Phase rule

Phases :- A phase may be defined as any part of a system which is -

a) homogeneous and separated from other parts of the system by a distinct boundary.

b) Physically and chemically different from other parts of a the same system. and

(c) mechanically separable from other parts of the sestem.

Examples illustrating phases are given below:

System	Phases
i) Ice and water	2 Phases : 1 solid and 1 liquid
ii) Water and water vapour	2 Phases : 1 liquid and 1 gaseous
iii) Ice, water and water vapour	3 Phases : 1 solid, 1 liquid and 1 gaseous.
iv) Two immiscible liquids, e.g- CS_2/H_2O, CCl_4/H_2O etc.	2 Phases : both liquids.
v) $CaCO_3$, CaO and CO_2	2 Phases : both solids.

Components : The number of components of a system at equilibrium is defined as the smallest number of independently variable ~~com~~ constituents by means of which the composition of each phase present can be expressed either directly or in the form of a chemical equation.

e.g - The water system, the water system consist of three phases.

Ice $\rightleftharpoons$ water $\rightleftharpoons$ water vapour.

The composition of any phases (Ice, water or water vapour) in eqm, be expressed in terms of the single constituent i.e. H_2O. So it is a one component system.

ii) Sulpher system consisting of four phases – Monoclinic (s), Rhombic (s), liquid (l) and Vapour (g) is one component system because the composition of each phasses can be expressed in terms of one constituent – sulpher.

iii) Decomposition of $CaCO_3$ by heat can be expressed according to the equilibrium

$$\underset{\text{(solid)}}{CaCO_3} \rightleftharpoons \underset{\text{(solid)}}{CaO} + \underset{\text{(Gas)}}{CO_2}$$

Thus there are three different constituents forming three different phases. But the composition of each phase can be expressed in terms of any two of the constituents. For example,

a) If the constituents are CaO and CO_2, then

Phase		Composition
$CaCO_3$	$\longrightarrow$	$CaO + CO_2$
CaO	$\longrightarrow$	$CaO + 0\,CO_2$
CO_2	$\longrightarrow$	$0\,CaO + CO_2$

b) If the constituents chosen are $CaCO_3$ and CO_2, then,

Phase		Composition
$CaCO_3$	$\longrightarrow$	$CaCO_3 + 0\,CO_2$
CaO	$\longrightarrow$	$CaCO_3 - CO_2$
CO_2	$\longrightarrow$	$0\,CaCO_3 + CO_2$

Similarly composition of the three phases can be expressed in terms of $CaCO_3$ and CaO. Thus the dissociation of $CaCO_3$ by heat is a two component system.

Degree of freedom or Variance - Degrees of freedom or variance of a system is the smallest number of variable factors i.e. temperature, pressure and concentration of the components which must be arbitrarily fixed in order that the conditions of the system may be completely defined.

Phase rule

Statement : The phase rule may be stated as "Provided the equilibrium between any ~~two~~ no. of phases is not influenced by gravity, electrical force or magnetic force or by surface action but influenced only by temp, pressure and composition then no. of degrees of freedom (F) of the system is related to the no. of components (C) and the phases (P) by the eqn,

$$F = C - P + 2$$ for any system at eqm at a definite temp. & pressure.

Derivation :- Let us consider a heterogeneous closed system having 'C' no. of components (denoted by 1, 2, 3 . . . C) & 'P' no of phases (denoted by I, II, III . . . P) in eqm. Since the system is in eqm, it implise that

1. chemical potential of each component in different phases must be same, chemical eqm.
2. all the phases must be at same temp - thermal eqm. &
3. all the phases must be under same pressure.

Let us start with assumption ~~at~~ that all the components are present in all P phases.

The system can be defined completely by specifing the following variables.

Variables	Number
a. Temp. of the system	1
b. Pressure of the system	1
c. Conc. (or mole fraction) of each component in all 'P' Phases. Since each phase contains 'c' components concn. variables for one phase will be 'c'. Therefore, total concn. variables for 'P' phases will be	PC.

Total no. of variables $= PC + 2$

But all the (PC+2) variables are not independent because of the restrictions imposed by the eqm conditions.

The restricted conditions which must be satisfied for the system being at eqm can be calculated as follows —

I. The sum of mole fraction of all the components in a phase is unity we can write the following eqns for ~~eqm~~ when there are 'p' phases (I, II, III ...) & each phase contains 'c' components (1, 2, 3, ...).

For phase I : $x_1^I + x_2^I + x_3^I + \cdots + x_c^I = 1$

" " II : $x_1^{II} + x_2^{II} + x_3^{II} + \cdots + x_c^{II} = 1$

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" " P : $x_1^P + x_2^P + x_3^P + \cdots + x_c^P = 1$

$\therefore$ Total no. of eqm $= P$.

That is due to molefraction condition, 'P' no. of restriction imposed on the system.

At eq^m the chemical potential of each component in various phases must be equal. let 'μ' stands for chemical potential.

For component 1 : $\mu_1^{I} = \mu_1^{II} = \mu_1^{III} = \mu_1^{IV} = \dots = \mu_1^{P}$ .... (P-1) eq^n

" " 2 : $\mu_2^{I} = \mu_2^{II} = \mu_2^{III} = \mu_2^{IV} = \dots = \mu_2^{P}$ .. (P-1) eq^n

" " 3 : $\mu_3^{I} = \mu_3^{II} = \mu_3^{III} = \mu_3^{IV} = \dots = \mu_3^{P}$ --(P-1) eq^n

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" " c : $\mu_c^{I} = \mu_c^{II} = \mu_c^{III} = \mu_c^{IV} = \dots = \mu_c^{P}$ --- c eq^n.

Hence this condition imposed = c (P-1) restrictions.

$\therefore$ Total no. of restrictions = P + C(P-1)

Therefore, the no. of independent variables i.e. degree of freedom (F) required to define a system completely = (total no. of variables) – (Number of restricting condition)

$$= (PC + 2) - [P + C(P-1)]$$
$$= PC + 2 - P - CP + C$$
$$= C - P + 2.$$

$\therefore \boxed{F = C - P + 2} \rightarrow$ This is phase rule.

This phase rule holds good when there is no rxn. bet^n components and eq^m of system affected by temp, pr. and composition only.

When components are interact each other. Then some additional restriction imposed on the composition variables. The no. of ~~sa~~ such restriction depends on the rxn. If g denotes such restritions, the no of degree of freedom will be diminished by the no. g. There fore, in such cases, the degree of freedom $F = C - P + 2 - g = (C - g) - P + 2$

$$= C' - P + 2$$