

TABLE IV. Activation energies at constant pressure for shear viscosity in H₂O.

P (kbar)	$E_p \pm 0.5$ (kcal/mole) Temperature interval (°C)				
	10, 5	5, 0	0, -5	-5, -10	-10, -15
0	5.1	5.1	(5.4) ^a	(5.8)	(6.1)
1	4.0	4.1	4.6	5.0	5.1
2	3.8	3.9	4.3	4.9	4.9
3	3.9	3.9	4.3	5.1	5.3
4	4.0	4.0	4.4	5.7	...
5	4.2	4.2	4.7	...	...

^aParentheses denote extrapolated values from the supercooled region.

any effects of hydrogen bonding, one estimates²⁰ κ for water in the range 0.01–0.1. Therefore, if water at higher density is behaving more like a normal liquid, it is not surprising to find a decrease of κ with compression since the shape of the molecule is becoming relatively more important.

It is well-known that many dynamic processes in water exhibit a non-Arrhenius temperature dependence. In our earlier relaxation studies^{1,19} of compressed water in the temperature range 10 °C to 90 °C and our diffusion study² of D₂O from 10 °C to 200 °C, we have shown that the activation energies for relaxation, self-diffusion, and shear viscosity decrease with increasing density. Since the non-Arrhenius behavior is very pronounced at temperatures below 10 °C, we calculated approximate activation energies for each temperature interval at which we carried out our measurements. The activation energies at constant pressure E_p and constant density E_v for shear viscosity are given in Tables IV and V. In spite of the fact that the E_p and E_v are subject to relatively large error (± 0.5 kcal/mole) because of the calculation procedure using only one pair of η values at two temperatures, one can nevertheless detect some trends with temperature and pressure. As expected, both E_p and E_v will increase with decreasing temperature and go through a slight minimum at pressures of about 2 kbar or densities ~ 1.050 – 1.075 g/cm³. Above these pressures and/or densities there is again a rise in the activation energies. This observation is in agreement with expectation because the increase of density first distorts the random hydrogen bond network leading to a minimum in viscosity, but further compression again increases E_p and E_v due to increased repulsive core interactions. After all, in normal molecular liquids compression leads to an increase in the magnitude of activation energies for various dynamic properties. Our findings are in agreement with the results of molecular dynamics calculations on compressed water by Stillinger and Rahman.²¹ Another observation worth mentioning is the comparable magnitude of E_p and E_v under the same experimental conditions. In this way water differs from the behavior of normal molecular liquids, where we usually find $E_p \approx 2E_v$.

Speedy and Angell⁸ have recently shown that many physical properties of water at atmospheric pressure can be correlated by an expression²²

$$X = A(T/T_s - 1)^{\gamma} \quad (7)$$

where X is the physical property, A and γ are constants, and T_s is the temperature of a thermodynamic singularity. Their atmospheric pressure data extend for some properties into the supercooled region. It is interesting to note that an expression of this form describes well our shear viscosity and proton T_1 data from -15 °C to 90 °C over the range of pressures measured. The temperature $T_s \approx 228$ °K obtained by fitting our experimental data agrees with the value reported by Angell *et al.*²³ Further work dealing with the applicability of Eq. (7) on other data including also self-diffusion and deuteron T_1 data in compressed liquid heavy water at low temperatures is in progress in our laboratory.

IV. CONCLUSIONS

The anomalous behavior of shear viscosity and proton spin-lattice relaxation time, T_1 , with initial compression of liquid water at temperatures below approximately 40 °C becomes more pronounced at temperatures below 0 °C. The fact that extremes of our pressure range at each temperature correspond to ice I and high pressure ice V enables us to draw some general conclusions about the dynamic structure of water under these experimental conditions. The main difference between the ice I and ice V are the decreased distance of closest non-hydrogen-bonded neighbors and the distortion of hydrogen bond angles. One can expect that the initial compression first distorts hydrogen bonds and thus weakens them, and therefore reorientation of water molecules will be facilitated under these conditions. Needless to say that the same is true for the behavior of shear viscosity. Only above density of approximately 1.075 g/cm³ further compression will hinder molecular motions due to increased packing and stronger short-range repulsive interactions. This picture of the compression effects on water is in agreement with the results of molecular dynamics calculations by Stillinger and Rahman.²¹

A general picture of the effects of temperature and pressure on dynamic properties can be illustrated by Fig. 5, which shows the effect of pressure and temperature on shear viscosity in water in the tempera-

TABLE V. Activation energies at constant volume for shear viscosity in H₂O.

Density ρ (g/cm ³)	$E_v \pm 0.5$ kcal/mole Temperature interval (°C)				
	10, 5	5, 0	0, -5	-5, -10	-10, -15
1.000	5.2	4.9	(5.4) ^a	(5.9)	(6.0)
1.025	4.6	4.0	4.5	6.1	5.7
1.050	4.0	3.9	4.5	4.9	5.2
1.075	3.9	3.5	4.3	4.6	4.9
1.100	3.8	3.9	4.1	4.6	5.0
1.125	4.2	3.8	4.0	4.9	5.3
1.150	3.8	3.8	4.5	4.9	...

^aParentheses denote extrapolated values from the supercooled region.

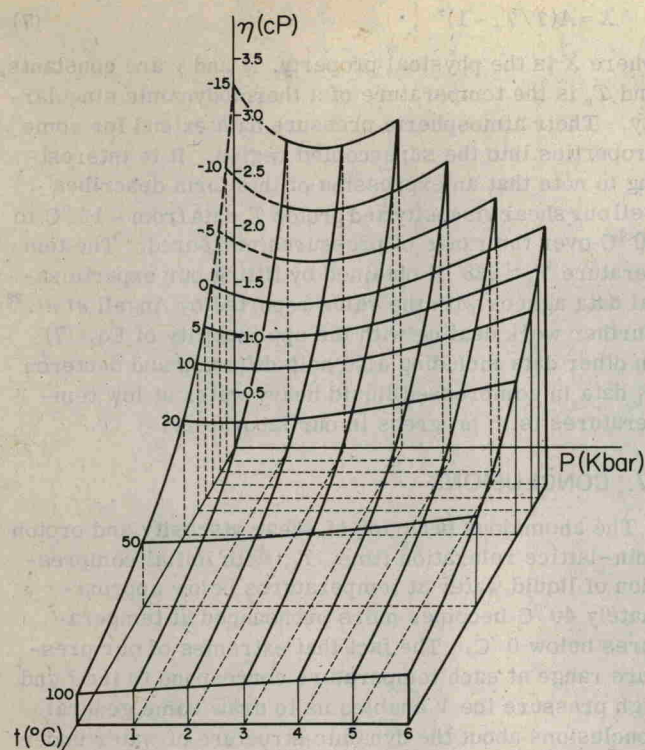


FIG. 5. Shear viscosity relief map as a function of temperature and pressure in liquid H_2O .

ture range -15°C to 100°C . We emphasize that analogous figures exhibiting maxima or minima can be constructed for the proton T_1 , self-diffusion, chemical shift in H_2O , and self-diffusion, shear viscosity, and deuteron relaxation in D_2O . The important finding of general validity which is clear from Fig. 5 is that both temperature and pressure have a parallel effect on the dynamic structure of water—both P and T increase molecular motional freedom at low temperatures and pressures. On the other hand, above ~ 2 kbar and at temperatures above $\sim 40^\circ\text{C}$, pressure and temperature exhibit just the opposite effect on dynamic properties, as is the case for normal liquids. It is quite understandable that compression of a normal liquid slows down the motional processes due to increased packing and stronger repulsive interactions. One may conclude that at high temperatures and high compression, behavior of water resembles that of normal molecular liquids.

In our earlier study¹ of H_2O , we proposed that compression changes the coupling between the rotational and translational motions of water molecules and that the Debye equation fails to describe the effects of den-

sity on reorientational motions. Using the same procedure for analysis of our experimental data at temperatures below 10°C we arrive at the same conclusions. It is interesting to find that even at lower temperatures the $(1/T_1)_H$ vs η/T plots are linear in an isochoric experiment. In summary, the results indicate that increasing the density of liquid water has two effects. It causes (a) the temperature independent coupling between translation and rotation to decrease, presumably until it is limited by the shape of the molecule and (b) an initial increase of rotational and translational motions until the effects of molecular packing become important. Detailed analysis of the self-diffusion data and deuteron relaxation in liquid heavy water under comparable experimental conditions will be published shortly.

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