point a, the system is in molten state. As it is cooled, there is no change till the point b is reached. At the point b, solid B begins to separate as the melt becomes saturated with respect to B. ab represents the cooling of the homogeneous melt. As the temperature is lowered further, more and more solid B crystalizes out and the melt becomes richer with respect to the other component A and its composition moves along bO. The amount of solid B crystallizing out at a given point c can be obtained by applying the lever rule as:

$$\frac{\text{Mass of solid B}}{\text{Mass of melt}} = \frac{cy}{cx} \qquad \ldots\ldots\ldots\ldots (7.8)$$

On further cooling eutectic temperature (T_e) is reached when maximum amount of B crystallizes out. At this point solid A begins to separate out and the melt is in equilibrium with solid A and solid B. The system becomes invariant ($F = 2 - 3 + 1 = 0$) so that the temperature remains constant. When the whole melt gets solidified, the temperature of the solid mixture falls along de. If the process is reversed from the point e by heating, the changes take place in the reverse order.

7.4.1 Phase Diagram of Simple Eutectic

Based on the miscibility of two components in the molten state and the nature of the solid phases that separate out during cooling, there may be different types of solid-liquid equilibria. Out of these, the simplest and the most important class is the one forming simple eutectic mixture.

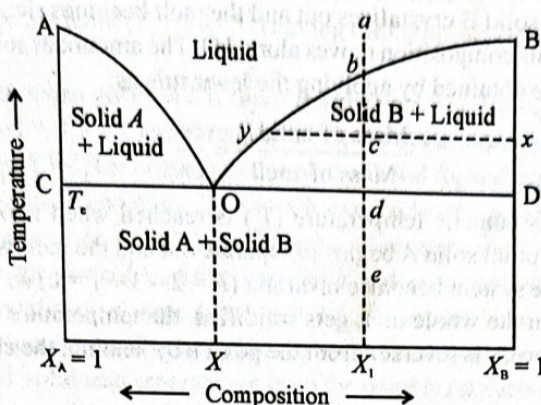A general phase diagram for a system of two components A and B forming simple eutectic is shown in Figure 7.4.

Fig. 7.4 Temperature-composition diagram of a binary system forming simple eutectic

The temperatures corresponding to A and B are the melting points of pure A and pure B respectively. Addition of B to A lowers the melting point of A along AO. Thus, AO is the melting point curve of A in presence of B. Similarly, BO is the melting point curve of B in presence of A. The system along AO and BO has two phases at equilibrium and hence univariant ($F = 2 - 2 + 1 = 1$). These are known as liquidus curves.

The curves AO and BO meet at the point O where three phases, namely, A(s), B(s) and the melt are at equilibrium. At the point O, the system is invariant ($F = 2 - 3 + 1 = 0$). This means that none of the varibles can be changed without disturbing the equilibrium. If one of the variables is changed, then one of the phases will disappear. Thus, on lowering the temperature, the melt disappears while on increasing the temperature, one of the solid phase disappears. The composition corresponding to O has the lowest melting point and is known as the **eutectic point** and the composition X is known as the **eutectic composition**. The temperature corresponding to O is known as the eutectic temperature (T_e). *The eutectic mixture has a definite composition and a sharp melting point. If melts giving a liquid of the same composition. However, eutectic mixture is not a compound as its components are not present in stoichiometric composition and the mixture is heterogeneous in nature.*

Above the liquidus curve (AOB) only the liquid phae (melt) exists. The system is bivariant ($F = 2 + 1 + 1 = 2$), i.e., both the temperature and the composition must be specified in order to define the system completely. Below the solidus curve COD, only the solid phases can exist (solid A + solid B). In the areas between the solidus and the liquidus, solid and liquid phases can be present. Within the curve AOC, solid A + melt can exist while in the are BOD, solid B + melt can exist. The systems within these areas is univariant ($F = 2 - 2 + 1 = 1$).

Let us now consider the phase changes that result when a melt of composition X_1 is cooled from point a to e along the constant composition line abcde, known as isopleth. At the

7.4 PHASE DIAGRAM OF TWO COMPONENT SYSTEMS

For a two component system, $C = 2$, the phase rule of such a system may be expressed as

$$F = C - P + 2$$
$$= 2 - P + 2$$
$$= 4 - P \qquad \qquad \text{............ (7.6)}$$

Thus, for systems having one phase, which may be gaseous, completely miscible liquid solution or solid solution, $P = 1$.

$$\therefore \quad F = 4 - 1 = 3$$

Therefore, three variables, namely, temperature, pressure and composition of the system will have to be specified in order to define the system completely.

For systems consisting of two phases, $P = 2$.

$$\therefore \quad F = 4 - 2 = 2$$

Thus, stating the values two variables, namely, temperature and composition is sufficient to define the system completely.

For system consisting of three phases, $P = 3$.

$$\therefore \quad F = 4 - 3 = 1$$

The system is univariant and stating the value of only one variable is sufficient to define the system completely.

In a two component system the various possible phase equilibria are liquid $\rightleftharpoons$ vapour, solid $\rightleftharpoons$ liquid, liquid $\rightleftharpoons$ liquid, solid $\rightleftharpoons$ vapour and solid $\rightleftharpoons$ solid. When we consider condensed systems like solid $\rightleftharpoons$ liquid equilibrium, it is found that such an equilibrium is unaffected by change in pressure. The system is studied under constant atmospheric pressure of 1 atm. For such condensed systems one degree of freedom, namely, pressure is already stated and hence their number is reduced one. The phase rule then reduces to

$$F = C - P + 1 \qquad \qquad \text{............ (7.7)}$$

This is known as **reduced phase rule**.

Thus, for a two component system, we have

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

The variables are temperature and composition. Hence, the solid $\rightleftharpoons$ liquid equilibria are represented on a temperature-composition diagram.

Phase Diagram (Two Component System)
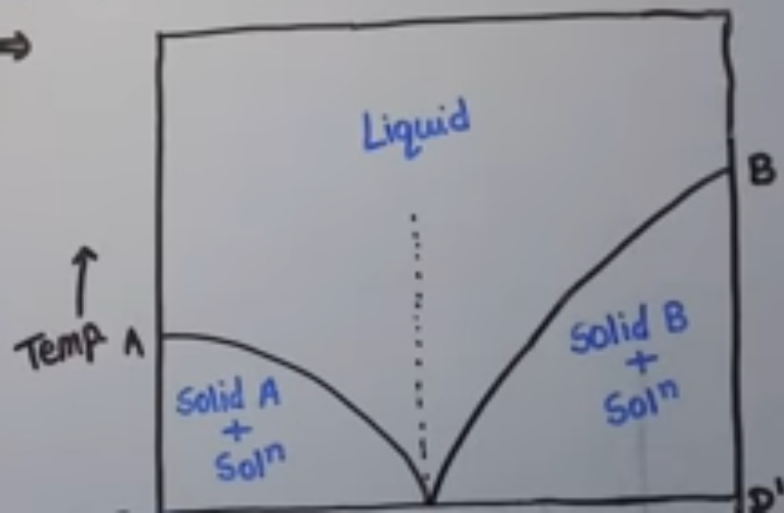
$$C = 2 \qquad F = 2 - P + 2 = 4 - P$$

For one Phase $\quad F = 4 - 1 = 3$

Temp. vs. composition ($P = $ constant)

Reduced Phase rule $\Rightarrow C - P + 1$

1) **Simple Eutectic System** $\Rightarrow$

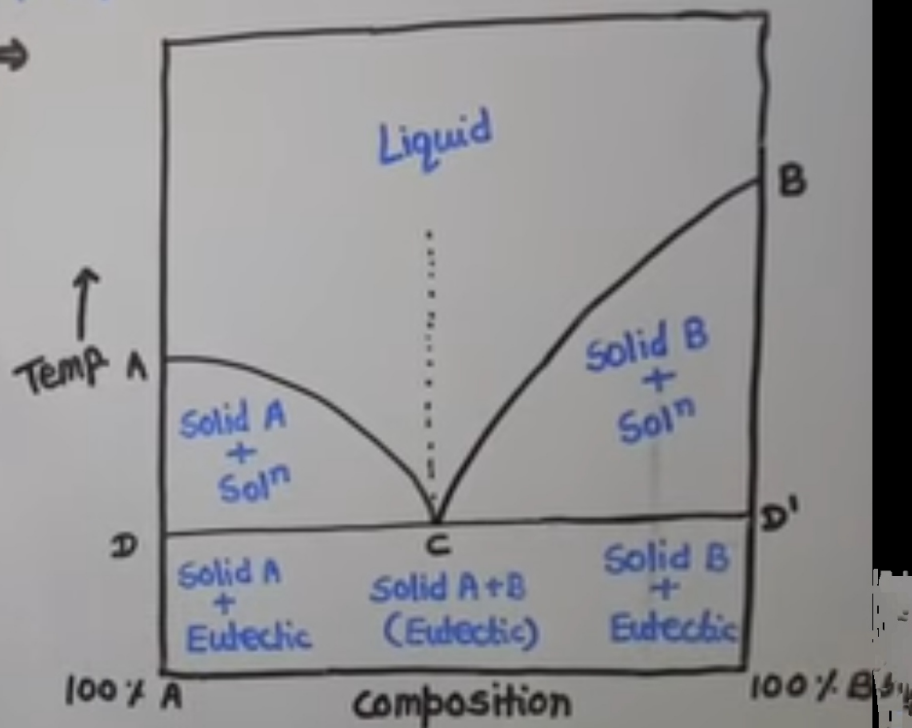- Solid A & B $\Rightarrow$ immiscible
  (Forms Eutectic Mix.)

Temp $\uparrow$ A

Liquid

B

Solid A + Soln

Solid B + Soln

Temp. vs. composition (P = constant)

Reduced Phase rule ⇒ $C - P + 1$

) **Simple Eutectic System** ⇒

Solid A & B ⇒ immiscible
    (Forms Eutectic Mix)

Temp ↑

Liquid

B

Solid B
+
Sol^n

Solid A
+
Sol^n

D

C

D'

Solid A
+
Eutectic

Solid A + B
(Eutectic)

Solid B
+
Eutectic

100% A

Composition

100% B

Curve EF is the fusion curve of rhombic sulphur. Along this curve rhombic sulphur exists in equilibrium with liquid sulphur. It shows the variation of melting point of rhombic sulphur with the change in pressure. Positive slope of the curve indicates that the melting point of rhombic sulphur increases with increase in pressure.

If a system on the curve OA is heated rapidly, monoclinic sulphur may not appear at O but the vapour pressure of the system continues along OD, which represents metastable equilibrium between rhombic sulphur and sulphur vapour. Similarly, if a system on the curve BC is cooled rapidly, monoclinic sulphur may not appear at B but the system continues to move along BD, which represents metastable equilibrium between liquid sulphur and sulphur vapour. Again, if a system of rhombic sulphur at high pressure is heated rapidlly, the system may pass over directly to liquid sulphur. The curve ED represents the metastable equilibrium between rhombic sulphur and liquid sulphur.

(iii) **Triple points:** In the phase diagram a triple point indicates the existence of three phases at equilibrium. At the triple point the system is invariant, i.e., both T and P are fixed and neither can be changed without disappearance of a phase.

Point O is the triple point where rhombic sulphur, monoclinic sulphur and sulphur vapour are at equilibrium ($S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_v$). The temperature and pressure corresponding to the triple point O are 95.6° C and 0.006 torr.

Point B is the triple point where monoclinic sulphur, liquid sulphur and sulphur vapour are at equilibrium ($S_\beta \rightleftharpoons S_\ell \rightleftharpoons S_v$). The temperature and pressure corresponding to the point B are 120° C and 0.04 torr respectively.

Point E is the triple point where rhombic sulphur, monoclinic sulphur and liquid sulphur are at equilibrium ($S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_\ell$). The temperature and pressure corresponding to the triple point E are 151° C and 1288 atm respectively.

Point D is the metastable triple point where rhomic sulphur, liquid sulphur and sulphur vapour ($S_\alpha \rightleftharpoons S_\ell \rightleftharpoons S_v$) are at equilibrium. The temperature and pressure corresponding to D are 114.5° C and 0.03 torr respectively.

In the light of the above discussion a brief description of the phase diagram of sulphur system is given in Table 7.2.

Table 7.2 Brief description of phase diagram of sulphur system

Location of the system	Status of the system	Degrees of freedom	Variables
AOEF	Rhombic sulphur	2	T and P
AOBC	Sulphur vapour	2	T and P
OEB	Monoclinic sulphur	2	T and P
CBEF	Liquid sulphur	2	T and P
OA	$S_\alpha \rightleftharpoons S_v$	1	T or P
OB	$S_\beta \rightleftharpoons S_v$	1	T or P
BC	$S_\ell \rightleftharpoons S_v$	1	T or P
OE	$S_\alpha \rightleftharpoons S_\beta$	1	T or P
BE	$S_\beta \rightleftharpoons S_\ell$	1	T or P
EF	$S_\alpha \rightleftharpoons S_\ell$	1	T or P
O	$S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_v$	0	—
B	$S_\beta \rightleftharpoons S_\ell \rightleftharpoons S_v$	0	—
E	$S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_\ell$	0	—
D	$S_\alpha \rightleftharpoons S_\ell \rightleftharpoons S_v$ (metastable)	0	—

7.3.2 Phase Diagram of Sulphur System

Sulphur exists in two allotropic modifications, rhombic sulphur (S_α) and monoclinic sulphur (S_β), the former being more stable form below 95.6° C. These along with liquid sulphur and sulphur vapour give rise to a number of single phase, two phase and three phase equilibria. As discussed in the earlier sections, a single phase equilibrium is bivariant ($F = 3 - P = 3 - 1 = 2$) and is represented by area in the phase diagram. In sulphur system there are four such areas. A two phase equilibrium is univariant ($F = 3 - P = 3 - 2 = 1$) and in the phase diagram represented by a line. In sulphur system there are six such lines. A three phase equilibrium is invariant ($F = 3 - P = 3 - 3 = 0$) and is represented by triple point. In sulphur system there are four triple points representing four three phase equilibia. The phase diagram of sulphur system is given in Figure 7.3.

(i) **Areas:** In the phase diagram of sulphur system there are four areas representing the existence of four single phase equilibria.
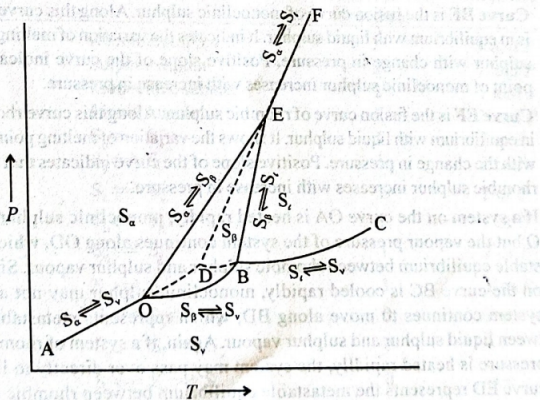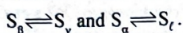

Fig 7.3 Phase diagram of sulphur system

The area on the left of AOEF represents the existence of rhombic sulphur, the area below AOBC represents sulphur vapour, the area of the left of CBEF represents liquid sulphur and the area enclosed within OBE represents the existence of monoclinic sulphur.

(ii) **Curves:** In the phase diagram, a curve represents the existence of two phase equilibrium and shows the variation of vapour pressure with changes in temperature. In the sulphur system, there are six two phase equilibria, viz., $S_\alpha \rightleftharpoons S_\beta$, $S_\alpha \rightleftharpoons S_v$, $S_\ell \rightleftharpoons S_v$, $S_\beta \rightleftharpoons S_\ell$, $S_\beta \rightleftharpoons S_v$ and $S_\alpha \rightleftharpoons S_\ell$.

Curve OA represents equilibrium between rhombic sulphur and sulphur vapour. It is the sublimation curve of rhombic sulphur and shows the variation of vapour pressure of rhombic sulphur with change in temperature.
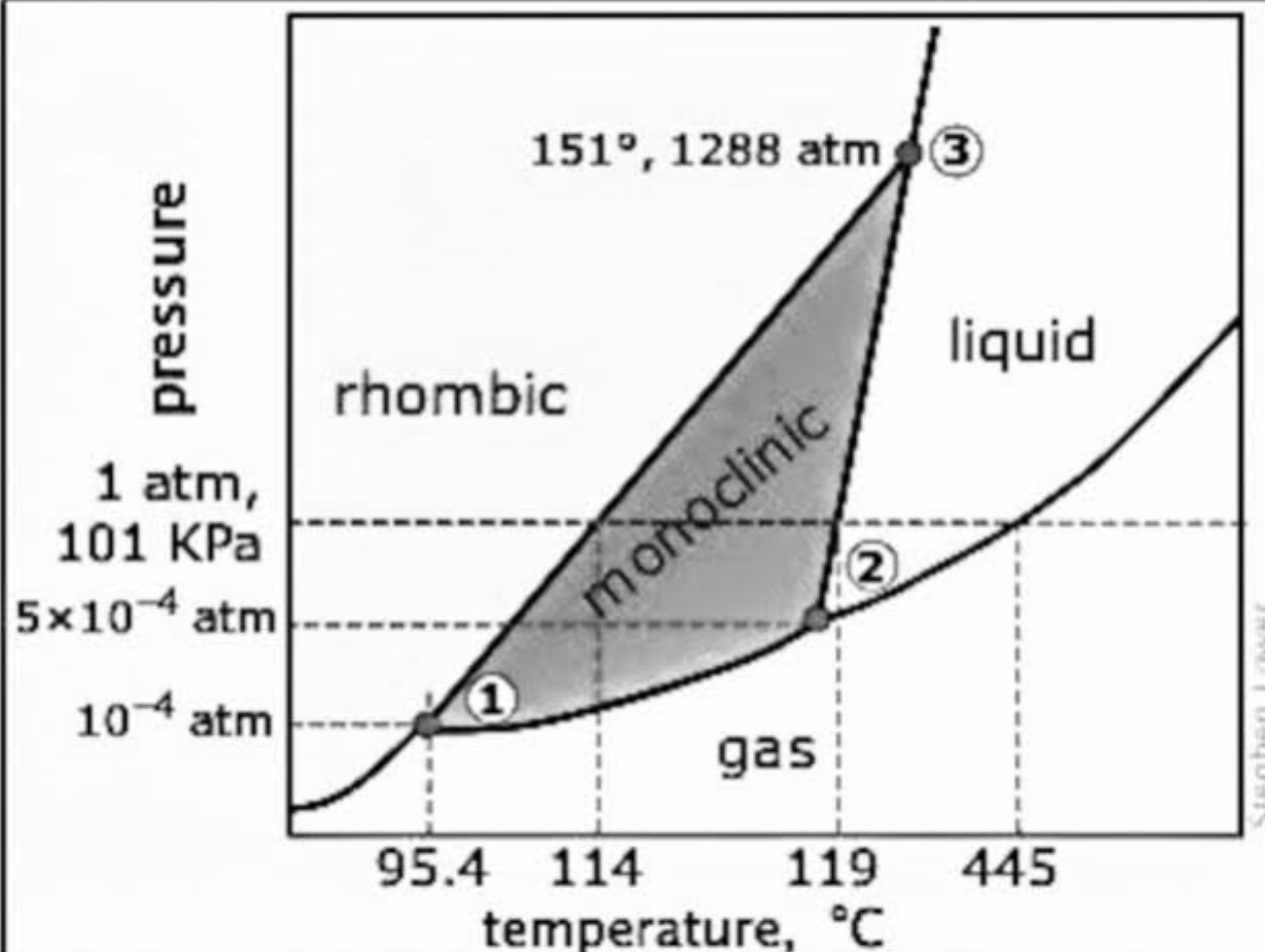
Curve OB is sublimation curve of monoclinic suphur and represents equilibrium between monoclinic sulphur and sulphur vapour. It shows the variation of vapour pressure of monoclinic sulphur with temperature.

Curve BC is the vapour pressure curve of liquid sulphur. Along this curve liquid sulphur and its vapour remain at equilibrium. It shows the variation of vapour pressure of liquid sulphur with temperature.

Curve OE is the transition curve for rhombic sulphur. Along this curve rhombic and monoclinic sulphur exist at equilibrium. It shows the effect of pressure on the transition temperature of rhombic to monoclinic sulphur. As the slope of the curve is positive it indicates that with increase in pressure the transition temperature also increases.

Curve BE is the fusion curve of monoclinic sulphur. Along this curve monoc is in equilibrium with liquid sulphur. It indicates the variation of melting poin sulphur with change in pressure. Positive slope of the curve indicates t point of monoclinic sulphur increases with increase in pressure.

Curve EF is the fusion curve of rhombic sulphur. Along this curve rhombic sulphur exists in equilibrium with liquid sulphur. It shows the variation of melting point of rhombic sulphur