

-1 N Na₂SO₄,^aObserved
 $D \times 10^5$
cm²/sec

0.28
0.33
0.29
0.39
0.56
0.55
0.90
1.01
0.86
0.76
1.07
1.60
0.78
1.03
0.80
4.86
1.24
1.14
1.34
1.88
2.24
2.27
1.46
1.26
1.81
1.54
1.25

verage deviation

-1 N K₂SO₄,^aObserved
 $D \times 10^5$
cm²/sec

0.33
0.67
0.71
0.50
0.40
0.90
0.86
0.83
0.82
0.66
1.40
0.98
1.04
1.30
1.44
0.90
0.84
1.17
1.59
0.82
0.87
3.92
2.48
0.87
0.75
1.46
2.06
2.37
1.44
1.04
0.58

rage deviation

From spectroscopic, dielectric, and x-ray diffraction studies, the modern view of water is that it retains the tetrahedrally coordinated structure of ice to a degree that decreases with increasing temperature. The molecules tend to arrange themselves in a tetrahedral manner in the solid because of the particular distribution of valence forces about the molecule. Upon melting, the regular structure is not completely destroyed, but persists over regions including tens or hundreds of molecules with the membership of the groups continually changing. The oxygen atoms tend to coordinate an extra hydrogen so that "hydrogen bonds" are formed between molecules. These bonds are stronger than ordinary intermolecular attractive forces.

The ratio of the activation volume to the molal volume is plotted for the three isotherms studied in Fig. 2. The compressibility data of Bridgman³ was used. The 25° isotherm of $\ln D$ in Fig. 1 shows the D increases with the initial increase of pressure above atmospheric.

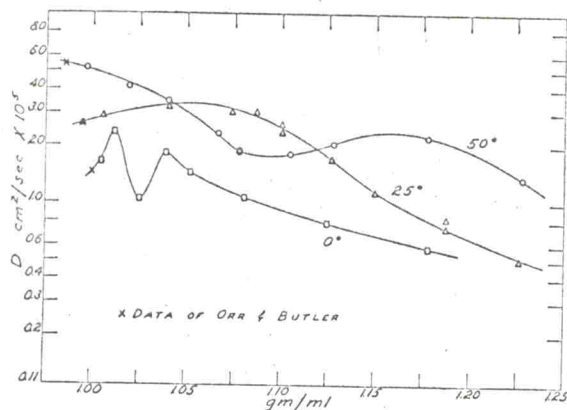


FIG. 1. Diffusion coefficients for the system THO-H₂O as a function of density.

This indicates that the tetrahedral structure in the water is broken down by pressure so that the average mobility of the molecules increases. The activation volume of 25° and 1 atmos is seen to be negative. From this we can conclude that the tetrahedral structure must be such that when a molecule migrates there is a localized collapse. As pressure is increased the percentage of molecules held in the characteristic tetrahedral structure apparently decreases and we find D slowly approaching a maximum while the activation volume approaches zero. Then, at the maximum in D (1500 atmos), $\Delta V^\ddagger/\bar{V}$ passes through zero. Further compression decreases D either because the tetrahedral structure is now completely destroyed, or because the effect of the increased compactness of the medium is greater than the influence of whatever remains of the structure. In any event, the activation volume increases because the local expansion necessary for activation is felt through a greater portion of the fluid as free volume is decreased. At 4000 atmos the slope of $\ln D$ vs P begins to decrease rather than increase and $\Delta V^\ddagger/\bar{V}$ goes

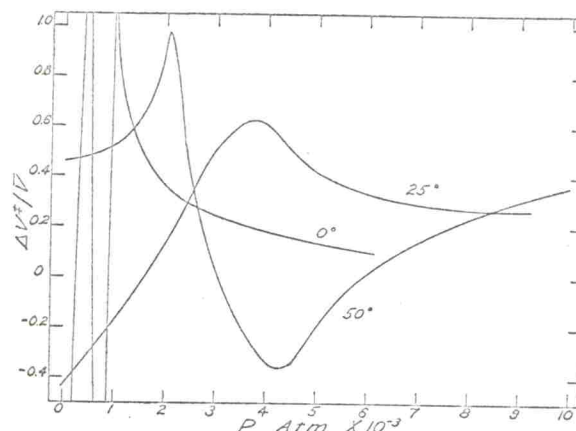


FIG. 2. Activation volume as a function of pressure. System: THO-H₂O.

through a maximum of 63 percent. The occurrence of this maximum and the relatively slow decrease of $\ln D$ and $\Delta V^\ddagger/\bar{V}$ beyond it indicate that a stabilized structure is forming in the same sense that such structures were formed in the organic solutions.^{1,2} That is, the configuration is becoming increasingly difficult to deform (either with increased pressure or during activation for diffusion), and diffusion takes place more and more through existing holes. Thus, we see that the activation volume settles down to approach an asymptote of about 25 percent of the molal volume.

Activation enthalpies are plotted versus pressure for 285, 298, and 310°K in Fig. 3. The change in activation entropy with pressure was calculated and is shown graphically in Fig. 4. The changes in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ calculated for the 25° isotherm are probably reasonably correct since 25° is the median temperature. With the initial application of pressure the structure begins to be broken down to decrease the order and increase the entropy level of the normal state. Thus, we see that the activation entropy (the difference between entropy levels of the initial and activated states) decreases in this range to a minimum of 17 cal/°K/mole below that

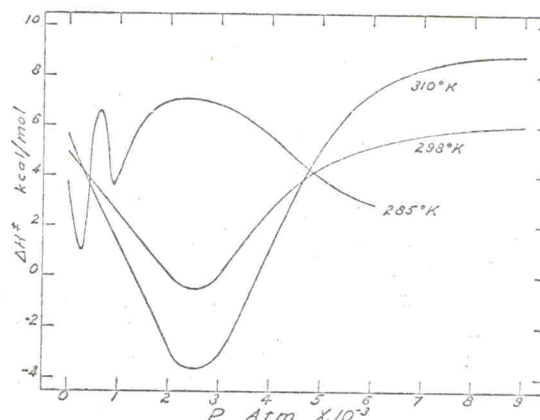


FIG. 3. Activation enthalpy as a function of pressure. System: THO-H₂O.