29th Lecture

B.Sc. Chemistry Hons) II

Date 13/05/2020
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Phase Rule

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One Component (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 Phases 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 enantiotopy with a transaction point at 95.6°C. Below this temp. S_R is stable, while above 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 $S_R \underset{}{\overset{95.6^\circ C}{\rightleftharpoons}} S_M \overset{120^\circ}{\rightarrow} S_L$

The phase diagram for the sulphur is shown in figure 1. The salient

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feature of the Phase diagram are described below. (i) The six curves AB, BC, CD, BE, CE, EG,

(ii) The three triple point B, C, E.

(iii) The four areas:-

ABG Marked 'Solid Rhombic)

BEC Marked 'Solid Monoclinic)

GECD Marked liquid Sulphur

ABCD marked Sulphur Vapour

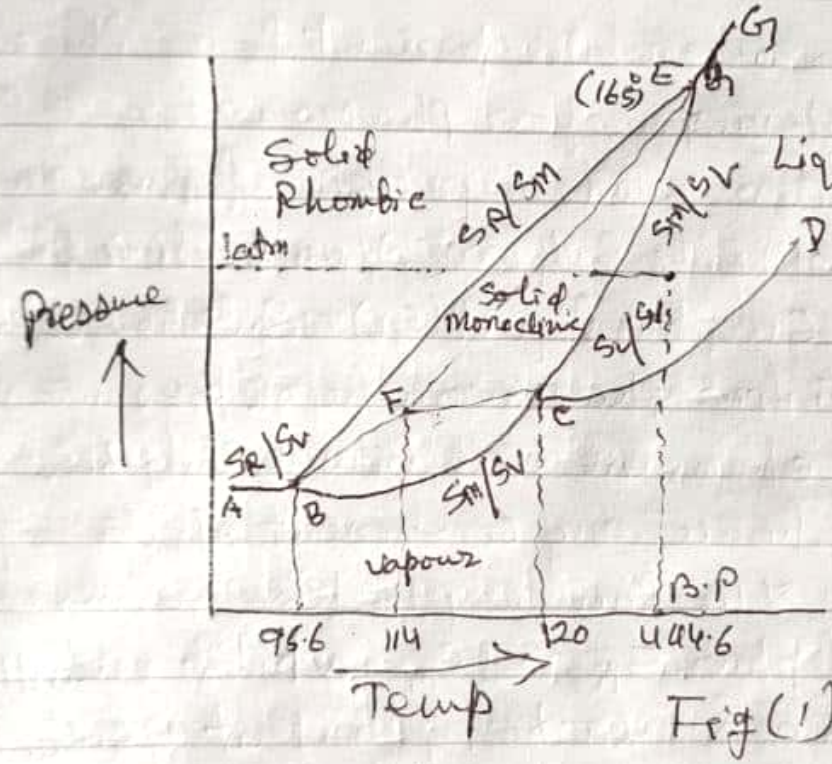

Fig (1)

Let us now discuss the significance of these features :-

(1) Curves :- These six curves divide the diagram in four areas :

Curve AB, the vapour Pressure Curve of SR :- Along this curve the two Phases SR and SV are in equilibrium. The system SR/SV has one degree of freedom.

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

Curve BC, the vapour pressure Curve of S_M shows variation of S_M with temp. S_M and S_V coexist in equilibrium along this Curve. The system S_M/S_V is monovariant

Curve CD, the V.P Curve of S_L :- S_L and S_V are in equilibrium so S_L/S_V = monovariant

Curve BE, the transition Curve shows the effect of Pressure and transition tem on S_R/S_M As two solid phases S_R/S_M is monovariant

Curve CE, the fusion curve for 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.

Curve EG, the fusion Curve for S_R → Here the two phases in equilibrium are S_R and S_L. The no. of phases being two, the system S_R/S_L is monovariant.

(2) The Triple Point B, C, E →

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

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

Triple Point C → The Curves BC, CD and CE meet at this point. The three phases S_M, S_L and S_V are in equilibrium. Here three

Phases and one Component the System $S_M/S_L/S_V$ is nonvariant.

Triple Point E → The two lines CE and BE having different inclination meet at E where the third 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.

(3) The Areas :→ The phase diagram of the sulphur system has four areas. These are labelled as rhombic ~~sulphur~~, monoclinic, liquid and vapour Sulphur. These represent single phase systems which have two degree of freedom.

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

That is each of the system S_R, S_M, S_L and S_V are bivariant.

(4) Metastable Equilibria :→
The change of S_R to S_M take place very slowly. If enough time for the change is not allowed and S_R is heated rapidly, it is possible to Pass well above the transition Point without getting S_M. In that case, there being three (S_R, S_L, S_V) only and one Component then the Phase diagram will consist of three curves, one triple point and three areas.