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herms at 5 percent

indicates

region is

10-15°C.

sely were stampol

24.0

13.8

8.10 39.3

24.2

9.70 6.02

3.93 2.10 6.70

6.40

4.60

4.30 4.06

 $4.13 \\ 3.73$

3.52

6.95ⁿ

4.58" 3.604

d with thermo-

egion where the iform to $\pm 1^{\circ}$ nutes) the heat p 40 seconds to removed and uns were made are shown in nes divided by ssibilities were

13.14

eted from Bridgman's³ data for solid sulfur. At espheric pressure it was assumed that the liquid the compressibility of the solid, and at 2000 sucheres one and one half times solid sulfur. The $\int_{C} \operatorname{error} \operatorname{in} \operatorname{calculating} D$ or the activation volume small no matter what reasonable assumption - Le. (About 5 percent for 100 percent error in the saf tessibility.)

In the mobile region (below 150°C) the activation tume is 1-3 atomic volumes: i.e., one-eighth to receighths of the molar volume of the eight-membered and are independent of pressure. This corresponds sity to the results obtained in many simple liquids e the same pressure range.4 In the viscous region the



FIG. 2. Diffusion coefficients versus pressure S36 in sulfur.

uid (silicone oil) activation volume starts at 2-6 atomic volumes and ned, the system apidly decreases to an atomic volume or less. As sulfur vas applied. (It s generally considered to exist in long chains in this ture.) Pressure ¹P. W. Bridgman, *Physics of High Pressure* (Macmillan Company, New York, 1931). ⁴R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 575 measured with a dead-weight

1953).



FIG. 3. Activation volume versus pressure.

region, it is apparent that the segment involved in a single move is a very small fraction of the chain.

Since the moving segment is so small, the motion is not greatly affected by the length of the sulfur chain. Therefore it is easy to see why the diffusion coefficient does not drop off rapidly in the region of greatly increasing viscosity.

The 195° isotherm containing iodine is intermediate in slope between the 175° and 210° isotherms run on pure sulfur, but the curve is displaced about 20 percent higher. In general, it can be said that the effect of the iodine is to lower the effective temperature of the melt 10-15°C.

The runs made at 20 atmospheres correspond closely to the result obtained by a different method¹ at atmospheric pressure, which gives greater confidence in the data.

The change of structure in liquid sulfur takes place with a decrease in volume and should therefore be displaced towards lower temperatures at high pressure. Since the melting point increases with pressure, it is evident that above some pressure only the "high pressure" liquid should exist. Our data indicate that above 1200-1500 atmospheres D increases with temperature at all temperatures, which is consistent with the above conclusion.

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