Classification of phase diagram :-

Phase diagrams are classified on the basis of no. of components. Hence we have (I) one component phase diagram (II) two component phase diagram & (III) three component diagram for one component system, two component system & three component system.

One component Phase diagram :-

a. General information :- In one component system only one & same substance exists in different phases & so there is no. degree of freedom with respect to composition. The only variables in these cases are two, viz. pr & temp.

Applying the phases rule in such cases we get,

i. Maximum no. of phase co-exist in eq^m :-

The phase rule is, $F = C - P + 2$ ---- (I)

[F = degree of freedom
C = component
P = phase]

For a one component system, C = 1. So the phase rule is reduced in the form, $F = 3 - P$ ---(II)

Normally 'P' becomes maximum when 'F' minimum & the minimum no. of degree of freedom possible in a system may be zero because 'F' cannot be negative i.e. F = 0.

So from eq^n (II) we can write P = 3.

That is in case of one component system three phase can exist in eq^m and never more than three.

1. WATER SYSTEM

Water system is one component and hence C = 1
Under ordinary condition three phases are possible
i) Solid - phases (ice) ii) liquid phases (water)
iii) gas - phase (vapour)

These three phase may exist singly, two phase in eqm or three phases in eqm, depending on the circumstances.

a) Water system containing only one phase
According to phase rule $F = C - P + 2$
$= 1 - 1 + 2$
$= 2$

i.e. system would be bivarient, this represent by area of phase diagram. Since three phases are possible. So three areas must be present in phase diagram. Also two variables (Pr & temp) must be specified to define the system completely.

b) When two phase co-exist in eqm,
Then we have $P = 2$, $C = 1$
According to phase rule, $F = C - P + 2$
$= 1 - 2 + 2$
$= 1$

i.e. system would be univarient, thus it would be necessary to specify only one variable (temp. or pr.) in order to define the system completely. Three such equilibria would expected, these are

i) Solid (ice) ⇌ liquid (water)
ii) ice ⇌ vapour
iii) water ⇌ vapour.

Since line in phase diagram represent such equilibria. So in phase diagram must contain three lines.

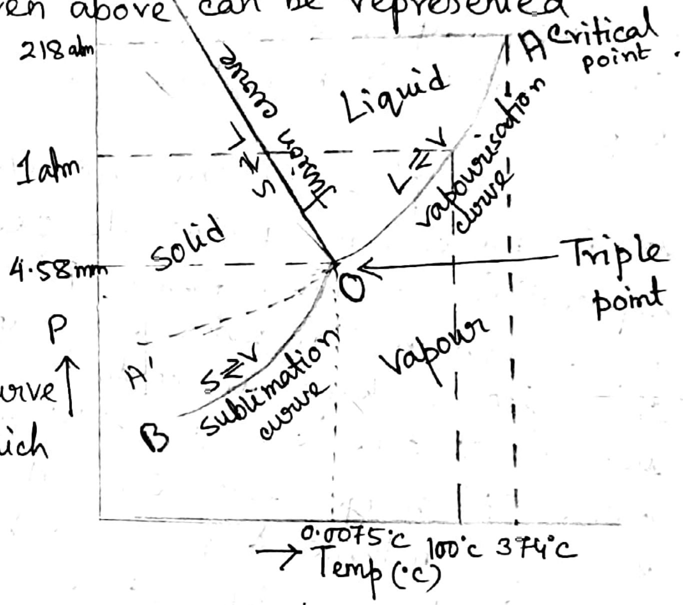
c) When three phase co-exist in equilibrium,

$P = 3, C = 1, F = 0$

That is, such a system would be non-varient. Thus the system is completely define automatically. there being no need to specify any variable. The point at which three phases co-exist In equilibrium is called triple point. For water system only one triple point is possible. This is actually intersection point of three line in phase diagram.

Phase diagram of water system :-

The informations given above can be represented graphically as —



The phase diagram consist of-

i) Curves : Three OA, OB & OC

ii) Triple point : Three curve meet at a point O which is triple point.

iii) Areas : Three areas AOB, AOC, BOC.

Description of phase diagram :

The salient features of water system are given below :

Curve (area/ point	Name	Phase in equilibrium	Degree of freedom
Curve OA	Vapourisation of liq(H_2O)	liq ⇌ vap.	1
Curve OB	Vap. pressure curve or sublimation curve of ice	solid ⇌ vap.	1
Curve OC	Fusion curve of ice	solid ⇌ liq	1
Curve OA'	Metastable vapourisation curve of liq.H_2O	liq ⇌ vap	1

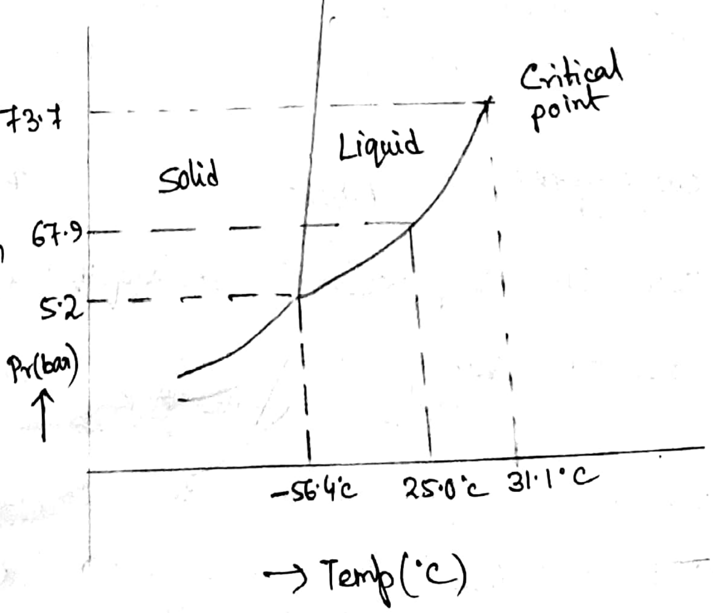
Curve /area/ point	Name	Phase in equilibrium	Degree of freedom
Area AOC	—	liq. H_2O	2
Area AOB	—	Vapour	2
Area BOC	—	Solid ice	2
Point 'O'	Triple point	solid ⇌ liq ⇌ vap.	0

▲ Metastable system :- The cooling of a liq. below its freezing point without separation of solid, is called super cooling of liq. The super cooled liquid exist in metastable state of eq^m with its vap.

In phase diagram, curve AO can be extended to A' by cooling below its freezing point without separation of ice. Hence A'O represent metastable eq^m. between liq. water & its vapour. As soon as a small ice is kept in contact with super cooled liq. it at once changes into the solid ice & the curve OA' merges into O'B. Thus meta-stable is very unstable & possesses higher vapour pressure than stable at same temp.

2. Phase diagram of CO_2 :-

The general features of the phase diagram are quite similar to those of water system except slope of 'OC' line. 'O' is triple point & 'B' is the critical point.



From the diagram it is clear that liq. CO_2 can exist at pressure above 5 atm. Hence under ordinary pressure (less than 5 atm.) solid CO_2 (called dry ice) will be dry. If we raise, the temp at this const pressure the dry ice will pass into vapour phase without liq phase. In ~~order~~ other words sublimation would occurs i.e. why dry ice is sublimate where as ice is melt.

3 <u>Sulpher System</u> :-

Sulpher system is one component system i.e. C = 1. Sulpher exists in polymorphic forms, some of which are unstable or metastable.

<u>Sulpher exists in four phases, namely</u>

a. Rhombic sulpher (SR), solid which is stable at ordinary temp.

b. Monoclinic sulpher (SM), solid which is stable ~~at ordina~~ above 95.5°C.

c. liquid sulpher (SL)

d. Sulpher vapour (Sv)

The phase rule gives following informations regarding the possible equilibria.

1. <u>Single phase equilibria are</u> :-

i) Rhombic S (SR) ii) Monoclinic S (SM)

iii) liq S (SL) iv) Sulpher vapour (Sv)

P = 1, C = 1, F = C − P + 2 = 1 − 1 + 2 = 2.

The system would be bivarient. There will be four single phase represented by FOUR AREAS in the phase diagram.

2. Two phase equilibria are :- There are six possible systems of two phases co-existing together namely,

i. $S_R - S_V$

ii. $S_M - S_V$

iii. $S_R - S_L$

iv. $S_M - S_L$

v. $S_L - S_V$

vi. $S_R - S_M$

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

The system would be univarient & will be completey define by spaicfing only one variable (temp or pr.)

There will be six two phases equilibria represented by <u>Six Curves</u> (lines) in phase diagram.

3. <u>Three phase equilibria</u> :- $P = 3$, $C = 1$

$F = 1 - 3 + 2 = 0$

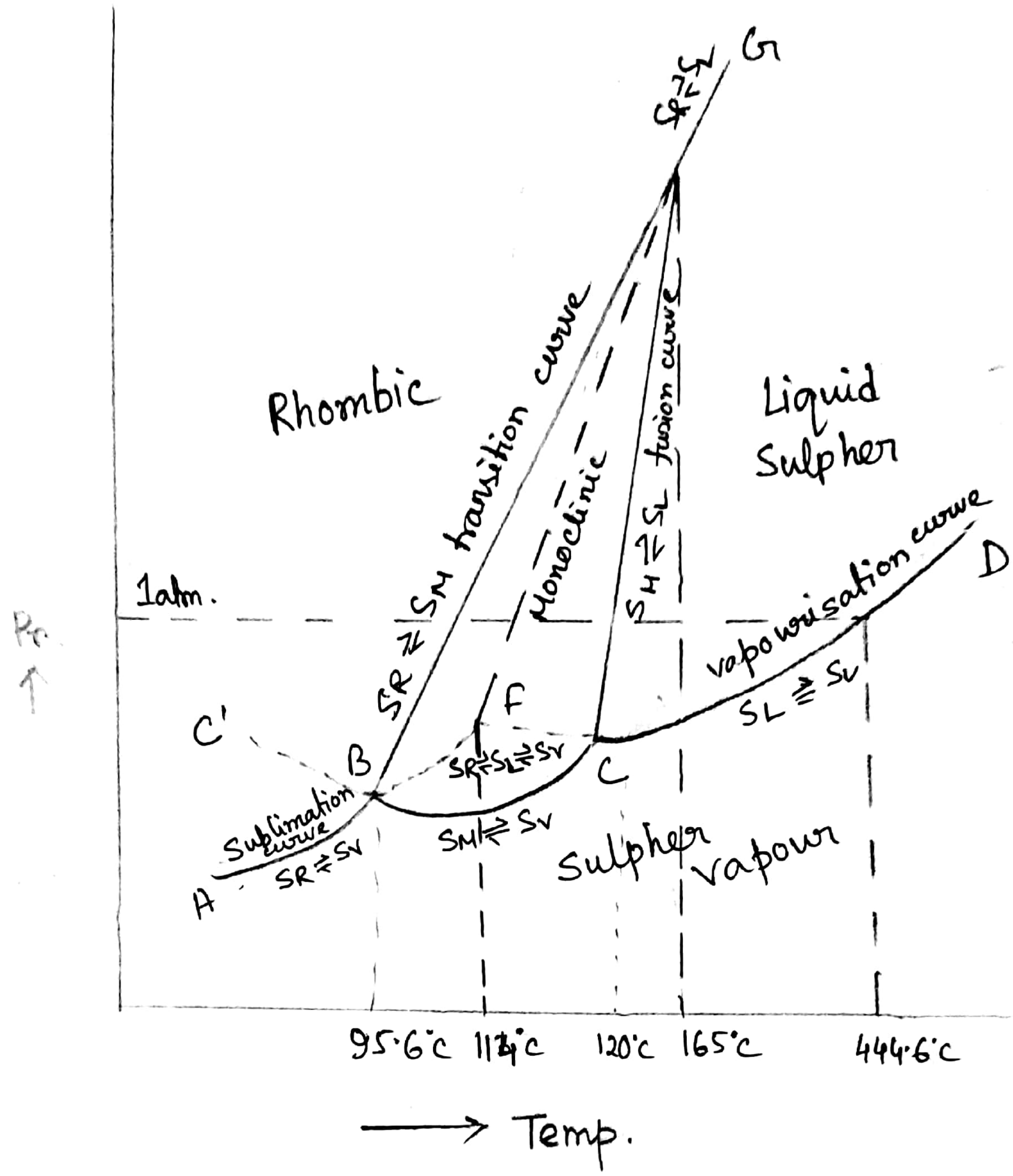
Such equilibria are non-varient in which all the parameters (variables) are automatically fixed. Such equilibria are represented by <u>Points</u>, <u>called triple point</u>. Four triple points are thus expected. These phase equilibria are -

i) $S_R - S_M - S_V$ ii) $S_R - S_M - S_L$ iii) $S_R - S_L - S_V$
iv) $S_M - S_L - S_V$

4. <u>Four phase equilibria can not exist</u> :-

If $P = 4$, $C = 1$, then $F = C - P + 2$
$= 1 - 4 + 2 = -1$

Thus in such case F becomes negative, which is meaningless. That is why four phase system is not possible.
The above informations can be graphically represented as —


G
SR ⇌ SL
Rhombic
SR ⇌ SM transition curve
Monoclinic
SM ⇌ SL fusion curve
Liquid
Sulpher
1atm.
Pr.
D
vapourisation curve
SL ⇌ SV
F
C'
B
SR⇌SL⇌SV
C
Sublimation curve
SR ⇌ SV
SM ⇌ SV
Sulpher vapour
A
95.6°C
114°C
120°C
165°C
444.6°C
Temp.