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PHASE RULE

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Phase rule:

It state that:
"provided the eqllbm b/w any no. of phase is not influenced by gravity, electrical or magnetic forces or by surface action & only by temp., press. & concent². then the no. of degree of freedom (F) of the system is related to the no. of components (C) & phases (P)

$$F = C - P + 2$$

Phase:

Any homogenous, physically distinct & mechanically separable portion of system having all the physical & chemical properties the same throughout the system".

→ A system may consist of one or more phases.

1) at freezing pt., water consist 3 phases. → Ice (s), → Water (l), → Water vap. (g)
2) A gas mixt, will const. only 1 phase
3) If two immiscible liq → (e.g benzene & H_2O ⇒ 2 phases)
4) " " miscible " → (e.g ethanol & H_2O ⇒ 1 phase)
5) A sol" of sub. e.g glucose in water ⇒ 1 phase
6) Each solid make new phase e.g each form of S.

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

3 phase.

$$Fe(s) + H_2O(g) \longrightarrow FeO(s) + H_2(g)$$ 3 phase.

⇒ A part of a system is homogenous if it has identical physical & chemical composition throughout the part.

Component :-

The smallest no. of undependent variable constituents, taking part in the state of eq/bm, by means of which the composition of each phase can be expressed in the form of chemical eq^n.

e.g. ① Ice (s) $\rightleftharpoons$ Water (l) $\rightleftharpoons$ Vap. (g)
one component system.

② Sulphur system (4 phases)
rhombic, monoclinic, liquid & vap.

⇒ no. of components of a system may alternatively be defined as the no. of chemical constituents of the system minus the no. of eq^n relating to those constituents in an eq/b^m state.

$$2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$$

$$K_{eq} = \frac{[KCl]^2[O_2]^3}{[KClO_3]^2} = [O_3]^3$$

Degree of freedom :- (or variance)

It is defined as the minimum no. of independently variables factors such as temp., press., concent., which must be arbitrarily fixed in order to define the system completely.

F = 3 trivariant
F = 1 univariant
F = 0 invariant
F < 0 disequilibrium.

Limitations of phase Rule :-

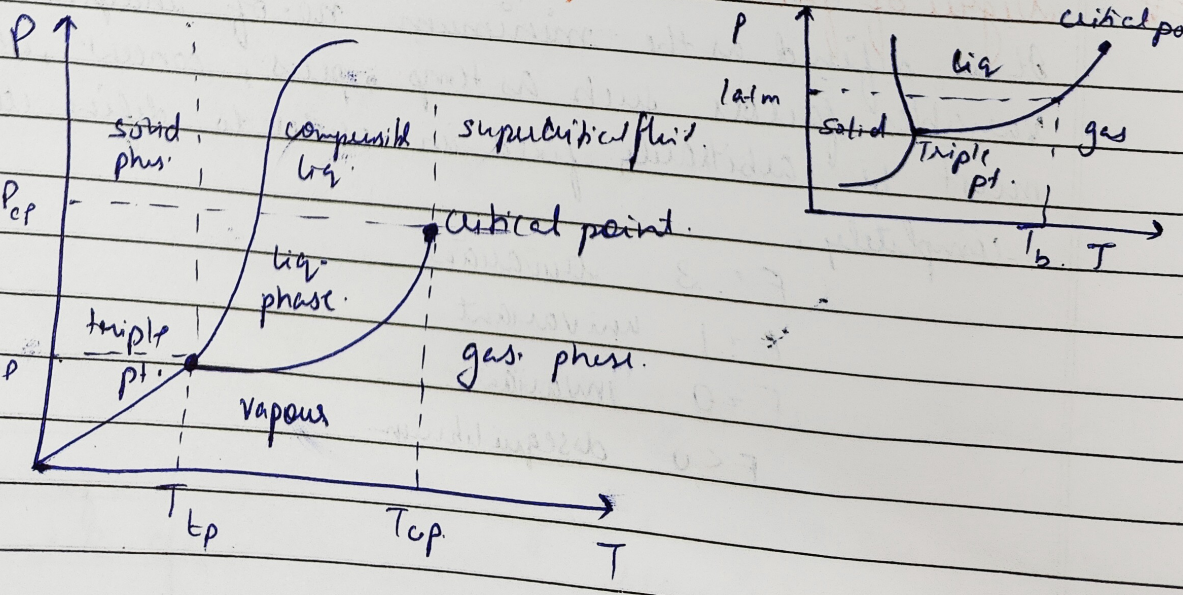
1) It is applicable for only those systems which are in eq/bm.
It is not much use for those systems which attain the eq/b^m state very slowly.

2) It applies only to a single eq/bm system. & provides no information regarding any other possible equilibria in the system.

3) It requires utmost care in deciding the no. of phases existing in an eq/b^m state, since it considers the no. of phases, rather than their amounts. Thus, even if a trace of a phase is present, it accounts towards the total no. of phases.

4) It conditions that all the phases of the system must be present simultaneously, under the identical cond^n of temp. & pr.

5) It conditions that S & I must not be in finely divided state; otherwise deviation occurs.



1. **Triple point**: the point on a phase diagram at which the three states of matter coexist.

2. **Critical point**: the point on a phase diagram at which the substance is indistinguishable b/w liq & gas state.

3. **Fusion (melting) (or freezing curve)**:
The curve that represents transitn b/w liq & solid stt.

4. **Vaporization (or condensatn) curve**:
the curve that represents the transition b/w gaseous & liq. states.

→ Sublimation curve that represents the transition b/w gaseous & solid states.

Components at triple point → 1
phase at " " → 3

Gibbs Phase Rule → $F = C - P + 2$

⇒ melting point of ice is ↓ by ↑ Pressure.

⇒ The melting curve or fusion curve of ice/water is very special. It has a negative slope (or tilted towards pres. axis) due to fact that when ice melts, molar vol. ↓. Ice melts at lower temp. at high pres.
e.g. The liq. formed b/w the skate & ice acts as a lubricant so that the skates moves gracefully across the ice. The skate apply a very high pres. on to the ice.

1. Disadvantages.

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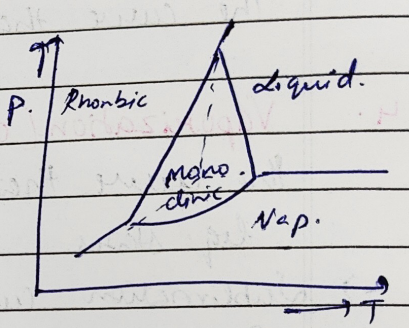
The Sulphur System :-

→ exist in two crystalline forms:
1) Orthorhombic S_8 2) Monoclinic S_4

⇒ Orthorhombic → yellow Sulphur
↳ commonly exist in normal cond^n.

⇒ Melting / Fusion curve:
→ negative slope due to the fact that when ice melts, the molar vol. ↓. ~~Ice~~ (done already)



Reduced / condensed phase rule :-

⇒ A solid liquid eq$^{lb^m}$ has practically no gas phase & the effect of P is small. Therefore experiments are conducted under atmospheric press$^{\circ}$. Thus keeping the press$^{\circ}$ const$^{\circ}$ of a system, in which vap$^{\circ}$ press$^{\circ}$ is not considered, it is called condensed system.
It will reduce the degrees of freedom of the system by one.

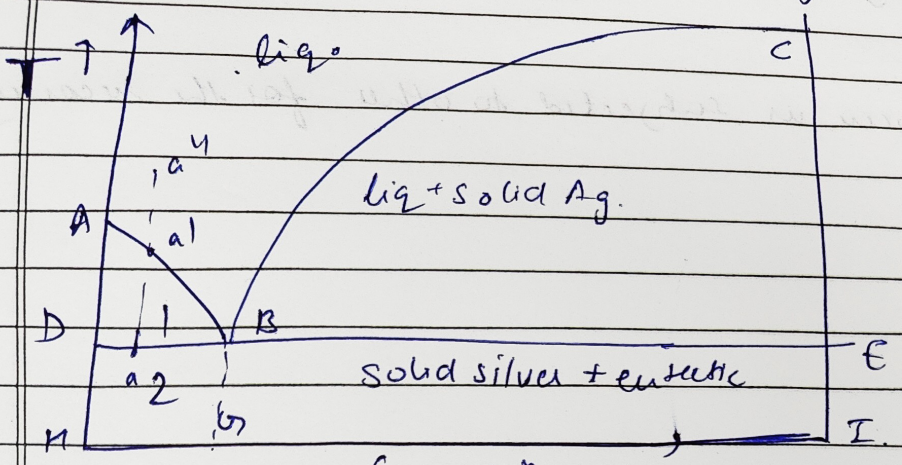
$$F = C - P + 1$$

just two variable → Temp$^{\circ}$ & conc$^{\circ}$.

Eutectic System :-

It is a mixt$^{\circ}$ of chemical compounds or elements that have a single chemical composition that solidifies at a lower temp$^{\circ}$. This comp$^{\circ}$ is called Eutectic comp$^{\circ}$. & temp$^{\circ}$ at which it solidifies is called Eutectic temp.

On diagram this intersection gives eutectic point



Pb-Ag System.

1. liq + solid pb.
2. Solid Pb + eutectic

Pattinson's process for desilverisation of Argentiferous lead :-

The process of heating argentiferous lead containing a very quantity of silver & cooling to get pure lead & liq. richer in silver is known as Pattinson's process

⇒ The argentiferous lead is melted & heated to a temp. above the melting pt. of pure Pb.
This system is then allowed to cool slowly & the temp. of the melt decreases along a'' - a'.
At a', solid lead starts separating.
As system further cools, more & more lead separates & liq. in eqbm with the solid lead gets richer in silver.

⇒ The lead that separates floats & is continuously removed by ladles.

→ After removing the lead that separates, the liq. is cooled further when it solidifies to give a mixt. of lead &

silver having the eutectic composition of 2·6 mass% of Ag.

⇒ This process is subjected to other for the recovery of silver.