

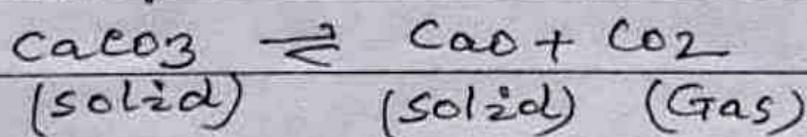
Deg II. Chem. subsidiary (Physical)

Topic :- Phase Rule

Component :- A Component is an element or Compound present in the system. This term according to "Herst" is, however, defined as

The number of components of a system at equilibrium is defined as the minimum number of molecular species in terms of which the composition of every Phase can be expressed by means of a chemical equation

Examples :- Consider the dissociation of  $\text{CaCO}_3$  by heat



this equilibrium consists of three Phases, two solid and one gaseous.

At first sight it appears to be a three Component system but actually it is a two Component system because the composition of every Phase can be expressed by taking any two of the constituents

① By taking  $\text{CaO}$  and  $\text{CO}_2$  as components -

<u>Phase</u>	<u>Components</u>
$\text{CaCO}_3$	$\text{CaO} + \text{CO}_2$
$\text{CaO}$	$\text{CaO} + 0\text{CO}_2$
$\text{CO}_2$	$0\text{CaO} + \text{CO}_2$

② By taking  $\text{CaCO}_3$  and  $\text{CaO}$  as components

<u>Phase</u>	<u>Components</u>
$\text{CaCO}_3$	$\text{CaCO}_3 + 0\text{CaO}$
$\text{CaO}$	$0\text{CaCO}_3 + \text{CaO}$
$\text{CO}_2$	$\text{CaCO}_3 - \text{CaO}$

Derivation of Phase Rule :-

Consider a heterogeneous system in equilibrium which consists  $C$  components distributed in  $P$  Phases. The degree of freedom of a system in equilibrium is the number of variables which be fixed arbitrarily to define the system completely. The number of such variables is given by the total number of variables of the system minus the number of variable which are defined automatically, by virtue of

the system being in equilibrium.

When a system is in equilibrium there can be one temperature and one pressure so these variables in total are 2 only. In order to define the composition of each phase it is necessary to specify  $(C-1)$  composition variables.

Thus for  $P$  phase the composition variables will be  $P(C-1)$

Thus the total number of variables of the system are  $P(C-1) + 2$

Now according to Thermodynamics when a system is in equilibrium, the chemical potential ( $\mu$ ) of a given component must be the same in every phase. Thus if there is one component in three phases say 1, 2, 3 then one of these say phase 1 is referred to as standard phase then this can be written in the form of two equations  $\mu_1 = \mu_2, \mu_1 = \mu_3$

Thus for each component in equilibrium in three phases two equations are known or in general for each component in  $P$  Phases  $(P-1)$  equations are known.

If there are  $C$  Components the number of equations or variables that are known from the conditions of equilibrium are  $C(P-1)$

Since chemical potential is a function of temperature, pressure and concentration it means that each equation represents one variable of the kind mentioned above.

The number of unknown variables or degree of freedom ( $F$ )

$$F = P(C-1) + 2 - C(P-1)$$

$$= P/C - P + 2 - P/C + C$$

$$F = C - P + 2$$

This equation is known as Gibbs' Phase rule.