No exception if perfectly applied.

willard gibbs

6. Phase Rule

Date

Page

kiya Ja sakta hai

can calculate effect of temperature, pressure and Concentration quantitatively on a heterogeneous system

Par

phase :- A phase is Homogenous (chemically homogeneous or), physically distinct, mechanically separate part of the system is called phase.

e.g water system.

Component :-

Phase rule is defined as:- when a heterogeneous system in equilibrium at definite temperature and pressure, the number of degree of freedom is equal to by 2 the difference the number of components and the phases provided that the equilibrium is not affected by external factor such as gravity, magnetic & electrical force.

GIBB'S PHASE RULE :-

When a heterogeneous system in equilibrium influenced (affected) by Temperature, Pressure and Concentration But not influenced by Elecitrical, magnetic force, gravity or by Surface tension etc.

$$F + P = C + 2$$

It is applicable for all universally persent Heterogenous system.

F = Number of degree of freedom

P = Number of phase

C = number of component

phase : A phase is chemically homogeneous, physically distinct, mechanically separate part of the system

e.g. Chemically homogeneous → means → System has identical physical properties and Chemical composition

physically → distinct (seperate) → means → the phase should have a definite bounding surface

mechanically separate → means → Each phase can be separate from every other phase by filtration, decantation, hand picking, etc.

e.g

(1) In air (salt - water)

If all salt is dissolved in the water, consists of only one phase

(2) In (water system)

At freezing point, an equilibrium exists where $\underbrace{\text{Ice, water and water vapour}}_{\text{the three phases}}$

- the three phases

- each are physically distinct, Homogeneous and definite boundaries b/w ice, water and water vapour

$$\boxed{\text{Ice} \rightleftharpoons \text{water} \rightleftharpoons \text{Water vapour}}$$

- The minimum No. of required chemical constituents which can be expressed directly or by mean of a chemical eq. composition of all the phase

minimum no. of constituent sufficient to determining the composition of all phase of system

Component :

- The minimum number of Independent Variable chemical constituent which are required to express the composition of each phase in the system directly or by means of a chemical equation.

$C = N - E$

no. of constituent (N); relation b/w them (E)

e.g

(1) water system

(1) Sulphur system → sulphur system consits four phases

(a) monoclinic sulphur (b) Rhombic sulphur

(c) liquid sulphur (d) Sulphur vapour

- The composition of each phase of the system can be expressed in terms

one constituent Sulphur

Hence, it is ~~one~~ one component system

(2) when calcium carbonate is heated in closed vessel

$$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$$

- There are Three phase $CaCO_{3(s)}$, $CaO_{(s)}$, $CO_{2(g)}$

- Thus, decomposition of $CaCO_3$ $\boxed{\text{gives}}$ $CaO_{(s)}$ and $CO_{2(g)}$

- System is Two Component system

- The composition of each phase of the system can be expressed in terms

any two of the three constituents system

kitne minimum variable
batane ki jarurat hai ke main
uska ~~State~~ pata kar saku called (Temp) - (Press) (Conc.)

Defined as the minimum no. of variable (T, P, Conc.) that can be changed independently without disturbing the no. of phase in equilibrium

Degree of freedom:

- Degree of freedom may be define as the number of intensive variable (Temperature, Pressure, ~~...~~ Concentration) that can be changed independently without disturbing the no. of phases in equilibrium

- A System having one degree of freedom → is a Uni-Variant or mono-variant System

- A System having two degree of freedom → bi-Variant System

- A System having three degree of freedom → tri-Variant System

- A System having zero degree of freedom → non-variant or invariant System

e.g (1) If all three phases are in equilibrium,
three no condition need to be specified
because the three phase can be in equilibrium only at particular temperature and Pressure

Ice(s) Water(l) water vapour(g)

→ The system is $\boxed{\text{no degree of freedom}}$ or $\boxed{\text{zero variant}}$

(2) - If temperature or pressure in altered. (changed)
- three phases will not remain in equilibrium
- one of phase disappears.

water(l) water vapour(g)

- Temperature and pressure is must to define the system completely

→ $\boxed{\text{Freedom is one}}$ or
System is $\boxed{\text{Univariant}}$ or $\boxed{\text{mono-variant}}$

- It is one component system as H_2O is the only chemical involved.
- water exists in three phase namely solid, liquid, gases/vapour

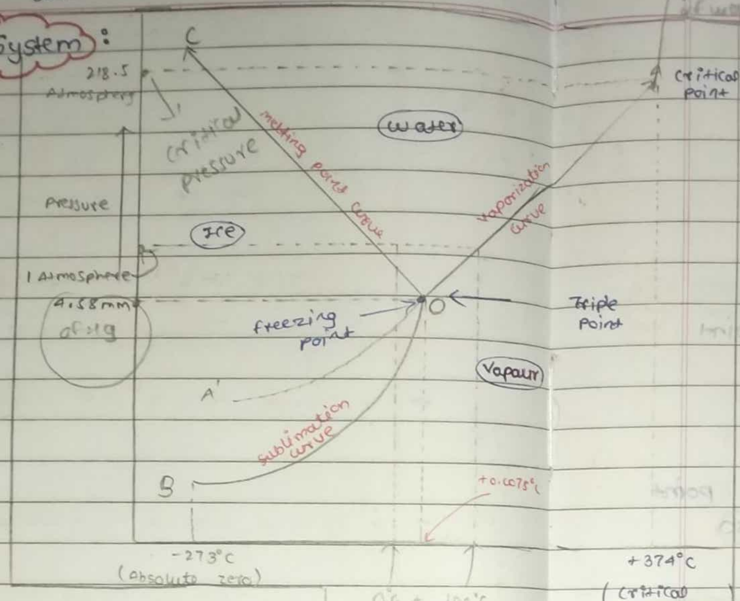
One Component System : (water)

The diagram consists of

(1) Curve : three curves are OA, OB and OC.

(2) Area : three curves divide the diagram into three area AOC, AOB, BOC

(3) Triple point : The three curves meet at point O which is known as triple point.



The phase diagram of water system

One Component System

Description of the phase Diagram :

Curves: ① Curve OA

(1) This curve known as Vapour Pressure curve because it gives the Vapour pressure at different temperature

(2) The curve start from O → which is freezing point of water. and end at A → which is critical temperature of water (374°C)

Beyond the point A → i.e. critical temperature ↳ the two phase liquid water and water vapour merge into each other

(3) along this curve there exist liquid water in equilibrium with water vapour.

(4) From this curve It is seen that any given temperature, there exists → fixed value of pressure

Similarly, for each vapour pressure, → temperature also has fixed value

(5) Thus, the degree of freedom on any point in this curve is one or univariant

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

** The number of phases is taken as two because liquid water and water vapour exist along the curve OA

② Curve OB :

(1) This curve is known as Sublimation curve

(2) Along this curve solid ice in equilibrium with vapour

(3) This curve shows the variation of vapour pressure with it vapour

(4) This curve start at O and end at B → which is absolute zero (-273°C)

(5) From this curve it is seen that each vapour pressure → can be maintained → only at a fixed temperature

(6) The system has one degree of freedom or it is univariant

applying phase rule, we have

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

(7) There are two phases exist in equilibrium along curve OB.

③ Curve OC :

(1) This curve is known as Fusion curve OR melting point

(2) along this curve ice in equilibrium with liquid water

(3) This curve start at O and End at C

(4) This curve indicates the effect of pressure on melting point of ice

(5) Inclination curve toward the pressure axis i.e Y-axis indicates melting point of ice is lowered by increases pressure

(6) degree of freedom is one or univariant

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

It mean that For any given pressure → melting point must have one definite value

(1) The three curves OA, OB and OC meet at a point which is known ~~triple point~~

(4) Triple point :

(2) At this point all the three phases namely water ice vapour

Thus the value of P = 3

(3) Applying the phase rule to this point

$$F = C - P + 2 = 1 - 3 + 2 = \underline{0}$$

(4) Thus the degree of freedom at triple point is zero

(5) It means that three phases can co exist in equilibrium only at a definite temperature and pressure

(6) Thus value of temperature and pressure → corresponds to point O are $\boxed{4.5\,mm \text{ of } Hg}$ and $\boxed{0.0098°C}$

(7) If pressure and temperature are varied three different cases :

- If pressure↑ is raised without changing the temperature → only liquid phases will be there.

  other two phase, ice and vapour will be converted into liquid

- If pressure↓ is lowered without changing the temperature → only vapour phases will be there.

  other two phase, ice and liquid will be converted into vapour

- If pressure and temperature are varied together

↓

all three curve (i.e OA, OB and OC

↓

will be depending upon value of pressure and temperature

(5) Areas AOB, BOC and AOC :

↳ The areas b/w curves OA, OB and OC are AOB, BOC and AOC

- In each area, a single phase i.e Solid ice, water and vapour

(1) In The Area AOB :

↳ only vapour phase exist

(2) In the Area AOC :

↳ only water phase exist

(3) In The Are BOC :

↳ only Ice exist

All these area are bivariant

$$F = C - P + 2$$
$$= 1 - 1 + 2$$
$$= \underline{2}$$

also called eutectic system

Two Component System : → mixture of two component → meaning How mass, composition, temperature

General characteristics

(1) maximum no. of phases will be 4

$P = C - F + 2$

$= 2 - 0 + 2$

$\boxed{P = 4}$

(2) maximum no. of degree of freedom will be 3

$F = C - P + 2$

$F = 2 - 1 + 2$

$\boxed{F = 3}$

Silver lead System : The Pb-Ag System consist of the following phase

(1) Solid lead
(2) Solid silver
(3) Solution of silver and lead
(ii) Eutectic solid sol. of Ag and Pb
(iv) Eutectic liquid sol. of Ag and Pb
(4) Vapour phase

But the B.P of silver & lead being considerably High, The vapour phase is practically absent.

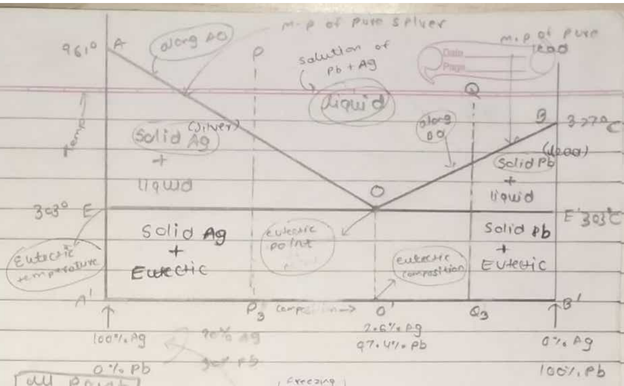
The effect of pressure is negligible, hence it is necessary to take into account the two variable Temperature Concentration

Such as solid - liquid System with the gas phase absent is called Condensed System.

The phase diagram is given below :

In this diagram : Following features are observed

(a) The curve AO (Freezing curve Ag) — or curve and curve
(b) The cure BO (Freezing curve Pb)
(c) the eutectic point O → when two curves meet at point O
(d) The area AOB



all point — freezing point

(1) Point A → represents the m.p of Pure Silver.
(2) Point B → represents the m.p of Pure lead.
(3) It can be seen from the diagram that

addition of Pb to pure Ag ⟶ lower the m.p of Ag

addition of Ag to pure Pb ⟶ lower the m.p of Pb

(4) All the point of curves AO and BO → represent the m.p of Ag and m.p of Pb in various mixture of Ag and pb

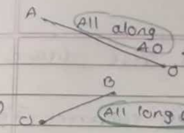
(5) AO → represent the m.p of curve silver or Freezing point curve of silver

Show the effect → addition of lead on the m.p of pure silver

BO → represent the m.p of curve lead or the f.p of curve silver

Show the effect → addition of silver on the m.p of pure lead

(6)



All along AO, Solid Ag and liquid are in equilibrium

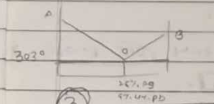
(7) All long BO, Solid Pb and liquid are in equilibrium

Hence AO and BO → Both represent univariant system

$F = C - P + 1$

$= 2 - 2 + 1$

$= 1$



(3) Eutectic point :

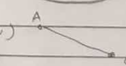
(8) The curve AO and BO intersect at point O at temperature 303°C

the point O is called Eutectic temperature or eutectic point

and corresponding to the composition (2.6% Ag + 97.4% Pb) which is called eutectic composition

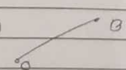
(1) All curve; point

(1) Curve AO : (i) AO is represent the m.p of Ag (961°
(ii) curve AO is called m.p of curve Ag or Freezing point curve of Ag
(iii) Show the effect → addition of Pb → on the m.p of pure Ag
(iv)



along curve AO → Solid Ag and liquid are in equilibrium

(2) Curve OB : (i) OB is represent m.p of pure pb (327°
(ii) curve OB is called m.p of curve Pb or freezing point of curve Pb
(iii) Show the effect → addition of Ag → on the m.p of pure pb
(iv)



along curve OB → Solid Pb + liquid are in equilibrium

$F = C - P + 1$

$= 2 - 2 + 1 = 1$

Date
Page

also called eutectic system

Two Component System : → mixture of two component → meaning How mult. composition, Temperature

General characteristics

(1) maximum no. of phases will be 4

$P = C - F + 2$

$= 2 - 0 + 2$

$\boxed{P = 4}$

(2) maximum no. of degree of freedom will be 3

$F = C - P + 2$

$F = 2 - 1 + 2$

$\boxed{F = 3}$

Silver lead System : The Pb - Ag System consist of the following phase

(1) Solid lead
(2) solid silver
(3) Solution of silver and lead
(iii) Eutectic Solid sol. of Ag and Pb
(iv) Eutectic liquid sol. of Ag and Pb
(4) Vapour phase

But the B.P of Silver & lead being considerably → High,

The vapour phase is practically absent.

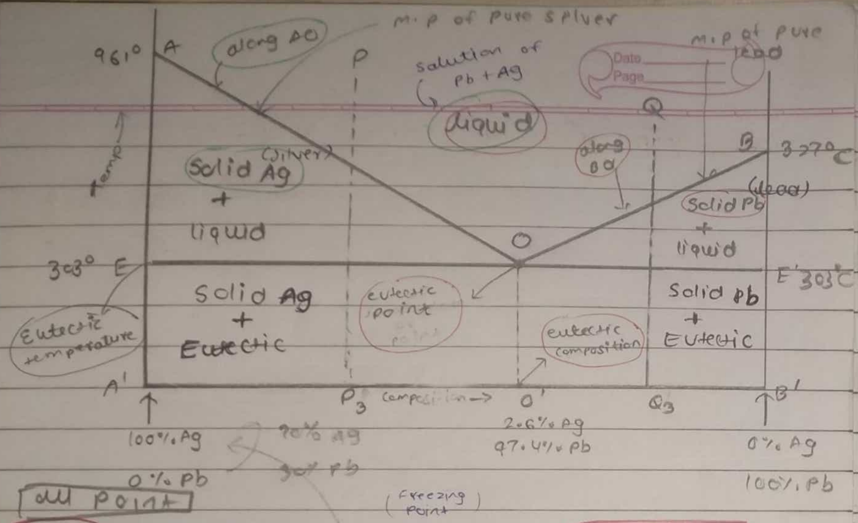
The effect of pressure is negligible, hence it is necessary to take into account the two variable → Temperature, Concentration

Such as solid - liquid system with the gas phase → absent is called Condensed System

The phase diagram is given below :

In this diagram : Following features are observed

(a) The curve AO (Freezing curve Ag)
(b) The cure BO (Freezing curve Pb) → AO curve and CP curve
(c) the eutectic point O → when two curves meet at point O
(d) The area AOB



all point

(1) Point A → represents the M.P of pure silver.

(2) Point B → represents the M.p of Pure lead.

(3) It can be seen from the diagram that

addition of Pb to pure Ag ⟶ lower the m.p of Ag

addition of Ag to pure Pb ⟶ lower the m.p of Pb

(4) All the point of curves

AO and BO → represent the m.p of Ag and m.p of Pb in various mixture of Ag and Pb

(5) AO → represent the m.p of curve silver or Freezing point curve of silver

show the effect → addition of lead on the m.p of pure silver

BO → represent the m.p of curve lead or the f.p of curve silver

show the effect → addition of silver on the m.p of pure lead

(6) A — All along AO — O, Solid Ag and liquid are in equilibrium

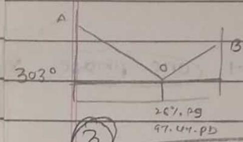
(7) O — All long BO — B, Solid Pb and liquid are in equilibrium

Hence AO and BO → Both represent univariant system

$F = C - P + 1$

$= 2 - 2 + 1$

$= 1$



(3) Eutectic point :

(8) The curve AO and BO intersect at point O at temperature 303°C

the point O is called Eutectic temperature or eutectic point

and corresponding to the composition (2.6% Ag + 97.4% Pb) which is called eutectic composition

(1) All curve; point

(i) Curve AO : (i) AO is represent the M.P of Ag (961°C)

(ii) curve AO is called m.p of curve Ag or Freezing point curve of Ag

(iii) Show the effect → addition of Pb → on the m.p of pure Ag

(iv) A — O along curve AO → Solid Ag and liquid are in equilibrium

(2) Curve OB : (i) OB is represent M.P of pure Pb (327°C)

(ii) curve OB is called m.p of curve Pb or freezing point of curve Pb

(iii) Show the effect → addition of Ag → on the m.p of pure Pb

(iv) O — B along curve OB → Solid Pb + liquid are in equilibrium

$F = C - P + 1$

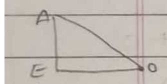
$= 2 - 2 + 1 = 1$

This phase diagram show $\boxed{\text{five distinct region}}$

① $\boxed{\text{The region above AOB}}$ → two component Ag and Pb are present only as homogeneous liquid sol.

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

As the system consists of only one phase in this area is $\boxed{\text{bivariant}}$.



It $\boxed{\text{means}}$ that both temperature and composition are required to define any point in this region

② $\boxed{\text{The region enclosed by the curve AOE}}$ → In this region solid Ag + liquid alloy are stable

③ $\boxed{\text{The region enclosed by the curve BOE}}$ → In this region solid Pb + liquid alloy are stable

④ $\boxed{\text{The region enclosed by EOO'A'}}$ → In this region solid Ag + eutectic are stable

⑤ $\boxed{\text{The region enclosed by E'OO'B'}}$ → In this region solid Pb + eutectic are stable advantage

Application of phase rule :

(1) It is applicable to both physical and chemical equilibria.

(2) It help us to predict → The behavior of a system → under different set of variable → Temperature, pressure and concentration

(3) phase rule is convenient method → which help to classifying equilibrium state → In terms of → Component, phases, degree of freedom

(4) The different system → which are having the same value of degree of freedom → they would behave similarly

(5) It have extensive use in study of Heterogeneous system

This phase rule is useful in → metallurgy; provide useful information about complex formation disadvantage

Limitation of phase rule :-

(1) phase rule → Con be applied → for system in equilibrium only

(2) Not easy to identify → No. of phases
→ No. of component
→ No. of degree of freedom

(3) It is not much help in case of
system which attain equilibrium state very slowly.

(4) It is applies only on a single equilibrium
and does not tell us about other possible equilibria present in the system

(5) This phase rule does not give any information
regarding the time taken for the system to attain equilibrium

(6) phase rule deal with → macro scopic study
and
It does not tell anything about → molecular structure