The Effect of Pressure on Diffusion in Water and in Sulfate Solutions

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Diffusion coefficients are presented as a function of pressure to 10 000 atmospheres for the following systems:

THO—H_2O 0°–25°–50°;
0.1 N $H_2S^{35}O_4$ —0.1 N H_2SO_4 0°–5°–25°–50°;
0.1 N $Na_2S^{35}O_4$—0.1 N Na_2SO_4 0°–25°–50°;
1.0 N $Na_2S^{35}O_4$—1.0 N Na_2SO_4 0°–25°–50°;
0.1 N $K_2S^{35}O_4$ —0.1 N K_2SO_4 0°–25°–50°.

The results are interpreted in terms of the activation volume and the tetrahedrally coordinated structure of water. It is found that pressure tends to break down the structure, and in certain regions an increase in diffusion coefficient with pressure is noted.

In the salt solutions the water structure is controlling with some added effects due to solvation and ionic interaction.

IN previous papers[1,2] a method for measuring diffusion in liquids under pressures to 10 000 atmospheres was presented, along with results for some organic solutions. In this paper results are presented for diffusion of tritiated water into ordinary water, for diffusion of S^{35} tagged 0.1 N sulfuric acid into untagged 0.1 N sulfuric acid, and for diffusion in 0.1 N Na_2SO_4, 1.0 N Na_2SO_4, and 0.1 N K_2SO_4. The tritiated water was obtained from Tracerlab, the S^{35} tagged H_2SO_4 from Oak Ridge National Laboratory of the U. S. Atomic Energy Commission. The ordinary water was de-ionized, and degassed water was obtained from the Boiler Water Laboratory by courtesy of F. G. Straub. The salts were cp quality.

The method of operation and for calculation of the diffusion coefficients is completely discussed in reference 1. The kinetic theory of liquids and the method for calculating the enthalpy of activation ($\Delta H^\ddagger$), the entropy of activation ($\Delta S^\ddagger$) above the value at atmospheric pressure ($\Delta S_0^\ddagger$), the activation volume ($\Delta V^\ddagger$), and the free energy of activation ($\Delta F^\ddagger$) are discussed in references 1 and 2.

The results will be discussed in terms of these concepts. The data are shown in Tables I–V.

SELF-DIFFUSION IN WATER

In Fig. 1 the diffusion coefficients are plotted against density using Bridgman's[3] compressibility data. The excellent agreement with the data of Orr and Butler[4] at atmospheric pressure is to be noted. As a matter of fact, the fritted glass was calibrated using their data at 25°C. Since each isotherm has a unique shape, it is apparent that the molecular geometry and mechanisms of motion depend upon more than merely density. This system will be analyzed primarily on the basis of changes in the activation volume. The activation volume is purely a function of a single isotherm, whereas $\Delta H^\ddagger$ and $\Delta S^\ddagger$ depend upon the displacements between the three isotherms. The structure obviously varies radically with temperature and thus $\Delta H^\ddagger$ and $\Delta S^\ddagger$ calculated on the basis of the three isotherms probably do not apply to any of them.

TABLE I. Measured diffusion coefficients for THO in H_2O.[a]

Temp. °K	Pressure atmos	Effective cell length cm	Observed $D\times10^5$ cm²/sec
273	136	0.504	1.65
273	252	0.504	2.37
273	600	0.504	1.06
273	900	0.504	1.84
273	1240	0.504	1.45
273	2040	0.557	1.08
273	3500	0.557	0.787
273	5900	0.611	0.584
298	1	0.504	2.64
298	245	0.504	2.90
298	1300	0.504	3.24
298	2050	0.557	3.06
298	2500	0.557	3.04
298	3000	0.557	2.62
298	3000	0.557	2.36
298	3975	0.557	1.71
298	5000	0.557	1.15
298	7000	0.611	0.753
298	7000	0.611	0.843
298	9175	0.611	0.515
323	235	0.504	5.15
323	735	0.504	4.17
323	1300	0.504	3.48
323	2100	0.557	2.33
323	2500	0.557	1.86
323	2500	0.557	1.89
323	3500	0.557	1.82
323	4450	0.557	2.07
323	7000	0.611	2.25
323	10050	0.665	1.38

[a] Maximum deviation in reproducibility 10 percent. Average deviation 5 percent.

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[1] R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267 (1953).

[2] R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 575 (1953).

[3] P. W. Bridgman, *The Physics of High Pressure* (Macmillan Company, New York, 1931).

[4] W. J. C. Orr and J. A. V. Butler, J. Chem. Soc. (London) 1935, 1273.