Gibbs Phase Rule

Gibbs phase rule was given by Willard Gibbs in 1876.

→ It states that if a heterogeneous system is influenced by temperature, pressure and concentration and not by any other action like gravity, electrical forces, magnetic forces or by surface action, then the sum of the phases (P) and degrees of freedom (F) is greater than the number of components (C) by 2. It is expressed mathematically as follows.

$$P + F = C + 2$$

or

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

where P is the number of phases
C is the number of components
F is the number of degrees of freedom.

Advantages of Phase Rule.

(i) Provide simple method of classifying equilibrium states of systems such as phases, components and degrees of freedom.

(ii) Indicates that different system having the same number of degree of freedom behave in like manner.

(iii) Explains the system behaviour when allowed ~~to allowed~~. to changes in the variable such as P, T & concentration

(iv) Phase rule is applicable to macroscopic systems.
∴ not compulsory to take in to account their molecular structure

(v) Applicable to physical as well as chemical equilibria.

(vi) PR predicts that under a given set of conditions
→ whether various substance would exist together in equilibrium
→ whether some of the substance would be interconverted.
→ whether some of the substance will completely disappear.

Limitations of PR

→ Applicable to heterogeneous system, so no use for such system which are slow in reaching the state of equilibrium.

→ PR is applicable to a single equilibrium state, so it never tells about the number of other equilibrium possible in the system.

→ In PR different variables are P, T & Conc. or composition But does not consider other factors like electric and magnetic influences

→ All the phases are required to be present under the same T, P & gravitational forces.

→ S or L phase should not be in finely divided form, otherwise vapour ~~phases~~ pressure may differ from the normal values

→ Does not take into consideration the quality of phases though it takes into account the no. of phases

Application of PR.

All the system are classified on the basis of number of components present.

PR is applicable to 1, 2, 3 etc component systems.

Phase diagram is an important medium which clearly indicate the equilibrium b/w different phases in a system.

→ Phase diagram is helpful for studying and controlling various processes such as phase separation, solidification of metals, the change of structure during heat treatment etc.

Phase Diagram. (PD)

It is a graphical representation of Pressure and temperature under which two or more physical states can exist together in a state of dynamic equilibrium.

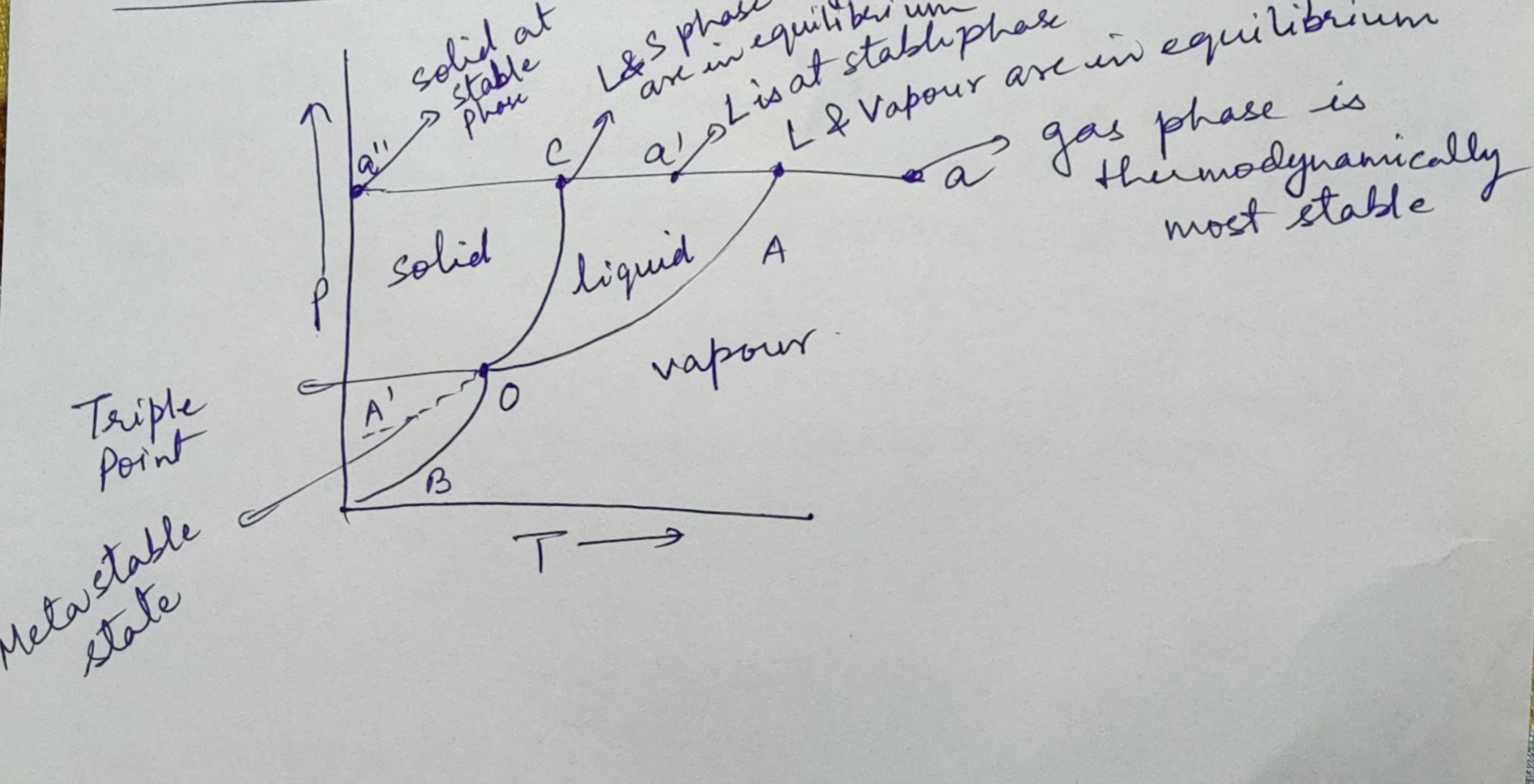
→ PD illustrate the condition of equilibrium between various phases of a substance

→ if T is plotted against P the diagram is called, P-T diagram.

→ PD enables the person to predict clearly the conditions under which a system can remain in equilibrium

PD consist of → Areas
→ Curves / Lines
→ Triple point
→ Metastable state

PD for One component system



(i) Areas — The diagram has 3 region as solid, (BOC)
Bivariant. liquid and vapour
(COA) (BOA)

Each of 3 areas shows condition of T & P under which the respective phase can exist
eg.
when 1 phase.

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

ie both T and P must be specified to define the state of the system.

(ii) Curves :— There are 3 lines or curves separating (Phase Boundaries) the areas and shows the condition of equilibrium between any 2 of the 3 phases

(a) AO represents the equilibrium (vapour-pressure curve).
Liquid ⇌ Vapour.

(b) OB (sublimation curve)
Solid ⇌ Vapour.

(c) OC (Melting or fusion curve or freezing point)
Solid ⇌ Liquid

(d) OA' (Metastable curve) unstable condition (super cooled)
Liquid can be cooled below freezing point without solidification. On adding small amount of seed crystal (solid), entire liquid solidifies rapidly.

Triple Point :-

The three lines on the PD intersect at a common point called the triple point.

→ It is the point at which all the 3 phases of the liquid can co-exist in equilibrium

Solid ⇌ liquid ⇌ Vapour.

$F = C - P + 2 = 1 - 3 + 2 = 0.$

No. degree of freedom.

Both T & P are fixed.

If there is any change in T or P the 3 phases would no longer co-exist and one of the phase will disappear.

Example – Water System (One component system)

Consist of 3 phases

Solid ⇌ liquid ⇌ Vapour.

Ice ⇌ Water ⇌ Vapour
(H_2O) (H_2O) (H_2O)

Since H_2O is the only chemical compound involved. It is a one component system

$C = 1.$

$F = C - P + 2 = 1 - P + 2 = 3 - P$

∴ Degree of freedom depends upon the number of phases present at equilibrium

3 different cases – (i) $P = 1$; $F = 3 - 1 = 2$ (bivariant System)
(ii) $P = 2$; $F = 3 - 2 = 1$ (Monovariant ")
(iii) $P = 3$; $F = 3 - 3 = 0$ (invariant System)

For 1 component system Maximum number of F is 2.