PAPER-I

Unit - 3

Phase Equilibria

Phase :- The physically distinct homogeneous and mechanically separable parts of a heterogeneous system are called phases.

Examples :-

(1). **Gaseous phase** – A gaseous mixture constitute a single phase because they are completely miscible.

(2). **Liquid phase** – Two or more liquids completely miscible gives rise to only one liquid phase but the liquids which are immiscible with each other constitute the no. of phases equal to the no. of liquids in the mixture.

water + ethanol — miscible (1- Phase)

water + Benzene — immiscible (2- phase)

(3). **Solid phase** – Each solid constitute a seperate phase unless a solid solution is formed.

*. **Component :-**

Component is defined as the minimum no. of variable constituents which are required to express the composition of each phase in the system.

Examples :-

(i) Ice ⇌ Water ⇌ Vapour

It is a three phase system but it is one component system, because the composition of each of the three phase present can be directly expressed as H_2O.

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(ii) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

There are three different phase but at least two of the three constituents are needed to represent the composition of all the three phases. The system is a two component system.

(iii) Sulphur exists in four phase, viz. rhombic sulphur, monoclinic sulphur, liquid & vapour. But since the composition of each phase can be expressed in terms of sulphur only, it is a one component system.

*. **Degree of freedom** :-

The no. of degree of freedom is defined as the minimum no. of intensive variable (temperature, pressure and composition) required to characterise the system completely.

Example :-

(i) **A gas system** — for given sample of a gas $PV = nRT$, any two of the three variable $PV = nT$ defined the system completely. Thus, the system has two degree of freedom or is bivariest.

(ii) Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapour

These three phase can co-exist in equilibrium only at one particular temperature and one particular pressure. Hence, the system has no degree of freedom or the system is invariest.

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*. Phase Rule :-

Gibb's Phase Rule :-

Gibb's Phase rule may be stated as follows-
In a heterogeneous system in equilibrium, the no. of degree of freedom plus the no. of phases is equal to the no. of components plus two.

i.e. $F + P = C + 2$

F = no. of degree of freedom.
P = no. of Phases.
C = no. of components
2 = Additional varibles of temperature & pressure besides concentration.

Advantage of Phases :-

The phase rule finds the extensive application in the study of heterogeneous system. Some of them are given below:-

1). It predicts under given condition whether a number of substances taken together would remain in equilibrium or would involved inter conversion or elemination of some of them.

2). It predicts the behaviour of the system with changes in the variables that governs the system in equilibrium.

3). It has been found extremly useful in metalurgy.

4). It can give information regarding the complex formation between various components.

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5). It deals with macroscopic system mainly and not concerned with molecular structure.

Problems :-

Q. Determine the no. of degree of freedom in each of the following system. Suggest the variables that could correspond to these degree of freedom.

a). Liquid water and water vapour in equilibrium.

b). Liquid water and water vapour in equilibrium at a pressure of 1 atm.

Sol^{n}. From Gibb's phase rule—

$$F + P = C + 2$$

or $$F = C - P + 2$$

a). In Case-a

$C = 1$ Hence, $F = 1 - 2 + 2 = 1$.

i.e. Only one variable T or P need to be specified.

b). In Case-b

P is constant, the degree of freedom reduces by 1.

Hence, the phase rule equation becomes

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

In this case $C = 1$ & $P = 2$

$$F = 1 - 2 + 1 = 0.$$

The system under the given condition is thus invariant.

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