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## VOLUME 21, NUMBER 8

## The Effect of Pressure on Diffusion in Liquid Sulfur\*

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Diffusion coefficients have been measured in liquid sulfur to 2500 atmospheres pressure for isotherms at 140°C, 150°C, 175°C, and 210°C. One isotherm was also obtained at 195°C for sulfur containing 0.75 percent iodine. The motion in the viscous region is characterized by very small activation volumes which indicates that the moving segment is very small. This shows why the drop in diffusion rate in the transition region is small compared with the increase in viscosity. The iodine reduces the "effective temperature" 10–15°C. Above 1200–1500 atmospheres only one form of liquid sulfur seems to exist.

IFFUSION coefficients have been measured in liquid sulfur to 2500 atmospheres pressure (or to the freezing pressure) at 140°C, 150°C, 175°C, and 210°C. One isotherm (195°C) was also obtained using sulfur containing 0.75 percent iodine. The method used was guite similar in principle to that described in a previous paper for atmospheric pressure work.1 The diffusion of S35 (obtained from Oak Ridge National Laboratory) into ordinary sulfur was measured in cylindrical fritted glass pellets of coarse porosity. The concentration gradient was measured by sanding off slices and counting the activity under carefully controlled geometrical conditions. The pellet thickness was measured by micrometer after each slice was taken. The sulfur was purified by the method of Bacon and Fanelli<sup>2</sup> as in the atmospheric pressure work.

The inside of the bomb used in the high pressure work is shown in Fig. 1. Thin-walled lead capsules



FIG. 1. Interior view of high pressure bomb with furnace.

\* This work was supported in part by the U. S. Atomic Energy Commission. <sup>1</sup> R. L. Saxton and H. G. Drickamer, J. Chem. Phys. 21, 1361, (1953).

<sup>2</sup> R. F. Bacon and R. Fanelli, Ind. Eng. Chem. 34, 1043 (1942).

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which fit the fritted glass pellets closely were stamped out. The pellet was inserted in a capsule, the edges were filled with sulfur, and a thin layer of radioactive sulfer was placed on the surface. The top was covered with heavy silicone grease and the capsules placed in to steel supporting sleeve which prevented lateral  $d_{e}$ .

TABLE I.

Temperature °C	Pressure atmos	Diffusion coefficient cm²/sec ×107
140	0	24.0
140	440	13.8
140	760	S.10
150	0	39.3
150	1100	24.2
175	0	9.70
175	520	6.02
175	1000	3.93
175	2000	2.10
210	0	6.70
210	20	. 6.40
210	300	4.60
210	560	4.30
210	900	4.06
210	1200	4.13
210	2000	3.73
210	2400	3.52
195ª	$O^{a}$	13.1ª
195ª	500ª	6.95ª
195ª	1200ª	4.58ª
195ª	2000ª	3.604

\* For the system, sulfur-iodine. All points are the average of two deteminations agreeing within  $\pm 10$  percent.

formation. The pressure transmitting fluid (silicone of was added, the connections were tightened, the system was pumped to pressure, and heat was applied. (It took 10-40 seconds to get to temperature.) Pressure was applied with a hand pump and was measured with a Bourdon gauge calibrated against a dead-weight gauge. The temperatures were measured with thermocouples placed inside the bomb. In the region where the capsules were, the temperature was uniform to  $\pm 1^{\circ}$ 2°C. At the end of the run (30-120 minutes) the head was cut off. It usually took about 20 to 40 seconds to cool below freezing. The pellets were removed and analyzed as described previously. All runs were made in duplicate. The diffusion coefficients are shown in Table I and Fig. 2, the activation volumes divided by the atomic volume, in Fig. 3. Compressibilities were AUGUST, 194,

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eted from Bridgman's<sup>3</sup> 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 wee-eighths 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 <sup>1</sup>P. W. Bridgman, *Physics of High Pressure* (Macmillan Company, New York, 1931). <sup>4</sup>R. 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 method<sup>1</sup> 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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