Phase diagram:

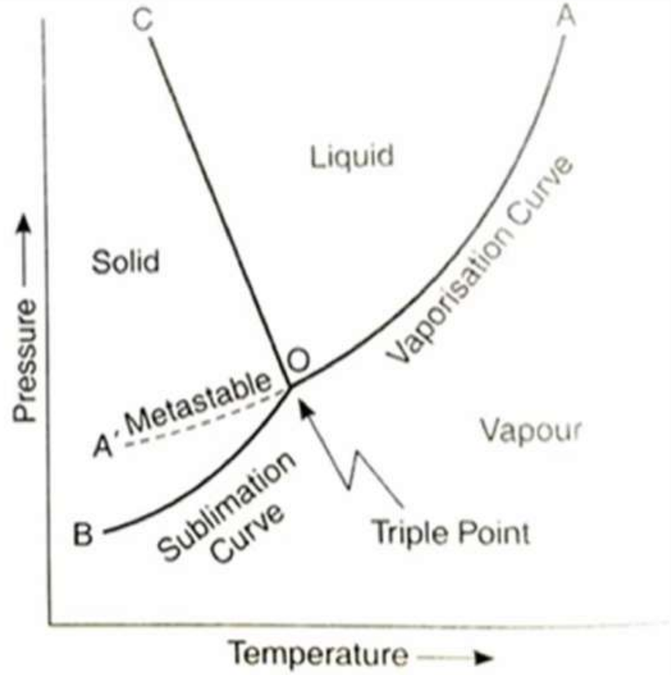

Fig. 6.1 A typical phase diagram of a one-component system.

Phase diagram may be defined as **a plot showing the conditions of pressure and temperature under which two or more physical states of a system can exist together in a state of dynamic equilibrium**. Phase diagram consists of three important features.

1. Areas or Regions
2. Curves or Lines
3. Triplet point

Let us consider a phase diagram for a one component system.

1. Areas or Regions :

The diagram has three areas namely BOC (solid) , COA (liquid), AOB (vapour). Each of the three areas shows the conditions of temperature and pressure under which the respective phase can exist.

Applying the phase rule equation to the system when only one phase is present, we have

$F = C - P + 2$; for one component system, C=1 and P=1

$F = 1 - 1 + 2$

$= 2$ – bivariant .

Therefore, in order to define the condition of the phase, both pressure and temperature must be stated.

2. Curves or Lines:

There are three curves meeting at the point O and divide the diagram into three areas. These curves show the conditions of equilibrium between any two of the three phases, i.e., solid $\rightleftharpoons$ liquid ; liquid $\rightleftharpoons$ vapour ; solid $\rightleftharpoons$ vapour.

i) **Solid-liquid line (Curve OC) :-** This line represents the equilibrium between solid and liquid i.e., solid ⇌ liquid and is referred to as melting curve or fusion curve.

ii) **Liquid-vapour line (Curve OA) :-** This line represents the equilibrium between liquid and vapour, i.e., liquid ⇌ vapour and is referred to as the vapour pressure curve or vaporisation curve for the liquid.

iii) **Solid-vapour line (Curve OB) :-** This line represents the equilibrium between solid and vapour, i.e., solid ⇌ vapour and is referred to as the sublimation curve.

Applying the phase rule equation to a one component, two phase systems, we have

$$F = C - P + 2$$
$$= 1 - 2 + 2$$
$$= 1 - \text{univariant}.$$

3) Triple point :

The three boundary lines intersect at a common point called the triple point. A triple point shows the condition under which all the three phases coexist in equilibrium. Applying the phase rule equation .

$$F = C - P + 2$$
$$= 1 - 3 + 2 = 0 - \text{invariant}.$$

Metastable equilibrium :-

Generally , the liquid freezes on cooling which is represented by the curve AO in the present phase diagram. If the liquid is cooled so carefully that crystals are not formed, the curve AO can be extended to A'. This means that the liquid can be cooled far below the freezing point without being converted into solid form. The supercooled liquid is an unstable condition since on the slightest disturbances, e.g., Introduction of a seed crystal, the entire liquid solidifies rapidly. Thus, the curve OA' represents a meta stable equilibrium.

$$\text{Supercooled liquid} \rightleftharpoons \text{vapour}$$

ONE COMPONENT SYSTEM :

According to phase rule equation, we have

$$F = C - P + 2$$

when there is one component in the system existing in one phase i.e., C = 1 and P = 1 then the degree of freedom (F) as calculated from phase rule is

$$F = 1 - 1 + 2 = 2.$$

Hence all the system of one component can be completely described graphically on paper, by taking two variable factors like pressure and temperature.

Water – System :

This is the most common example of the one component system. The three phases in the system are

$$\text{Ice} \rightleftharpoons \text{Water} \rightleftharpoons \text{Vapour}$$
$$\text{(Solid)} \quad \text{(liquid)} \quad \text{(Gaseous)}$$

The above three phases may occur in four possible combinations in equilibrium as :

i) Liquid $\rightleftharpoons$ Vapour

ii) Liquid $\rightleftharpoons$ Solid

iii) Solid $\rightleftharpoons$ Vapour

iv) Solid $\rightleftharpoons$ Liquid $\rightleftharpoons$ Vapour

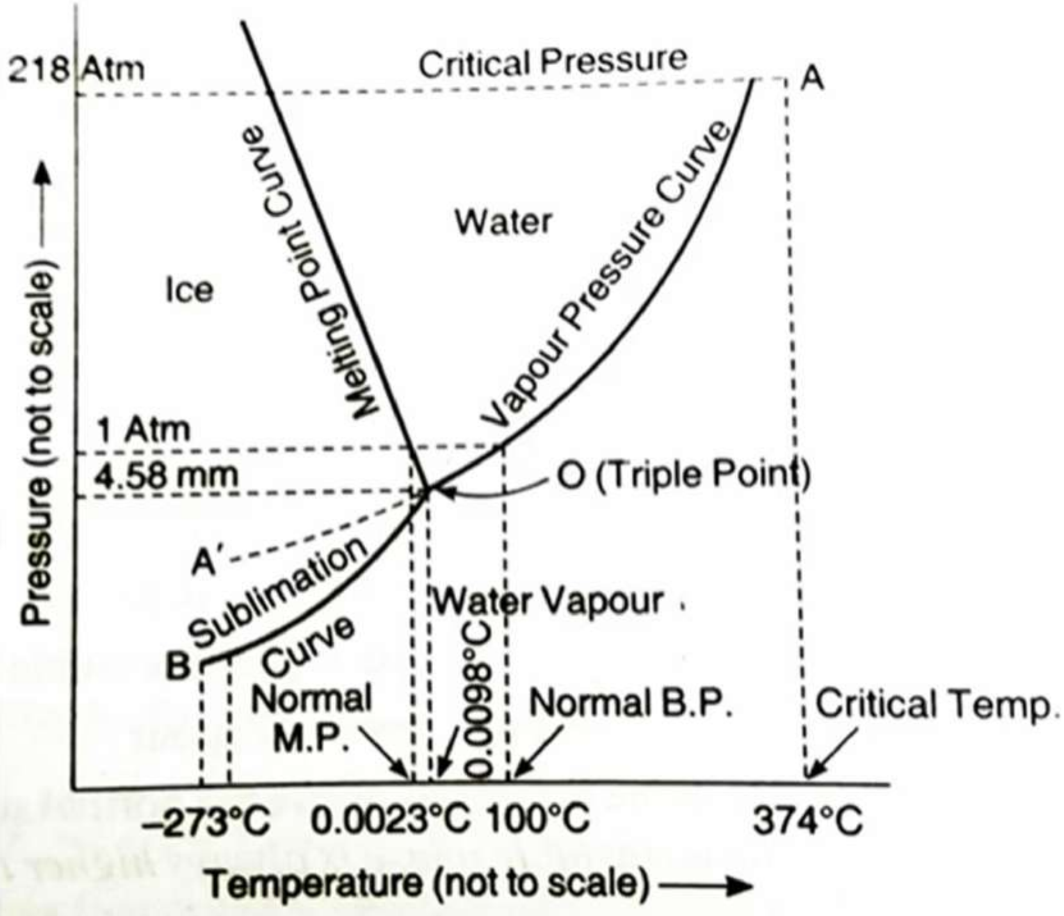

Fig. 6.2 Phase diagram of the water system

This phase diagram consists

i) The stable curves OA,OB and OC
ii) One metastable curve OA'
iii) Three areas AOC, BOC, AOB.
iv) Triple point O

1) Curves :

i) Curve OA(Vapourisation curve) :-

This is the vapour pressure curve of water . It represents the equilibrium between water and vapour at different temperatures. At every point of the curve the two phases are present. The starting point of curve is O, which is the freezing point of water (0.0098°C at 4.58mm). This curve ends at A, the critical temperature(374^{0}C at 218 atm).

Applying the phase rule equation .

$$F = C - P + 2 \qquad [\because C=1 ; P=2]$$
$$= 1 - 2 + 2$$
$$= 1 - \text{univariant} .$$

ii) OA' curve :-

The dotted curve OA' is a continuation of the OA curve and represents the vapour pressure curve of supercooled water. This curve is known as **metastable curve**. When slight disturbance is there, the supercooled phase at once changes to solid ice and the curve merges into OB.

Applying the phase rule equation

$$F = C - P + 2 \qquad [\because C=1;\ P=2]$$

$$= 1 - 2 + 2$$

$$= 1 \text{ – Univariant.}$$

iii) OB curve (Sublimation curve) :-

It is the sublimation curve. The curve starts from point O and ends at B (-273°C)

Applying the phase rule equation .

$$F = C - P + 2 \qquad [\because C=1 ; P=2]$$

$$= 1 - 2 + 2$$

$$= 1 - \text{univariant.}$$

iv) OC Curve (Melting point curve or Fusion curve) :

The curve shows the equilibrium between ice and water at various pressures. It is known as melting point curve. There is no limit for the curve OC. It goes upto a point corresponding to 2000 atmospheric pressure at -20°C.

Applying the phase rule equation .

$$F = C - P + 2 \qquad [\because C=1 ;P=2]$$

$$= 1 - 2 + 2$$

$$= 1 - \text{univariant} .$$

2) Areas:

Pressure and **temperature** are the two quantities to define the system completely at any point in an area.

In water system, there are three areas

i) AOB – Vapours of water only

ii) BOC – Ice only

iii) COA – Water in liquid form only.

Applying the phase rule equation .

$$F = C - P + 2 \qquad [\because\ C=1\ ; P=1]$$

$$= 1 - 1 + 2$$

$$= 2 - \text{Bivariant}\ .$$

3) Triple point:

It is the point where the three curves OA, OB and OC meet together. At this point, all the three phases are in equilibrium. At point O, temperature and pressure are fixed at 0.0098°C and 4.58mm respectively.

Applying the phase rule equation .

$$F = C - P + 2 \qquad [\because C=1 ; P=3]$$

$$= 1 - 3 + 2$$

$$= 0 - \text{invariant} .$$

Conclusion : The main features of the phase diagram are

System	Phase	Degree of Freedom
i) Curves (OA, OA',OB, OC)	2	1
ii) Areas (AOB, BOC, COA)	1	2
iii) Triple Point (O)	3	0

TWO COMPONENT SYSTEM :

For a two component system, Phase rule can be written as

$$F = C - P + 2$$

$$F = 2 - P + 2$$

$$F = 4 - P$$

This phase equation can be applied to two component systems which have 2,3 or 4 phases, but not for only one phase because the system will have three degrees of freedom

$$F = 4 - 1$$

$$= 3$$

Thus, for defining such system, we must have three different variables; pressure, temperature and composition. It is necessary to have three coordinate axes which cannot be easily represented on a paper. For this reason, we have chose two variables out of three and the third variable is kept constant.

Example:- For a solid-liquid equilibrium, the gas phase is absent and the affect of pressure on the equilibrium is negligible. Such a system where pressure is kept constant is called a condensed system and the new phase equation is called reduced phase equation.

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

Solid - liquid equilibrium :

The solid-liquid equilibria are divided into different types

i) The two components are completely miscible
ii) The two components are partially miscible
iii) The two components are immiscible

Type one is important and further divided into different types.

a) The two components do not form any compound and on solidification they simply form a mixture known as eutectic mixture.

   Example : Ag- Pb system

Silver-lead system (Ag – Pb) :

It is a two component system, the two components being Ag and Pb. The various possible phases are

i) Solid Silver
ii) Solid Lead
iii) Solution of silver and lead in molten state (liquid melt)
iv) Vapour

Since, the boiling points of silver and lead are high, the vapour phase is practically absent and thus Ag – Pb system consists of only solid and liquid phases.

The phase diagram of the system consists of two curves OA and OB intersecting at point 'O'.

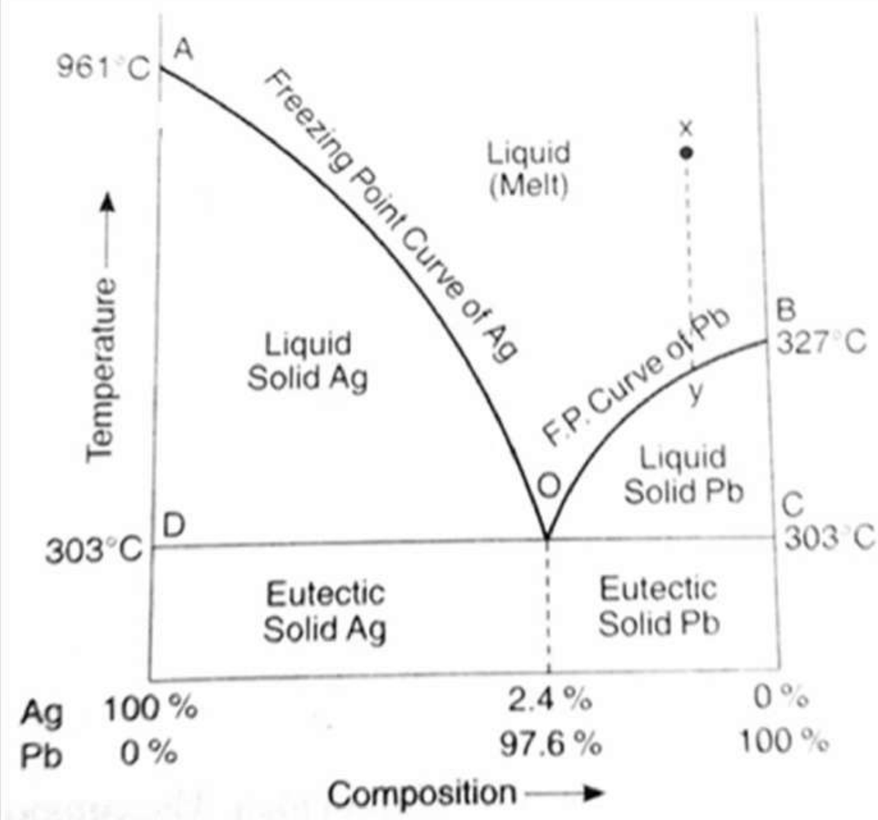

Fig. 6.3 Phase diagram of the silver-lead system

i) Curves (AO and BO) :

Point A represents the melting point of the pure silver (961°C) and point B that of pure lead (327°C). All these points on the curve AO and BO represents the melting points of various mixtures of silver and lead obtained by the addition of lead to pure silver (AO curve) or silver to pure lead (BO curve). Curves AO and BO represent the melting point curves of silver and lead respectively. Since addition of a metal to another pure metal lowers the melting point, the curves AO and BO are also referred to as **freezing point curves of silver and lead respectively.**

All along the curves AO and BO, the added metal goes into the solution and the separation of the original metal occurs till the point O is reached. At point O the solution becomes saturated with the added metal and hence the melting point of silver and lead does not fall further.

Thus the point O represents the lowest possible temperature (303°C) in the system and corresponds to fixed composition having 2.4% silver and 97.6% lead. The point O is called the **eutectic point**.

Applying the reduced phase rule equation .

$$F' = C - P + 1 \qquad [\because \; C=2\;;P=2]$$

$$= 2 - 2 + 1$$

$$= 1 - \text{Univariant}$$

ii) Eutectic point(O) :

This is the point where the two curves AO and BO meet together. At this point, three phases (solid Ag, solid Pb and their liquid solution) coexist. Therefore, point O has no degree of freedom, i.e., it is invariant.

Applying the reduced phase rule equation.

$$F' = C - P + 1 \qquad [\because \; C=2; P=3]$$

$$= 2 - 3 + 1$$

$$= 0 - \text{invariant}$$

The point O is called the eutectic point, the temperature (303°C) and composition of the components (2.4% Ag + 97.6% Pb) corresponding to the **eutectic point** and are called the **eutectic temperature** and **eutectic mixture** respectively.

Eutectic mixture :

It may be defined as a liquid mixture of the components which has the lowest freezing point as compared to all other liquid mixtures of the same constituents.

iii) Areas :

There are three areas above the line COD and two areas below the line COD.

a) The area above the curve AOB:

In this region, only the liquid melt (alloy) exists i.e., there is only one phase

$$F' = C - P + 1 \qquad [\because C=2; P=1]$$
$$= 2 - 1 + 1$$
$$= 2 \text{ – bivariant}$$

b)The area AOD :

This region has solid Ag and liquid melt i.e., there are two phases.

$$F' = C - P + 1 \qquad [\because C=2; P=2]$$
$$= 2 - 2 + 1$$
$$= 1 - \text{Univariant}$$

c) The area BOC :

This region has solid Pb and liquid melt i.e., there are two phases.

$$F' = C - P + 1 \qquad [\because C=2; P=2]$$
$$= 2 - 2 + 1$$
$$= 1 - \text{Univariant}.$$

d) The areas DOE and COE :

These areas are present below the line COD. Both areas have two phases; i.e., solid Ag + eutectic in the area DOE and solid Pb + eutectic in the area COE.

Applying the reduced phase rule equation .

$$F' = C - P + 1 \qquad [\because \; C=2;\; P=2]$$

$$= 2 - 2 + 1$$

$$= 1 - \text{Univariant} .$$