



FIG. 4. Activation entropy as a function of pressure.
System: THO-H₂O.

at 1 atmos. The minimum ΔS^\ddagger occurs in the same pressure region as does the zero activation volume. At this point the local expansion for activation becomes positive and the entropy of the activated state increases rapidly. The increase of ΔS^\ddagger continues (more gradually at higher pressure) until about 7000 atmos, where it levels to about the same value as at 1 atmos ($\Delta S_P^\ddagger - \Delta S_0^\ddagger \approx 0$). We saw above that the activation volume became virtually constant at this same pressure. The leveling of ΔS^\ddagger further substantiates the conclusion that a stabilized configuration has formed. Stabilized, that is, in the sense that the most probable configuration does not change greatly with pressure.

As a matter of general interest, $\Delta F_P^\ddagger - \Delta F_0^\ddagger$ was calculated at 25°. In Table VI below it is seen that the free energy of activation goes through a minimum at about 1500 atmos and then increases steadily. The total increase in 9000 atmos is 17 percent of ΔH_0^\ddagger ($\Delta H_0^\ddagger = 5000$ cal/mol).

From the isotherm of $\ln D$ in Fig. 1 it is seen that at 50° the diffusion coefficient decreases with the initial application of pressure as is normally expected. Thus, it appears that the tetrahedral structure does not control molecular motion to any prominent extent in the low pressure range at 50°. The activation volume increases from 45 percent of molal volume at 1 atmos to a maximum of 99 percent at 2000 atmos, while D continually decreases in this range. From this we infer that the decreasing free volume causes the local expansion necessary for activation to be felt over an increasingly larger portion of the liquid. Compressing beyond 2000 atmos the activation volume is seen to decrease rapidly and pass through zero to reach a minimum at 4200 atmos. At the same time, D drops rapidly beyond 1800 atmos, goes through a minimum at 3000, and rises slowly until a maximum is reached at 5800 atmos. These trends in the activation volume and diffusion coefficient lead to the conclusion that the free volume has been reduced to a point where, at 2000 atmos, the same situation is beginning to prevail as existed at 25° and 1 atmos. Namely, the tetrahedrally coordinated

structure controls the motion. D decreases more rapidly between 1800 and 2500 atmos because the average mobility of the molecules is decreasing as they become more and more tied up in the structure. Also, the activation volume decreases rapidly indicating that the activation process is beginning to involve collapse of the structure. Beyond 3000 atmos the structure begins to break down, the diffusion coefficient increases, and the major volume effect during activation becomes the localized collapsing of the structure so that ΔV^\ddagger becomes negative. $\Delta V^\ddagger/\bar{V}$ continues to decrease and goes through a minimum at 4200 atmos and then becomes zero again at 5800 where D is at a maximum. Above 5800 atmos the effect of whatever remains of the tetrahedral structure is no longer predominant, and the local expansion for diffusion becomes positive again. At 10 000 atmos $\Delta V^\ddagger/\bar{V}$ is 0.37 and appears to be leveling. It is anticipated that with further compression the activation volume would pass through a maximum and then settle to some constant lower value as the "stabilized" configuration is formed, as was the case at 25°.

It is to be noted in Fig. 3 that the enthalpy of activation is negative between 2300 and 2800 atmos at 298° and between 1400 and 3750 atmos at 310°. Even taking into consideration the tetrahedral structure and hydrogen bonding it is difficult to conceive of a situation wherein a molecule activated for diffusion would be at a lower energy level than it was in the initial state. It must be concluded then that the negative ΔH^\ddagger arises entirely as a result of the fact that at a given density the structure is radically different for the three widely separated isotherms we have studied.

At first glance one might feel that we have fixed the maximum and minimum in the low pressure range of the 0° isotherm with an insufficient amount of data (see Fig. 1). Although it is true that the position of these "critical" points may be shifted within the limits of experimental error, we are confident of their existence. The experimental runs were consistent within themselves, and also, other work on salt solutions (Figs. 7-9) has led us to expect such behavior in water and aqueous solutions. (See also the sulfuric acid data in Fig. 5.)

Since 0°C and 1 atmos is a triple point for water, it is to be expected that the liquid phase would contain large regions of the tetrahedrally coordinated structure in this pressure and temperature range. This accounts

TABLE VI. $\Delta F_P^\ddagger - \Delta F_0^\ddagger$ for self-diffusion in water at 25°C.

P (atmos)	$\Delta F_P^\ddagger - \Delta F_0^\ddagger$ (cal/mole)
500	-82
1000	-134
1500	-156
2000	-141
3000	-17
5000	416
7000	675
9000	843