PHASE RULE

Q1) Define Phase, Components, Degree of Freedom.

Ans**) Phase:** A phase is physically distinct, chemically homogeneous and mechanically separable part of a heterogeneous system.

Component: A component is defined as the minimum number of independent species necessary to define the composition of all the phases present in the system either directly or in the form of chemical equation.

Degree of Freedom or Variance: Degree of freedom is defined as the number of factors which may be varied without altering the number of phases in a system. **Or**

The degree of freedom or variance of a system is defined as the minimum number of variable factors such as temperature, pressure and concentration which must be arbitrarily fixed in order to define the system completely.

Q2) Define Gibb's Phase Rule and give its equation.

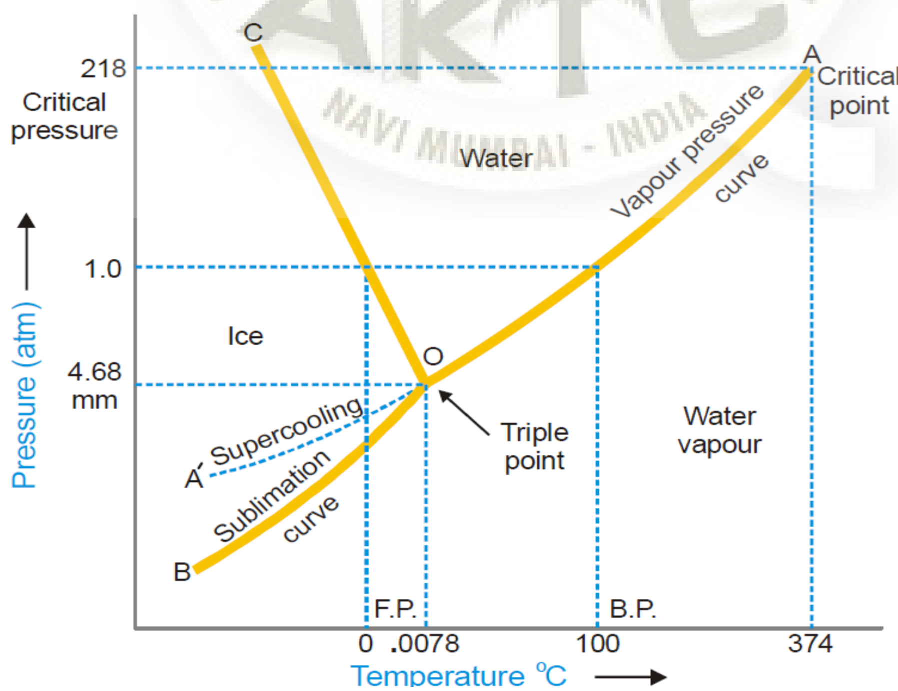
Ans) The Gibb's Phase rule can be defined as "The sum of the number of phases and degrees of freedom of any system exceeds the number of component by two.

$$F+P = C+2, \quad F=C-P+2$$

where, F= Degree of Freedom, C = Components, P = Number of Phases

Q3) Explain the application of Gibb's Phase Rule to one component system (water system).

Ans) **One Component system:** The example of one component system is the water system



THE WATER SYSTEM : This system consists of 3 phases –ice, water, vapour and one component ie H_2O

The salient features of the phase diagram of water system are

a)The curves OA,OB,OC

b)The Triple Point "O"

c)The areas AOC,AOB,BOC

Now, Let us discuss the significance of each of these features.

1)The Curves OA,OB,OC

These three curves meet at a point "O" and divide the diagram into three areas.

Curve OA: Curve OA is the vapour pressure curve of water. It represents the vapour pressure of liquid water at different temperatures. The two phases water and watervapour coexist in equilibrium along this curve. The curve OA terminates at 'A' called the critical Point (218.5atm and 374°C) ,where the liquid and vapour are indistinguishable from each other and thereafter only one phase is left. When the vapour pressure is equal to one atmosphere the corresponding temperature as indicated on the phase diagram is the boiling point (100°C) of water.

Curve OB: The sublimation curve of ice, shows the vapour pressure of solid ice at different temperatures. The two Phases: Solid ice and water vapour coexist in equilibrium along this curve. At the lower limit ,the curve OB terminates at absolute Zero (-273°c) where no vapour exists.

Curve OC: The fusion curve of ice .Here ice and water co-exist in equilibrium .Along curves OA,OB,OC there are two phases in equilibrium and one component .

Therefore, $F = C - P + 2,$

$= 1 - 2 + 2$

$=1$

As these curve having one degree of freedom the systems are called monovariant.

2) The Triple Point 'O': The curves OA,OB.OC meet at the triple point 'O 'where all the three phases ice/water/water vapour coexist in equilibrium. This occurs at 0.0075°c and vapour pressure of 4.58 mm of Hg. Since there are three phases and one component.

We have , $F = C - P + 2$, $F= 1 - 3 + 2$,Thus $F = 0$

i.e. the system at the triple point is non-variant.

Thus, if either pressure or temperature is changed the three phases would not exists and one of the phases would disappear. Since the triple point is validly attained.

3) Areas AOC, AOB, BOC: The areas or regions between the curves show the conditions of temperature , pressure under which a single phase- ice, water or vapour is capable of stable existence.

Area AOC represent condition for 1 – phase system ie water.

Area BOC represents condition for 1 –phase system ie ice.

Area AOB represents condition for 1 – phase system ie water vapour

As all the three areas have one phase and one component ,

Therefore, $F = C - P + 2$, $F=1 - 1 + 2$, Thus $F= 2$

Thus each area system is bivariant.

4) Metastable system : Super Cooled Water/Vapour

The vapour pressure curve for water (AO) can be continued past the triple point as shown by the dotted line OA'. This means water can be super cooled by carefully eliminating solid particles. The super cooled water vapour system is metastable (Unstable) .On slightest disturbance or introducing a crystal office, the metastable system reverts to the stable system i.e ice /vapour system.

Q4) Define and explain Reduced or Condensed Phase Rule equation.

Ans) For two components system the degrees of freedom is three, therefore a phase can be defined by three variables i.e. temperature ,pressure and composition. So for constructing a phase diagram of a two components systems three dimensional space models are required.

To simplify this, it is a usual practice to choose any two of the three variables , assuming the third to be constant, for constructing a simple phase diagram for two components system. Thus the degree of freedom of the system was reduced to one . Therefore, the phase rule equation for a two component system can be written as,

$$F = C - P + 2$$

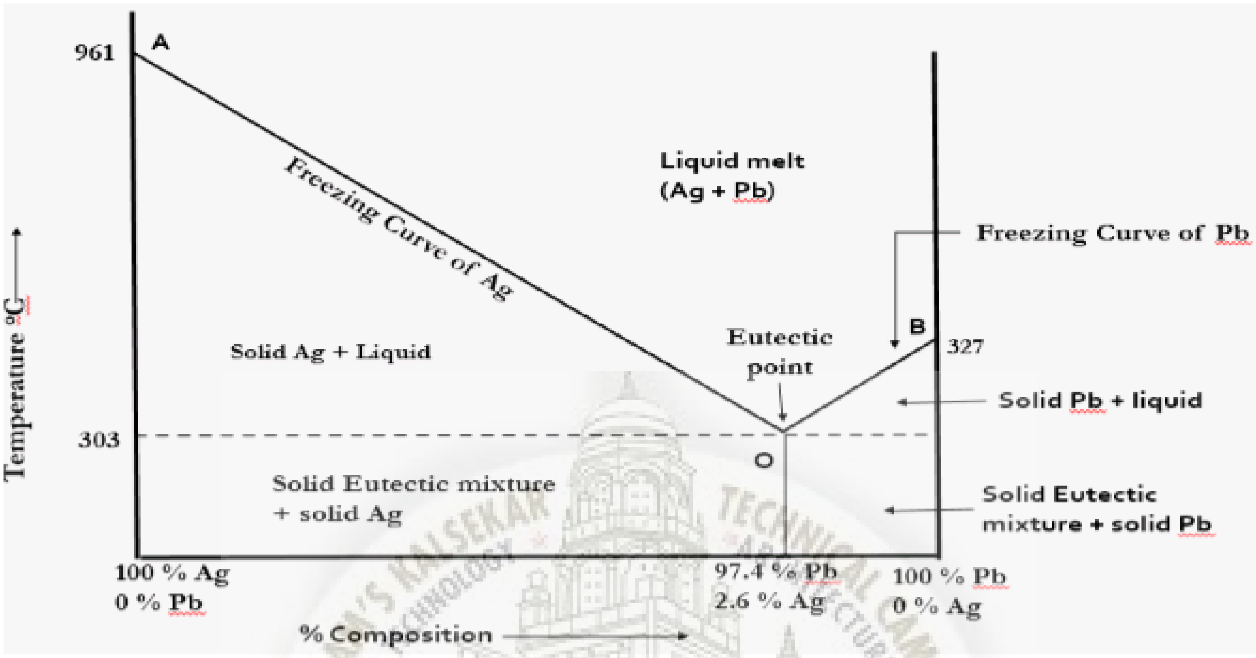
$$F - 1 = C - P + 2 - 1$$

$$F^1 = C - P + 1 \ldots\ldots\ldots(.1)$$

where F^1 is new degree of freedom of the system. Equation (1) is known as Reduced or condensed phase rule.

Q5) Explain application of Reduced Phase rule two Component system(Lead-Silver System).

Ans)**Two Component System:** Lead Silver or Pb-Ag system is a two components system



The two metals : Lead and silver are completely miscible in the molten state and they form a homogeneous solution . They do not react with each other to form any compound.

The equilibrium diagram of Lead –Silver system is as shown above.

The Phases are : a)Solid silver (Ag) b)Solid lead(Pb)

c) Solution of molten silver and lead d)Vapour

The boiling points of silver and lead are very high , the vapour phase is practically absent.

The salient features of Pb –Ag phase diagram.

a) Two curves : AO and BO

b) Eutectic Point : O

c) Three areas: i) Above AO ii)Below AO iii)Below BO

i) The Point 'A' represents the freezing or melting solid silver. The curve AO shows that the addition of lead lower the melting point along it . The phases in equilibrium along AO are solid silver and solution of silver and lead.

Applying the Reduced phase rule: $F^1 = C - P + 1$

$$F^1 = 2 - 2 + 1$$

$$F^1 = 1$$

Thus, the system is monovariant or univariant

ii)**The Curve BO :** The point B represents the freezing point or melting point of solid lead (327°C) and the curve BO shown that the melting point is lowered by the addition of silver. The phases in equilibrium along BO are solid lead and solution of lead and silver .This system is also univarient.

iii)The Eutectic Point 'O': The two curves AO and BO intersects at point 'O' which is called the Eutectic Point .This point being common to both the curves represents the conditions under which three phases.

Solid Lead, Solid Silver , The liquid (Pb + Ag)Co-exist

Applying the reduced phase rule equation :

$$F^1 = C - P + 1$$

$$F^1 = 2 - 3 + 1$$

$$F^1 = 0$$

Thus the system Ag/Pb solution at the point 'O' is non varient i.e. has no degree of freedom . The point 'O' is called as Eutactic point i.e lowest temp .at which the liquid melt can exist.

iv)Area above AOB: It represents solution of Pb-Ag . Along this area only one phase exists

i.e homogeneous mixture of Pb +Ag. Apply reduced phase rule to any point in this area.

We have,

$$F^1 = C - P + 1$$

$$F^1 = 2 - 1 + 1$$

$$F^1 = 2$$

So, the system in this area is bivariant.

Q6) Give the applications and limitations of Phase Rule.

Ans)1) Phase rule is applicable to both physical and chemical equilibrium.

2) The nature or quantities of the components do not have any role.

3) Different systems behave in a similar fashion if they have same degrees of freedom.

4) The nature of the system can be predicated under different sets of variable conditions like

whether different substances can co-exist or be inter converted under different sets of condition.

Limitations Of The Phase Rule:

1) This rule can be applied only to systems that have attained equilibrium ,so it is of no value for system which may attain equilibrium very slowly.

2) In phase rule ,various variables are temperature, pressure and composition. This phase rule does not consider electric and magnetic influences.

3) Phase rule takes into account the number of phases and not their quantities.

Q7) Using phase rule , find the number of phases, degree of Freedom(F) in the following systems at equilibrium :

Ans) **1) In the water system,**

Ice (s) → Water (l) → Watervapour (g)

P = 3 , C = 1 , F = C - P + 2 , F = 1- 3+ 2 , F = 0

2) A gaseous mixture of Nitrogen and Hydrogen

P = 1, C= 1, F= C-P + 2 ,F= 2

3) Saturated solution of NaCl

NaCl → NaCl -water → watervapour

solid Liquid Gas

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

4) Mixture of rhombic and monoclinic sulphur

Rhombic Sulphur → Monoclinic Sulphur

(Solid) (Solid)

P= 2, C= 1, F = 1-2+2 , F = 1

5) Mixture of Oxygen and Nitrogen

P= 1, C= 1, F= 1-1 + 2 , F= 2

6) Ice → Water equilibrium

P= 2 , C = 1, F = 1-2 + 2 , F = 1

7) $CaCO_3 \rightarrow CaO + CO_2$

(s) (s) (g)

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

8) Dissociation of NH_4Cl in a closed vessel

$NH_4Cl \rightarrow NH_4Cl \rightarrow NH_3 + HCl$ (If the proportion of NH_3 and HCl are equivalent)

(s) (g) (g) (g)

P= 2, C= 1 , F = 1-2 + 2 ,F = 1

If the proportion of NH_3 and HCl are in excess

P = 2, C =2, F = 2-2 + 2 ,F = 2

9) Dissociation of $CuSO_4$

$CuSO_4 .5H_2O \rightarrow CuSO_4 .3H_2O + 2H_2O$

(Solid) (Solid) (Gas)

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

10) $Fe + H_2O \rightarrow FeO + H_2$

(s) (l) (s) (g)

P = 3, C = 3 , F = C-P + 2 ,F = 3 -3 + 2 ,F = 2

11) A homogeneous solid solution of salt contains a single phase

eg) Mohr's salt ($FeSO_4 . (NH_4)_2SO_4 . 6 H_2O$) , P = 1

12) Glucose solution in water

P = 1 , Single phase

13) $2CH_3COOH \rightarrow (CH_3COOH)_2$

P = 3 , C = 1 , F = 0

Note : CH_3COOH exist in the form of double molecules entirely in the solid state, to a great extent in the liquid state and only to a smaller extent in the vapour state. This is the equilibrium state where all three phases exist due to association.

14) Monoclinic Sulphur → Liquid Sulphur

(s) (l)

P = 2 , C = 1 , F = 1-2+2 , F = 1

15) $MgCO_3$ →MgO + CO_2

(s) (s) (g)

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

16) I_2 → I_2

(s) (g)

P = 2 , C = 1, F = 1-2+2, F =1

17) PCl_5→PCl_3 + Cl_2

(s) (l) (g)

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

18) Emulsion of oil in water

P= 2, C =2, F= 2-2 + 2, F = 2

19) Sulphur in equilibrium

(Four forms of sulphur : Rhombic Sulphur , Monoclinic Sulphur , Liquid Sulphur , Sulphur vapour

There are two solid phases Rhombic and monoclinic , a liquid phase and vapour phase.

Then, P = 4, C = 1 , F = C-P +2 =1-4+ 2 ,F = -1 which is impossible .

Therefore the maximum number of phases which can exist in equilibrium in the sulphur system is only 3**,** **S_R → S_M → S_L → S_V**

(s) (s) (l) (g)

P= 3 , C = 1, F =0 which is correct

20) H_2O (l) → 1/ 2H_2 (g) +) O_2 (g)

P= 2, C=1 , F= 1

21) H_2O (l) → H_2 (g) + H_2O (g)

P= 2 , C = 2 ,F= 2

22) A gas in equilibrium with its solution in a liquid

C = 2 , P= 2, F = 2

23) A solution of a solid in a liquid in equilibrium with solvent vapour.

F =2, P =2 ,C=2

24) Two partially miscible liquids in the absence of vapour.

F = 2 , p= 2 ,c = 2

25) NH3 (g)

P=1, C = 1, =F= 2
