COVA DR53 0037

The Effect of Pressure on Diffusion in Liquid Sulfur*

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(Received March 16, 1953)

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.

DIFFUSION 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 quite similar in principle to that described in a previous paper for atmospheric pressure work.[1] The diffusion of S^{35} (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[2] 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 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 sulfur was placed on the surface. The top was covered with heavy silicone grease and the capsules placed in a steel supporting sleeve which prevented lateral deformation. The pressure transmitting fluid (silicone oil) 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 ±1°-2°C. At the end of the run (30–120 minutes) the heat 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

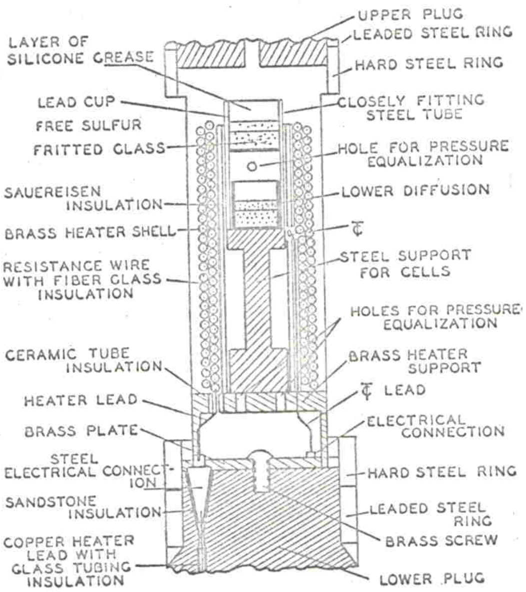

Fig. 1. Interior view of high pressure bomb with furnace.

Table I.

Temperature °C	Pressure atmos	Diffusion coefficient cm²/sec ×10⁷
140	0	24.0
140	440	13.8
140	760	8.10
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
195[a]	0[a]	13.1[a]
195[a]	500[a]	6.95[a]
195[a]	1200[a]	4.58[a]
195[a]	2000[a]	3.60[a]

[a] For the system, sulfur-iodine. All points are the average of two determinations agreeing within ±10 percent.

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* This work was supported in part by the U. S. Atomic Energy Commission.

[1] R. L. Saxton and H. G. Drickamer, J. Chem. Phys. 21, 1361, (1953).

[2] R. F. Bacon and R. Fanelli, Ind. Eng. Chem. 34, 1043 (1942).