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-H₂O 0°-25°-50°; $0.1 N H_2S^{35}O_4 - 0.1 N H_2SO_4 0^{\circ}-5^{\circ}-25^{\circ}-50^{\circ};$ $0.1 N \text{ Na}_2\text{S}^{35}\text{O}_4 - 0.1 N \text{ Na}_2\text{SO}_4 \quad 0^\circ - 25^\circ - 50^\circ;$ 1.0 N Na₂S³⁵O₄-1.0 N Na₂SO₄ 0°-25°-50° 0.1 N K₂S³⁵O₄ -0.1 N K₂SO₄ 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 S³⁵ tagged 0.1 N sulfuric acid into untagged 0.1 N sulfuric acid, and for diffusion in 0.1 N Na₂SO₄, 1.0 N Na₂SO₄, and 0.1 N K₂SO₄. The tritiated water was obtained from Tracerlab, the S35 tagged H2SO4 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 (ΔH^2) , the entropy of activation (ΔS^{\ddagger}) above the value at atmospheric pressure (ΔS_0^{\ddagger}) , the activation volume (ΔV^{\ddagger}) , and the free energy of activation (ΔF^{\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' compressibility data. The excellent agreement with the data of Orr and Butler⁴ 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 ap-

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¹ R. C. Koeller and H. G. Drickamer, J. Chem. Phys. 21, 267

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.

parent 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 ΔH^{\ddagger} and ΔS^{\ddagger} depend upon the displacements between the three isotherms. The structure obviously varies radically with temperature and thus ΔH^{\ddagger} and ΔS^{\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 H2O.ª

Temp. °K	Pressure atmos	Effective cell length cm	Observed $D \times 10^{3}$ cm ² /sec	
273 273 273 273 273 273 273 273 298 298 298 298 298 298 298 298 298 298	$\begin{array}{c} 136\\ 252\\ 600\\ 900\\ 1240\\ 2040\\ 3500\\ 5900\\ 1\\ 245\\ 1300\\ 2050\\ 2500\\ 3000\\ 3000\\ 3000\\ 3000\\ 3975\\ 5000\\ 7000\\ 7000\\ 7000\\ 7000\\ 7000\\ 2500\\ 2500\\ 2500\\ 2500\\ 2500\\ 2500\\ 3500\\ 4450\\ 7000\\ 10050\\ \end{array}$	0.504 0.504 0.504 0.504 0.504 0.557 0.557 0.557 0.504 0.504 0.504 0.504 0.504 0.557 0.57 0.57 0.577 0.577 0.577 0.577 0.5	$\begin{array}{c} 1.65\\ 2.37\\ 1.06\\ 1.84\\ 1.45\\ 1.08\\ 0.787\\ 0.584\\ 2.64\\ 2.90\\ 3.24\\ 3.06\\ 3.04\\ 2.62\\ 2.36\\ 1.71\\ 1.15\\ 0.753\\ 0.843\\ 0.515\\ 5.15\\ 4.17\\ 3.48\\ 2.33\\ 1.86\\ 1.89\\ 1.82\\ 2.07\\ 2.25\\ 1.38\end{array}$	

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

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blume). It increases cent at 2000 atmos at 3200 atmos, and 00 beyond where it ure. The very low t, as in the case of loose and permits of local expansion. molecular orientaincreasing pressure vation to be more and the activation vious that radical e in order to cause th the limited data ould be pure conation. In previous reasing activation indicating that an such a degree that red for activation and more through we must assume this system after

BuOH at 40°C.

 ΔF_0^{\ddagger} (cal/mole)

66		
178		
543		
973		
1170		
1310		
	178 543 973 1170	178 543 973 1170

settles again to

nd the change in nction of pressure e most important calculated as an 40° isotherms of very dissimilar, it tained from the licable to either observed is that he range 3100 to e what type of gative activation parent from the pes of structures attempt will be ime.

, that in spite of her variables for ation rises conems studied. wledge financial ing Corporation imission.