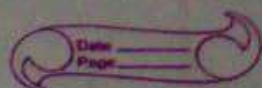


10/10/20

Phase Equilibrium



Phase - It is defined as any homogeneous and physically distinct part of a system which is separated from other parts of the system by definite bounding surfaces.

Homogeneous 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.

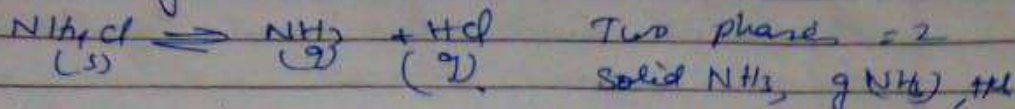
The independent chemical constituents is the one whose concⁿ can be varied independent of other constituents of the system.

1 component like H_2O solid $H_2O \Rightarrow$ ice, liquid $H_2O \Rightarrow$ water, vapour $H_2O \Rightarrow$ water vapour.
Every phase is single constituent i.e. H_2O .

Two component eg. **hydrated system** : $Na_2SO_4 \cdot 7H_2O$, $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4 , water present in solid, liquid or (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.



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

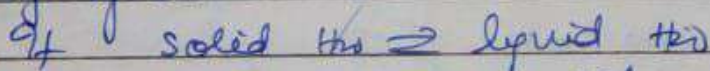
$$\text{NH}_4\text{Cl} \rightarrow x \text{NH}_3 + x \text{HCl}$$

If dissolution is carried out in arbitrary 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.



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



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

Total no. of variables:

- (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 ' concn terms & thus for ' P ' phases, one has to specify all $P \times C$ values = $P \times C$.

Total no. of variables that need to be specified = $C \times P + 2$

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
- $$x_{1(1)} + x_{2(1)} + x_{3(1)} + \dots + x_{C(1)} = 1$$
- $$x_{1(2)} + x_{2(2)} + x_{3(2)} + \dots + x_{C(2)} = 1$$
- $$x_{1(3)} + x_{2(3)} + x_{3(3)} + \dots + x_{C(3)} = 1$$
- $$\vdots$$
- $$x_{1(P)} + x_{2(P)} + \dots + x_{C(P)} = 1$$

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

(i) Thermodynamic condition of phase equilibrium
the chemical potential of any component
will have same value in all the P phases

$$\mu_1(1) = \mu_1(2) = \mu_1(3) = \dots = \mu_1(P)$$

$$\mu_2(1) = \mu_2(2) = \mu_2(3) = \mu_2(4) = \dots = \mu_2(P)$$

$$\mu_3(1) = \mu_3(2) = \mu_3(3) = \dots = \mu_3(P)$$

!

$$\mu_C(1) = \mu_C(2) = \mu_C(3) = \mu_C(4) = \dots = \mu_C(P)$$

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

$$\text{Total no. of equations} = P + C(P-1)$$

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

$$F = (P+2) - P + CP + C$$

$$F = C - P + 2$$

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

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. H₂O, S $P=3$ $F = 1 - 3 + 2 = 0$