10/10/20 Phase Equilibria

Phase : It is defined as any homogenous and physically distinct part of a system which is seperated from other parts of the system by definite bounding surfaces.

Homogenous means it has identical physical properties and chemical composition throughout the whole of the system

Gases → one phase, since gases are completely miscible with one another in all proportions

Liquids → No. of phases is equal to the number of layers present in the system

Solids → every solid has a single phase, but in solid solution is equal to no. of solids present

2) No. of components :- It is the smallest no. of independent chemical constituents by means of which the composition of each / every phase can be expressed

The independent chemical constituents is the one whose conc^{n} can be varied independent of other constituents of the system

1 Component like H_2O Solid H_2O ⇒ liq H_2O liquid H_2O ⇒ water vapour Solid H_2O ⇒ water vapour Every Phase is single constituent i.e H_2O

Two Component eg hydrate system : $Na_2SO_4.H_2O$ $Na_2SO_4.7H_2O$, $Na_2SO_4.10H_2O$ Na_2SO_4, water present in solid, liquid & (g) water vapour

No. of Components = 2.

$CaCO_3 \rightarrow CaO + CO_2$ No. of phases = 3

(S) (S) (g) No. of Components = 2

system has 3 components, but 2 components is sufficient to define the system to express the composition of all the three phase.

$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$ Two phase = 2 solid NH_3, g NH_3, HCl

If system is in vaccum, the no. of components is 1 In gaseous phase both HCl & NH_3 are present in equal amounts

$NH_4Cl \rightarrow x\,NH_3 + x\,HCl$

If dissociation is carried out in arbitary amounts of NH_3 or HCl. then no. of components is 2.

Degrees of Freedom:- It is minimum no. of independent variables such as T, P & concentrations that must be ascertained so that a given system in equilibrium is completely defined.

Solid $\rightarrow$ liquid $\rightarrow$

If there is only one phase, two parameter T & P is required to describe the state of system. $F = 2$

If solid $\rightleftharpoons$ liquid

Temp at which a solid melts depends upon external pressure. Value of one of the variables is fixed then its others will automatically fixed.

At 0°C, 1 atm, ice melts. so one variable is sufficient to define the state of the system either Temp. or Pressure. System has one degree of freedom

Derivation of Phase Rule.

Consider a heterogenious system of 'P' phases at equilibrium containing in 'C' components. Let us assume that 'C' components are present in all 'P' phases.

Total no. of variable;

(1) Temp. of system = 1

(2) Pressure of System = 1

(3) concn of each & every component in all 'P' phases. For each phase, we have to specify the value of 'C' concentrations & Thus for 'P' phases, one has to specify all PC values = PC.

Total no. of variables that need to be specified = CP + 2

Values of these variables can be obtained by solving the equations which are applicable when the system is at equilibrium.

Types of equations

(1) In any one phase, the sum of amount fractions = 1

$x_{1(1)} + x_{2(1)} + x_{3(1)} + \cdots + x_{c(1)} = 1$

$x_{1(2)} + x_{2(2)} + x_{3(2)} + \cdots + x_{c(2)} = 1$

$x_{1(3)} + x_{2(3)} + x_{3(3)} + \cdots + x_{c(3)} = 1$

$\vdots$

$x_{1(P)} + x_{2(P)} + \cdots + x_{c(P)} = 1$

There will be same no. of equations as no of phases. Here the total no is P

(ii) Thermodynamic condition of phase equilibria
The chemical potential of any component will have same value in all the P phase,

$\mu_{1(1)} = \mu_{1(2)} = \mu_{1(3)} = \cdots = \mu_{1(P)}$

$\mu_{2(1)} = \mu_{2(2)} = \mu_{2(3)} = \mu_{2(4)} = \cdots \mu_{2(P)}$

$\mu_{3(1)} = \mu_{3(1)} = \mu_{3(3)} = \cdots \mu_{3(P)}$

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$\mu_{C(1)} = \mu_{C(2)} = \mu_{C(3)} = \mu_{C(4)} = \cdots = \mu_{C(P)}$

For each component there is $(P-1)$ equations & hence for 'C' components the no of equations will be $C(P-1)$

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

Variance = Total no of variables that need to be specified — Total no of equations that are available

$f = (PC+2) - P + CP + C$

$f = C - P + 2$

This is phase rule which connects the no of phases & components with the variance of the system

When $C=2$ then if $P=1$, $f = 2-1+2=2$

$C=2$ if $P=2$ $f = 2-2+1 = 1$

if $P=3$ $f = 2-3+2 = 1$

If $C=1$, if $P=1$ $f = 1-1+2 = 2$

$P=2$ $f = 1-2+2 = 1$

eg: H_2O $P=3$ $f = 1-3+2 = 0$