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Phase Rule

→ It is used for the quantitative analysis of thermal equilibrium

→ Gibb's Phase Rule -

- Provided the equilibrium between the no. of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action & only by temperature, pressure & concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) & of phases (P) by the phase rule equation,

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

for any system at equilibrium at a definite temperature and pressure.

→ Phase :

- Any homogenous, physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of system.
- Eg : * A system with CO_2 gas → 1 phase (gas)
  * A system of miscible water & alcohol → 1 phase (liquid)
  * A system of immiscible water & ether → 2 phase
  * $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ → 3 phases

    ↙ 2 solids ↘ 1 gas.

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→ Components :
→ the smallest number of independent variable constituents, taking part in the state of equilibrium by means of which composition of each phase can be expressed in the form of a chemical equation

OR

number of chemical constituents of the system minus the number of equations relating to these constituents in an equilibrium state, i.e, $C = N - E$

Eg: * In the water system,

$$Ice\,(s) \rightleftharpoons Water\,(l) \rightleftharpoons Vapour\,(g)$$

Chemical composition of all 3 phases is H_2O ⇒ 1-component system.

* Sulphur System consists of 4 phases { rhombic, monoclinic, liquid, vapour } chemical composition is S

⇒ One Component System

* In the thermal decomposition of $CaCO_3$,

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

$N = 3$

$E = 1$

$\Rightarrow C = 3 - 1 = 2$

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Degree Of Freedom, (or), Variance -

- the minimum number of independently variable factors, such as temperature, pressure & composition of the phases, which must be arbitrarily specified in order to represent perfectly the condition of a system.

Eg :* In case of water system Ice(s) $\rightleftharpoons$ Water(l) $\rightleftharpoons$ Vapour(g)

- no need of a condition to be specified as the 3 phases can be at equilibrium at particular T & P.

$\Rightarrow$ Zero-Variant / Non-Variant / Invariant

* Water(l) $\rightleftharpoons$ Vapour(g)

- either T or P to be specified

$\Rightarrow$ Monovariant / Univariant

* Vapour (g)

- both T & P to be specified

$\Rightarrow$ Bivariant

* For a gaseous mixture of N_2 & H_2 -

- both T & P, because if temperature & pressure are fixed, volume automatically becomes definite.

$\Rightarrow$ 2 Degrees of freedom (Bivariant)

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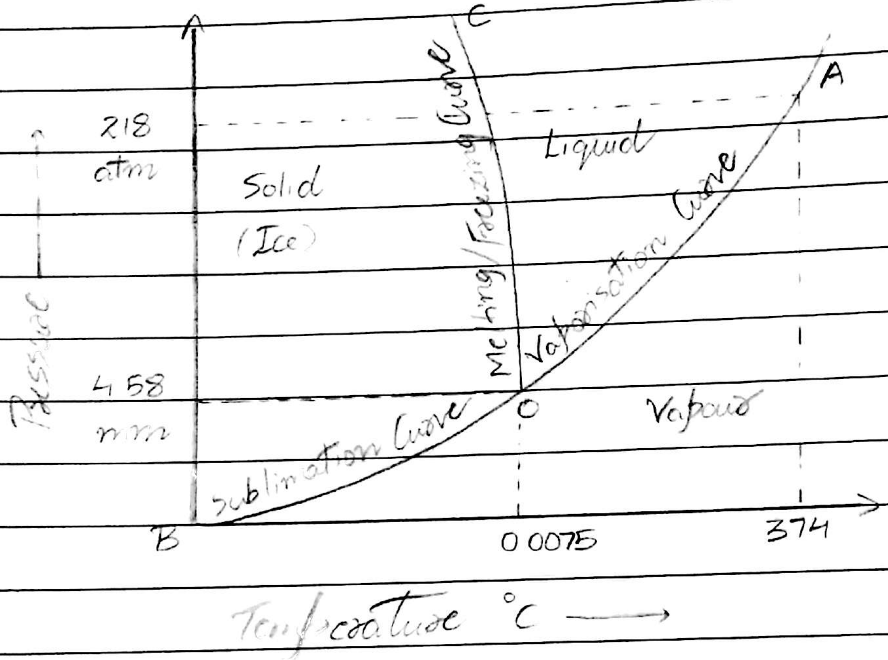
(B)

→ One Component System-

(A) Water System:



O ≡ Triple Point : All 3 states co-exist.

At O, $P = 3$

$C = 1$

$\Rightarrow F = -3+1-2 = 0$

$\Rightarrow$ System is invariant.

OA, OC, OB : Co-Existent Curves [$P=2, C=1 \Rightarrow F=1$]

Areas AOB, AOC & BOC are fields of existence of vapour, liquid & ice phase. $\Rightarrow P=1,\ C=\cancel{3}1 \Rightarrow F = 1-1+2$

$= 2.$

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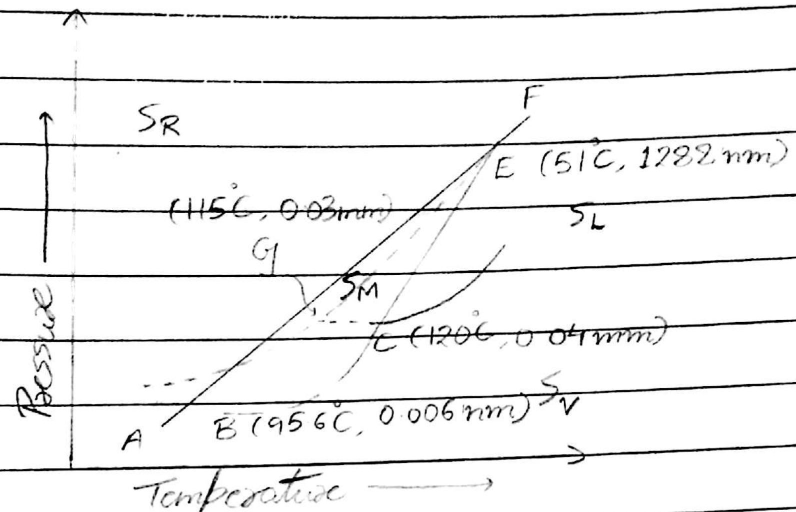
(B) Sulphur System -



As F can't be -ve ⇒ only 3 phases can co-exist at a time.

3 stable triple points:

$B \rightarrow S_R, S_M, S_V$

$C \rightarrow S_M, S_L, S_V$

$E \rightarrow S_R, S_M, S_L$

→ Eutectic System -

2. A binary system consisting of two substances, which are miscible in all proportions in the liquid phase, but which do not react chemically is called eutectic (easy to melt) system.

Eg: a mixture of Pb & Ag.

* Eutectic Mixture: a 'solid solution' of 2 or more substances having the lowest freezing point of all the possible mixture of the components

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* Eutectic Point : 2 or more solid substances capable of forming solid solutions with each other have the property of lowering each other's freezing point, & the minimum freezing point attainable corresponding to the eutectic mixture, is called the eutectic point (means lowest melting point)

* Application of eutectics -
  - low melting alloy are used in safety devices (eg. as plugs in automobiles), fire sprinklers & as 'fail-safe' device in boilers.

→ Lead Silver System -
  - Simple Eutectic formation
  - a 2 component system with 4 possible phase - solid Ag, solid Pb, solution of Ag + Pb & vapour.

Note : Phase Rule for two-component alloy systems -
  - P = 2 ⇒ F has the highest value of 3
    - ⇒ phase diagram may be represented as 3-D of pressure, temperature & composition which can't be conveniently shown on paper.

- A solid liquid equilibrium of an alloy has no gas phase & effect of pressure is negligible ∴ experiments are conducted by keeping P constant of a system in which vapour phase is not considered is Known as condensed system.

⇒ The Phase Rule changes to, $F = C - P + 1$

2 Reduced (or Condensed) Phase Rule.

⇒ It has 2 variables – Temp. & composition; & solid-liquid equilibria is represented by temp-composition diagrams

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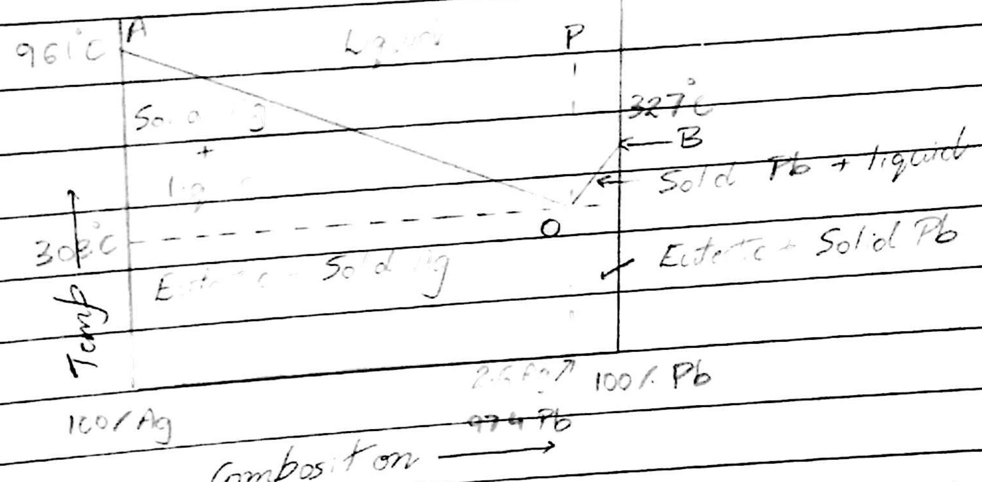
2 As the gas phase is practically absent & P is neglected, using the condensed phase rule, $F = C - P + 1 = 2 - P + 1 = 3 - P$.



AO ≡ Freezing Pt. Curve of Ag, $F = 3 - P = 3 - 2 = 1$ ⇒ univariant.

BO ≡ Freezing Pt Curve of Pb ⇒ univariant

O ≡ Eutectic Point

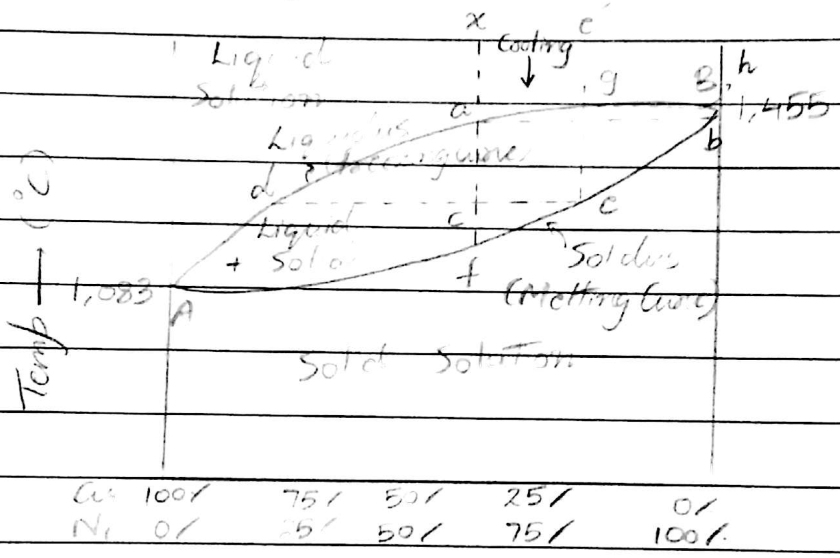
2 3 phases: Solid Ag, Solid Pb & their solution, co-exist

2 represents a fixed composition ($Ag = 2.6\%$, $Pb = 97.4\%$)
(Eutectic Composition)

2 No mixture of Pb & Ag has a melting pt. lower than the eutectic temperature.

→ Cu - Ni Alloy System -

- soluble in each other in all proportions in solid states.
- freezing pt. of Cu & Ni are resp. 1083°C & 1452°C
- addition of Ni to Cu raises the f.p while addition of Cu to Ni depresses the f.p.
- f.p. of mixture of any composition of Cu & Ni lies b/w individual f.p. of Cu & Ni



* Effect of Cooling -

- For any mixture of Cu & Ni in molten state, say x, F=2(2-1+1)
- When cooled directly to A, F = 1 (2-2+1) & system can't be further cooled without affecting the conc. The solid that appears is neither pure Cu nor pure Ni but a solid solution of Cu & Ni.
- ratio of Ni to Cu is ↑ than in original liquid (x) in b & hence, the liquid becomes richer in Cu. As Cu tends to diminish the f.p the liquid, if cooled, will now freeze at a still lower temp.
- due to exothermic nature of change from liquid to solid, rate of cooling is slowed down.

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→ The system at c consists of liquid with composition d in equilibrium with solid solution of composition e.

→ ⇒ dce is the tie line that gives the composition of the liquid solution ~~of comp~~ in equilibrium with solid solution

Using lever rule at c,

$$\frac{\text{Amount of solid}}{\text{Amount of liquid}} = \frac{dc}{ce}$$

⇒ residual liquid (after separation of solid phase) becomes richer in Cu & poorer in Ni

→ the composition of liquid solution moves along aA, while that of solid along Bf

→ At f, system solidifies as such.