Phase Equilibrium

Dr. Virender Singh

~~Conditions~~ Q. Discuss the Phase Diagram for water system.

Ans. A Phase Diagram is a plot giving the conditions of equilibrium between various Phases of a given system. The number of the Phases that coexist for a system in equilibrium depends upon the temp. and Pressure.

H_2O system:-

Under normal conditions water exists in Phases namely liquid water, ice and water vapours. Various Phases which can exist in equilibrium are:-

$H_2O(l) \rightleftharpoons H_2O(g)$, $H_2O(s) \rightleftharpoons (H_2O(g)$, $H_2O(s) \rightleftharpoons H_2O(l)$

Overall $H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$

The (P-T) Phase diagram of water system consists of:- (i) Three curves OA, OB & OC

(ii) Curve OA' metastable curve

iii Three areas AOC, AOB, BOC

(iv) A Point O called the triple Point.

(A) Curve OA, the vapour Pressure curve of water:- Curve OA represents equilibrium between liquid water and water vapours at different temperatures. $H_2O(l) \rightleftharpoons H_2O(g)$ The curve starts from Point O, the freezing Point of water and terminates at A which is critical Point (218 Atm, Temp 374°C). At Point A only only ice Phase exist. Along this curve the Degree of freedom is one. $F = C - P + 2$, $F = 1 - 2 + 2 =$

It means for a given value of Pressure, there is fixed value of temp.

(B) Curve OA', the metastable curve for supercooled water:-

When water in the curve OA is rapidly cooled, then it is Possible that the ice may not appear at triple point O and we may get liquid water below its freezing point. The water is then said supercooled water. and the curve OA' represents the metastable equilibrium between liquid and vapour phases. If a small crystal of ice is added to the supercooled liquid, the liquid at once solidifies and changes into ice and the curve OA' merges into curve OB.

Ⓒ **Curve OB, the sublimation curve of ice:-**

~~vapour at var~~ The curve OB represent equilibrium between ice and vapour at different T&P. The Degree of freedom is one.

Ⓓ **The curve OC, melting point curve of ice:-**

It represents $H_2O(s) \rightleftharpoons H_2O(l)$. Degree of freedom is one

Ⓔ **Areas AOC, AOB and BOC:-**

These areas shows the conditions of pressure and temp at which a single phase ice, water or vapour exist. These areas are bivariant system as from phase rule $f = C - P + 2$, $C = 1$, $P = 1$ so $f = 2$

Ⓕ **Triple point 'O':-** The curve OA, OB and OC meet at the triple point. At this point all the three phases ie ice, water and vapours exist in equilibrium. This point corresp. to a definite temp (0.0075°C) and pressure (4.58 mm of Hg). At T.P. Degrees of freedom is zero

$$F = C - P + 2$$

$$C = 1,\ P = 3 \quad \text{So} \quad F = 1 - 3 + 2 = 0$$

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$$f = C - P + 2$$

$C = 1$, $P = 3$ so $f = 1 - 3 + 2 = 0$

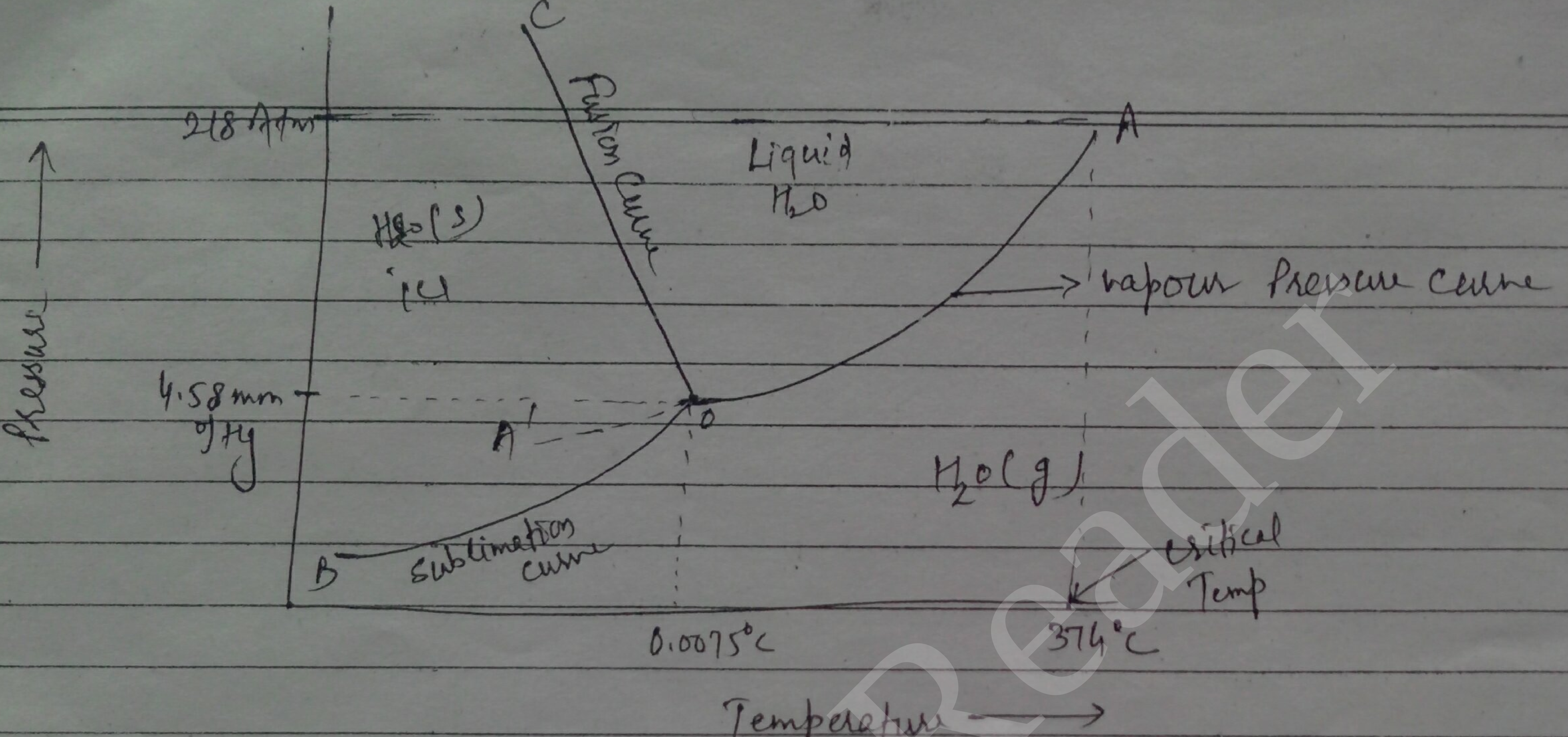


Fig:- The Phase Diagram for water system.

The variation of vapour Pressure with temperature is quantitatively given by clapeyron-clausius equation:-

$$\frac{dP}{dT} = \frac{\Delta H_v}{T(V_g - V_l)} \qquad \frac{dP}{dT} = \frac{\Delta H_s}{T(V_g - V_s)} \qquad \frac{dP}{dT} = \frac{\Delta H_f}{T(V_l - V_s)}$$

or

$$\ln\frac{P_2}{P_1} = \frac{\Delta H_v}{R} \times \left\{\frac{T_2 - T_1}{T_1 T_2}\right\}$$

Main features of water system:

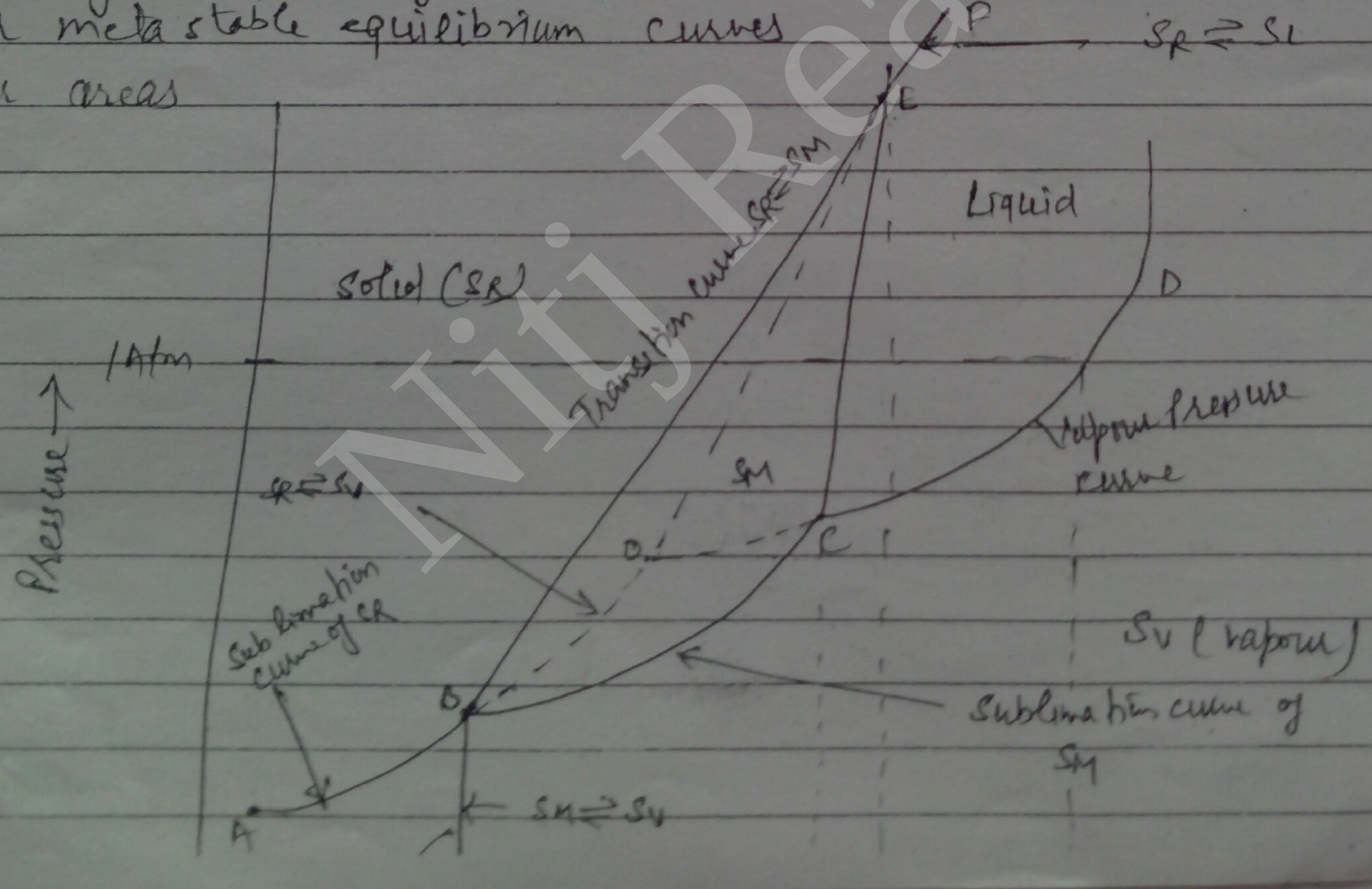
Features	No. of phases	Degree of freedom
Curves OA, OA', OB, OC	2	one
Areas AOC, AOB, BOC	1	TWO

Q. Discuss Phase Diagram for Sulphur System.

Ans: It is a one component system comprising of four phases which are

(1) Rhombic sulphur, SR] solid
(2) Monoclinic sulphur, SM]
(iii) Sulphur Liquid, SL
(iv) Sulphur Vapour, SV

The Phase Diagram of S-system shows (i) six equilibrium curve AB, BC, CD, BE, CE, EF
(ii) Four metastable equilibrium curves
(iii) four areas



⑥

The two crystalline form of sulpher namely sulpher rhombic (SR) and monoclinic sulpher (SM) exist in equilibriums with each other at a Temperature of 95.6°C. The rhombic sulphur is stable below 95.6°C whereas monoclinic sulpher is stable above 95.6°C. At 120°C monoclinic sulpher melts into sulpher liquid (SL).

$$S_R \overset{95.6^\circ C}{\rightleftharpoons} S_M \overset{120^\circ C}{\rightleftharpoons} S_L$$

It may be noted that all the four Phases cannot coexist as this is forbidden by Phase rule

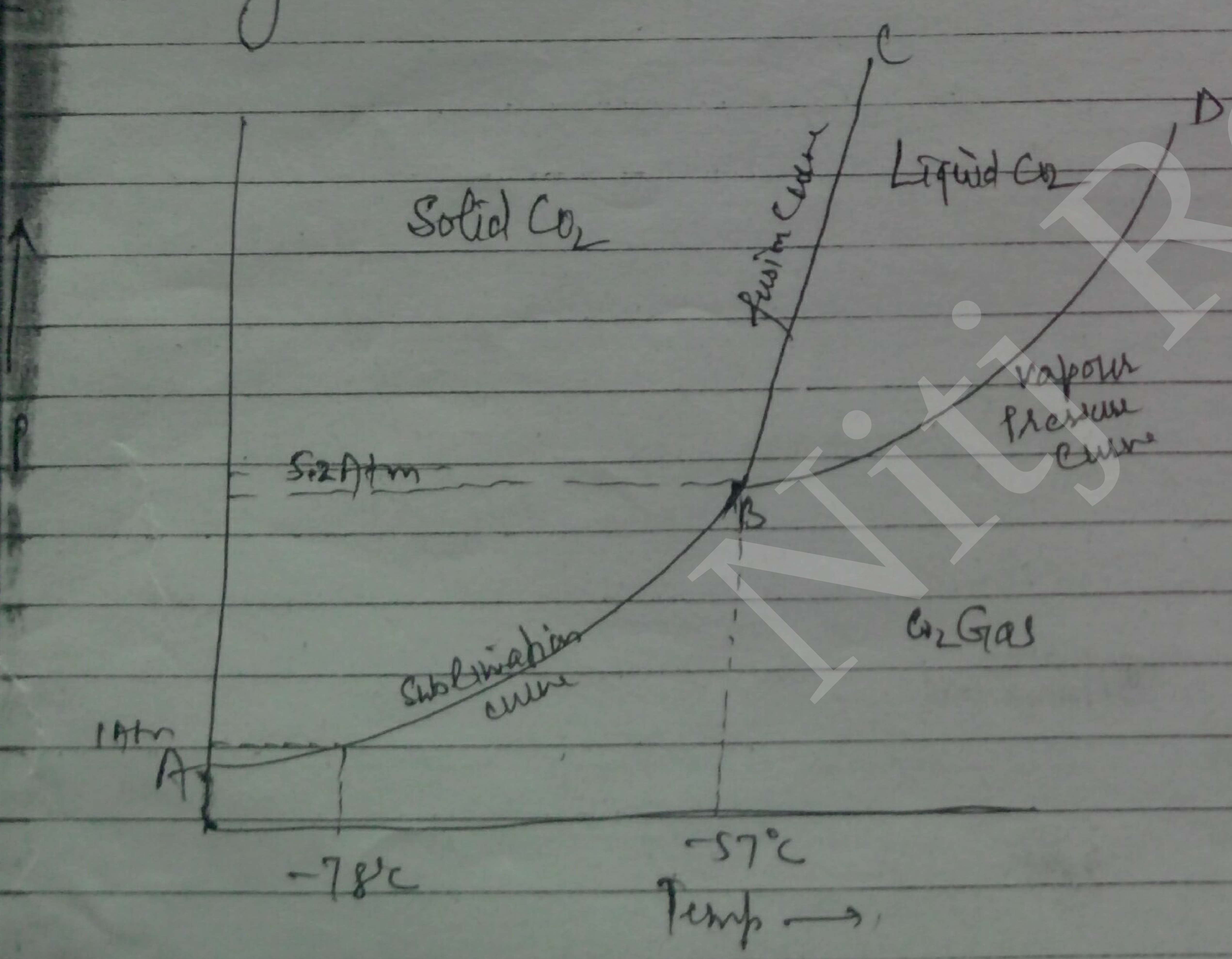
$F = C - P + 2$, $C = 1$, $P = 4$, $F = 1 - 4 + 2 = -1$ A negative variable is not possible.

The characteristics of Phase Diagram of Sulpher system are :-

Feature	Equilibrium or No of Phases	Degree of freedom
(1) The curve AB and metastable curve BO	$S_R \rightleftharpoons S_V$	1
② Curve BC and metastable curve BG	$S_M \rightleftharpoons S_V$	1
③ Curve CD and metastable curve CO	$S_L \rightleftharpoons S_V$	1
④ Curve EF and metastable curve EO	$S_R \rightleftharpoons S_L$	1
⑤ Curve BE	$S_R \rightleftharpoons S_M$	1
⑥ Curve CE	$S_M \rightleftharpoons S_L$	1
Areas:- (i) Area toward left of ABEF	S_R	2
(ii) Area Enclosed by BEC	S_M	2
(iii) Area Right of DCBG	S_L	2
(iv) Area Below ABCD	S	2

	Equilibrium	Degree of freedom
Triple Point B	$S_R \rightleftharpoons S_M \rightleftharpoons S_V$	0
Triple Point C	$S_M \rightleftharpoons S_L \rightleftharpoons S_V$	0
Triple Point E	$S_R \rightleftharpoons S_M \rightleftharpoons S_L$	0
Metastable Triple Point O	$S_R \rightleftharpoons S_L \rightleftharpoons S_V$	0

CO_2 System :-



CO_2 system is a one component system. The Phase diagram contains three curve and three areas and one triple Point.

Ⓐ **Curve AB** :- It is the sublimation curve along which solid CO_2 is in equilibrium with gas

Ⓑ **Curve BD** :- BD is vapour pressure curve along which ~~solid~~ liquid CO_2 is in equilibrium with gas CO_2.

Ⓒ **Curve BC** :- It is fusion curve along which solid CO_2 and liq. CO_2 are in equilibrium

Ⓓ **Triple Point B** :- B is the triple Point at which all the three Phases co-exist. The temp. of the system at this Point is -57°C and Pressure is 5.2 Atm.

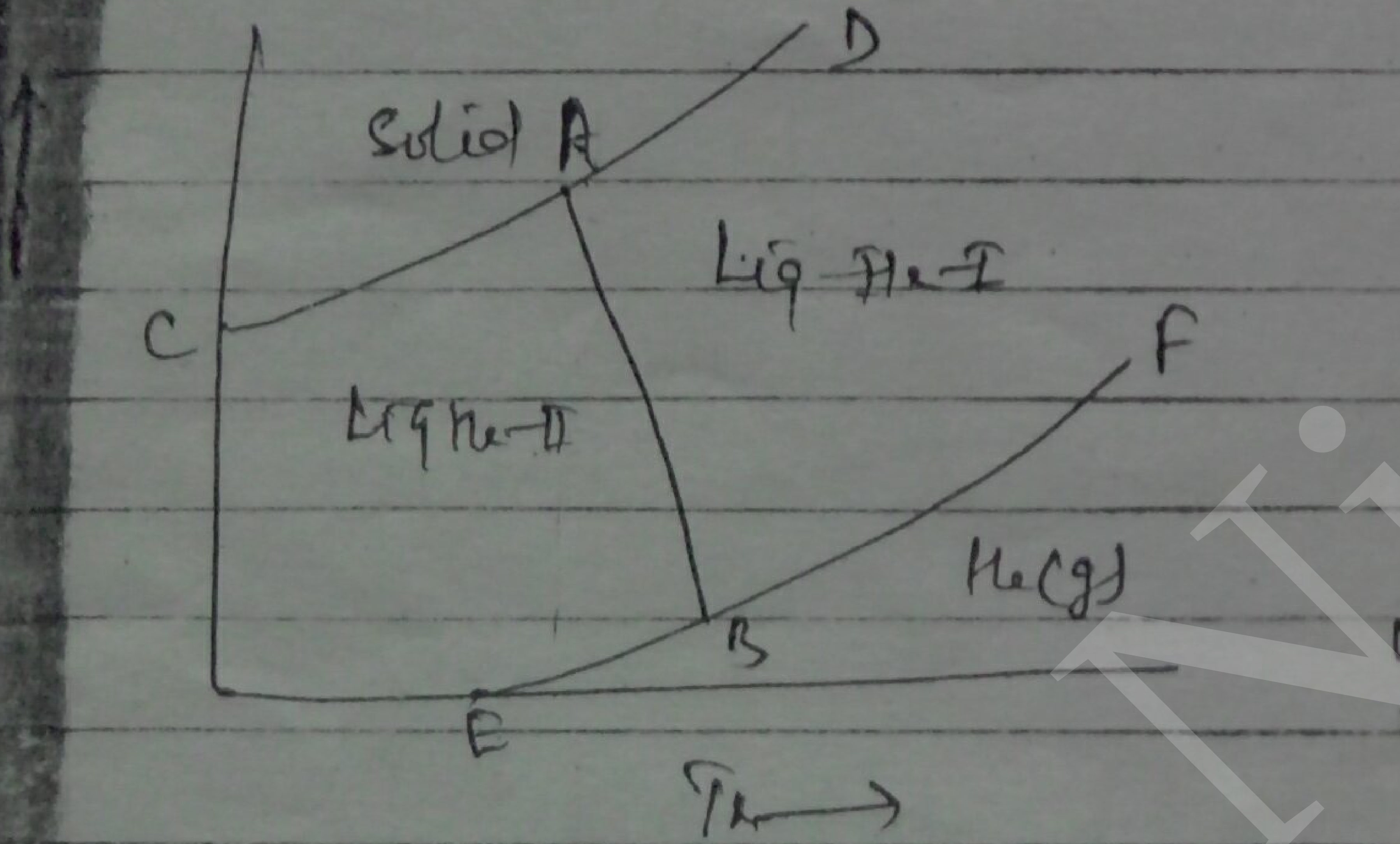
Ⓔ **Dry ice** :- A significant feature of CO_2 system is that the ~~vapour~~ & even at atmosphere Pressure (1 Atm), CO_2 gas can be directly solidified without the appearance of liquid phase merely on cooling to −78°C. Due to this reason solid CO_2 is called dry ice.

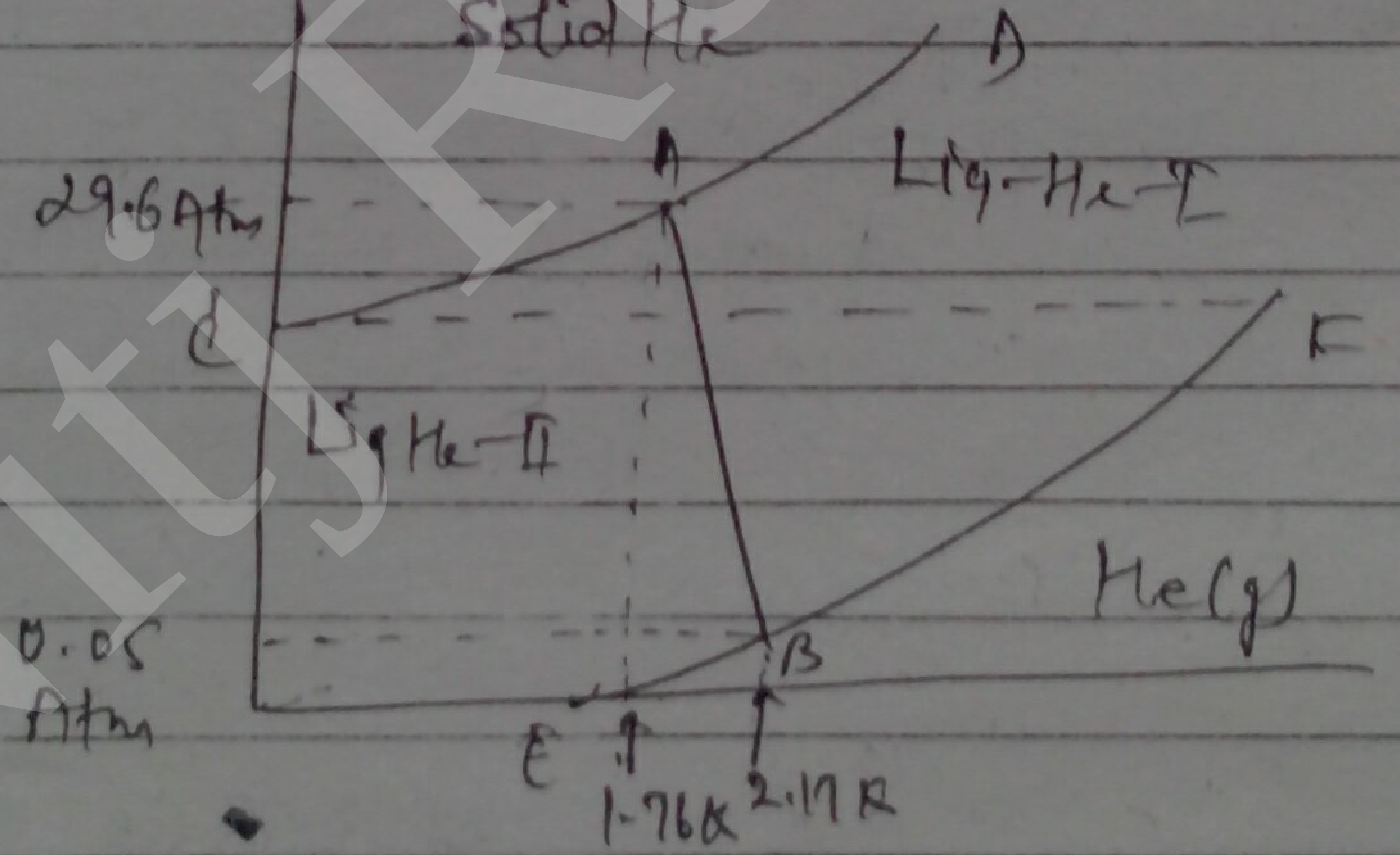
The other feature is that fusion curve is tilted away from Pressure axis.

CO_2 gas has very high vapour Pressure even at low temp (−57°C)

Solid $CO_2 \rightleftharpoons$ Liq CO_2 equilibrium exist at high Pressure of 5.2 Atm.

The Liquid Helium System :- Discuss! -





AB, AC, AD, BE, BF } 5 curves

two triple Point - A, B

Helium is the only Pure substance that can exist in two different isotropic liquid Phase: Liquid-He-I & Liquid He-II. There is no solid ⇌ liquid ⇌ vapour triple Point. There are however two triple Points A and B showing Equilibria.

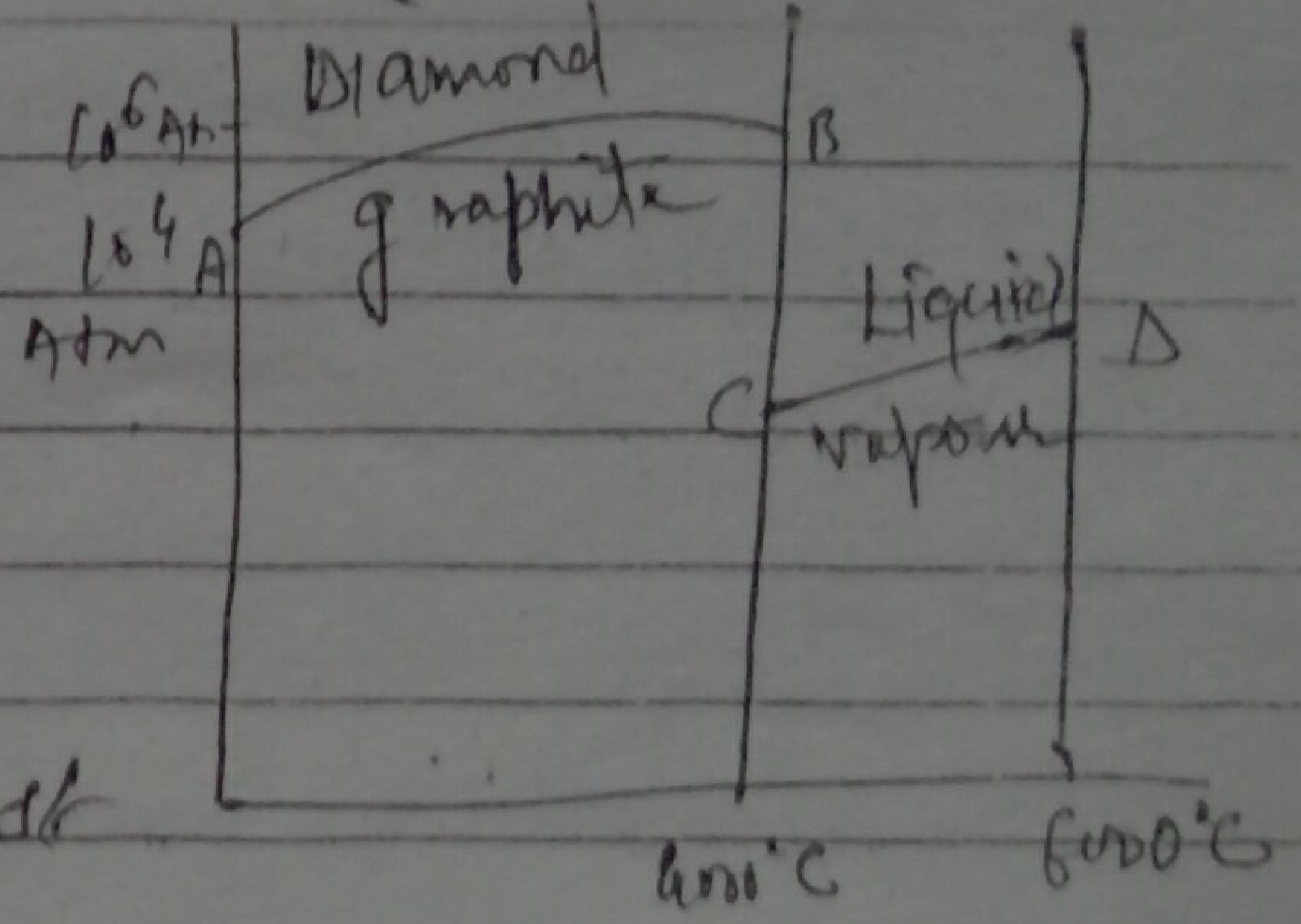
For Point A = Solid He ⇌ Liq He-I ⇌ Liq He-II   For Point B :- Liq He-I ⇌ Liq He-II ⇌ He(g)

Triple Point A exist at 1.76 K and 29.6 Atm and triple Point B at 2.17 K and 0.05 Atm Pres

The transition between He-I and Liq He-II in Presence of Helium vapour is known as (λ) lambda transition. The transition Point is called λ Point. The curve AB representing $He\ I \rightleftharpoons He-II$ transition is called lambda curve.

Liq He-II displays unusual properties in vicinity of 0K. It is a super- super fluid because it has extremely low viscosity.

The Carbon System :—



The phase Diagram for carbon system three curves AB, CD, BC. It is Possible to convert graphite into Diamond by compressing it at high pressure of 2×10^6 Atm and at a high temperature of 4000°C. However Practically no container can withstand these extremes of P & T. But in presence of catalyst such as cobalt and tantalum this transformation can be achieved at 2000°C & 70000 Atm Pressure.

Derivation of Phase Rule for two component system :—

Ans.— Phase Rule equation is $F = C-P+2$

For a two component system ($C=2$) Phase Rule is $F = 2-P+2 = 4-P$

Since minimum no. of phases in a system can be one so (for $P=1$) $F = 4-1 = 3$

Degree of freedom is three, it means three variables i.e. temp, Pressure & Composition of the system have to be ~~constant~~ specified to define the system.

Since it is difficult to represent three variables on a graph, three types of Possible diagrams are Possible:

(1) P-T Diagram ② T-C Diagram ③ C-P Diagram

Out of these, the ~~most~~ convenient is Temp-composition diagrams in which Pressure is kept Constt. For eg ~~in a~~ solid ⇌ Liquid equilibria, the vapour phase is generally ignored and the effect of Pressure is very small on equilibrium. The measurements of the Temp and and concentration in condensed systems are usually carried out at 1 atm Pressure.

As one variable is less P = Const. So $F = C - P + 1$. This is known as reduced Phase rule equation or condensed Phase Rule equation.

Que: Define a Eutectic System. Discuss lead-silver system & write its significance.

Eutectic system :- A eutectic system is defined as a two component system which do not react with each other but are completely miscible in molten state.

Lead - Silver system :- It is a two component system having three Phases (i) solid Lead (ii) solid silver (iii) solution of molten Pb & Ag. As the boiling point of Pb & Ag are high so vapour phase is ignored.

The Curve BC :- freezing Point curve of silver :- Point B represent the freezing Point of silver (961°C). The curve BC shows that addition of Pb to Ag decreases the freezing Point of Ag. BC represent the freezing point curve of silver. ~~The freezing point of silver falls along the Curve BC.~~ Along this curve solid Ag exist in equilibrium with liquid solution of Pb in Ag.

* Applying the reduced Phase rule equation to curve BC = $F = C-P+1$, $2-2+1=1$
we find that system is univariant.

* It is seen that along this curve the lead that is added goes into solution and silver separates outs. The separation of silver continues till Point O is reache

* At Point O, the solution becomes saturated with respect to lead and no more lead dissolves into it. hence the melting Point of silver does not fall further.

* The eutectic composition is fixed at Point O. which is 97.4% Pb and 2.6% Ag. and the eutectic temperature is 303°C.

② Curve AC, the freezing Point curve of lead:-

Pure lead melts at 327°c and the addition of silver lowers its melting Point along AC. Thus AC is the freezing Point curve of lead.
Therefore, along this curve, solid lead is in equilibrium with liquid solution of silver in lead of varying composition.
Applying the reduced Phase equation $F = C-P+1 = 2-2+1 = 1$
Thus it is a univariant system.

③ Eutechic Point Ⓒ :-

The curve AC and BC meet at Point C which is called eutectic Point.
At this Point three Phases, solid Ag, solid Ag and solution of both are in equilibrium
Applying reduced Phase rule $F = C-P+1 = 2-3+1 = 0$
The Point 'O' represent the non-variant system. Both variable temp (303°) and composition (97.4% Pb and 2.6%.Ag) are fixed.

System	% Salt in the Eutectic	
NH_4Cl & ice	20%	−16°C
NH_4NO_3 & ice	43%	−18°C
$NaNO_3$ & ice	33.3%	−18.1°C
$NaCl \cdot 2H_2O$ & ice	23.0%	−22.0°C
	5	
KI & ice	52.0%	−23.0°C
$CaCl_2 \cdot 6H_2O$ & ice	15.2%	−55.9°C

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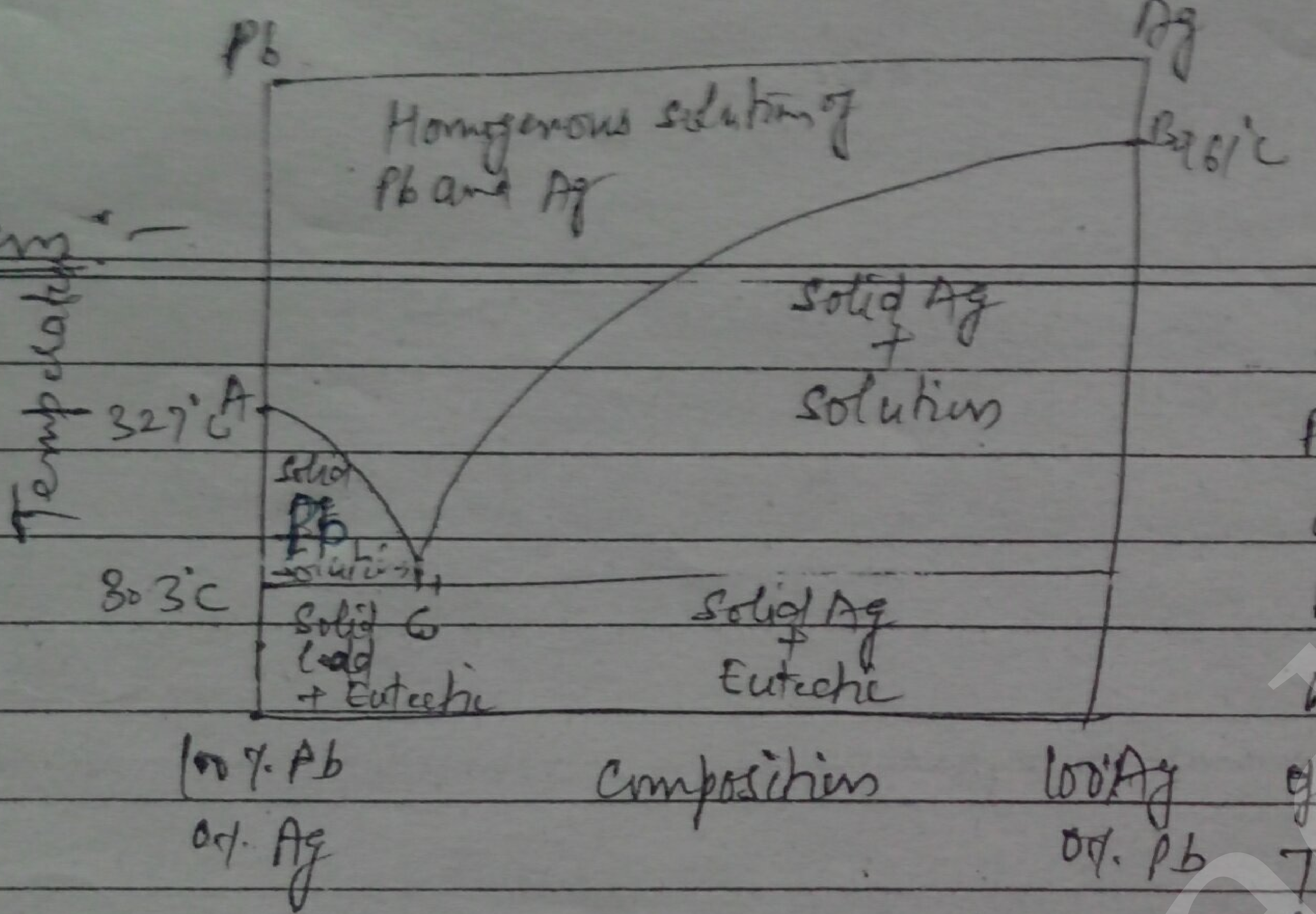
Phase Equilibrium
Part-III

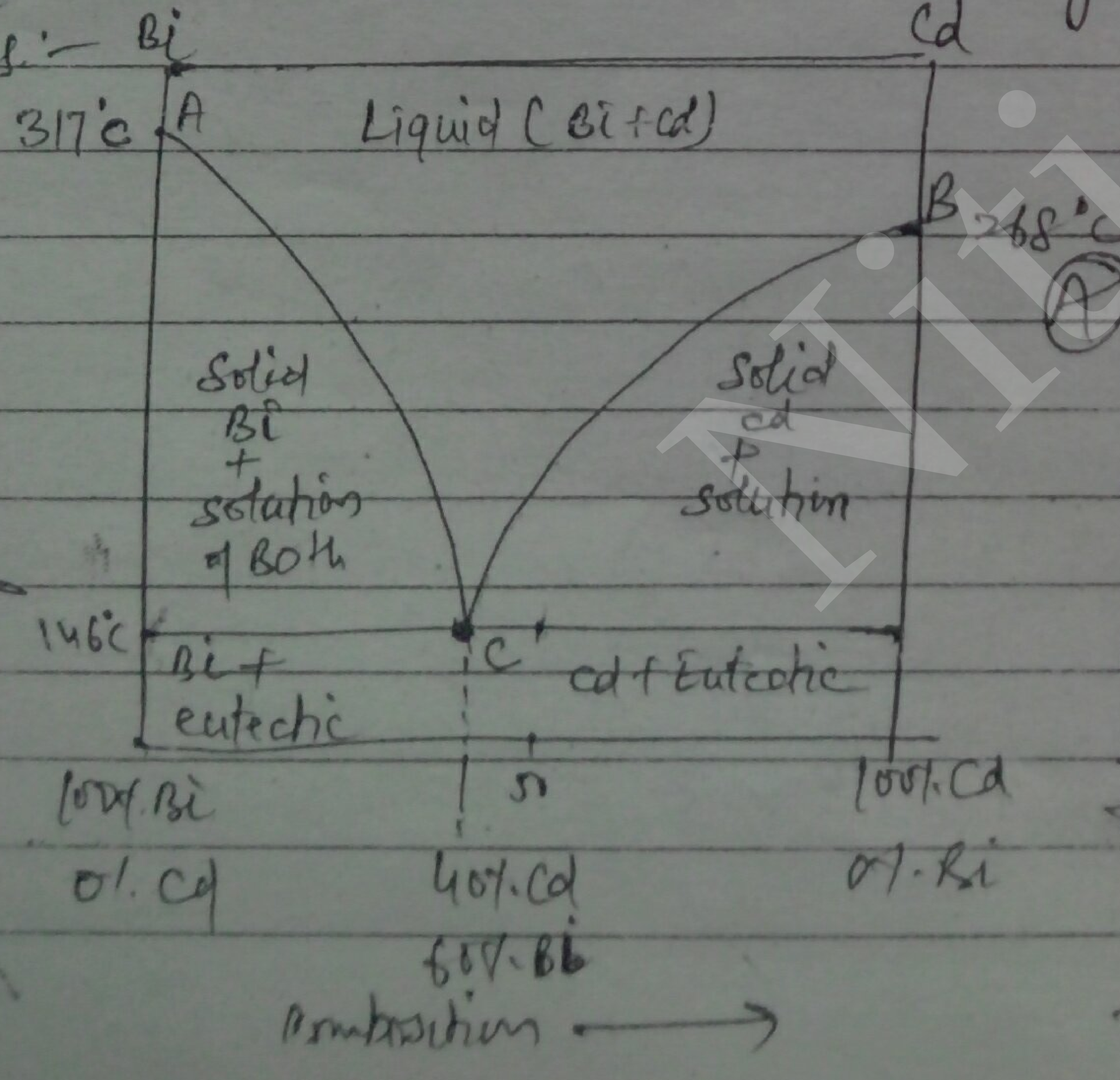
Pb-Ag system:-



Significance:- The Phase diagram of Pb-Ag system has significance in desilverisation of lead. ~~By~~ The argentiferous lead (~~[illegible]~~ galena PbS) which contain 0.1% Ag, the concentration of Ag can be increased to 2.6%. The Process of raising the Relative Proportion of Silver in the alloy is known as Pattinson's Process.

Q Discuss Phase Diagram of Bismuth-Cadmium system. Ⓑi Ⓒd ⟶ BC-category = Reservation 40%.

Ans:-



Ans:- It is a two component system, having three phases ① solid ~~Bi~~ Bi ② solid Cd + solution of molten Bi & Cd.

Ⓐ The curve AC:- Pure Bismuth melts at 317°C and the addition of Cd to molten bismuth lower its freezing point along the curve AC. The AC curve is the freezing point curve of Bismuth.

Along AC the solid ~~Cd~~ Bi exist in equilibrium with solution.

From Reduced Phase Rule $F = C - P + 1$ $C = 2$ $P = 2$

$= 2 - 2 + 1 = 1$

Thus system is univariant.

(B) The Curve BC :- The curve BC represent the freezing point curve of Cadmium. Along this curve addition of Bi to cadmium lowers its freezing point Along this curve BC, Cadmium freezes out. In The area below BC, two phases in equilibrium are solid Cd and liquid solution. Since in this region P = 2 F = 1 ie the system is univariant.

(C) The Eutectic Point (C) :-

At the eutectic Point C, three Phases coexist :- Solid Bi, Solid Cd and Liquid. The composition of the eutectic is 40% Cadmium & eutectic temp is 146°C. At C no of Phase = 3 So F = 0 system is invariant.

(D) The area below eutectic point :- In this region solid Bi & Solid Cd exist So P = 2, F = 1, Thus only temperature need to be specified to describe system completely

(E) Area above ACB :- In this region homogenous mixture of molten ~~Bi and~~ Bi & Cd exist, So P = 1, F = 2 Thus In this region temp & Composition can be varied without changing the number of Phases.

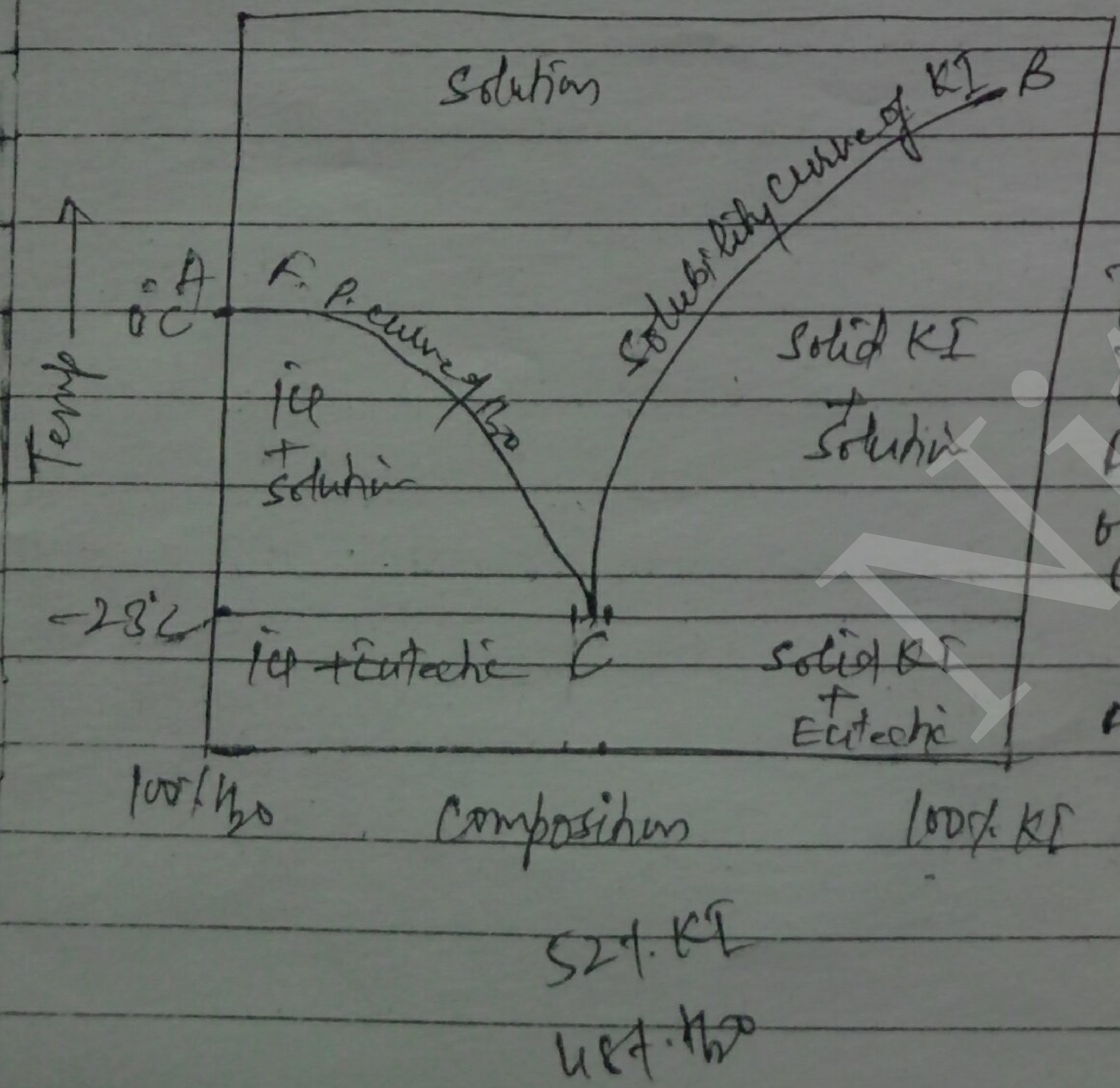
Q Discuss the Phase Diagram of Potassium Iodide Water system & Application (3)

One essential feature of a salt (KI) – water system is that melting point of salt is very high, even higher than the critical temp of H_2O (374°C). It is therefore not possible to represent the melting point of both the components in the Phase digram.

(A) The Curve AC :- A is the freezing Point of ice (0°C). As Potassium iodide is added some of KI dissolves in water which was in contact with the ice. If the addition of KI

is continued, there will be a change in the concentration of the solution. and decrease in in the freezing point take place Along curve AC which is known as freezing point curve of lead. Along this curve the solution (containing KI in water) is in contact with ice. At the point solution become saturated and therefore KI also separates out as another solid phase. Along this curve no of phase is two :- ① ice + ② solution of KI in H_2O
So degree of freedom $F = C - P + 1$ is one ie system is univariant.

(B) **Eutectic Point C :-** The Point 'C' represent the eutectic point at which three Phases are in equilibrium, solid ice, solid KI and solution of KI in water.
The eutectic composition is = 52% KI and 48% H_2O and eutectic temp is −23°C.
At this Point $P = 3$, so $f = 0$ system is invariant.



(C) **The Curve BC ; Solubility Curve of Potassium Iodide :-** The curve BC shows the effect of temp. on solubility of KI Therefore BC curve is called solubility curve of KI. Curve BC is also a univariant system having degree of freedom $F = 1$. Along this curve solid KI is in equilibrium with solution of KI in water.

Application: The significance of this Phase diagram is in make freezing mixtures. Which can generate a system with low temperature.

Azeotrope :- An azeotrop is a mixture of two or more liquids in such a way that its components can not be altered by simple distillation. This happens because when an azeotrope is boiled, its vapour has the same proportion as the liquid.

Positive Azeotrope :- Each azeotrope has a characteristic boiling point. If the boiling pt of an azeotrope is less than the boiling point temp of any of its constituents it is called Positive Boiling Azeotrope.

Ethanol = 95.63%   Water : 4.37% ⟶ 78.2°C

Ethanol = 78.4°C   water : 100°C

Positive azeotrops are also called ~~maximum~~ minimum boiling mixtures or Pressure maximum azeotropes.

Negative Az :- If the B.Pt of an azeotrop is greater than the boiling point of any of its constituents it is called -ve Azeotrope.

HCl 20.2%   Water 79.8% by weight   110°C

Hcl ~~water~~ - 84°C H_2O 100°C

Neg. Azeotropes are also called maximum boiling mixtures or Pressure minimum azeotrops.

Mr Virender Singh Phase Equilibria Part-I

Phase :- A Phase may be defined as any homogenous and Physically distinct part of a system which is bounded by a surface and is mechanically separable from other parts of the system.

* A phase has all the Physical and chemical properties same thoroughout.

Component :- The term component may be defined as the minimum no. of chemical constituents in terms of which the composition of each Phase can be expressed either directly or in terms of equation.

For example water system represent a one component system as

$$H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(v)$$

All these three Phases can be chemically represented by H_2O.

Degree of freedom :- No of component is given by formula

$C = N - E$ Where N = Total no of species (substituents)

E = no. of independent equations relating the conc. of N species

If constituents are given as ions then a solution be electrically neutral also counts as one equation.

Q KCl-NaCl-H_2O system is regarded as 3 component while KCl-NaBr-H_2O as a four component - why?

Ans It is because in case of KCl-NaCl-H_2O, even upon exchange of ions no new chemical species are formed. So only 3-components are there but in case of KCl-NaBr-H_2O system exchange of ion can take place and they can give new chemical constituents as represented by equation

$$KCl + NaBr \rightleftharpoons KBr + NaCl$$

So total 5 species are here KCl, NaBr, H_2O KBr, NaCl and can be represented by one chemical equation i.e. $E = 1$

So no of component = $C = N - E = 5 - 1 = 4$

egree of freedom :- The degree of freedom of a system is defined as minimum no. of independent variables such as temp., Pressure and concentration which must be specified in order to define the system completely.

If degree of freedom, f = 0, system is invariant

If f = 1, system is monovariant. Pressure is fixed for a given temp. Both cannot be changed independently.

If f = 2, system is bivariant, i.e. it can be defined by specifying two variable and both temp. & pressure can be changed independently.

Q. What are the differences in Phase diagram of water system & CO_2 system.

water System	CO_2 system
① In case of water system, the fusion curve ~~sdp~~ slopes toward the Pressure Axis. This indicates that with increase of pressure, melting point of ice decreases.	① In case of CO_2 system, the fusion curve slopes away from the pressure axis. This indicates that with increase of pressure melting point of solid CO_2 increases. The factor $\frac{dT}{dP}$ of the clausius-clapeyron equation is positive, which indicates that $V_e > V_s$. volume of liquid CO_2 is more than volume of solid CO_2.
② The solid water (ice) can exist in equilibrium with water (l) S ⇌ L even at low Pressure of 4.58 mm of Hg.	② While solid CO_2 can exist in equilibrium with liquid CO_2 (S ⇌ L) only at a very high pressure of 5.2 atm.
③ Vapour Pressure of water is low at low temp.	③ The vapour pressure of ~~solid~~ CO_2 is very high even at very low temperature.
④ There exist one metastable curve in water system.	④ There exist no metastable curve in CO_2 system.

4.2 CONDITIONS FOR EQUILIBRIUM BETWEEN PHASES

A system having more than one phase is said to be in equilibrium if following conditions are satisfied.

1. Thermal Equilibrium : In this state the temperature of all the phases must be same otherwise heat will flow from one part of the system to another part. Consider a system having two phases 1 and 2 at temperatures T_1 and T_2 respectively. Let S_1 and S_2 be the entropies of these phases. Suppose dq is the amount of heat transferred from phase 1 to phase 2 at equilibrium. Then,

The Entropy Change of phase 1 *i.e.*, $dS = -\frac{dq}{T_1}$

The Entropy Change of phase 2, $dS_2 = \frac{dq}{T_2}$

Total entropy change of the system $= \frac{-dq}{T_1} + \frac{dq}{T_2}$

For a system in equilibrium $dS = 0$

i.e. $dS_1 + dS_2 = 0$

$\therefore$ $\frac{-dq}{T_1} + \frac{dq}{T_2} = 0$

or $\frac{dq}{T_1} = \frac{dq}{T_2}$

$\therefore$ $T_1 = T_2$

2. Mechanical Equilibrium : According to this condition, all the phases of the system be under the same pressure. Otherwise, the volume of one phase will increase while that of other phase will decrease. This can be proved as follows :

Suppose a system having phases 1 and 2 is in equilibrium at constant volume and temperature. Further, let the volume of phase 1 increase by a small amount dV, as a result, the volume of phase 2 decreases by the same amount. If P_1 and P_2 are pressures of phase 1 and 2 respectively then,

the change in work function of phase 1 *i.e.*, $dA = +P_1\,dV$

Change in work function of phase 2, *i.e.* $dA_2 = -P_2\,dV$

At equilibrium the change in free energy, $(dA)_{V,T} = 0$

or $dA = dA_1 + dA_2 = P_1\,dV - P_2\,dV = 0$

$\therefore$ $P_1 = P_2$

3. Chemical Equilibrium : In the state of chemical equilibrium, the chemical potential of a component must be same in all the phases.

It may be recalled that chemical potential is in the molar free energy *i.e.* it is the change in free energy which takes place at constant temperature and pressure, when one mole of a component is transferred from one phase to another, keeping the amount of all other components constant. It is represented by μ.

Consider, a system having two phases A and B. The components 1, 2, 3 ... C, are distributed between these phases. The temperature and pressure of each phase is assumed to be constant. Suppose a small amount dn_1 of component 1 is transferred from phase A to phase B. If $(\mu_1)_A$ and $(\mu_1)_B$ are the chemical potentials of component 1 in the phases A and B respectively, then

the decrease in free energy of component 1 in phase A $= (\mu_1)_A\,dn_1$

the increase in free energy of component 1 in phase B $= (\mu_1)_B\,dn_1$

The free energy change for the system is the sum of free energy changes of various phases. Thus

$$dG = dG_A + dG_B \ldots$$

Also, for a two phase system, we have

$$dG = -S\,dT + V\,dP + (\mu_1)_A\,dn_1 + (\mu_1)_B\,dn_2 \ldots$$

At constant T and P, $dT = 0$ and $dP = 0$ so that

$$(dG)_{T,P} = (\mu_1)_A\,dn_1 + (\mu_1)_B\,dn_2$$

For a closed system at equilibrium, $dG = 0$

$\therefore$ $-(\mu_1)_A\,dn_1 + (\mu_1)_B\,dn_2 = 0$ (Negative sign indicates the decrease in free energy)

or $(\mu_1)_A = (\mu_1)_B$

It follows that for a two phase system at equilibrium, the chemical potential of a component 1 is same in both the phases.

In general for a component i distributed in phases, A, B, C, ... of a multiphase system at equilibrium, we can write

$$(\mu_i)_A = (\mu_i)_B = (\mu_i)_C$$

It follows that *for a multiphase system at equilibrium, the chemical potential (μ_i) of a component i is same in all the phases.*

4.3 THE GIBBS PHASE RULE

The phase rule put forward by J. Williard Gibbs, *states that for a heterogeneous system in equilibrium, the number of degrees of freedom, F is related to the number of components, C and the number of phases, P as*

$$F = C - P + 2$$

DERIVATION OF THE PHASE RULE

The degrees of freedom, F, of a system is given by the difference of the total number of variables required to specify the system and the number of independent equations available to define the system at equilibrium. Thus,

Degrees of freedom = (Total number of variables) − (Number of independent equations for the system in equilibrium) ...(1)

Total number of variables in a system can be calculated as follows :

Consider a single phase system containg two components. If the concentration of one component is known, the concentration of other can be simply obtained by the difference. Hence, the phase having two components can be defined by one concentration term. Similarly, a single phase containing three components can be defined by the knowledge of two concentration terms. If the same concept is extended, we can say a simple phase containing C components can be completely defined by (C − 1) concentration terms. If instead of single phase there are P number of phases having C components then the number of concentration terms required will be P (C – 1). Besides, concentration variables then are two more variables i.e. temperature and pressure of the system.

Thus, the total number of variables = P (C – 1) + 2 ...(2)

Next, we calculate the number of independent equations which are required for equilibrium between phases.

From thermodynamic considerations, we know that when a system is in equilibrium, the chemical potential of each constituent is same in all the phases.

Consider a system having *i*th component distributed in three phases namely 1, 2 and 3. The chemical potential of *i*th component must be same in all the three phases in equilibrium i.e.

$$(\mu_i)_1 = (\mu_i)_2 = (\mu_i)_3$$

This can be represented by two equations viz.

$$(\mu_i)_1 = (\mu_i)_2$$
$$(\mu_i)_2 = (\mu_i)_3$$

Hence, for a system of three phases, two equations are required to define each component. In general, for a system having P phases, (P – 1) number of equations are required for each component. Now, if there are C components present in P phases, then

The number of independent equations = C (P – 1) ...(3)

Substituting the values from equations (2) and (3) in equation (1), we get the degrees of freedom of a system as

$$F = [P(C-1)+2]-[C(P-1)]$$

or

$$\boxed{F = C - P + 2} \qquad ...(4)$$

Equation (4) is the phase rule which relates the number of phases and the number of components with the degrees of freedom of a system.

Worked Examples

Example 1. *Calculate the number of degrees of freedom in the following systems. Indicate the variables that need to be specified for these equilibria.*

(i) Water (l) ⇌ Water (V)

(ii) Water (l) ⇌ Water (g) at 1 atm pressure.

Solution : Phase rule is :

$$F = C - P + 2$$

(i) $H_2O\,(l) \rightleftharpoons H_2O\,(g)$ is one component system

$$\therefore \quad C = 1, P = 2$$
$$\therefore \quad F = 1 - 2 + 2 = 1$$

As the system has only one degree of freedom therefore, only one variable T or P has to be specified.

(ii) $H_2O\,(l) \rightleftharpoons H_2O\,(g)$ at 1 atm pressure.

$$C = 1, P = 2.$$

There is a restriction of constant pressure (1 atm), degree of freedom reduced by one.

Hence, the phase rule becomes

$$F = C - P + 1$$
$$\therefore \quad F = 1 - 2 + 1 = 0$$

The system has zero degree of freedom and is invariant.

Example 2. *Calculate the number of components and the number of degrees of freedom in an aqueous solution of sodium chloride.*

Solution : In this case

$$C = 2, P = 1$$
$$\therefore \quad F = C - P + 2$$
$$= 2 - 1 + 2 = 3$$

The variables for the system are T, P and concentration of the solution.

4.4. PHASE DIAGRAM

A **phase diagram** *is a plot giving the conditions of equilibrium between various phases of a given system.* The number of phases that coexist for a system in equilibrium depends upon the temperature and pressure of the system. These conditions of pressure and temperature are experimentally determined and plotted as pressure temperature (P – T) diagram. The P – T diagrams or the phase diagram contain a number of lines, areas and triple points. Phase diagrams of some systems are discussed ahead.

4.5. PHASE EQUILIBRIUM OF ONE COMPONENT SYSTEMS

According to phase rule, the degrees of freedom of a one component system is given by

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

or

$$F = 3 - P \qquad ...(1)$$

For a one-component system we can write the phase rule equation as :

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

Three cases may arise depending upon the number of phases in the system.

Case I. When there is only **one phase present,**

$$\therefore \quad F = 3 - 1 = 2$$

The system is **bivariant** *i.e.* it can be completely defined by specifying the two variables, temperature and pressure. In this case both the temperature and pressure can be varied independently. **Thus a single phase is represented by an area of P–T graph.**

Case II. When there are **two phases** in equilibrium,

$$P = 2$$
$$F = 3 - 2 = 1.$$

The system then has one degree of freedom and is called as **monovariant.** In this system, the pressure cannot be changed independently. The pressure is fixed for a given temperature. **A two-phase system is represented by a line on a P–T graph.**

Case III. When there are **three phases** in equilibrium,

$$F = 3 - P = 3 - 3 = 0$$
$$F = 0$$

The system has zero degree of freedom and is called as **non variant or invariant.** This condition can be attained at a definite temperature and pressure. The system is, completely defined and no external conditions are required to be specified. **A three-phase system is depicted by a point on the P–T graph.** At this point, the three phases (solid, liquid, vapour) are in equilibrium and, it is termed as the **Triple point.**