



6MHM+G6C, Chatrapati Colony, Barshi, Maharashtra  
413401, India

Latitude  
18.242615°

Longitude  
75.688745°

Local 01:51:14 PM  
GMT 08:21:14 AM

Altitude 446.5 meters  
Monday, 28-03-2022



GPS Map Camera



**Barshi, Maharashtra, India**

**6MHJ+VX3, Chatrapati Colony, Barshi,  
Maharashtra 413401, India**

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**Long 75.682622°**

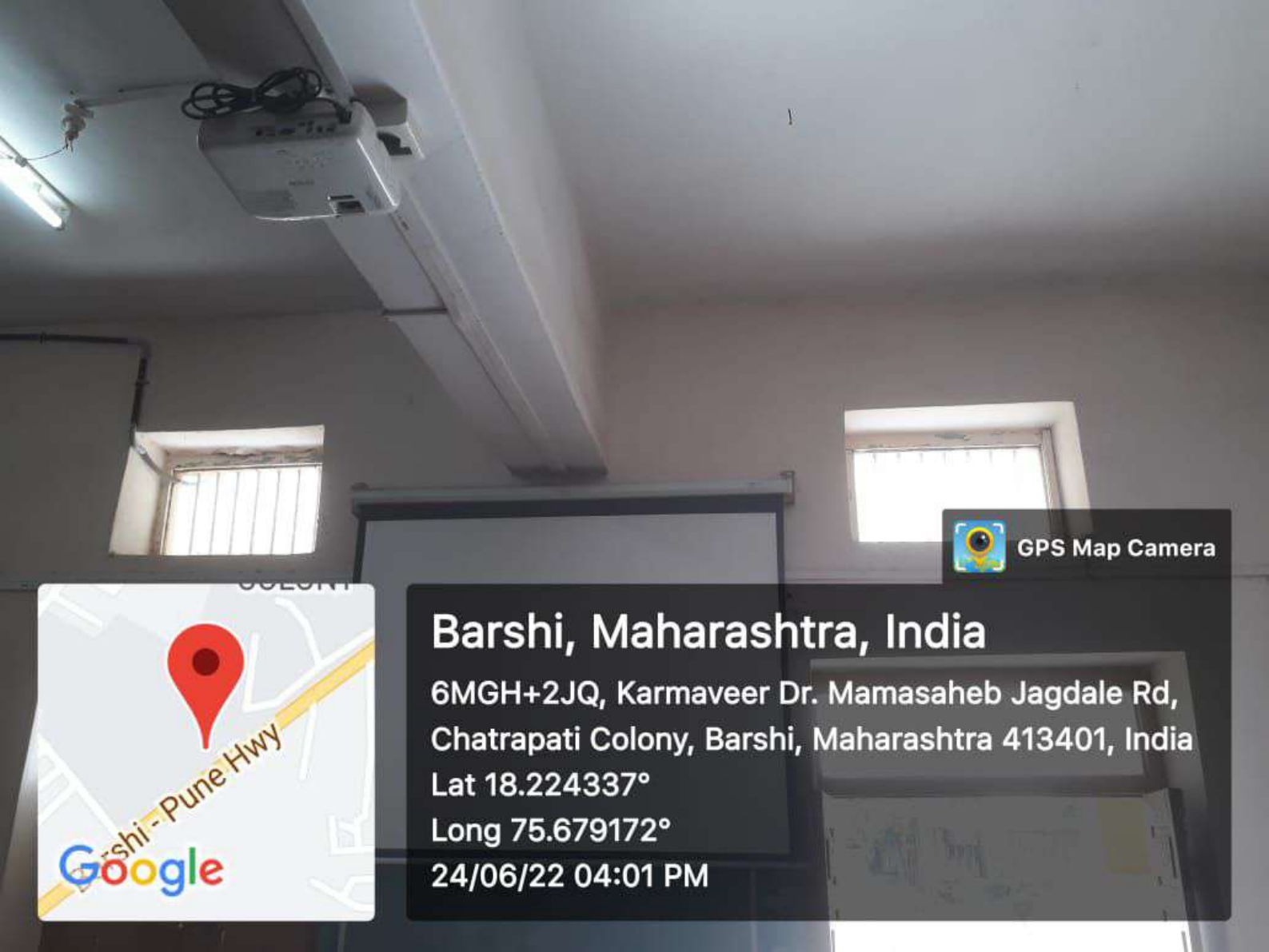
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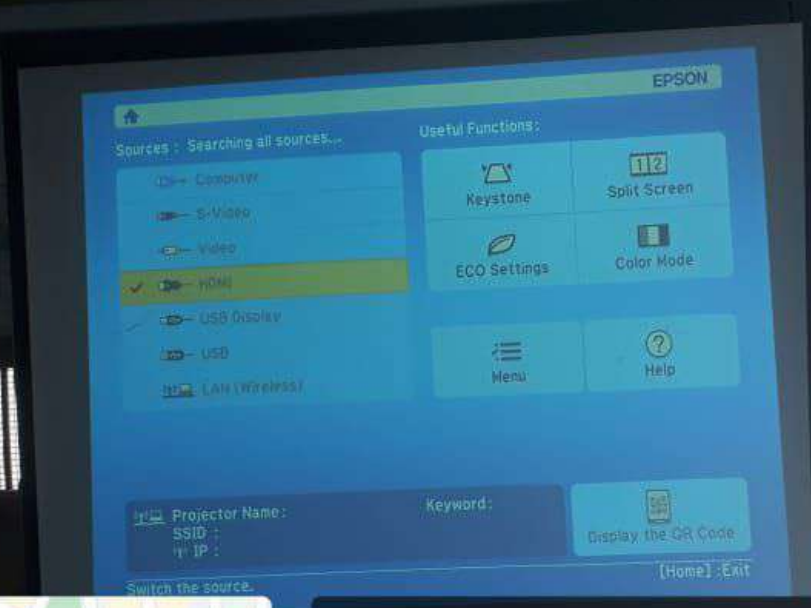
## Barshi, Maharashtra, India

6MGH+2JQ, Karmaveer Dr. Mamasahab Jagdale Rd,  
Chatrapati Colony, Barshi, Maharashtra 413401, India

Lat 18.224337°

Long 75.679172°

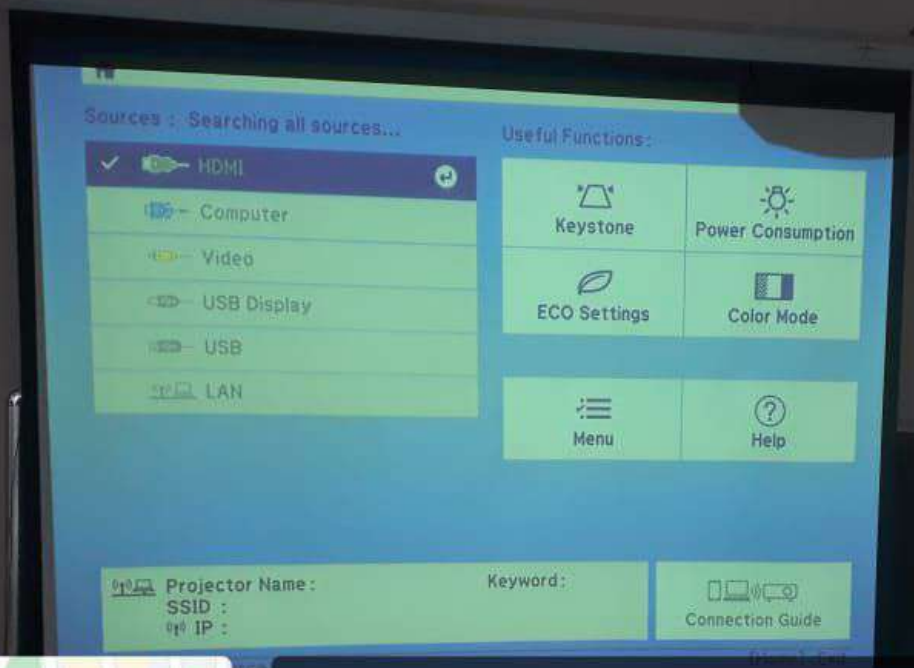
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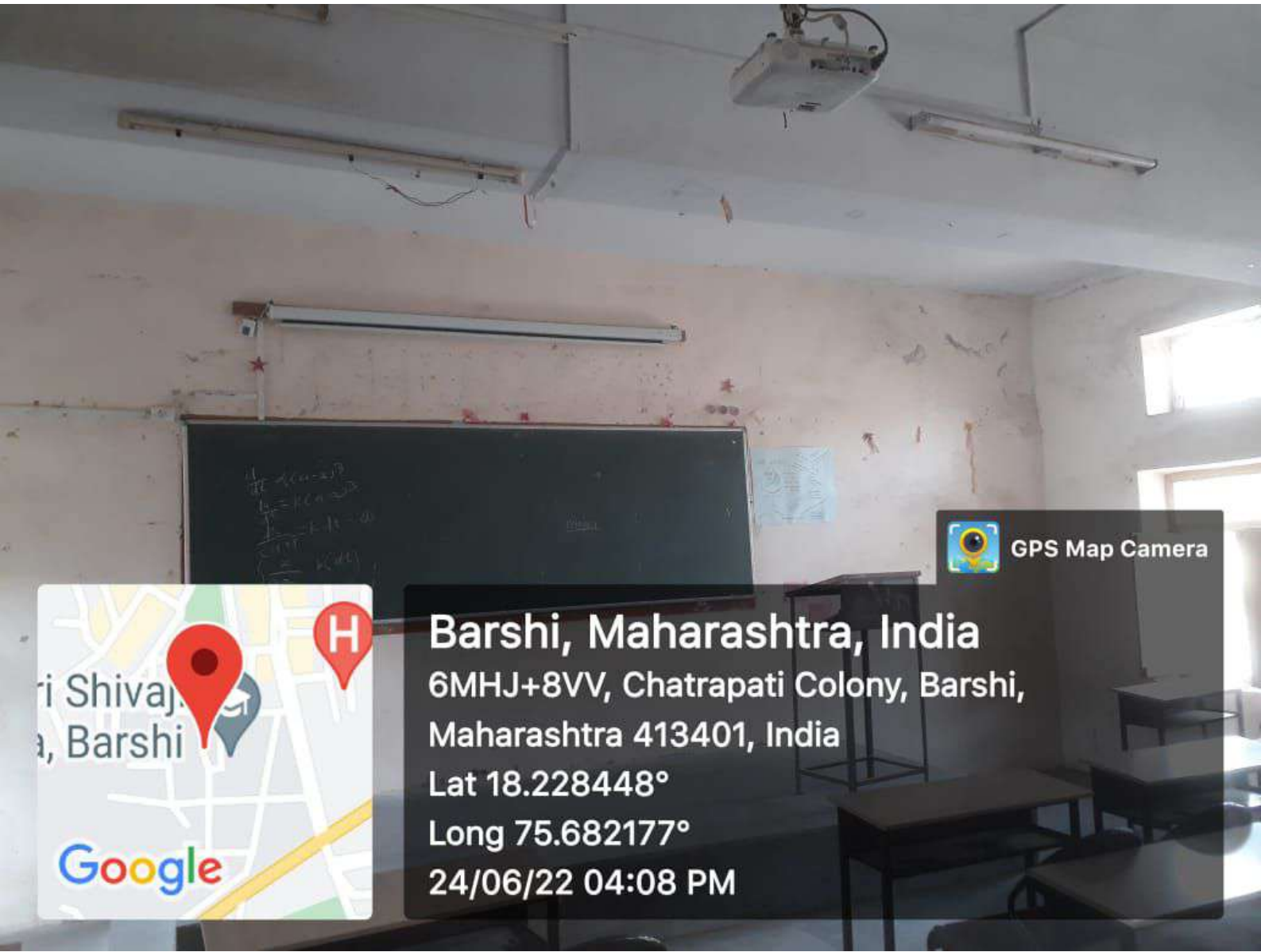
**Barshi, Maharashtra, India**  
**6MHJ+8VV, Chatrapati Colony, Barshi,**  
**Maharashtra 413401, India**  
**Lat 18.228448°**  
**Long 75.682177°**  
**24/06/22 04:05 PM**



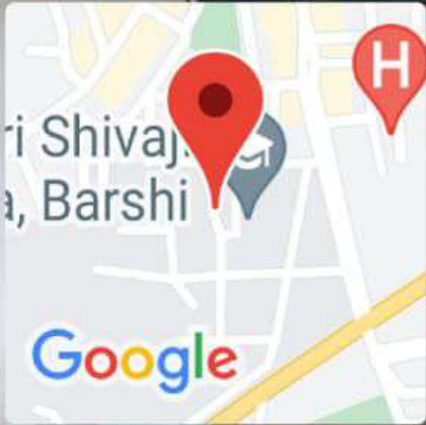
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**Barshi, Maharashtra, India**  
**6MHJ+8VV, Chatrapati Colony, Barshi,**  
**Maharashtra 413401, India**  
**Lat 18.228448°**  
**Long 75.682177°**  
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**Barshi, Maharashtra, India**

6MHJ+8VV, Chatrapati Colony, Barshi,  
Maharashtra 413401, India

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Long 75.682177°

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**B.Sc. III, semester V**

**Phase Equilibria**

**By**

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**System:** Part of the universe under study.

**Homogeneous system:** It has only one phase throughout.

**Heterogeneous system:** It has more than one phases.

**Phase( P ):** It is homogenous part of the system which is physically distinct and separated from other parts of the system by definite bounding surface. Eg. Freezing of ice. **3**

**Component( C ):** It is the minimum number of chemical constituents which are essential to express the composition of every phase present in the system directly or in the form of a chemical equation. Eg. Freezing of ice. **1**

**Variance or degrees of freedom (F):** It is the minimum number of variables which must be fixed or stated in order to describe the system at equilibrium completely. Eg. Freezing of ice. **0**

**Phase Rule:**

Phase rule was deduced by Willard Gibbs in 1876. It is applicable to all heterogenous systems and helps to know the effect of temperature , pressure and concentration on the system.

It can be stated as the sum of the number of phases and degrees of freedom of any system exceeds the number of components by 2.

$$P+F=C+2 \qquad \text{OR}$$
$$F=C-P+2 \dots \dots \dots (1)$$

# Phase

Example	Phases	P
Air	V (Gases)	1
Water + acetone	L	1
Water + benzene	L+L	2
$\text{CaCO}_3 (\text{S}) = \text{CaO}(\text{S}) + \text{CO}_2(\text{G})$	S+S+ V	3
Water	Ice + water + vapour	3

# Component

Example:	Compositions	C																				
Water system	Ice: $XH_2O$ Water: $YH_2O$ Vapours : $ZH_2O$	1																				
Sulphur	Rhombic: S Monoclinic: S Liquid: S Vapour: S	1																				
Salt and water	L : salt and $H_2O$	2																				
$CaCO_3 = CaO + CO_2$	<table border="0" style="width: 100%;"> <tr> <td style="text-align: left;">phase</td> <td style="text-align: right;">components</td> </tr> <tr> <td colspan="2"><math>CaCO_3</math> (solid) = <math>CaCO_3 + 0CaO</math></td> </tr> <tr> <td></td> <td style="text-align: right;"><math>= CaCO_3 + 0CO_2</math></td> </tr> <tr> <td></td> <td style="text-align: right;"><math>= CaO + CO_2</math></td> </tr> <tr> <td colspan="2"><math>CaO</math>(Solid) = <math>0CaCO_3 + CaO</math></td> </tr> <tr> <td></td> <td style="text-align: right;"><math>= CaCO_3 - CO_2</math></td> </tr> <tr> <td></td> <td style="text-align: right;"><math>= CaO + 0CO_2</math></td> </tr> <tr> <td colspan="2"><math>CO_2</math>(Gas) = <math>CaCO_3 - CaO</math></td> </tr> <tr> <td></td> <td style="text-align: right;"><math>= 0CaCO_3 + CO_2</math></td> </tr> <tr> <td></td> <td style="text-align: right;"><math>= 0CaO + CO_2</math></td> </tr> </table>	phase	components	$CaCO_3$ (solid) = $CaCO_3 + 0CaO$			$= CaCO_3 + 0CO_2$		$= CaO + CO_2$	$CaO$ (Solid) = $0CaCO_3 + CaO$			$= CaCO_3 - CO_2$		$= CaO + 0CO_2$	$CO_2$ (Gas) = $CaCO_3 - CaO$			$= 0CaCO_3 + CO_2$		$= 0CaO + CO_2$	2
phase	components																					
$CaCO_3$ (solid) = $CaCO_3 + 0CaO$																						
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	$= CaO + 0CO_2$																					
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	$= 0CaCO_3 + CO_2$																					
	$= 0CaO + CO_2$																					

# Degree of Freedom

Example:	Facts	F	Variance of system
Given mass of pure gas	$PV=RT$	2 (from P,V,T)	Bivariant
Solution of salt	Solubility $\propto$ Temp.	1 (C or T)	Univariant
Pure liquid	Vapour Pressure $\propto$ Temp.	1 ( T or P)	Univariant
water with three phases	Triple point	0	nonvariant

## Phase Diagram:

The conditions of equilibrium of a system can be conveniently studied by means of Gibb's phase rule using a diagram or graph known as **Phase Diagram**.

If P is plotted against T: **P-T diagram** : Useful for single component systems.

If T is plotted against C: **T-C diagram**: Useful for two component systems.:

## True and metastable equilibrium:

**True equilibrium**: In any system when the same state is obtained by approach from either direction, it is called a state of true equilibrium. Ex. Ice (S)  $\leftrightarrow$  water (L)

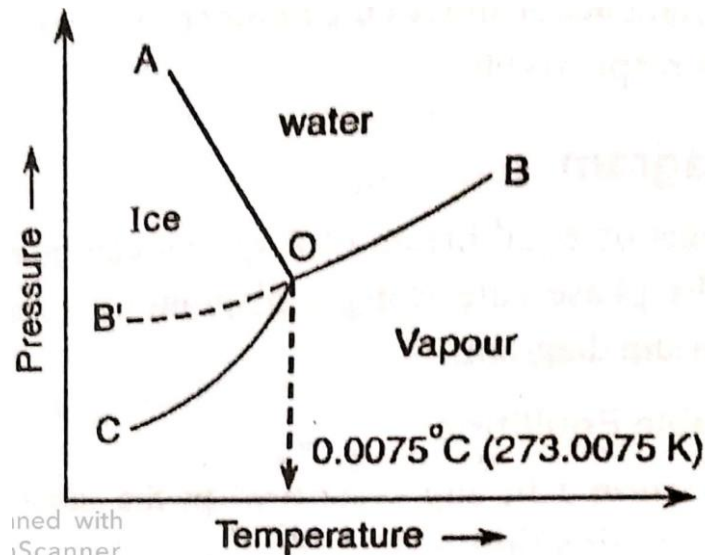
**T, P**

**Metastable equilibrium**: State of metastable equilibrium in any system can be obtained only by **careful approach from only one direction** is called a state of true equilibrium.

Ex. Supercooled water ( $H_2O$  at  $-4^\circ C$ )  $\leftrightarrow$  ice

- Not possible to obtain liquid water at  $-4^\circ C$  by melting ice.
- Possible to obtain liquid water at  $-4^\circ C$  by **careful** cooling of water.
- by slight disturbance, shock, stirring it immediately converted into ice.

# One component system: water system



Salient feature	Name	Phases	P=	F=C-P+2	Variance
Curve OC	sublimation curve of water	Ice + vapour	2	1	monovariant
Curve OA	FP curve of water/MP curve of ice	Water+ ice	2	1	monovariant
Curve OB	B.P curve of water	vapours+water	2	1	monovariant
Curve OB'	Metastable curve of supercooled water	Vapours + supercooled water	2	1	monovariant
Point: O	triple point	Ice+water+vapours	3	0	Invariant or Nonvariant
Area BOC	Single phase	vapours	1	2	Bivariant
Area AOB	Single phase	water	1	2	Bivariant
Area AOC	Single phase	ice	1	2	Bivariant

Salient feature	Name	Phases	P=	F=C-P+2	Variance F
Curve MO	Sublimation curve of $S_R$	$S_R$ and $S_V$	2	1	monovariant
Curve OL	Sublimation curve of $S_M$	$S_M$ and $S_V$	2	1	monovariant
Curve LP	B.P. Curve of $S_L$	$S_L$ and $S_V$	2	1	monovariant
Curve ON	Transition curve of $S_R$ to $S_M$	$S_R$ and $S_M$	2	1	monovariant
Curve LN	M.P. Curve of $S_M$	$S_M$ and $S_L$	2	1	monovariant
Curve OM'	Metastable curve	Superheated $S_R$ and $S_V$	2	1	monovariant
Curve LM'	Metastable curve	Supercooled $S_L$ and $S_V$	2	1	monovariant
Curve NM'	Metastable curve	Superheated $S_R$ and supercooled $S_L$	2	1	monovariant
point O	Triple point	$S_R, S_M, S_V$	3	0	nonvariant
point L	Triple point	$S_M, S_L, S_V$	3	0	nonvariant
point N	Triple point	$S_R, S_L, S_M$	3	0	nonvariant
point M'	Triple point	$S_R, S_L, S_V$	3	0	nonvariant
Area MON	Single phase area	$S_R$	1	2	Bivariant
Area MOLP	Single phase area	$S_V$	1	2	Bivariant
Area OLN	Single phase area	$S_M$	1	2	Bivariant
Area PLN	Single phase area	$S_L$	1	2	bivariant

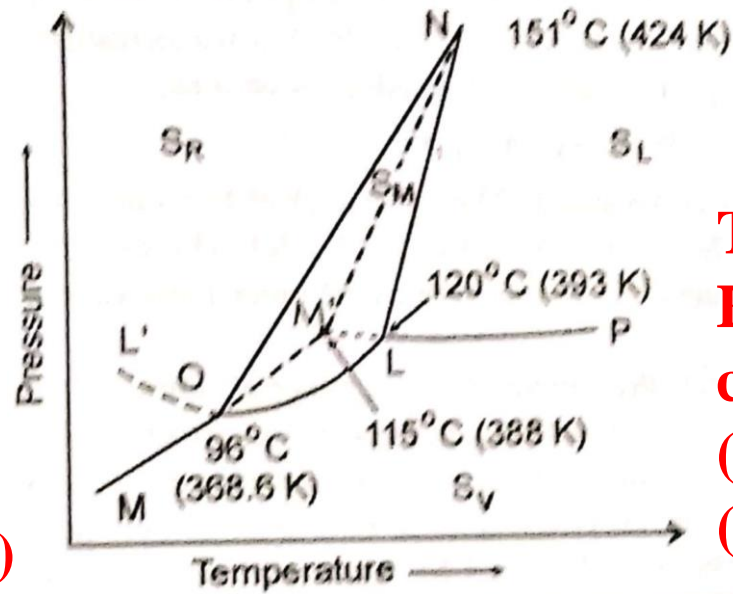
## Sulphur system:

### Crystalline form

Allotropy(element),

Polymorphism

(substance) or (compound)



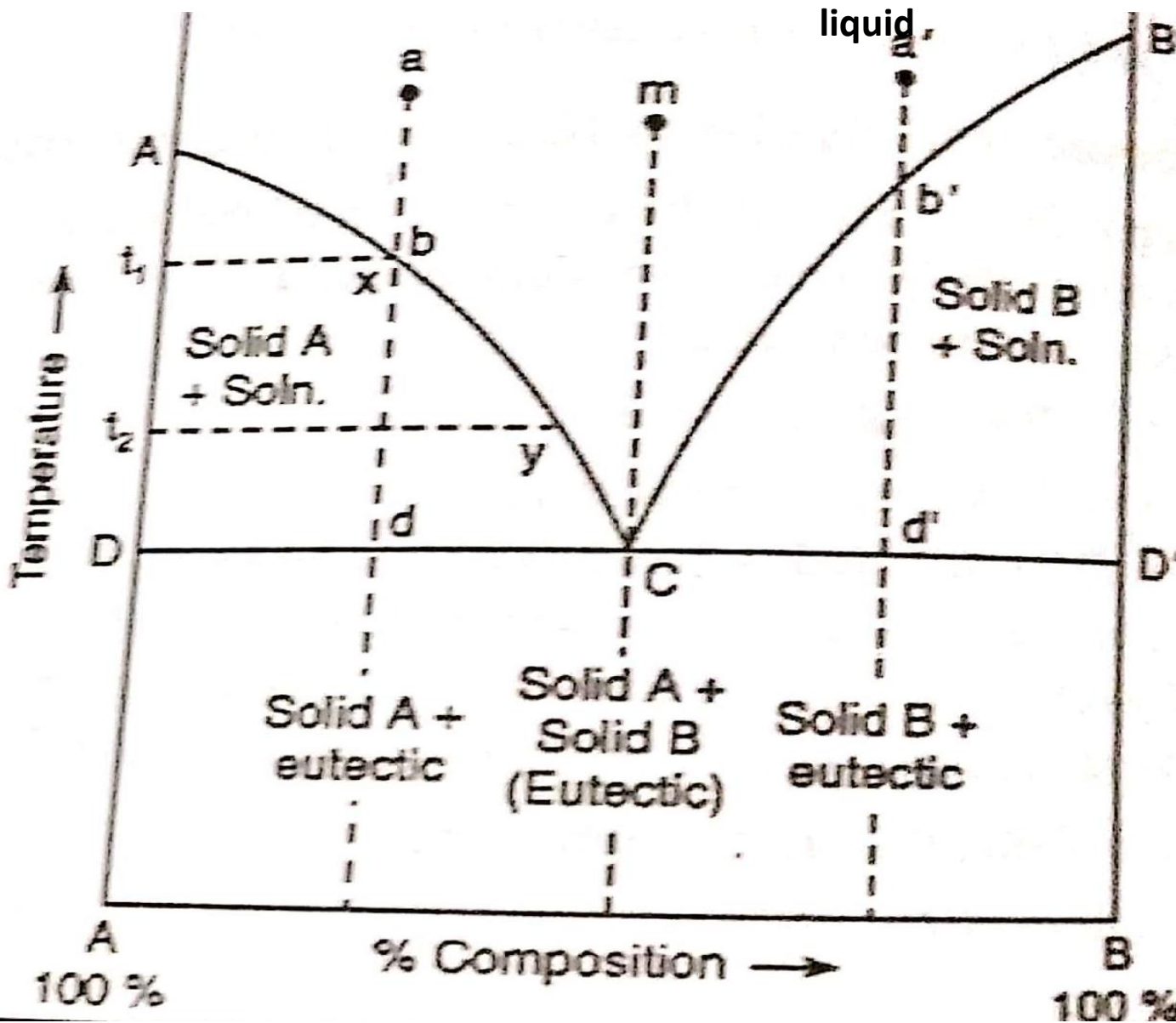
Transition point,  
Enantiotropy,  
conversion,  
(substance) or  
(compound)

# Two component system (condensed system):

- Phase rule is  $F=C-P+2$
- Suppose  $C=2$ ,  $P=1$  then  $F=2-1+2=3$
- $T$ ,  $P$ ,  $C$  are required to be stated or fixed
- **Three coordinate axes** at right angle to each other gives three dimensional figure.
- Generally for simplicity or **convenience**, we draw plane diagram with 2 variables and **third variable** is supposed as **constant**.
- PT diagram, TC diagram, CP diagram
- In solid liquid equilibria, **vapor phase is neglected** and  $P$  is kept constant.  $P$  is negligible
- The system in which only solid & liquid phases are considered is called as condensed system.
- One variable is fixed or constant.
- So degree of freedom reduces by 1
- **Reduced** phase rule is  $F'=C-P+1$



# Two component system: Type I: Simple Eutectic system:

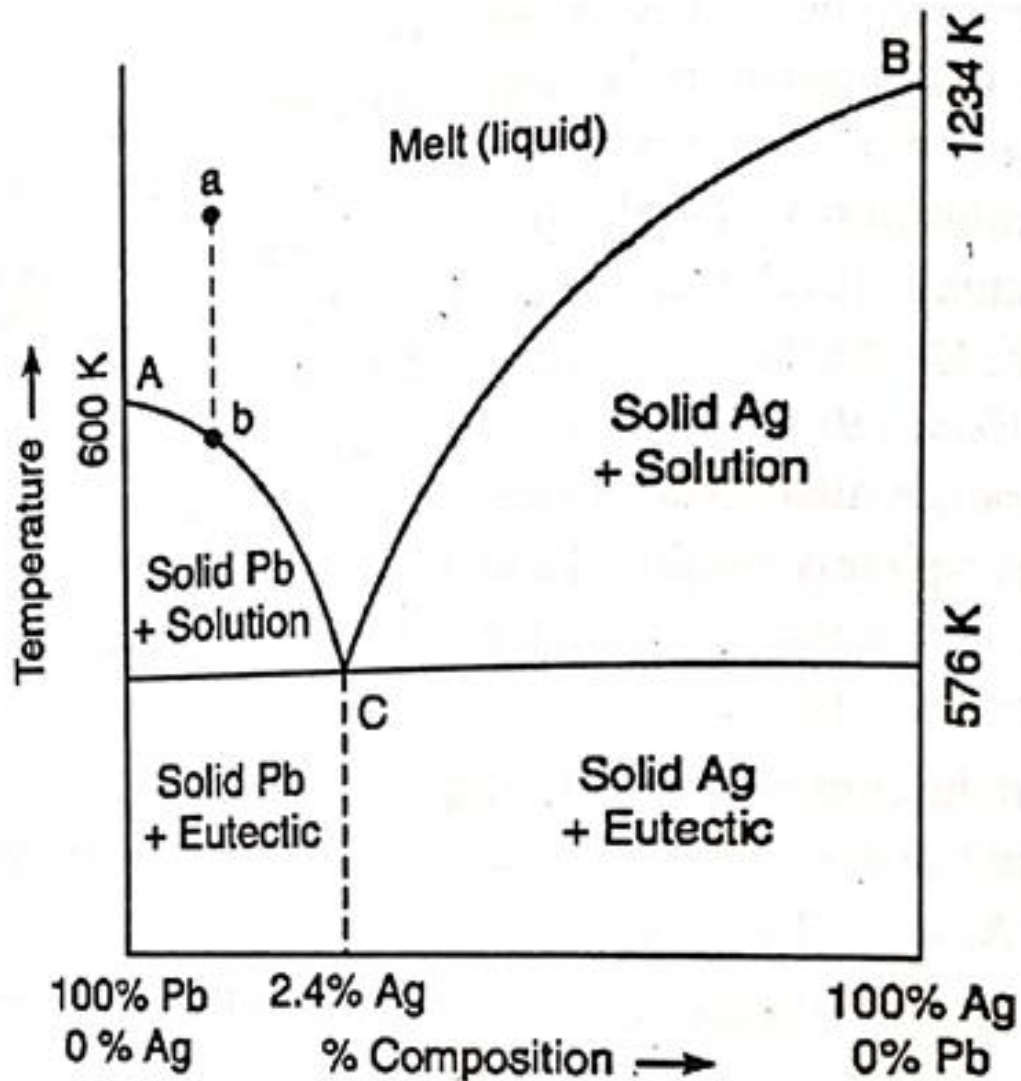


- Curve AC or CA
- a to b to d
- Curve BC or CB
- a' to b' to d'
- Point C
- Eutectic temp & composition
- Special case m  
liq comp = eutectic  
composition
- Solidus & liquidus

**Point A and B are freezing points or melting points of pure A and B respectively**

Salient feature	Name	Phases	P=	F'=C-P+1	Variance
Point: C	Eutectic point	Solid A + Solid B + soln	3	0	nonvariant
Curve AC	FP curve of A	Solid A + soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Curve BC	F.P curve of B	Solid B+ soln	2	1	monovariant
	liquidus : gives information about the composition of liquid phase				
Solidus AD	i.e 100% A				
Solidus BD'	gives information about the composition of solid phase. i. e 100% B				
Solidus DD'	gives information about the composition of solid phase. i. e % of A and B				
Area above AOB	Solution of A and B with diff composition P=1, hence F'=2, bivariant				
Area Below DD'	Solid solution mixture of A and B with different composition , P=1, hence F'=2, bivariant				
Area within AOD	Solid A + soln, P=2, hence F'=1, monovariant				
Area within BOD'	Solid B + soln, P=2, hence F'=1, monovariant				

# Pb-Ag System

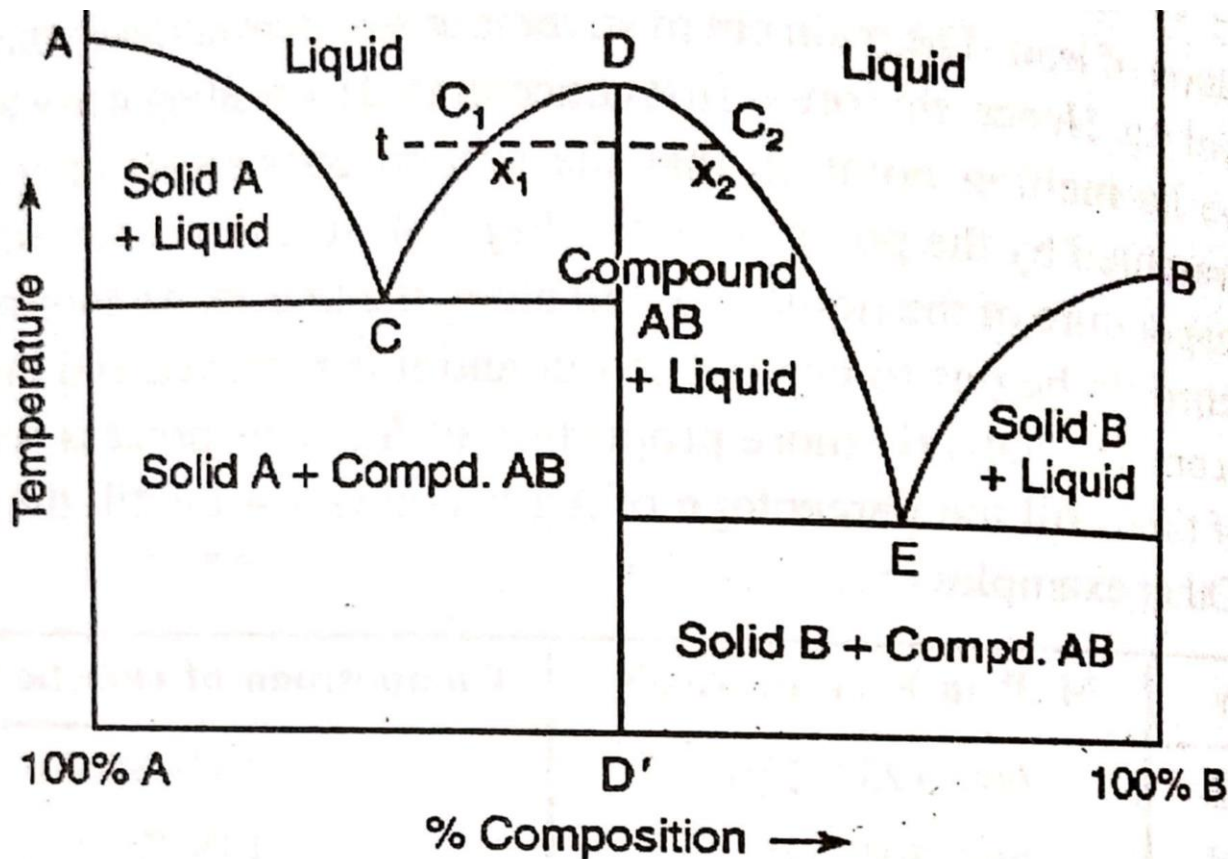


- Curve AC
- Curve BC
- Point C
- Desilverisation of lead

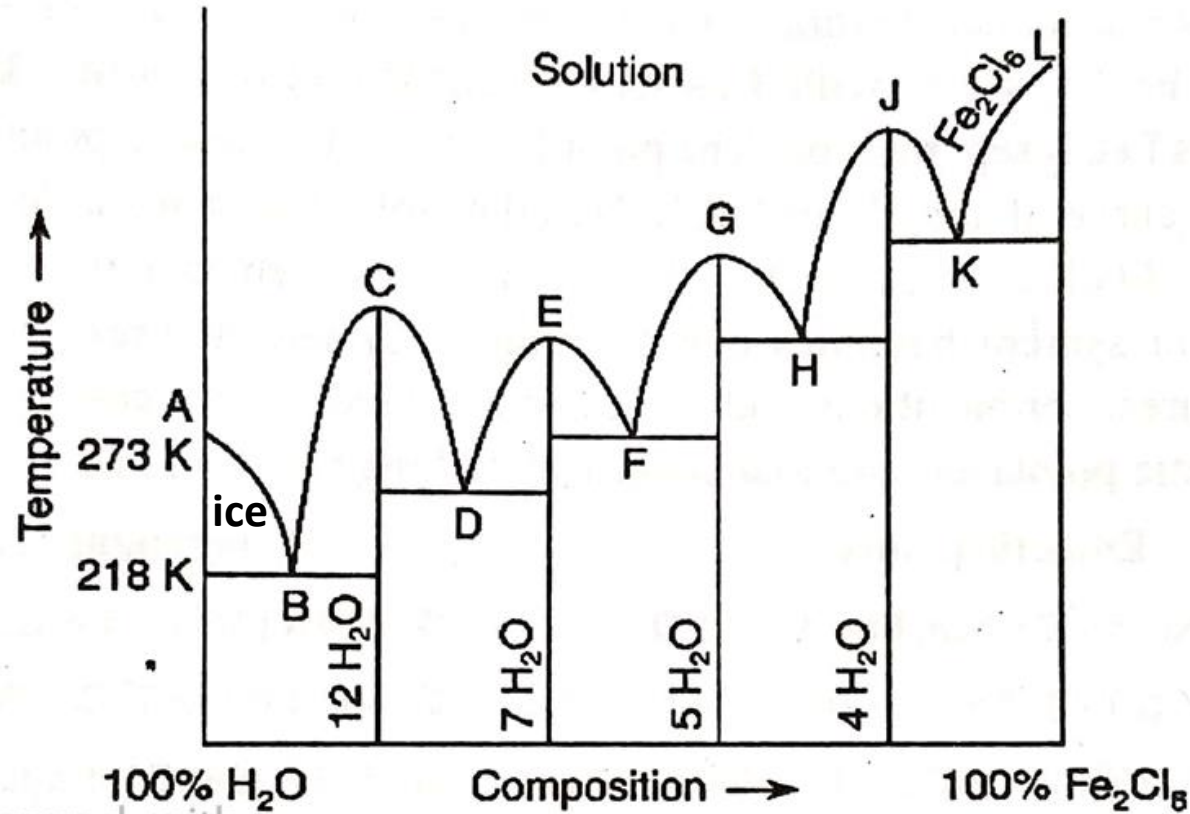
# Two component system: Type II:

## Formation of a compound with congruent MP:

Reduced phase rule:  $F' = C - P + 1$



- Congruent MP
- Compound AB
- Curve AC, BE, CDE
- equilibria
- point D,
- point C,E
- $x_1, x_2$  composition
- retroflex solubilities
- curve DC, DE
- line DD'
- horizontal lines passing through C & E are solidus



# Water-ferric chloride system

Curves AB, BCD, DEF, FGH, HJK, KL

## Eutectic points

B : 218 K (− 55°C) - ice, Fe<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O

D : 299 K (26°C) - Fe<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O, Fe<sub>2</sub>Cl<sub>6</sub>·7H<sub>2</sub>O

F : 303 K (30°C) - Fe<sub>2</sub>Cl<sub>6</sub>·7H<sub>2</sub>O, Fe<sub>2</sub>Cl<sub>6</sub>·5H<sub>2</sub>O

H : 328 K (55°C) - Fe<sub>2</sub>Cl<sub>6</sub>·5H<sub>2</sub>O, Fe<sub>2</sub>Cl<sub>6</sub>·4H<sub>2</sub>O

K : 339 K (66°C) - Fe<sub>2</sub>Cl<sub>6</sub>·4H<sub>2</sub>O, Fe<sub>2</sub>Cl<sub>6</sub>

## Congruent M. P.

C : 310 K (37° C) - Fe<sub>2</sub>Cl<sub>6</sub>·12H<sub>2</sub>O

E : 305.5 K (32.5° C) - Fe<sub>2</sub>Cl<sub>6</sub>·7H<sub>2</sub>O

G : 329 K (56° C) - Fe<sub>2</sub>Cl<sub>6</sub>·5H<sub>2</sub>O

J : 346.5 K (73.5° C) - Fe<sub>2</sub>Cl<sub>6</sub>·4H<sub>2</sub>O

## Explanation of P, C, F for some systems

(i) **Ice  $\rightleftharpoons$  Water  $\rightleftharpoons$  Vapour** : It is one component system (*i.e.*  $\text{H}_2\text{O}$ ) and there are three phases *i.e.*  $C = 1$ ,  $P = 3$ , hence by applying the phase rule we get,

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

*i.e.* degree of freedom is zero and system is non-variant.

(ii) **NaCl solid with saturated solution, ice and vapour** : It is two component system ( $\text{NaCl}$  and  $\text{H}_2\text{O}$ ) and there are four phases *i.e.* solid  $\text{NaCl}$ , ice, solution and vapour. Thus,  $C = 2$ ,  $P = 4$ , hence applying phase rule we get,

$$F = C - P + 2 = 2 - 4 + 2 = 0$$

*i.e.* degree of freedom is zero and system is invariant.

(iii) **Unsaturated solution of KI and vapour** : It is two component system ( $\text{KI}$  and  $\text{H}_2\text{O}$ ) and there are two phases *i.e.*, solution and vapour. Thus,  $C = 2$ ,  $P = 2$ , hence applying the phase rule we get,

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

*i.e.* degree of freedom is two and system is bivariant.

(iv)  $\text{CaCO}_{3(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_{2(g)}$  : It is two component system as composition of any phase can be explained with the help of two components by using a chemical equation. There are three phases (two solids and one gas phase).

*i.e.*  $C = 2, P = 3$ , hence applying the phase rule we get,

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

*i.e.* degree of freedom is one and system is univariant.

(v)  $S_L \rightleftharpoons S_V$  : It is one component system (*i.e.*, sulphur) and there are two phases,  $S_L$  and  $S_V$ , hence applying the phase rule,

$$F = C - P + 2 = 1 - 2 + 2 = 1 \text{ and system is univariant.}$$

(vi) Solution of cane sugar in a beaker at room temperature : Here there are two components *i.e.*, cane sugar and water (solvent) and phases are two *i.e.*, solution and vapour. Hence, applying the phase rule we get,

$$F = C - P + 2 = 2 - 2 + 2 = 2 \text{ and system is bivariant.}$$

(vii)  $S_R \rightleftharpoons S_M \rightleftharpoons S_V$  : This is the one component system as  $S_R$ ,  $S_M$  and  $S_V$  are different forms of the same chemical individual, sulphur. There are three phases (two solids  $S_R$  and  $S_M$  and one gas phase) *i.e.*, the degree of freedom is zero as,

$$F = C - P + 2 = 1 - 3 + 2 = 0 \text{ and system is non-variant.}$$

(viii)  $\text{NH}_4\text{Cl}_{(s)} \rightleftharpoons \text{NH}_3_{(g)} + \text{HCl}_{(g)}$  : Here the number of components is one because each phase can be explained with the help of only one chemical component  $\text{NH}_4\text{Cl}$ . There are two phases *i.e.*, solid  $\text{NH}_4\text{Cl}$  and homogeneous gaseous mixture of  $\text{NH}_3_{(g)}$  and  $\text{HCl}_{(g)}$  *i.e.*,  $C = 1$ ,  $P = 2$  and hence by applying the phase rule we get,

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

*i.e.*, the degree of freedom is one and system is univariant.

(ix) A mixture of benzene and water at room temperature : It is two component system *i.e.*, benzene and water with the help of which composition of every phase can be explained. There are three phases *i.e.*, two liquids (as benzene and water are immiscible) and one vapour phase. Thus,  $C = 2$ ,  $P = 3$  and hence applying the phase rule we get,

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

*i.e.*, the degree of freedom is one and system is univariant.





THANK  
YOU