

for the fact that at 0° D rises from 1.45×10^{-5} at 1 atmos to a maximum of 2.35×10^{-5} in only 250 atmos (see Fig. 1). As rapidly as D rises to the maximum at 250 atmos, it falls again to a minimum of 1.06×10^{-5} at 600 atmos; ascends once more to a maximum of 1.85×10^{-5} at 900 beyond where it decreases gradually with pressure. The initial rise is explained by the same arguments used above concerning the breakdown of the structure and increase of mobility with pressure. The descent between 250 and 600 atmos must be caused by a secondary formation of the structure which ties up the molecules to decrease their mobility. Then once again this secondary structure suffers a breakdown with increasing pressure and D rises to its maximum at 900 atmos. The activation volume, plotted in Fig. 2, follows the same trends as would be expected on the basis of the arguments presented above for the 25° and 50° isotherms. At 1 atmos it is extremely negative, passes through zero at 250, becomes excessively large and positive, then descends to pass through zero at 600 atmos; between 600 and 900 atmos it goes extremely negative again and then ascends to some high positive value a little beyond 900 atmos. From this last positive maximum, $\Delta V^\ddagger/\bar{V}$ descends rapidly to 1.00 at 1000 and then more slowly to 0.36 at 2000 atmos. Beyond 2000 the descent is very gradual to 0.10 at 6000 atmos. It appears that with suitable compression, $\Delta V^\ddagger/\bar{V}$ would approach zero as an asymptote. From the gradual decline of D and of $\Delta V^\ddagger/\bar{V}$ beyond 2000 atmos it appears that the "stabilized" configuration is forming.

Bridgman³ gives data for the viscosity of water as a function of pressure at 0, 10.3, 30, and 75°C. He observed anomalous behavior at temperatures below 30°C in that the viscosity decreases with the initial application of pressure. The effect diminishes with increasing temperature. At 0° the viscosity at 1000 atmos is 92 percent of that at 1 atmos and then increases rapidly with pressure; at 10° a minimum of 95 percent of the value at 1 atmos is found at about 1200 atmos; no decrease is observed at 30 or 75° but the initial increase is very slow. These trends in the viscosity could be the result of breakdown of the tetrahedral water structure with increasing pressure and temperature. The effect is of a lesser extent and smaller magnitude than that we have observed in the case of diffusion. For all the

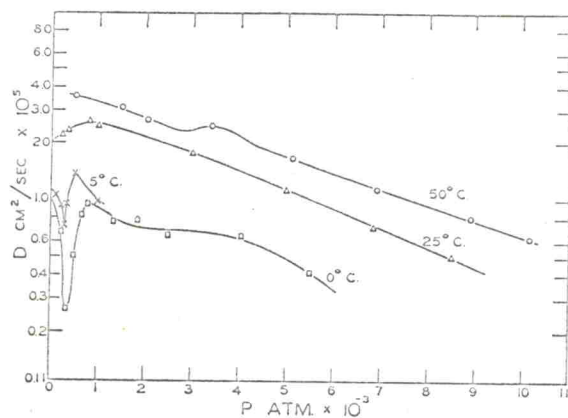


FIG. 5. Diffusion coefficients as a function of pressure. System: 0.1 N H₂SO₄-0.1 N H₂S²O₄.

systems we have studied it has been true that diffusion is more sensitive to pressure than is viscosity. The Stokes-Einstein equation predicts that the product of diffusion coefficient times the viscosity should be a constant. That this does not hold for water is seen in Table VII below where the product of the relative viscosity times the diffusion coefficient is shown for 25 and 0°C. The product may be approaching a constant value at 0° in the high pressure range.

0.1 N H₂S²O₄ IN 0.1 N H₂SO₄

Insofar as structure is concerned, the situation is probably much more complicated in sulfuric acid than in water. Along with having the tetrahedral water structure, the additional complication of solvation exists in the acid. The large size of the sulfate radical and its unbalanced valence forces probably cause further deviations from the water characteristics. It is impossible to give a unique interpretation to the diffusion data we have gathered. We shall not attempt to account for the effects of solvation or the sulfate radical but shall analyze the data giving consideration only to the characteristic tetrahedrally coordinated structure of water.

Isotherms of the diffusion coefficient are shown in a semilogarithmic plot against pressure in Fig. 5. Four temperatures were studied: 0, 5, 25, and 50°C. The ratio of the activation volume to the molal volume was calculated for the 0, 25, and 50° isotherms using compressibility data for water and is plotted in Fig. 6.

The isotherms in Fig. 5 show that D increases with the initial application of pressure at 25°C. Thus, it appears that the tetrahedral structure (modified by the acid) is a controlling factor for diffusion. Increasing pressure destroys the structure to increase the average sulfate mobility and D increases. The maximum value of D is found at about 900, and beyond this it decreases at a very steady rate with pressure. The activation volume (Fig. 6) is negative at one atmosphere and increases to pass through zero at about 900 atmos, where D was seen to be at a maximum. As in the case of water,

TABLE VII. The viscosity-diffusivity product for water.

Pressure atmos $\times 10^{-3}$	$D\eta/\eta_0 \times 10^{-5}$	
	0°	25°
0	1.46	1.40
1	1.60	1.78
2	1.05	1.87
3	0.876	1.62
4	0.810	1.17
5	0.792	0.91
6	0.794	0.77
7		0.69
8		0.62
9		0.57