

**Lecture no. 3**  
**One Component Systems**  
**(Water System)**

# One component system

➤ Here, one component is the smallest number by which the composition of each phase is expressed. This means,  $C = 1$

➤  $F = C - P + 2 \rightarrow F = 1 - P + 2 = 3 - P$

➤ *Maximum Number of Phases:*

$$F_{min} = 3 - P_{max}$$

$$0 = 3 - P_{max}$$

$$P_{max} = 3$$

➤ *Maximum Number of F:*

$$F_{max} = 3 - P_{min}$$

$$F_{max} = 3 - 1$$

$$F_{max} = 2$$

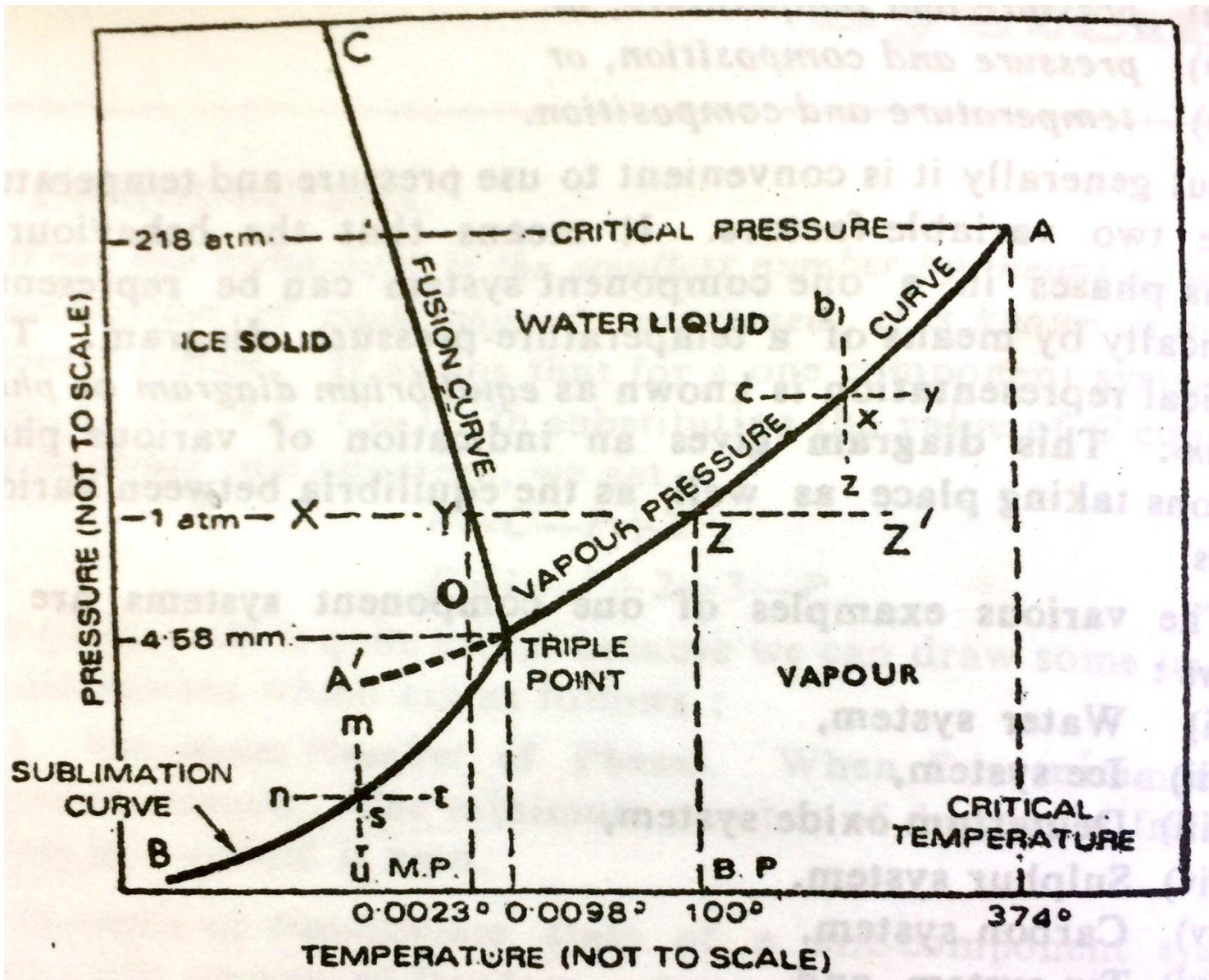
✓ This means, to define completely one component system, we have to mention two variable factors.

✓ The two variable factors can either be;

Pressure and temperature, or

Pressure and composition, or

Temperature and composition



# Various examples for one component system:

- 1) *Water system,*
- 2) *Ice system,*
- 3) *Deuterium oxide system,*
- 4) *Sulphur system,*
- 5) *Carbon system,*
- 6) *Phosphorus system.*

## Water system

- H<sub>2</sub>O is the only chemical compound involved → One component system*
- Three possible phases, namely, Solid (ice), Liquid (water), vapour*
- Three forms of equilibria:*

*Liquid  $\leftrightarrow$  Vapour*

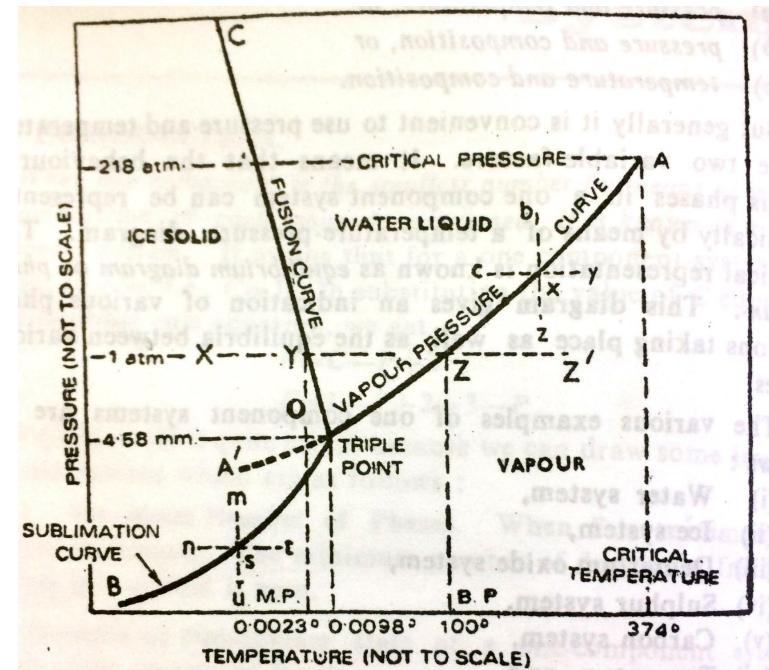
*Solid  $\leftrightarrow$  Vapour*

*Solid  $\leftrightarrow$  Liquid*

# Water (H<sub>2</sub>O) system, phase diagram, (pressure-temperature diagram)

The phase diagram consists of:

- I. Curves. There are three curves; OA, OB, and OC.
- II. Triple point. The above three curves meet at the point O, this point is known as triple point.
- III. Areas. The three curves divide the diagram into three areas: AOB, AOC, and BOC.
- IV. Metastable equilibrium. The curve OA' represents the metastable equilibrium.



# Water (H<sub>2</sub>O) system, phase diagram,

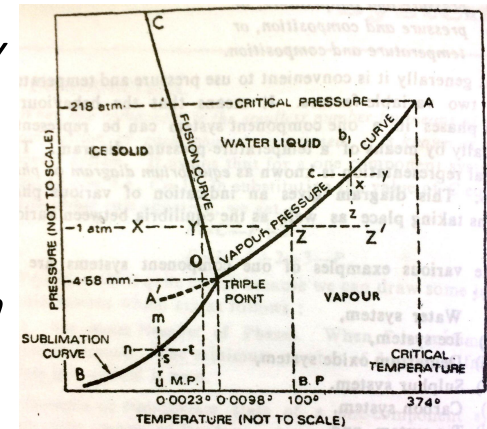
## I. Curves:

### 1. OA curve.

- It is known as the **vapour pressure curve of liquid water** because it gives the vapour pressure of water at different temperatures.
- The curve starts from O (freezing point) and ends at A (the critical temperature of water, 374°C).
- Critical temperature is the T at which the boundary surface between a liquid and its vapour is disappeared.

### **SCF!!**

- This curve presents the equilibrium Liquid  $\leftrightarrow$  Vapour. This means liquid water and vapour merge into each other.
- On any point on this curve,  **$P = 2$ , so  $F = 1 - 2 + 2 = 1$ .**
- For any given temperature there exists a fixed value of pressure. Similarly, for each vapour pressure, temperature has also a fixed value.
- For example, at 1 atm, water and vapour can be in equilibrium at one point only (the boiling point of water, 100°C)

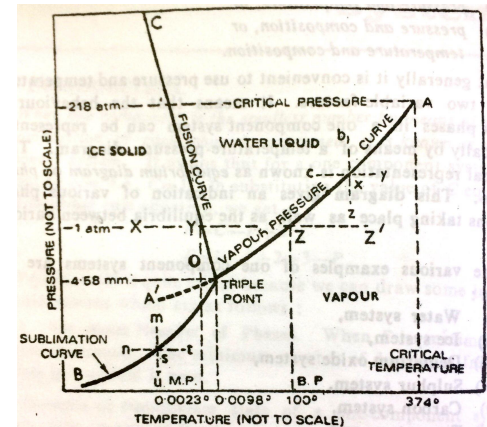


# Water (H<sub>2</sub>O) system, phase diagram,

## 1. Curves:

### 2. OB curve.

- It is known as the **vapour pressure curve of ice**, or **sublimation curve**.
- Along this curve, ice is in equilibrium with its vapour.
- The curve starts at point O, and ends at point B (point of absolute zero, -273°C). **No more vapours.**
- Along this curve, there are two phases  $F = 1 - 2 + 2 = 1$ .
- Thus, the system is univariant. This means, for each temperature there can be one and only one pressure, and vice versa.
- Please note that, the curve OB is not a prolongation of OA, but steeps rather rapidly.



# 1. Curves:

## 3. OC curve.

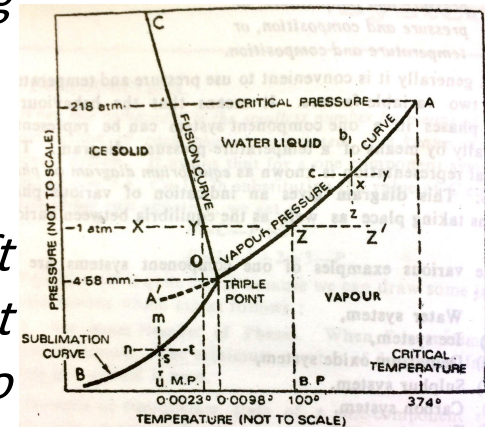
- It is known as the melting point or **fusion curve of ice**.
- This curve inclines towards the pressure axis (Y-axis).
- This means that, the melting point of ice is lowered by the increase of pressure. This can be understood as follow:

i. Ice and water are in equilibrium at  $0^{\circ}\text{C}$ , ice occupies more volume than the corresponding amount of water at the same temperature.

ii.  $\text{Ice} \leftrightarrow \text{water}$   
(more volume) (less volume)

iii. If we increase the pressure, equilibrium will shift in that direction in which the volume is reduced. It means more ice would melt into water. This also means the melting point is lowered by increasing the pressure.

iv. The freezing point of water at a pressure off  $4.58\text{mmHg}$  is  $0.0098^{\circ}\text{C}$ , whereas at higher pressure of  $760\text{mmHg}$ , it is lowered to  $0.0023^{\circ}\text{C}$ .





# Application of Clapeyron Eqn. to Solid/Liquid Phase

∴

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}$$

Clapeyron  
Equation

- **Process:** fusion (melting)

$T$  = melting point,  $T_m$

$\Delta H$  = enthalpy ( $\Delta_f H$ )

$\Delta V$  = volume ( $\Delta_f V$ )

(slope of a line on the phase diagram)

$$\frac{dp}{dT_m} = \text{slope of line} = \frac{\Delta_f H}{T_m \Delta_f V}$$

- **Inverting:**

$$\frac{dT_m}{dp} = \text{change in } T_m \text{ with } p = \frac{T_m \Delta_f V}{\Delta_f H}$$

- What is  $\Delta_f V$ ?

$$\Delta_f V = V_l - V_s$$

$$V = 1/\text{density} = 1/\rho = 1/\text{gcm}^{-3} = \text{cm}^3\text{g}^{-1}$$

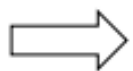
$$\Delta_f V = 1/\rho_l - 1/\rho_s \quad (\text{a volume change per unit amount})$$

- Sign of slope:

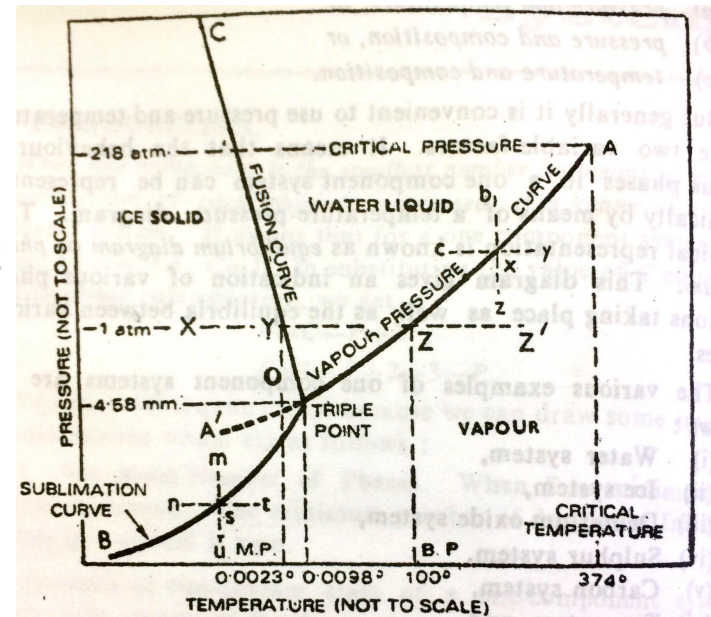
Water       $dp/dT = -ve = \frac{\Delta_f H}{T_m \Delta_f V}$

and       $\Delta_f H = \text{positive}$

$\therefore \Delta_f V = -ve$



$\rho_s < \rho_l$       (and so ice floats)

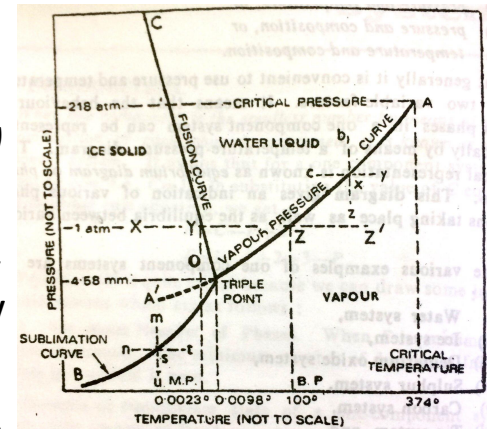


# Water (H<sub>2</sub>O) system, phase diagram,

## II. Points:

### Triple point O.

- *The point at which the three curve OA, OB, and OC meet.*
- *At this point, all the three phases (ice, water, and vapour) are co-exist.*
- *$F = 1 - 3 + 2 = 0$ , this means the three phases can only co-exist at one temperature and pressure (0.0075°C and 4.58mmHg).*
- *At this point neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases.*



# Water (H<sub>2</sub>O) system, phase diagram,

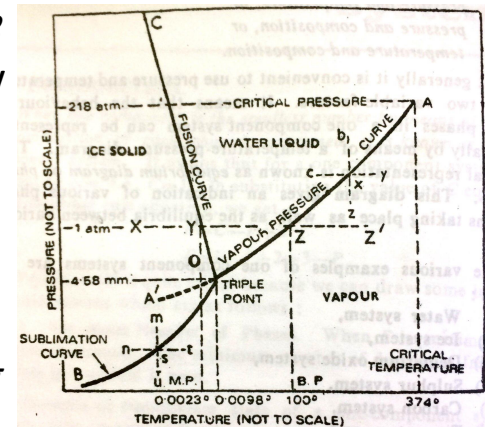
## III. Areas or Regions:

### Areas AOB, BOC, and AOC

- *In each area, a single phase is existed. Vapour exists in AOB area, water is only existed in the area AOC, while ice (solid phase) is existed only in the area BOC.*
- *All areas are bivariant.  $F = 1 - 1 + 2 = 2$*

## IV. Metastable Equilibrium

- *Sometimes, it is possible to cool water below its freezing point without the separation of solid ice.*
- *This water is then said to be in a state of metastable equilibrium or it is considered to be super-cooled.*
- *As soon as a small ice particle is kept in contact with the super-cooled liquid, it at once changes into the solid ice.*
- *This can be presented in the diagram by the curve OA`.*



	<i>Area</i>	<i>Phase exists</i>	<i>Component</i>
(i)	Area <i>AOC</i>	ice	H <sub>2</sub> O
(ii)	Area <i>COB</i>	water	H <sub>2</sub> O
(iii)	Area below <i>BOA</i>	vapour	H <sub>2</sub> O

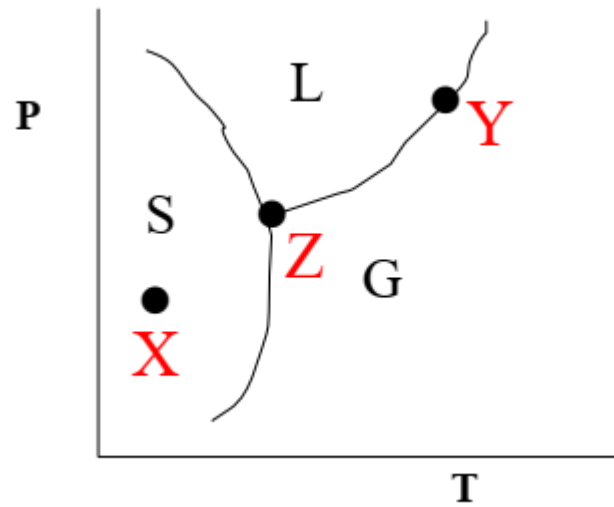
Thus, for every area contains

$$C = 1 \quad \text{and} \quad P = 1$$

Therefore, applying phase rule on areas

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

Hence, each area is a *bivariant system*. So, it becomes necessary to specify both the temperature and the pressure to define a one phase-system.



- At X

$$P = 1 \text{ (solid)}$$

$$F = C - P + 2$$

$$= 2$$

must specify 2 variables to locate position on diagram

- At Y

$$P = 2 \text{ (L + G)}$$

$$F = 1$$

position determined by only 1 variable

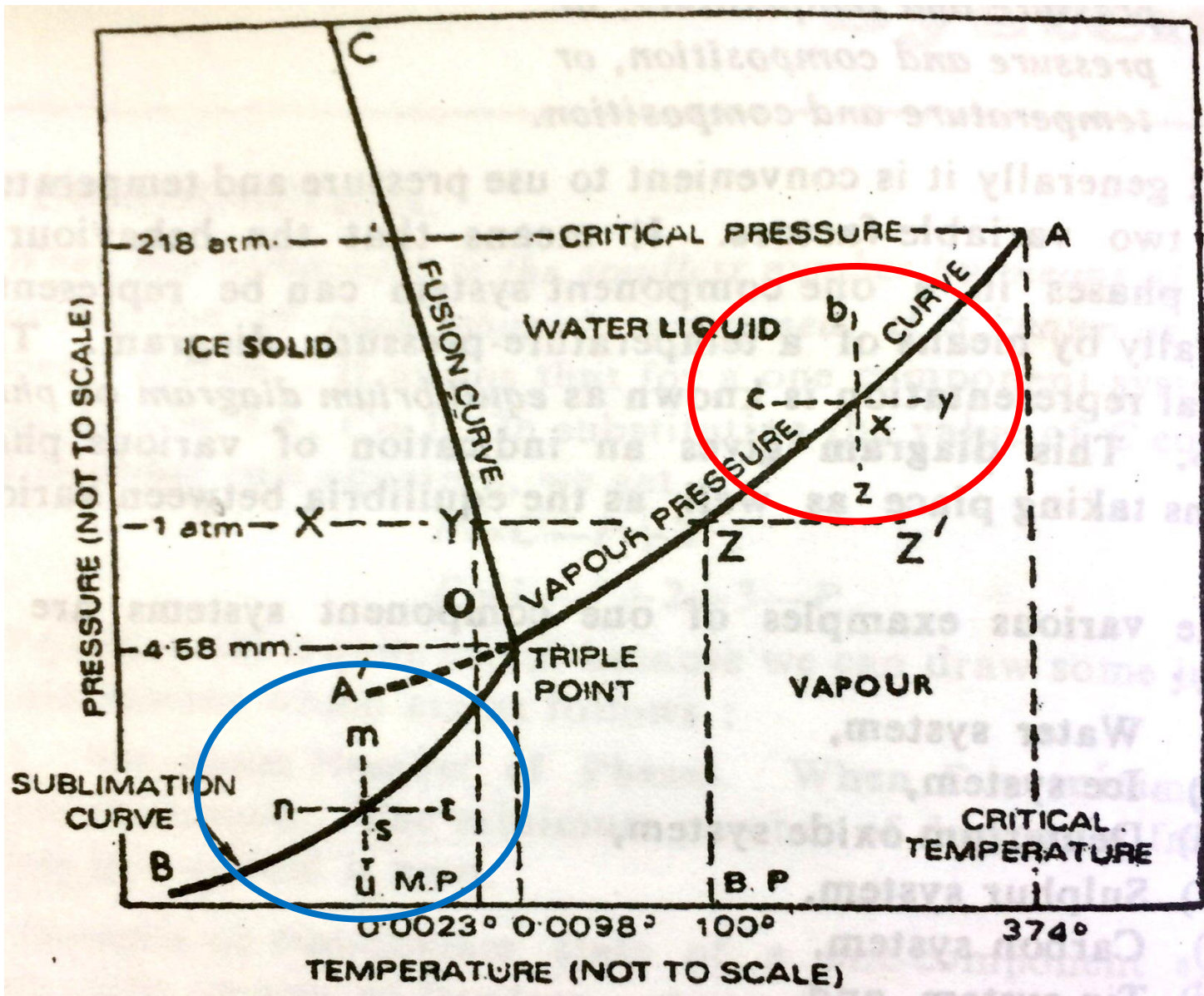
- At Z

$$P = 3 \text{ (S + L + G)}$$

$$F = 0$$

can only co-exist for fixed p and T

<i>Curve/ area/ point</i>	<i>Name of the system</i>	<i>Phases in equilibrium</i>	<i>No. of phase (P)</i>	<i>Degree of the freedom (F)</i>
Curve OB	Vapourisation curve	Liquid & vapour	02	01(Univariant)
Curve OA	Sublimation curve	Solid & vapour	02	01(Univariant)
Curve OC	Fusion curve	Solid & liquid	02	01(Univariant)
Curve OA'	Metastable vaporization curve	Liquid & vapour	02	01(Univariant)
Area AOC		Ice	01	02(Bivariant)
Area BOC		Water	01	02(Bivariant)
Area AOB		Vapour	01	02(Bivariant)
Point O		Ice & water & vapour	03	0(Invariant)



Xb line

XC line

XY line

XZ line





# Sulphur System

# ALLOTROPY

Existence of an element into more than one physical forms is known as allotropy.

## Example

Allotropic Form of Carbon

Coal

Diamond

Graphite

# The Sulphur System

It is a **one-component, four-phase system**. The four phases are:

**(a)** Two solid polymorphic forms:

**(i)** Rhombic Sulphur ( $S_R$ )

**(ii)** Monoclinic Sulphur ( $S_M$ )

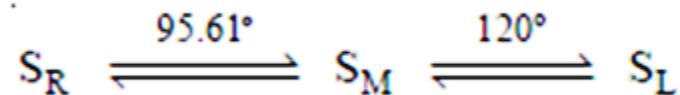
**(b)** Sulphur Liquid ( $S_L$ )

**(c)** Sulphur Vapour ( $S_V$ )

All the four phase can be represented by the only chemical individual 'sulphur' itself and hence one component of the system.

**The two crystalline forms of sulphur  $S_R$  and  $S_M$  exhibit enantiotropy with a transition point at 95.6°C.**

Below this temperature  $S_R$  is stable, while above it  $S_M$  is the stable variety. At 95.6°C each form can be gradually transformed to the other and the two are in equilibrium. At 120°C,  $S_M$  melts. Thus,



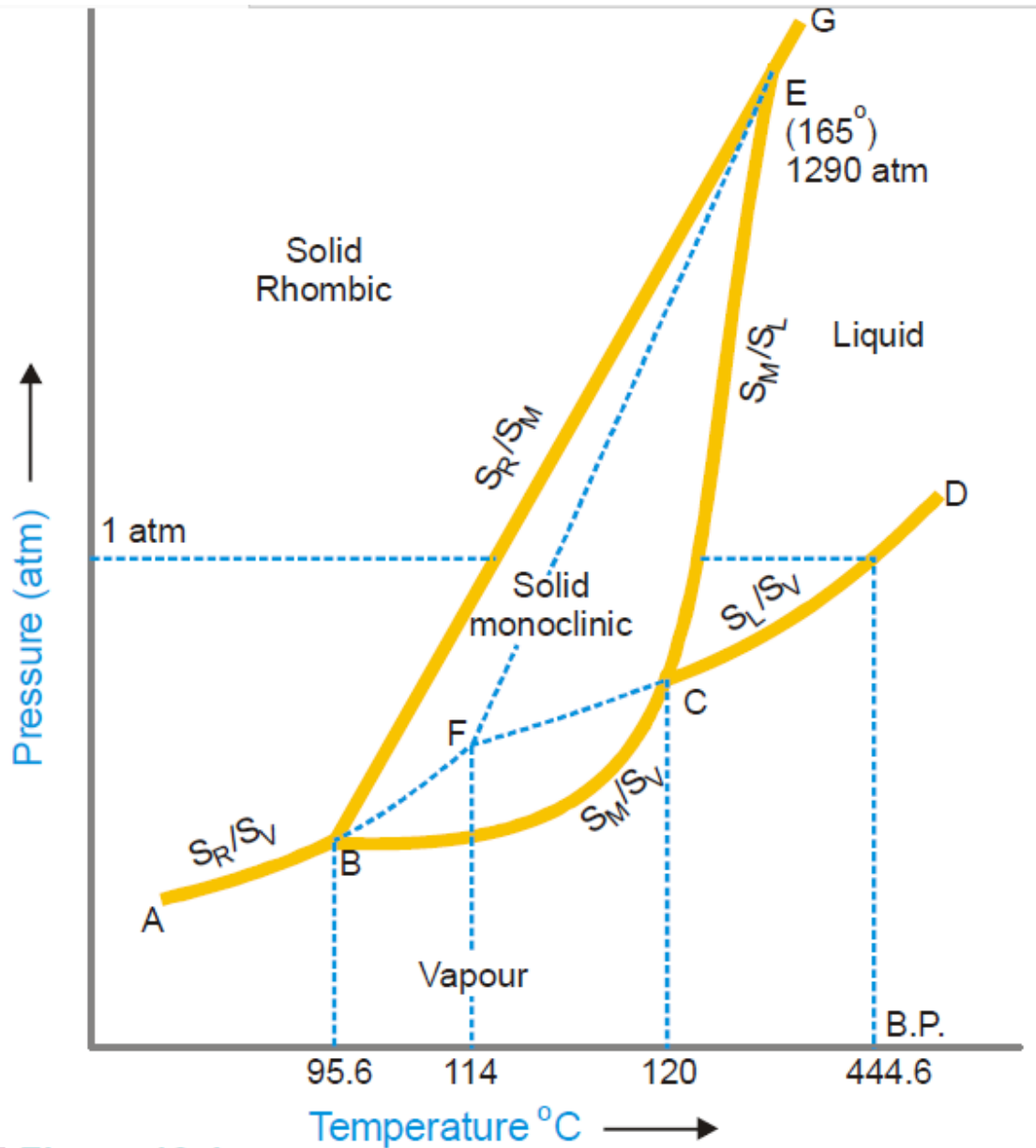
Four Phases are as follows

Rhombic Sulphur

Monoclinic Sulphur

Sulphur Liquid

Sulphur Vapour



# Salient feature of phase diagram



The phase diagram for the sulphur system is shown in Figure The salient features of the phase diagram are described below.

(i) The six curves  $AB$ ,  $BC$ ,  $CD$ ,  $BE$ ,  $CE$ ,  $EG$

(ii) The three Triple points  $B$ ,  $C$ ,  $E$

(iii) The four areas:

$ABG$  marked 'solid Rhombic'

$BEC$  marked 'solid Monoclinic'

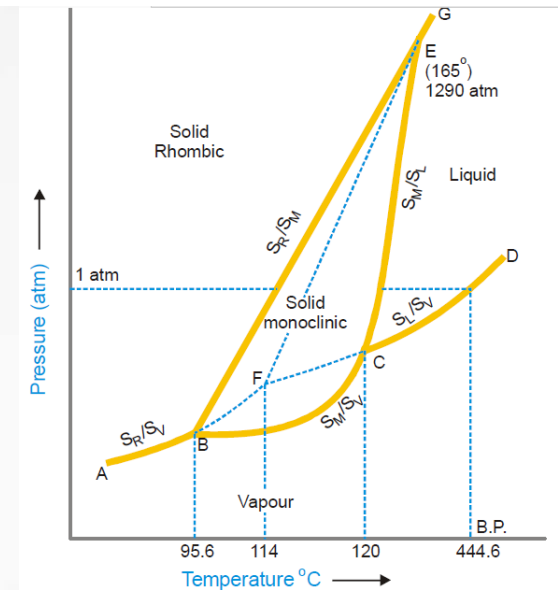
$GECD$  marked 'liquid Sulphur'

$ABCD$  marked 'Sulphur vapour'

(vi) *Meta-stable triple point (F).*

# Curves

- Six curves AB, BC, CD, BE, CE, EG
- Curve AB Vapour pressure curve of Rhombic sulphur
- Curve BC Vapour pressure curve of monoclinic sulphur
- Curve CD vapour pressure curve of liquid sulphur
- Curve BE transition curve
- Curve CE fusion curve of monoclinic sulphur
- Curve EG fusion curve for Rhombic sulphur

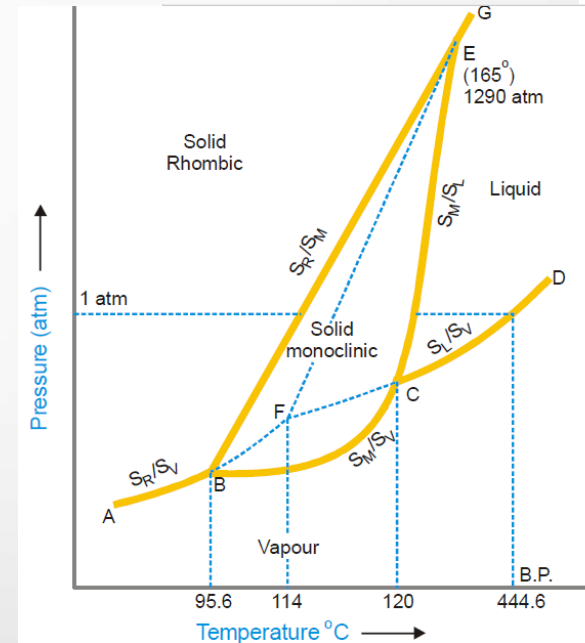




# Area

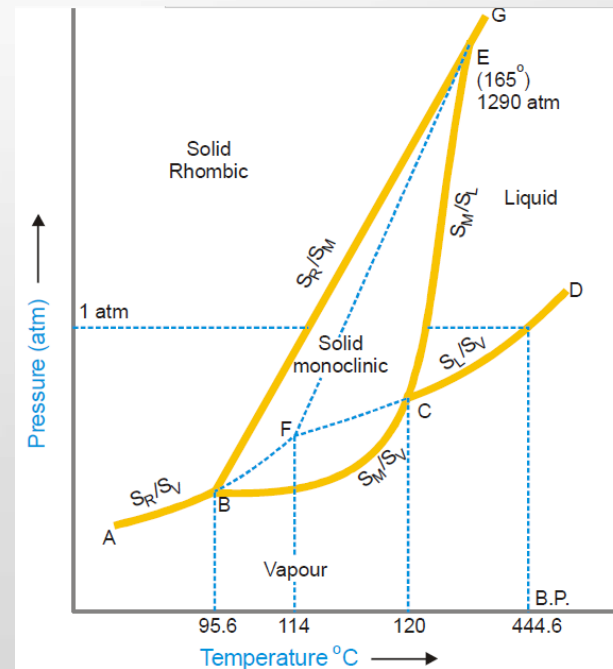
Sulphur system phase diagram has four areas.

- ✓ Rhombic sulphur.  $\longrightarrow$  ABG
- ✓ Monoclinic sulphur.  $\longrightarrow$  BEC
- ✓ Liquid sulphur.  $\longrightarrow$  GECD
- ✓ Sulphur Vapour.  $\longrightarrow$  ABCD
- Each represent **single phase**.
- Degree of freedom is **two** i.e **bivariant**



# Triple point

- There are **three** triple point in sulphur system which are as follows.
- Triple point at B.
- Triple point at C.
- Triple point at E.



The phase diagram for the sulphur system is shown in Figure . The **salient features of the phase diagram** are described below.

- (i) The six curves *AB, BC, CD, BE, CE, EG*
- (ii) The three Triple points *B, C, E*
- (iii) The four areas:

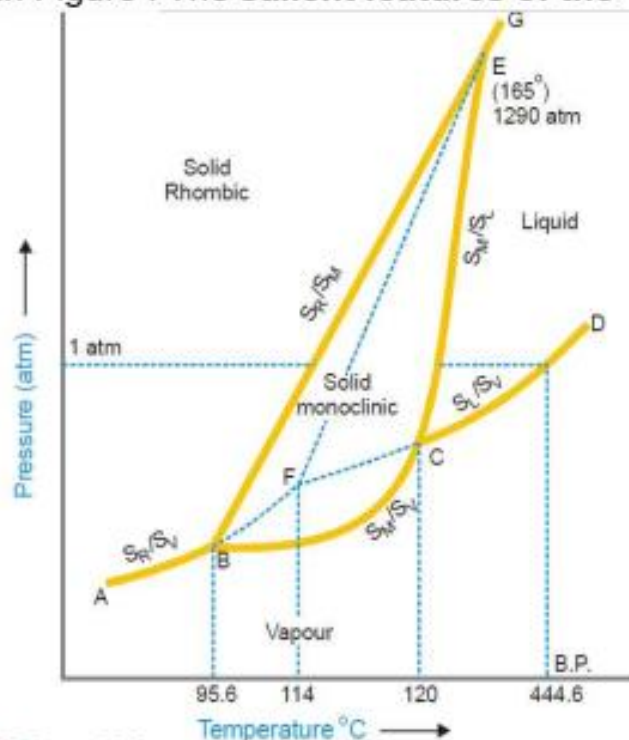
*ABG* marked 'solid Rhombic'  
*BEC* marked 'solid Monoclinic'  
*GECD* marked 'liquid Sulphur'  
*ABCD* marked 'Sulphur vapour'

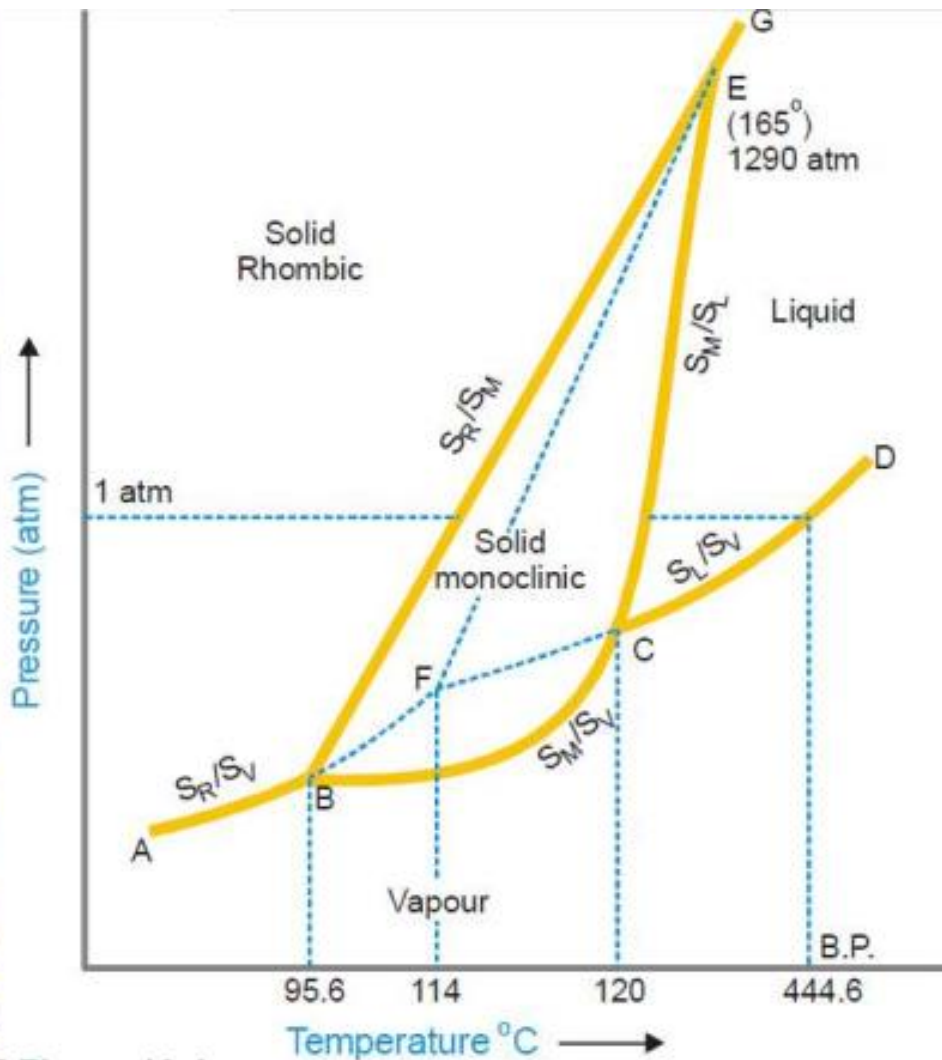
Let us now proceed to discuss the significance of these features :

**(1) The curves *AB, BC, CD, BE, CE, EG***

These *six curves* divide the diagram into *four areas*.

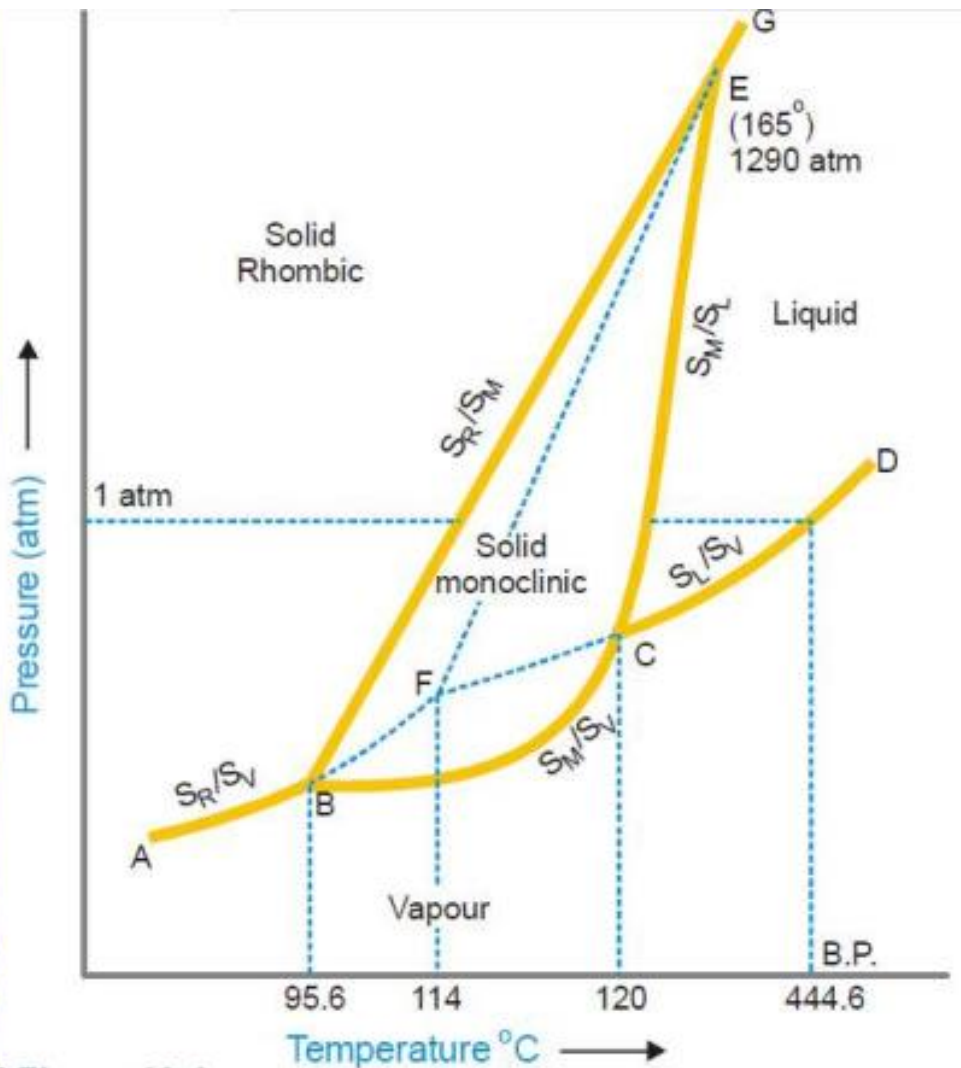
**Curve *AB*, the Vapour Pressure curve of  $S_R$ .** It shows the vapour pressure of solid rhombic sulphur ( $S_R$ ) . Along this curve the two phases  $S_R$  and sulphur vapour ( $S_V$ ) are in equilibrium. The system  $S_R/S_V$  has one degree of freedom,  
 $F = C - P + 2 = 1 - 2 + 2 = 1$  i.e., it is *monovariant*.



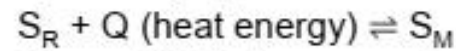


**Curve BC, the Vapour Pressure curve of  $S_M$ .** It shows variation of the vapour pressure of monoclinic sulphur ( $S_M$ ) with temperature.  $S_M$  and  $S_V$  coexist in equilibrium along this curve. The system  $S_M/S_V$  is *monovariant*.

**Curve CD, the Vapour Pressure curve of  $S_L$ .** It depicts the variation of the vapour pressure of liquid sulphur ( $S_L$ ) with temperature.  $S_L$  and  $S_V$  are in equilibrium along CD. The two phase system  $S_L/S_V$  is monovariant. One atmosphere line meets this curve at a temperature (444.6°C) which is the boiling point of sulphur.



**Curve BE, the Transition curve.** It shows the effect of pressure on the transition temperature for  $S_R$  and  $S_M$ . As two solid phases are in equilibrium along the curve, the system  $S_R/S_M$  is *monovariant*.

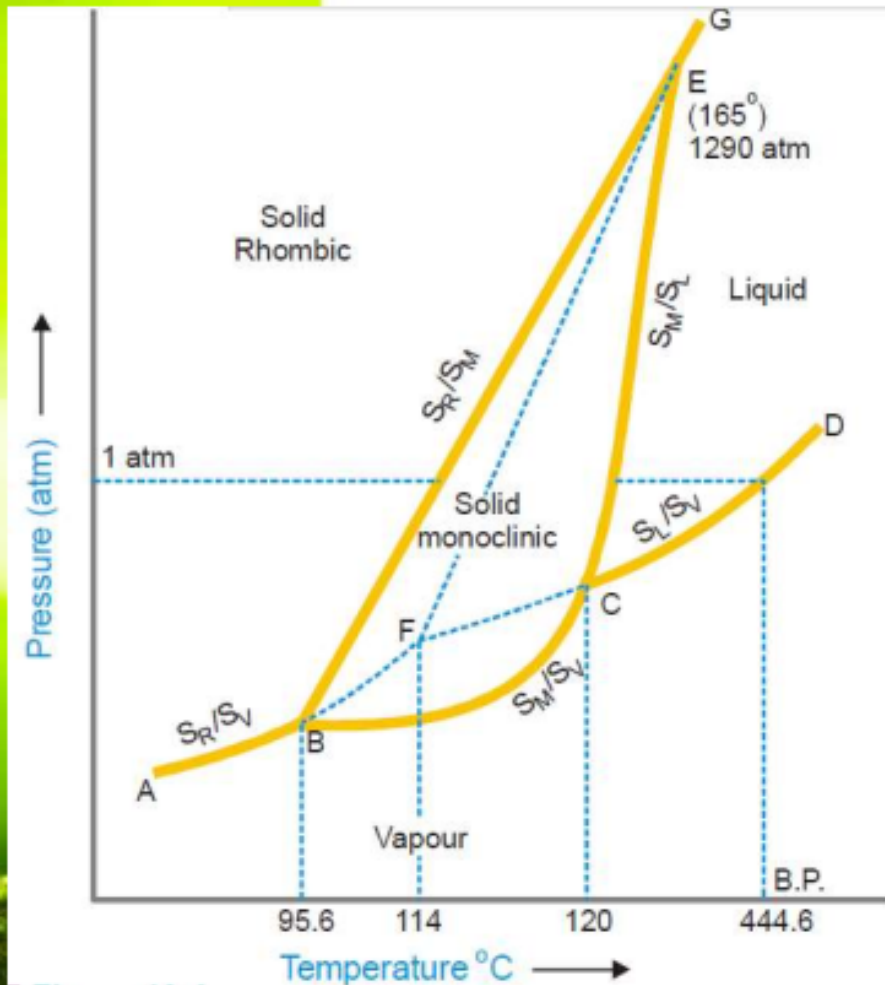


Thus, with the increase of pressure the transition temperature is raised .

**Curve CE, the Fusion curve of  $S_M$ .** It represents the effect of pressure on the melting point of  $S_M$ . The two phases in equilibrium along this curve are  $S_M$  and  $S_L$ . The system  $S_M/S_L$  is *monovariant*. With a slight increase of volume, the melting point will rise by increase of pressure .

**Curve EG, the Fusion curve for SR.** Here the two phases in equilibrium are SR and SL. The number of phases being two, the system SR/SL is *monovariant*.

## (2) The Triple points B, C, E



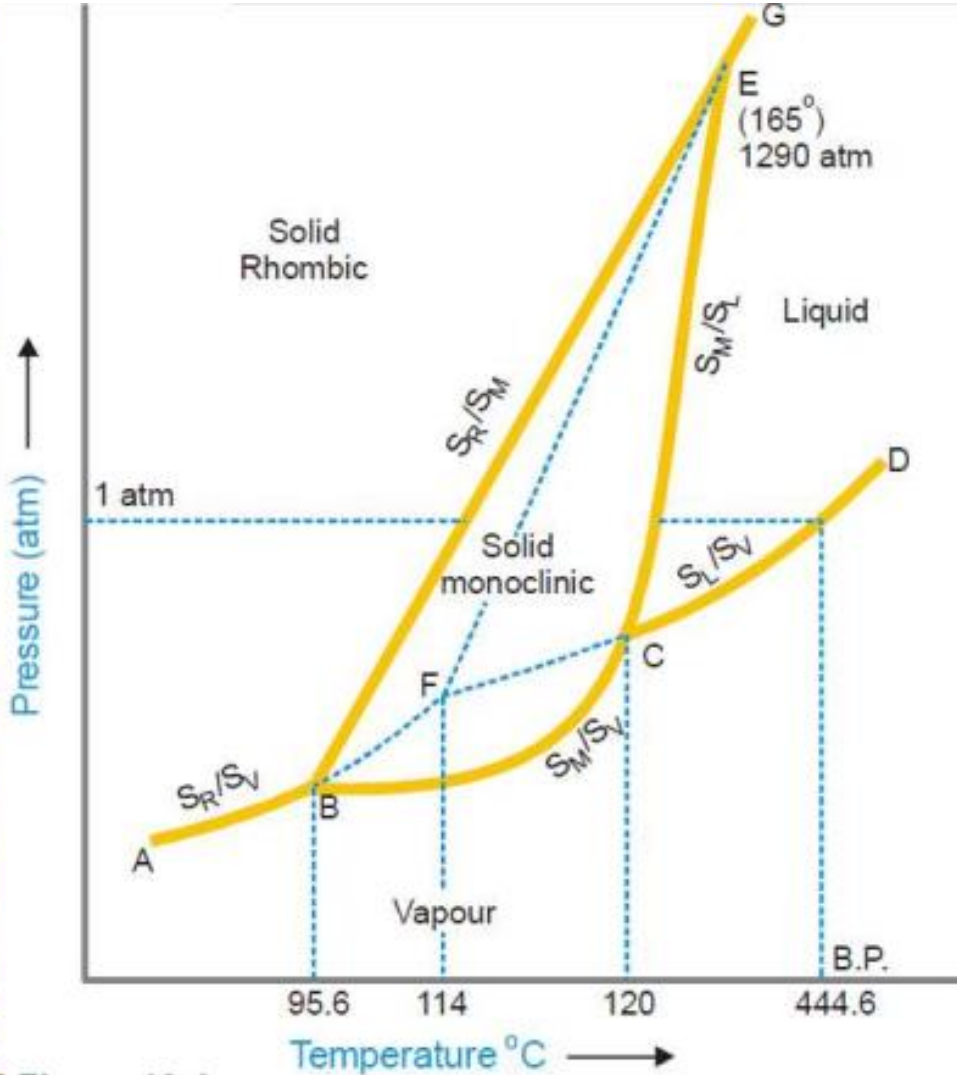
**Triple point B.** This is the meeting point of the three curves AB, BC and BE. Three phases, are in equilibrium at the point B. The system  $S_R/S_M/S_V$  is *nonvariant*.

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

At B,  $S_R$  is changed to  $S_M$  and the process is reversible. Thus the temperature corresponding to B is the *transition temperature* (95.6°C).

**Triple point C.** The curves BC, CD, CE meet at the point C. The three phases in equilibrium are  $S_M$ ,  $S_L$  and  $S_V$ . There being three phases and one component, the system  $S_M/S_L/S_V$  is *nonvariant*. The temperature corresponding to C is 120°C. This is the melting point of  $S_M$ .

**Triple point E.** The two lines CE and BE meet at E where a third line EG also joins. The three phases  $S_R$ ,  $S_M$  and  $S_L$  are in equilibrium at the point E and is *nonvariant*. At this point gives the conditions of existence of the system  $S_R/S_M/S_L$  at 165°C and 1290 atmospheres pressure.



### (3) The Areas

The sulphur system has **four areas** or **regions**. These are rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour.

These represent single phase systems with two degrees of freedom,

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

That is, each of the systems  $S_R$ ,  $S_M$ ,  $S_L$ , and  $S_V$  are *bivariant*.

### **(1) The curves AB, BC, CD, BE, CE, EG**

These *six curves* divide the diagram into *four areas*.

**Curve AB, the Vapour Pressure curve of  $S_R$ .** It shows the vapour pressure of solid rhombic sulphur ( $S_R$ ) at different temperatures. Along this curve the two phases  $S_R$  and sulphur vapour ( $S_V$ ) are in equilibrium. The system  $S_R/S_V$  has one degree of freedom,

$F = C - P + 2 = 1 - 2 + 2 = 1$  *i.e.* it is *monovariant*.

**Curve BC, the Vapour Pressure curve of  $S_M$ :** It shows variation of the vapour pressure of monoclinic sulphur ( $S_M$ ) with temperature.  $S_M$  and  $S_V$  coexist in equilibrium along this curve. The system  $S_M/S_V$  is *monovariant*.

**Curve CD, the Vapour Pressure curve of  $S_L$ :** It depicts the variation of the vapour pressure of liquid sulphur ( $S_L$ ) with temperature.  $S_L$  and  $S_V$  are in equilibrium along *CD*. The

two phase system  $S_L/S_V$  is monovariant. One atmosphere line meets this curve at a temperature ( $444.6^\circ\text{C}$ ) which is the boiling point of sulphur.



**Curve BE, the Transition curve:** It shows the effect of pressure on the transition temperature for  $S_R$  and  $S_M$ . As two solid phases are in equilibrium along the curve, the system  $S_R/S_M$  is *monovariant*.

The transformation of  $S_R$  and  $S_M$  is accompanied by increase of volume (density of  $S_R = 2.04$ ;  $S_M = 1.9$ ) and absorption of heat *i.e.*,



Thus, the increase of pressure will shift the equilibrium to the left (*Le Chatelier's Principle*) and the transition temperature will, therefore, be raised. This is why the line *BE* slopes away from the pressure axis showing thereby that the **transition temperature is raised with increase of pressure**.

Curve *CE*, the Fusion curve of  $S_M$ . It represents the effect of pressure on the melting point of  $S_M$ . The two phases in equilibrium along this curve are  $S_M$  and  $S_L$ . The system  $S_M/S_L$  is *monovariant*. As the melting or fusion of  $S_M$  is accompanied by a slight increase of volume, the melting point will rise by increase of pressure (*Le Chatelier's principle*).

Thus the curve *CE* slopes slightly away from the pressure axis. The curve ends at *E* because  $S_M$  ceases to exist beyond this point.

Curve *EG*, the Fusion curve for  $S_R$ . Here the two phases in equilibrium are  $S_R$  and  $S_L$ . The number of phases being two, the system  $S_R/S_L$  is *monovariant*.

## (2) The Triple points **B**, **C**, **E**

**Triple point B.** This is the meeting point of the three curves  $AB$ ,  $BC$  and  $BE$ . Three phases, solid  $S_R$ , solid  $S_M$  and  $S_V$  are in equilibrium at the point  $B$ . There being three phases and one component, the system  $S_R/S_M/S_L$  is *nonvariant*.

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

At  $B$ ,  $S_R$  is changed to  $S_M$  and the process is reversible. Thus the temperature corresponding to  $B$  is the *transition temperature* ( $95.6^\circ\text{C}$ ).

**Triple point C.** The curves  $BC$ ,  $CD$ ,  $CE$  meet at this point. The three phases in equilibrium are  $S_M$ ,  $S_L$  and  $S_V$ . There being three phases and one component, the system  $SM/SL/SV$  is *nonvariant*. The temperature corresponding to  $C$  as indicated on the phase diagram is  $120^\circ\text{C}$ . This is the melting point of  $S_M$ .

**Triple point E.** The two lines  $CE$  and  $BE$ , having different inclinations away from the pressure axis, meet at  $E$  where a third line  $EG$  also joins. The three phases  $S_R$ ,  $S_M$  and  $S_L$  are in equilibrium and the system at the point  $E$  is *nonvariant*. This point gives the conditions of existence of the system  $S_R/S_M/S_L$  at  $155^\circ\text{C}$  and 1290 atmospheres pressure.

### (3) The Areas

The phase diagram of the sulphur system has **four areas** or **regions**. These are labelled as rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour. These represent single phase systems which have two degrees of freedom,

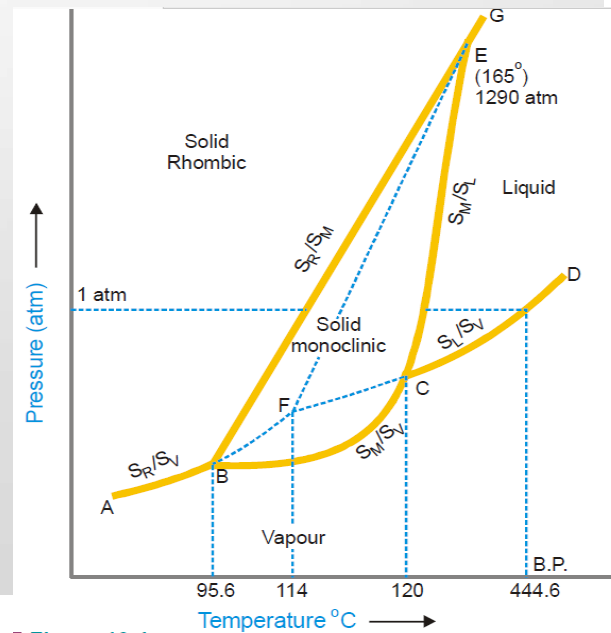
$$F = C - P + 2 = 1 - 1 + 2 = 2$$

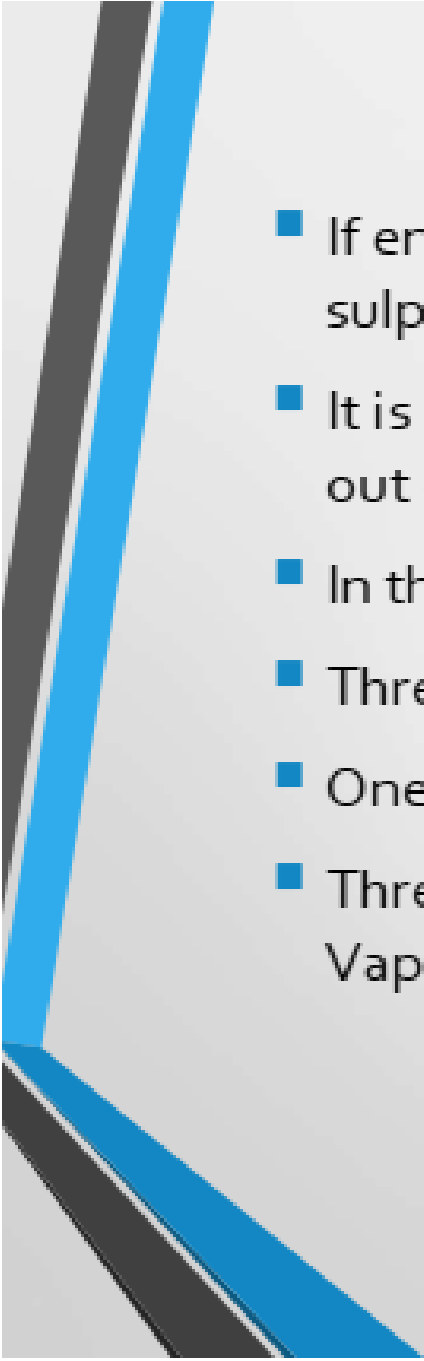
That is, each of the systems  $S_R$ ,  $S_M$ ,  $S_L$ , and  $S_V$  are *bivariant*.

# Meta stable equilibrium

A phase that can be produced by a very rapid change in system conditions( temperature, pressure)or in some case

The metastable state may persist indefinitely as the movement towards equilibrium is virtually imperceptible over long period of time.



- 
- If enough time for the change is not allowed and rhombic sulphur is heated rapidly
  - It is possible to pass well above the transition point without getting monoclinic sulphur.
  - In that case phase diagram will consist of
    - Three curves
    - One triple curve
    - Three areas (rhombic sulphur, liquid sulphur, sulphur Vapour )

## Dashed curve BF, Vapour pressure curve of metastable rhombic sulphur

- Continuation of vapour pressure curve AB of stable rhombic sulphur.
- The metastable phase rhombic sulphur and sulphur vapour are in equilibrium.
- It has one degree of freedom.
- The Vapour pressure curve of supercooled liquid sulphur

## Curve CF, Vapour pressure curve of super cooled liquid sulphur

- On super cooling liquid sulphur, dash curve CF is obtained
- Metastable equilibrium between liquid sulphur and sulphur Vapour

## Dashed curve FE, the melting curve of metastable of Rhombic sulphur

- The two metastable phase rhombic sulphur and liquid sulphur are in equilibrium.
- Melting point of rhombic sulphur increase with pressure.

# Metastable Equilibrium

- 3 Dashed curve:
  - curve BF (sublimation curve of metastable  $S_R$ )
  - curve CF (vapour press. Curve of supercooled liquid sulphur)
  - curve FE (fusion curve of metastable  $S_R$ )
- One triple point F
- 3 areas:
  - Area ABFE (Metastable  $S_R$ )
  - Area ABFCD (Sulphur vapours)
  - Area DCFE (supercooled liquid sulphur)