous phase and the pressure will not have much influence. In the case of solid-liquid equilibrium, the experiments are generally carried out at constant pressure.

Thus the system in which only the solid and liquid phases are considered and the gas phase is ignored is called a **condensed system**. This reduces the degree of freedom of the system by one. The phase rule equation is then written as

$$\boxed{F' = C - P + 1} \quad \dots\dots\dots (3)$$

This equation is called **reduced phase rule or condensed phase rule**.

For a two component system the phase rule equation is written as

$$\begin{aligned} F' &= C - P + 1 \\ &= 2 - P + 1 = 3 - P \quad \dots\dots\dots (4) \end{aligned}$$

The above equation is known as the **reduced (condensed) form of phase rule for two component system**.

There are various types of solid-liquid equilibria of which only two of them are taken here.

1. Those equilibria in which the components are completely miscible with one another in liquid state. They do not form any compound on solidification. They give rise to merely an intimate mixture known as eutectic.

Some examples of this system are

- 1) lead-silver system
- 2) Lead-Antimony system
- 3) Zinc-cadmium system
- 4) Potassium iodide- water system

2. Those equilibria in which the components enter into chemical combination . They give rise to one or more compounds.

Examples of this system are :

- 1) Zinc-magnesium system
- 2) Calcium chloride – Potassium chloride system
- 3) Gold-Tellurium system.

Classification of two component system

The two component systems are classified into the following three types :

- i) Simple eutectic formation
- ii) a) Formation of compound with congruent melting point.
b) Formation of compound with incongruent melting point.
- iii) Formation of solid solution.

i) Simple eutectic formation :

A system with two substances which are completely miscible in the liquid state , but completely immiscible in the solid state is known as **eutectic system**. In this system the substances do not react chemically.

Among the mixtures of different proportions of two substances, the mixture which has the lowest melting point is known as the eutectic mixture.

The temperature and composition corresponding to the point eutectic point is called eutectic temperature and eutectic composition respectively.

ii) a) Formation of compound with congruent melting point :

In this type of binary alloy system the two substances form one or more compounds with definite proportions. Of the compounds, a compound is said to possess congruent melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of the solid.

b) Formation of compound with incongruent melting point :

Of the above compounds, a compound is said to possess incongruent melting point, if it decomposes completely at a temperature below its melting point yielding a new solid phase with a composition different from that of the original.

iii) Formation of solid solution :

In this type, when two substances, especially metals, are completely miscible in both the solid and liquid states, they form solid solutions where mixing takes place in the atomic levels. A solid solution can be formed only when the difference between the atomic radius of two metals is not greater than 15%.

6.6 Simple eutectic systems

The general phase diagram for binary alloy systems is shown in Fig 4.2 . Here the pressure does not have the considerable effect. Hence, the other two variables viz, temperature and compositions are taken into account.

Components A and B.

When small quantities of B are added to A gradually, the melting point of A falls along the curve AC. In the same way when small quantities of A are added to B gradually, the melting point B falls along the curve BC. Hence, AC and BC are the freezing point curves of A and B respectively.

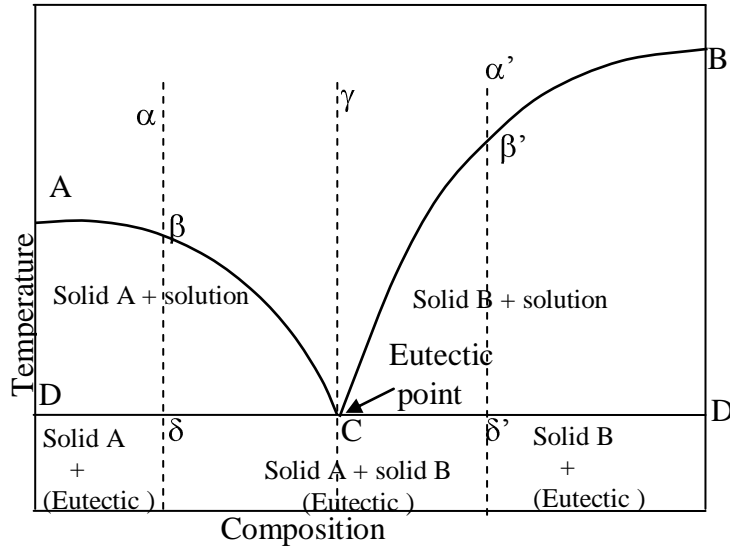


Fig 6.2 The simple Eutectic system

The curves AC and BC meet at the point C. At this point the three phases solid A, solid B and their solution coexist. The degree of freedom is zero here and the system is therefore invariant. Also only at this point C, the liquid can exist at the lowest temperature. Since the mixture of components A and B of composition corresponding to the point C has the lowest melting point, the point C is called the **eutectic point**.

The temperature and composition corresponding to the point C is called eutectic temperature and eutectic composition respectively.

Consider a liquid mixture of composition represented by a point α cooled at constant pressure. The temperature falls without any change of composition until the point β on the curve AC is reached. At this temperature t_1 , the solid A will separate out. The system now consists of two phases and hence monovariant. As cooling continues, the component A keeps on separating out and the solution becomes relatively richer in B. The temperature and the solution composition both change along AC. Thus at the

temperature t_1 , solid A is in equilibrium with solution of composition X and at temperature t_2 , it is in equilibrium with solution of composition Y. It is clear therefore, in the area ACD, solid A is in equilibrium with solutions of varying composition given by the curve AC depending upon the temperature.

When the temperature reaches a point represented by δ , the solid B also begins to separate out. On further cooling the system, solid A and B separate out together in constant ratio so that the composition of the solution remains constant. The temperature also remains constant for some time. When the liquid solution has been completely solidified and the system consists only of a mixture of solid A and B, it becomes monovariant. Further cooling will result in the fall of temperature below the line DD into the area in which only the two solids coexist as shown.

In the same way, if the composition of liquid mixture is on the right of the eutectic point C, as represented by point ' α ', similar series of changes will be obtained on cooling.

Construction of Phase diagram by Thermal analysis (or) cooling curve

Thermal analysis is a method involving a study of the cooling curves of various compositions of a system during solidification. The shape of the freezing point curves for any system, especially those involving metals can be determined by thermal analysis.

The data obtained from thermal analysis along with recorded curves are called as thermogram. These thermograms are characteristic of a particular system composed of either single or multi component materials. Thermograms indicate the system in terms of temperature, dependencies of its thermodynamic properties. Let us discuss in detail the cooling curves or time-temperature curves of some simple systems.

Example 1 :

If a pure substance say x , in molten state is cooled slowly and the temperature is noted at different time interval. The graph plotted between temperature and time (the cooling curve) will be of the form shown in Fig 6.3 (a). In this diagram ab denotes the rate of cooling of molten liquid and the liquid starts solidifying at the freezing point b . Now the temperature remains constant until the liquid melt is completely solidified. Solidification completes at the point 'c'. The horizontal line 'bc' represents the equilibrium between the solid and liquid melt. After the point 'c', the temperature of the solid begins to decrease along the curve 'cd'.

Example 2 :

When a molten liquid containing two components (say A and B) is cooled slowly then the cooling curve is different and one such curve is shown in Fig 6.3 (b). As before, initially the rate of cooling is continuous. When it reaches the point 'b' one substance (either A or B) begins to solidify out of the melt, which is indicated by a break and the rate of cooling is different.

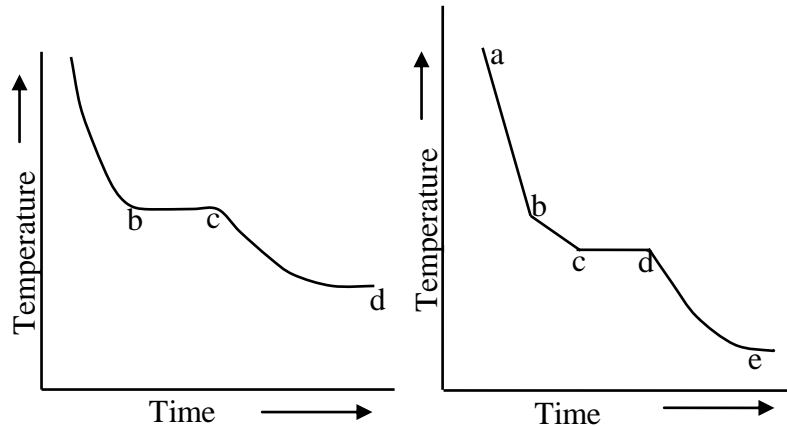


Fig 6.3(a) Cooling curve of a Pure solid

Fig 4.3(b) Cooling curve of a mixture A + B

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, which forms the eutectic mixture (line cd). After the break point 'd' cooling of solid mass begins. The temperature of horizontal line 'cd' gives the eutectic temperature.

The temperature measurements are done with a sensitive thermometer and the arrest points are determined with good precision.

A number of mixtures of A and B are taken with different composition. Each mixture is heated to the molten state and their cooling curves are drawn separately for each mixture. From the cooling curves of various compositions, the main phase diagram can be drawn by taking the composition in X-axis and temperature in Y-axis. Any point on this line indicates the appearance of the solid phase from the liquid. The area above this curve is only liquid phase.

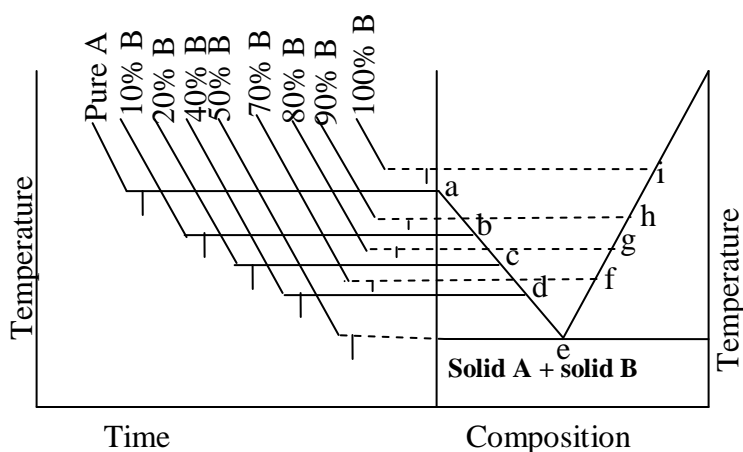


Fig 6.4 Cooling curve of various compositions of two solids

Uses of Cooling curves

1. Cooling curves are used to find the percentage purity of the compounds.
2. It is used to find the melting point of the compounds
3. Thermal analysis is useful in derivation of phase diagram of any two component system
4. Used to find the composition of the alloy.
5. Used to analyse the behaviour of the compounds.

6.7 Lead –Silver system

It is a two component system . The two metals are completely miscible in liquid state and do not form any compound . There is almost no effect of pressure on this system. The temperature-composition phase diagram is shown in Fig.6.5. It contains lines, areas and the eutectic point.

i) The curve AC:

The curve AC is the freezing point curve of pure lead. The melting point of lead decreases gradually along the curve AC, with the continuous addition of silver. Thus the curve AC is showing the effect of addition of silver on the melting point of pure lead. All along the curve AC two phases –solid lead and liquid are in equilibrium.

According to reduced phase rule equation

$$\begin{aligned} F' &= C - P + 1 \\ &= 2 - 2 + 1 = 1 \end{aligned}$$

$$\text{i.e, } F' = 1$$

i.e., the system is univariant.

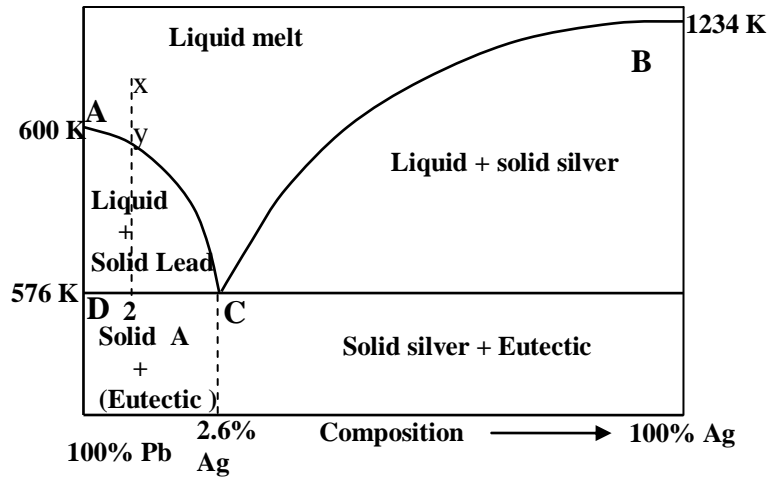


Fig 6.5 Lead-Silver System

ii) The curve BC

Curve BC is the freezing point curve of pure silver and represents the effect of addition of pure lead on the melting point of pure silver. All along the curve BC two phases –solid silver and liquid are in equilibrium.

According to reduced phase rule equation.

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

$$= 2 - 2 + 1 = 1, \text{ i.e. } F' = 1 \text{ (The system is univariant)}$$

iii) Point C (Eutectic point)

Point C is the eutectic point where solid silver, solid lead and their solution coexist. The curves AC and BC meet at point C. Since the experiment is carried out at constant pressure, the number of degree of freedom for the system at the eutectic point C is zero on the basis of reduced phase rule.

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

$$= 2 - 3 + 1 = 0; \quad \text{i.e., } F' = 0$$

The system is non-univariant.

Eutectic composition is 2.6% silver and 97.4% lead and the corresponding temperature is 576 K.

iv) Areas

The area above the line ACB has a single phase (molten Pb+Ag).

According to reduced phase rule equation,

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

$$= 2 - 1 + 1 = 2; \quad \text{i.e., } F' = 2$$

The system is bivariant.

Both the temperature and composition have to be specified to define the system completely.

The area below the line AC (solid Ag + liquid melt), below the line BC (solid Pb + liquid melt) and below the eutectic point 'C' have two phases and the system is univariant.

According to reduced phase rule equation,

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

$$= 2 - 2 + 1 = 1 \quad \text{i.e., } F' = 1$$

Application of Pattinson's process :

The phase diagram of lead-silver is useful in the extraction of silver from the argentiferous lead ore which has a very small percentage of silver. This process is known as **Pattinson's process**.

Let x represent the molten argentiferous (Pb + Ag alloy) lead containing very small amount of silver in it. It is a homogeneous liquid and on cooling, the temperature falls but

without change in concentration till any point y on the curve AC is reached.

On further cooling, lead begins to separate out and the solution becomes richer in silver. Further cooling will shift the system along the line yc. More of lead separates as solid till the point C is reached when the percentage of Ag rises to 2.6%. This process of increasing the relative proportion of silver in the alloy is known as **Pattinson's process of desilvering of lead.**

Uses of Eutectic system :

1. Eutectic systems are useful in predicting the suitable alloy composition.
2. It is used in the preparation of solders which are used for joining two metal pieces together.

Review questions

1. State the phase rule and what are the merits and demerits of phase rule?
2. State the condensed phase rule
3. Explain Phase, component and degree of freedom.
4. Describe the water system
5. Briefly describe the construction of phase diagram using thermal analysis.