Phase equilibrium

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

eg. ① A gas mixture constitutes a single phase, since gases are completely miscible.

② CCl_4 and H_2O form two phases, since they are immiscible.

③ Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapour is a three phase system.

Components: The no. of components of a system at equilibrium is defined as the smallest no. of independently variable constituents by means of which the composition of each phase can be expressed either directly or in terms of chemical equations.

eg. ① Water exists in three phase,

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

But, it is a one-component system.

② Sulphur exists in four phases, viz. rhombic sulphur, monoclinic sulphur, liquid and vapour. But it is a one-component system.

③ An aqueous solution of sucrose is a two-component system.

In a chemically reacting system, the no. of components is given by, $\boxed{C = N - E}$ where, N is the no. of chemical species.

E is the no. of independent chemical eqns relating the conc^n of N species.

Each independent chemical equations ~~sub~~ involving the constituents is count as one. If ions are involved ~~electrically~~ electrical neutrality is also count as one restriction (E).

Degree of freedom:

The degree of freedom of a system is defined as the no. of independent variables such as Temperature, Pressure and concentration (composition) which must be specified in order to define the system completely.

If $F=0$, the system is called invariant; if $F=1$, univariant (monovariant) if $F=2$, it is bivariant, etc.

Conditions for Equilibrium between Phases:

① **Thermal Equilibrium**: All the phases must be at the same temperature to prevent flow of heat from one phase to another.

Let us consider two phases α and β at temperatures T_α and T_β respectively. Let, S_α and S_β be the entropies of the two phases and let dq be the heat transferred from phase α to phase β at equilibrium.

$\therefore$ Entropy change, $dS = dS_\alpha + dS_\beta$

$$\because \; dS_\alpha = \frac{-dq}{T_\alpha} \quad \text{and} \quad dS_\beta = \frac{dq}{T_\beta}$$

$$\therefore \left(-\frac{dq}{T_\alpha}\right) + \left(\frac{dq}{T_\beta}\right) = 0.$$

$$\Rightarrow T_\alpha = T_\beta.$$

② **Mechanical Equilibrium**: All the phases must be under the same pressure otherwise the volume of one phase will increase than the other.

Let α-phase is expanded to β-phase by the volume change dv. Then the change in Helmholtz free energy

at constant temperature is given by:

$$dA = -dA_\alpha + dA_\beta = 0 \qquad (\text{At eq}^m)$$

But, $dA_\alpha = -P_\alpha \cdot dV$ and $dA_\beta = -P_\beta \cdot dV$. (At const. T)

$\because$ At equilibrium, $dA_\alpha = dA_\beta$

$$\Rightarrow P_\alpha = P_\beta$$

③ <u>Chemical Equilibrium</u>:

For a system of many phases at equilibrium, the chemical potential of a component i is the same in all the phases.

Let us consider a closed system of P phases designated as $\alpha, \beta, \gamma \ldots P$ which contain C components as $1, 2, 3, \ldots C$ at constant temperature and pressure.

$\therefore$ The Gibbs free energy of each phase is given by,

$$G_\alpha = f(T, P, n_i)_\alpha$$

$$G_\beta = f(T, P, n_i)_\beta$$

$$G_P = f(T, P, n_i)_P$$

where, $i = 1, 2, 3, \ldots i \ldots C$

We know,

$$dG = dG_\alpha + dG_\beta + dG_\gamma + \ldots$$

For multicomponent system,

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$

At constant T and P, $dT = 0$ and $dP = 0$.

$$\therefore (dG)_{T,P} = \sum_i \mu_i dn_i$$

For an infinitesimal transfer of mass from one phase to another,

$$dG = \sum_{i=1} \mu_{i\alpha} dn_{i\alpha} + \sum_{i=1} \mu_{i\beta} dn_{i\beta} + \sum_{i=1} \mu_{i\gamma} dn_{i\gamma}$$

We know that for a closed system at eq^m, $G = 0$

$$\therefore \sum_i \mu_{i\alpha} dn_{i\alpha} + \sum_i \mu_{i\beta} dn_{i\beta} + \ldots\ldots = 0$$

As the system is in equilibrium, the total mass of each component at equilibrium is constant.

Thus,
$$dn_{1\alpha} + dn_{1\beta} + dn_{1\gamma} + \ldots\ldots + dn_{1P} = 0$$
$$dn_{2\alpha} + dn_{2\beta} + dn_{2\gamma} + \ldots\ldots + dn_{2P} = 0$$
$$dn_{i\alpha} + dn_{i\beta} + dn_{i\gamma} + \ldots\ldots + dn_{iP} = 0$$
$$dn_{c\alpha} + dn_{c\beta} + dn_{c\gamma} + \ldots\ldots + dn_{cP} = 0$$

For the above relations to remain zero for all variations of n, we must see that the following requirement is satisfied.

$$\mu_{1\alpha} = \mu_{1\beta} = \mu_{1\gamma} = \ldots\ldots = \mu_{1P}$$
$$\mu_{2\alpha} = \mu_{2\beta} = \mu_{2\gamma} = \ldots\ldots = \mu_{2P}$$
$$\mu_{c\alpha} = \mu_{c\beta} = \mu_{c\gamma} = \ldots\ldots = \mu_{cP}.$$

i.e. For a multiphase system at equilibrium, the chemical potential μ_i of component i is same in each phase.

Gibbs Phase Rule:

It states that, "If the equilibrium in a heterogeneous system is not influenced by electrical, magnetic or gravitational forces, the no. of degrees of freedom (F) of the system, the no. of components (C) and the no. of phases (P) of the system are related ~~to~~ by the equation:

$$\boxed{F = C - P + 2}$$

Derivation:

Let us consider a homogeneous system of P phases and C components. We know that the degree of freedom of a

system in equilibrium is the no. of variables which must be fixed arbitrarily to define the system completely.

For a ~~comp~~ one component system, there are as many concentration variables as the no. of phases. Thus, for each component, we have P concentration variables.

∴ For C components, the no. of concentration variables $= C \times P$.

~~Consider~~ In addition, Pressure and Temperature are two external variables.

∴ Total no. of variables $= CP + 2$.

Also, for each phase there is an equation of state.

∴ For P phases, ~~the phas~~ no. of phase equations $= P$.

Also, for two phases, we have one chemical potential equation.

For three phases, the no. of chemical potential equation $= 2$.

∴ For P phases, the no. of chemical potential equation $= P-1$

As there are C components, the no. of chemical potential equations $= C(P-1)$.

∴ Total no. of equations $= P + C(P-1)$.

∴ Degrees of freedom (F) = Total no. of variables − Total no. of equations;

$$\Rightarrow F = CP + 2 - \{P + C(P-1)\}.$$

$$\Rightarrow F = CP + 2 - P - CP + C.$$

$$\boxed{\Rightarrow F = C - P + 2}$$

Thermodynamic Derivation of Phase Rule Equation:

Let us consider a heterogeneous system having C components ($C_1, C_2, C_3, \ldots C_C$) and P phases ($P_\alpha, P_\beta, P_\gamma, \ldots P_P$). Let us count the no. of intensive variables variants. The pressure and temperature are counted as two. The composition of a phase can be specified by specifying the composition of (C-1) components.

∴ There are P phases, the total no. of composition variable is $P(C-1)$.

At this point, total no. of intensive variable is $\{P(C-1)+2\}$.

At equm the chemical potential of a component J must be the same in every phase.

$$\therefore \mu_{J,\alpha} = \mu_{J,\beta} = \mu_{J,\gamma} = \ldots\ldots \text{ for P phases.}$$

i.e. there are (P-1) equations of this kind to be satisfied for each component J.

∴ For C components, no. of equation $= C(P-1)$.

Each such equm. reduces our freedom to vary one of the $\{P(C-1)+2\}$ intensive variables.

$$\therefore F = P(C-1) + 2 - C(P-1).$$

$$\Rightarrow F = PC - P + 2 - CP + C$$

$$\Rightarrow \boxed{F = C - P + 2}$$

Phase Equilibrium of one component system:

A one component system may consist of one phase, two phase or three phases.

Case I: When, $P = 1$, and $C = 1$,

$$F = C - P + 2 = 1 - 1 + 2 = 2.$$ i.e. Bivariant system.

Case II: When, $P = 2$ and $C = 1$.

$$F = C - P + 2 = 1 - 2 + 2 = 1.$$ i.e. Monovariant system.

Case III: When, $P = 3$ and $C = 1$,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$ i.e. Invariant system.

Phase Diagram of Water system (One component system):

An example of a one component phase equilibrium is the water system. If we ignore the dissociation of water, we would say that only one specie is present and there are no restrictions. i.e. $C = 1$.

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

If we consider dissociation of water,

i.e. $2H_2O \rightleftharpoons H_3O^+ + OH^-$

The system has three chemical species, one reaction equilibrium condition and one electroneutrality condition.

$$\therefore C = 3 - 2 = 1.$$

and $F = 2$.

Thus, whether or not we take dissociation into account, the system has one independent component and two degrees of freedom.

When, $C = 1$, then acc. to gibbs phase rule,

$$F = C - P + 2 = 1 - P + 2 \cancel{= 3}.$$

$$\Rightarrow F = 3 - P.$$

∴ P = 1, F = 2 represents area; P = 2, F = 1 represents line and P = 3, F = 0 represents point.

For a one component system, C = 1, F = 2, we can represent it by a point on a 2D Pressure v.s Temperature diagram where each point corresponds to a definite temp^r and pressure. Such a diagram is called Phase diagram.

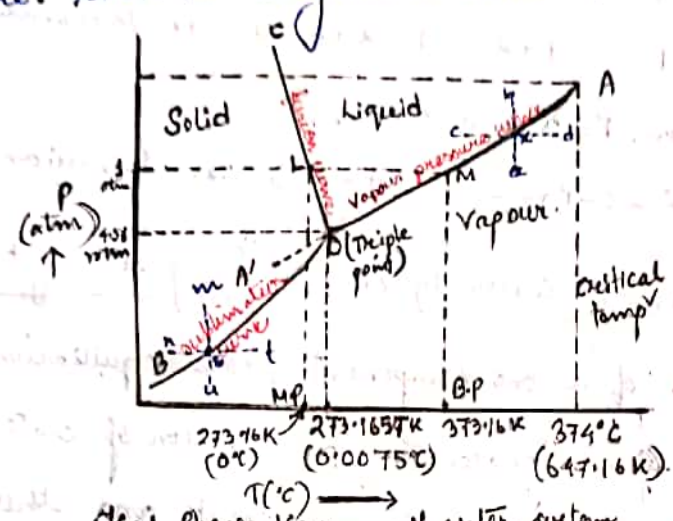

Fig: Phase diagram of water system

The phase diagram consists of three curves OA, OB and OC, each indicating the equilibrium between two phases. These curves divide the diagram into three areas. The area bounded by the curves OB and OC represents the solid phase, area bounded by the curves OA and OC represents the liquid phase and the area bounded by the curves OB and OA represents the vapour phase. The point O where the three curves meet represents the three phases in equilibrium.

Curve OA: It represents the equilibrium between liquid ~~and~~ water and vapour at different temperatures. It is called the vapour pressure curve of water. Here, since two phases are in equilibrium, hence F is 1.

At 373.16 K (100°C), the vapour pressure equals 1 atm (101.3 kPa). Thus, 373.16 K is the boiling point of water.

The curve OA has a natural upper limit at A, which is the critical temperature (374°C or 647.16 K), beyond which liquid water is no longer distinguishable from the vapour phase.

Curve OB: It represents the equilibrium between ice and vapour at different temperatures. It is called sublimation curve of ice. Here, no. of phases is two, hence degree of freedom is 1.

Curve OC: It represents the equilibrium between ice and liquid water. It is called the fusion curve of ice. The normal melting point of ~~water~~ ice is 0.0075°C which decreases slowly with increase in pressure. Thus, the melting ~~of~~ point of ice or freezing point of water is 0.0075°C at 4.58 mm (610 Pa) but is reduced to 0°C at 1 atm (101.3 kPa) pressure.

Metastable Curve OA': It represents the liquid water and water vapours in metastable equilibrium. The liquid below the freezing point is said to be in supercooled states. This state is an unstable state and is known as metastable state.

The point O: The three curves OA, OB and OC meet at point O at which solid, liquid and vapour phases co-exist in equilibrium. This point at 273.1675 K and 4.58 mm pressure is called a triple point. Here, no. of phases is 3, hence degree of freedom is zero.

A point on curve OA:

Let us consider a point 'x' representing the state of equilibrium on the line OA. Here liquid and vapour phases are in contact. If at constant temperature, the pressure is increased, the vapours will be compressed wholly into the liquid phase.

(along dotted line xb). Similarly, if at constant pressure, the temperature is decreased, the vapours will again change to the liquid form (along the dotted line xc). Then, the area above OA represents only the liquid phase.

On the other hand, if at the point x, the temp^r is kept constant and the pressure is decreased (along the dotted line xa), the whole of liquid will get converted into vapour form. Similarly, if at constant pressure, the temp^r is increased (along dotted line xd), the whole of the liquid will be changed to vapour phase. The area below OA represents only the vapour phase.

A point on curve OB:

Let us consider a point 's' representing the state of equilibrium on the curve OB. Here, ice and vapours are in contact. At the point s, if at constant pressure, the temp^r is decreased (along dotted line sn) or if at constant ~~pressure~~ temp^r, the pressure is increased, the whole of vapours get changed into solid ice. Thus, in the region above the curve, OB, only the ~~second~~ solid phase exists, Similarly, ~~be~~ in the region below the sublimation curve OB, only the vapour phase exists.

The Sulpher System:

Sulpher exists in two crystalline forms, i.e. (a) Rhombic (S_R) and (b) Monoclinic (S_M). Rhombic sulpher is stable at ordinary temperature and pressure. Above 95.6°C, monoclinic sulpher is stable and sulpher melts at 119°C. 95.6°C is the

transition temperature at which both the forms exist in equilibrium with each other. Two solid forms of sulphur can exist in equilibrium with each other and can undergo reversible transformation at the transition temp^r. Such a change is called enantiotropy. The liquid form of sulphur (S_L) undergoes changes in colour and viscosity when heated until it boils at 444°C. Sulphur, therefore exists in three forms:

(a) Solid sulphur (S_R) (b) Solid sulphur (S_M).

(c) Liquid sulphur (S_L) (d) Vapour sulphur (S_V).

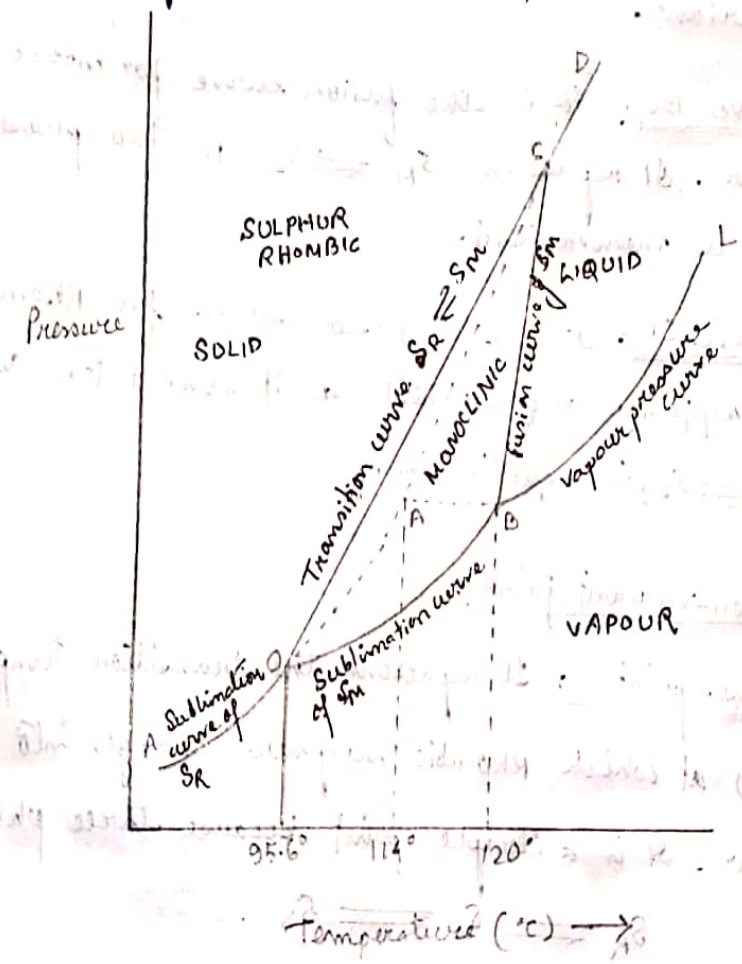

Fig: The Sulphur system.

The Various Curves:

Curve OA: It is the sublimation curve of Rhombic Sulphur. It represents $S_R \rightleftharpoons S_V$ i.e. Two phase equilibrium and hence it is monovariant.

(b) Curve OB: It is the sublimation curve of monoclinic sulphur (S_M). It represents $S_M \rightleftharpoons S_V$ i.e two phase equilibrium and hence equilibrium is monovariant.

(c) Curve BL: It is the vapour pressure curve of liquid sulphur. It shows $S_L \rightleftharpoons S_V$ i.e. Two phase equilibrium and hence equilibrium is monovariant.

(d) Curve OC: It is the transition curve. On this curve, both the phases in equilibrium ($S_R \rightleftharpoons S_M$) are solid. It is monovariant.

(e) Curve BC: It is the fusion curve for monoclinic sulphur. It represents $S_M \rightleftharpoons S_L$ i.e. two phase equilibrium and hence monovariant.

(f) Curve CD: It is the fusion curve for Rhombic sulphur. The system is monovariant as it constitutes two phases ($S_R \rightleftharpoons S_L$) in equilibrium.

The Non-variant points:

(a) The point O: It represents the transition temperature (95.6°C) at which Rhombic sulphur changes into monoclinic sulphur. It is a triple point because three phases.

$$S_R \rightleftharpoons S_M \rightleftharpoons S_V.$$

exists in equilibrium here and it is non variant.

(b) The point B: It represents the melting point of monoclinic sulphur which is 120°C. At this ~~poin~~ triple point, the three phases are in equilibrium as —

$$S_M \rightleftharpoons S_L \rightleftharpoons S_R.$$ It is non-variant

(c) The point C: C is another triple point where phases $S_R \rightleftharpoons S_M \rightleftharpoons S_L$ are in equilibrium and it is non-variant. This point corresponds to the temperature 150°C and 1250 atm pressure.

Metastable equilibria:

Metastable equilibria are shown by the dotted lines in the figure.

(a) Dotted line OA': If rhombic sulphur is heated quickly at above 95.6°C, it will remain in equilibrium with its vapours ($S_R \rightleftharpoons S_V$) for several degrees above the transition temperature, i.e. along the curve OA', the metastable equilibrium ($S_R \rightleftharpoons S_V$) exists.

(b) Dotted line BA': If liquid sulphur is allowed to cool along the curve by the solid monoclinic sulphur may not separate at B. The line BA' represents metastable equilibrium ($S_L \rightleftharpoons S_V$). The point A' represents the melting point of meta-stable rhombic sulphur. The point A' is triple point where three phases exist in metastable equilibrium ($S_R \rightleftharpoons S_L \rightleftharpoons S_V$).

(c) Dotted line CA': This curve shows the effect of pressure on melting point of rhombic (metastable) sulphur. It is also called the fusion curve of metastable rhombic sulphur. Along this curve, S_R is in metastable equilibrium with the liquid.

Phase Equilibria for two component system:

For a two component system, the phase rule equation can be written as,

$$F = C - P + 2$$

$$\Rightarrow F = 2 - P + 2 = 4 - P.$$

Hence, if the no. of phases is one, degrees of freedom will be ~~are~~ three. viz. Pressure, Temp^r and composition.

If the no. of phases is two, degrees of freedom will be two.

If the no. of phases is three, degrees of freedom is one.

If the no. of phases is four, degree of freedom is zero.

Let, the two components are miscible in the liquid state. Here, the following cases are encountered—

① The two components are not miscible in the solid state and form a eutectic mixture.

② The two components form a stable compound with stable melting point.

③ The two components form a compound with incongruent melting point.

Lead - Silver System:

It is an example of simple eutectic system since these metals are completely miscible in the liquid state and don't react chemically to form any compound. The four phases taking part in equilibrium are —

① Solid lead ② Solid silver

③ Solution of lead and silver ④ Vapour.

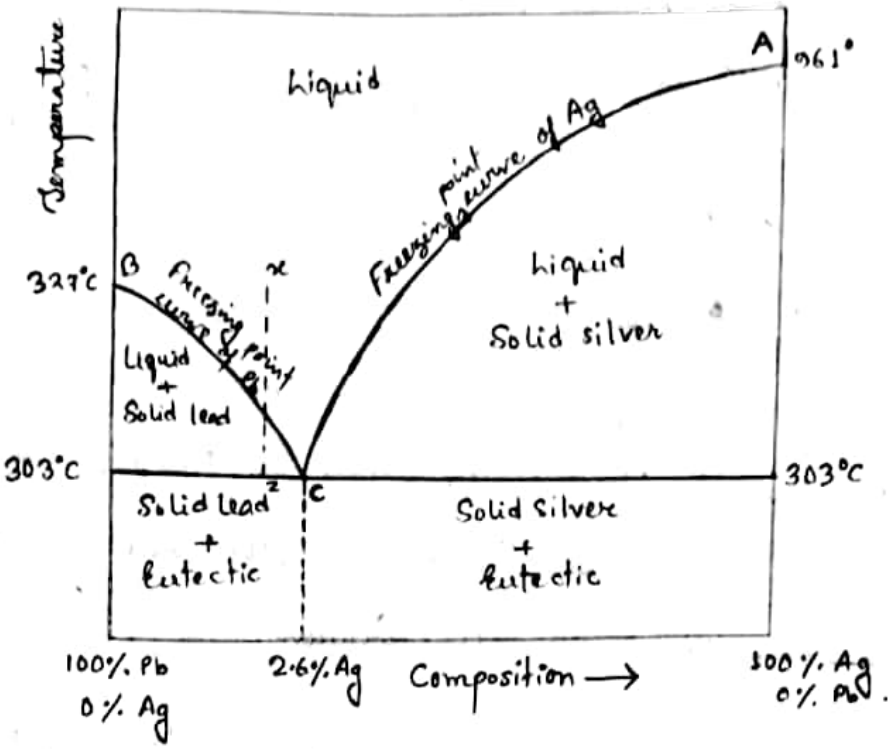

Fig : Lead - Silver System

Curve AC : The melting point of silver is 961°C. The continuous addition of Pb in it lowers the melting point along AC. The point A is the melting point of pure silver where pure solid silver, liquid silver and vapour coexist. The melting point of silver falls gradually with the addition of lead along AC. The lowest point is attained at C. At point C, the solution becomes saturated with respect to lead and if more lead is added, it separates out as a solid. AC curve is called the freezing point curve of silver.

Curve BC : The melting point of pure lead is 327°C. The point B represents the melting point of pure lead where pure solid lead, liquid lead and vapour coexist. The melting point of lead falls gradually with the addition of silver along BC. The lowest point

attained is C. At the point C, the solution becomes saturated with respect to silver and further addition of silver results in its separation as a solid. Curve BC is called freezing point curve of lead.

<u>Eutectic point</u> : Eutectic point is defined as the lowest temp^r at which the liquid mixture of two components can exist and if the liquid is cooled below this temp^r, both the components separate simultaneously in the solid form having the same composition as in the solution.

<u>Eutectic point C:</u> It is the point at which the ~~liquid can exist at~~ curves AC and BC meet. Here, three phases, solid Pb, solid Ag and their liquid solution coexist. Hence, here degree of freedom is zero.

The point C represents the lowest temperature (303°C) at which the liquid can exist and if the liquid is cooled below this temperature, both the components separate simultaneously in the solid form, having composition 97.6 % Pb and 2.4 % Ag. The temperature corresponding to eutectic point is called eutectic temperature. It is always lower than the melting points of the components constituting the mixture. The composition corresponding to the eutectic point is called eutectic composition.