

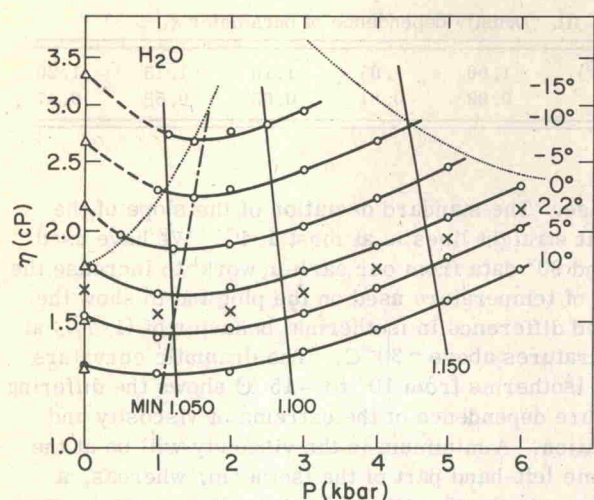


FIG. 2. Pressure dependence of shear viscosity in H_2O . X denotes values from Ref. 14. Δ denotes values from Ref. 7. Dotted lines denote phase boundaries (ice I and ice V).

ments¹ above 0 °C, and those below the freezing point fall on the isotherms when they are extrapolated into the supercooled region. Previous pressure measurements¹ at 10 °C are also plotted. They agree with the new data within 3%, which is about the error of our measurements.

The anomalous pressure dependence of shear viscosity and T_1 in H_2O is clearly seen from Figs. 2 and 3. The isotherms of both viscosity and proton T_1 have low pressure slopes which are opposite in sign to those found for normal liquids. It can also be seen that at lower temperatures the magnitude of these slopes increases.

Earlier work¹ has shown that $(\partial T_1 / \partial P)_{P=0} = 0$ at about 30 °C. At 10 °C the maximum in the curve is at about 2.2 kbar. This trend might be expected to continue as the temperature is decreased to -15 °C. However, it

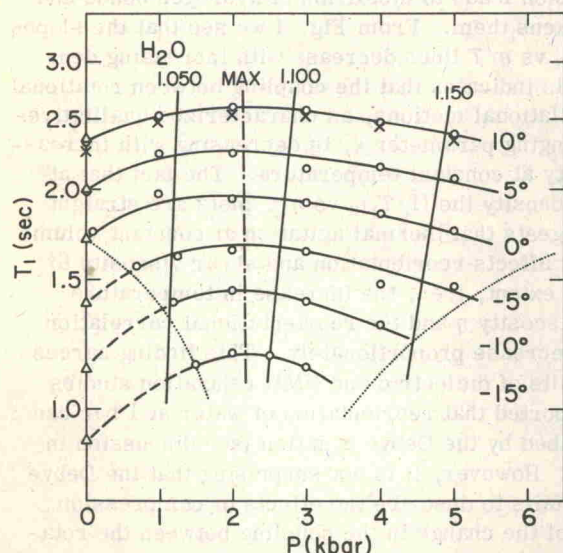


FIG. 3. Pressure dependence of the proton spin-lattice relaxation time T_1 in H_2O . X denotes values obtained in our earlier study (Ref. 1). Δ denotes values from Ref. 6. Dotted lines denote phase boundaries (ice I and ice V).

can be seen from Fig. 3 that the maximum falls between 1.9 and 2.2 kbar and there is no apparent temperature trend. This means that the position of the maximum must change rather sharply for it to be at 30 °C and 1 bar. Similarly Bett and Cappi¹⁴ have found that the minimum in the viscosity vs pressure curve at 33.5 °C is at 1 bar. At 10 °C the minimum was found to be at about 1.1 kbar. Our data show that the minimum moves up to 1.6 kbar at -15 °C. The positions of the maxima and minima are listed in Table II. It is interesting that the positions of the extremes in the viscosity and the relaxation are not at the same pressures and do not have the same temperature dependences. The discussion which follows will show they need not have the same behavior.

The analysis of the proton relaxation data follows the procedure used and discussed in our earlier study¹ of H_2O in the 10 °C to 90 °C temperature range. As pointed out in detail,¹ the data analysis involves several assumptions but enables one to reach qualitative conclusions about the effects of density and temperature on the dynamic behavior of water.

Since spin-rotation interactions are small¹⁶ at temperatures below 100 °C, H_2O relaxes primarily by dipole-dipole interaction, which is composed of inter- and intramolecular terms

$$\left(\frac{1}{T_1}\right)_{\text{observed}} = \left(\frac{1}{T_1}\right)_{\text{inter}} + \left(\frac{1}{T_1}\right)_{\text{intra}} \quad (1)$$

The intra term can be related to the correlation time τ_θ by

$$\left(\frac{1}{T_1}\right)_{\text{intra}} = \frac{3}{2} \frac{\gamma^4 \hbar^2}{r^6} \tau_\theta \quad (2)$$

where r is the distance between the protons in the water molecule, and γ is the magnetogyric ratio of the proton. τ_θ can be related to the viscosity by the modified Debye equation:

$$\tau_\theta = \frac{4}{3} \pi \frac{a^3 \eta}{kT} \kappa \quad (3)$$

where $\frac{4}{3} \pi a^3$ is the volume of the molecule, η is the viscosity, κ is the parameter introduced by McClung and Kivelson¹⁷ (see discussion in our earlier study).¹ Equations (2) and (3) can be combined to give the dependence of $(1/T_1)_{\text{intra}}$ on η/T .

Hubbard¹⁸ has derived the following equation, which

TABLE II. PVT conditions for shear viscosity minimum and T_1 maximum.

t (°C)	Pressure (bar)	
	η (minimum)	T_1 (maximum)
10	1.0 ± 0.1	2.2 ± 0.2
5	1.2	2.0
0	1.4	1.9
-5	1.5	2.1
-10	1.6	2.0
-15	1.6	2.2

relates $(1/T_1)_{\text{inter}}$ to the diffusion coefficient D

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{N\pi\gamma^4\hbar^2}{5aD} \left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 + \dots \right], \quad (4)$$

where N is the number density of the nuclei, a is the hydrodynamic radius, and b is the distance of the nucleus from the center of the molecule.

The modified Stokes-Einstein equation relates D and viscosity η :

$$D = \frac{kT}{C\pi a\eta} \quad (5)$$

The coefficient C can take on values of 6 or 4 for the hydrodynamic stick or slip limits, respectively. It has been found² that water more closely obeys the stick limit as would be expected considering the extent of hydrogen bonding. We will, therefore, assume that $C=6$ and combine Eqs. (4) and (5), which will give the dependence of $(1/T_1)_{\text{inter}}$ on η/T . If Eqs. (1)–(5) are all combined, the relationship between T_1 , η , ρ , and T will be obtained:

$$\left(\frac{1}{T_1}\right)_H = (c'\rho + c\kappa)\eta/T, \quad (6)$$

where

$$c = \left(\frac{3\gamma^4\hbar^2}{2r^6}\right) \left(\frac{4\pi a^3}{3k}\right), \quad (6'a)$$

$$c' = \frac{6\pi^2\gamma^4\hbar^2}{5k} \left[1 + 0.233\left(\frac{b}{a}\right)^2 + 0.15\left(\frac{b}{a}\right)^4 + \dots \right] \frac{N_0}{M} s, \quad (6'b)$$

where N_0 is Avagadro's number, M is the molecular weight, and s is the number of spins per molecule. If it is assumed that a , b , and r do not change with temperature and density, then both c and c' will not depend on T and ρ . We use the following values: $a=1.38$ Å, $b=0.92$ Å, $r=1.52$ Å.

If κ depends only on density, a plot of $(1/T_1)_H$ vs η/T at constant density would yield a straight line through the origin. The plot in Fig. 4 shows that this is indeed

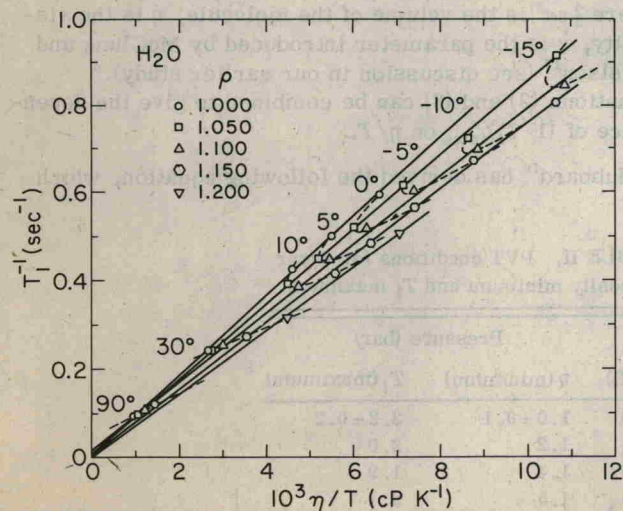


FIG. 4. Dependence of the observed proton relaxation rate $(1/T_1)_H$ upon η/T in H_2O at several constant densities.

TABLE III. Density dependence of parameter κ .

$\rho(\text{g/cm}^3)$	1.00	1.05	1.10	1.15	1.20
κ	0.93	0.81	0.65	0.58	0.47

the case. The standard deviation of the slope of the best fit straight lines is at most 1.4%. We have used 30° and 90° data from our earlier work¹ to increase the range of temperature used on the plot and to show the marked difference in isothermal behavior of $(1/T_1)_H$ at temperatures above $\sim 30^\circ\text{C}$. The dramatic curvature of the isotherms from 10° to -15°C shows the differing pressure dependence of the extrema of viscosity and relaxation. A minimum in the viscosity will be at the extreme left-hand part of the isotherm; whereas, a maximum in the T_1 will occur at the lowest point. Depending upon the curvature of the isotherm, these two points might be at different pressures (see Table II). If our assumptions are valid (see Ref. 1), the data suggest that κ is independent of temperature within experimental error and depends only on density, as shown in Table III.

Figure 4 can be qualitatively understood in terms of a simple physical picture based on the changes in the random hydrogen bond network. As is clear from Fig. 1 and Figs. 2 and 3, ice I and the high pressure ice V represent the boundaries of our experiments. The important structural features of ice V are the distorted hydrogen bonds and the closer approach between non-hydrogen-bonded neighbors. As Eisenberg and Kauzmann³ pointed out, such features permit relatively high densities without necessitating the complete rupture of hydrogen bonds. By compressing liquid water in the temperature range studied, we gradually go from an open structure with optimal tetrahedral order toward a more compact arrangement where non-hydrogen-bonded neighbors are in repulsive contact and where hydrogen bonds are distorted. The net result is that compression leads to distortion of hydrogen bonds and thus weakens them. From Fig. 4 we see that the slopes of $(1/T_1)_H$ vs η/T lines decrease with increasing density. This indicates that the coupling between rotational and translational motions, as characterized qualitatively by changing parameter κ , is decreasing with increasing density at constant temperature. The fact that at constant density the $(1/T_1)_H$ vs η/T plots are straight lines suggests that thermal agitation at constant volume obviously affects reorientation and shear viscosity to the same extent, i.e., the increase in temperature causes viscosity η and the reorientational correlation time to decrease proportionately. This finding agrees with results of dielectric and NMR relaxation studies which reported that reorientation of water at 1 bar can be described by the Debye equation (see discussion in Ref. 19). However, it is not surprising that the Debye equation fails to describe the effects of compression because of the change in the coupling between the rotational and translational motions of water with density. It should be emphasized that κ for molecular liquids is usually in the range ~ 0.1 – 0.3 . If one considers only the molecular shape of a water molecule and neglects