THE JOURNAL OF CHEMICAL PHYSICS VOLUME 54, NUMBER 2 15 JANUARY 1971

Relaxation Processes in Water. The Spin–Lattice Relaxation of the Deuteron in D_2O and Oxygen-17 in $H_2{}^{17}O$*

J. C. Hindman, A. J. Zielen, A. Svirmickas, and M. Wood
Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 1 June 1970)

An experimental study of the deuteron relaxation time T_1 has been made over a temperature range -18–178°C. The equation for the temperature dependence of the relaxation time is of the form

$$-\ln T_1 = \ln(ae^{b/T}+ce^{d/T}).$$

The data are interpreted in terms of an equilibrium leading to a species which relaxes by an isotropic rotational diffusion process. Using transition rate theory and a quadrupole coupling constant derived for the relaxing species from dielectric data, heats and entropies are calculated for both the equilibrium and rate processes. For the equilibrium $\Delta H = 6.8 \pm 0.2$ kcal mole^{-1} and $\Delta S = 24.8 \pm 0.9$ e.u. mole^{-1}. For the rate, $\Delta H^* = 2.50 \pm 0.06$ kcal mole^{-1} and $\Delta S^* = 3.6 \pm 0.1$ e.u. mole^{-1}. Similar measurements for the oxygen-17 relaxation time T_1 over the temperature interval -14–180°C yield for the equilibrium $\Delta H = 5.6 \pm 0.3$ kcal mole^{-1} and $\Delta S = 20.7 \pm 1.4$ e.u. mole^{-1}. For the rate, $\Delta H^* = 2.43 \pm 0.08$ kcal mole^{-1} and $\Delta S^* = 3.9 \pm 0.2$ e.u. mole^{-1}. The results are discussed in terms of models for the water structure, the species present in the liquid, the relaxation process and molecular motion in the liquid.

INTRODUCTION

A number of mechanisms have been proposed for the processes which lead to reorientation and relaxation of water molecules in liquid water. To a considerable degree these reflect the viewpoints of the various authors with respect to the nature of the structure and the species present in the liquid. An excellent review and discussion of various possibilities has been given by Eisenberg and Kauzmann.[1] In principle, information about both the nature of the relaxing species and the details of the molecular motion can be obtained from nuclear magnetic resonance relaxation measurements on water containing the isotopic species ^1H, ^2H, and ^{17}O. The simplest data to interpret are the spin–lattice relaxation times, T_1, for the ^2H and ^{17}O isotopes since for these the only correlation times involved are those for intramolecular motion.[2]

The fundamental equation relating the spin–lattice relaxation time T_1 to the correlation time τ_r for rotational motion is[3]

$$1/T_1 = (3/40)[(2I+3)/I^2(2I-1)] \times (1+\tfrac{1}{3}\eta^2)(e^2qQ/\hbar)^2\tau_r, \quad (1)$$

where I is the spin, η the asymmetry parameter, and e^2qQ/h the quadrupole coupling constant. The interpretation of the experimental data is complicated by the fact that there are three possible variables. The asymmetry parameter and the quadrupole coupling constant will depend on the nature of the relaxing species, e.g., whether it is a hydrogen-bonded or free water molecule. In this respect the deuteron represents the simplest case since the asymmetry parameter is small in both the gaseous[4] and hydrogen-bonded (ice)[5] water molecules. The correlation time is a simple parameter only if the rotational process is isotropic.

If the rotational motion is anisotropic, additional correlation times are introduced and the relations between the relaxation time and the correlation times involve factors dependent on the angular relation between the principal symmetry axis of the tensor of interest relative to the rotational axis.[6–10] The possibility of anisotropic rotation in water cannot be ignored in view of the fact that the relaxation processes in water generally exhibit a non-Arrhenius temperature dependence. If anisotropic rotation is responsible for the non-Arrhenius behavior, the expression for the temperature dependence of the relaxation time will be the sum of Arrhenius terms with different pre-exponential factors and apparent activation energies for relaxation of geometrically nonequivalent quadrupolar nuclei in the same molecule.[9,10]

There are, of course, other possible explanations for the non-Arrhenius temperature dependence of the relaxation processes. One such possibility, suggested by the general shape of relaxation time versus $1/T$ plots, is that there are two relaxation processes, one dominant at high temperature and a second important at low temperatures. In this simple case the resulting equation for the temperature dependence of the relaxation time would involve the sum of two exponentials. As noted in an earlier communication,[11] an adequate test of this or other possible complex relaxation process will require more precise experimental data than are presently available over a wide temperature range. In particular, the oxygen-17 data do not extend to a sufficiently high temperature.[11] The one set of deuteron relaxation measurements[12] over a wide temperature range (0–300°C) are not adequate for anything more than qualitatively defining the general shape of the curve for the temperature dependence of the relaxation time. Significant differences are noted between these data and those obtained by Woessner[6] for the temperature interval from 5–100°C. As is the case for the oxygen-17 data,[11] these latter results do not cover a sufficient temperature interval to permit a meaningful analysis. We have therefore made new measurements of both the deuteron and oxygen-17 relaxation times over

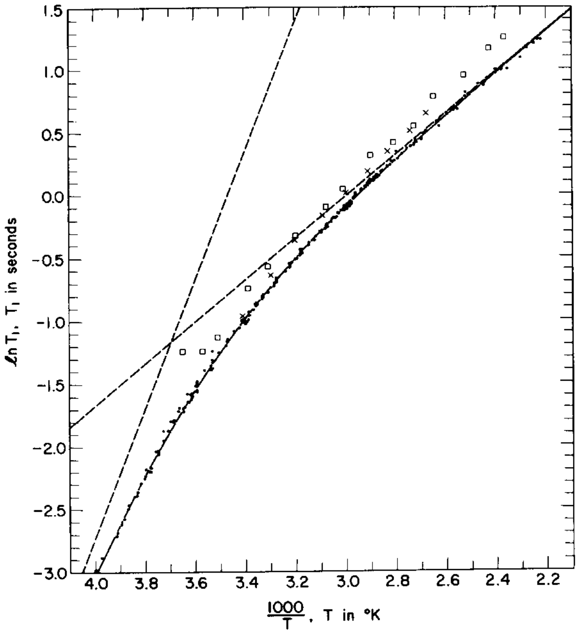

FIG. 1. Experimental data, D_2O, ●. Solid line, Eq. (2). Dashed lines, process I and II contributions, Eq. (2), constants from Table II. ×, Woessner.[8] ⊡, Powles, Rhodes, and Strange.[12]

a more extended temperature range. Since it is found experimentally that there is a marked curvature to the $\ln T_1$ vs $1/T$ plots at low temperature and a definite approach to Arrhenius-like behavior at the higher temperature, emphasis has been placed on extending the measurements as far as possible into the supercooled region to permit a better definition of the low temperature behavior.

Starting with the observation that the relaxation appears to be dominated by a single process at the high temperatures, it is found that the temperature dependence of the relaxation times can be explained by considering only two contributions to T_1. The resulting equation for the temperature dependence is of the form

$$-\ln T_1 = \ln(ae^{b/T} + ce^{d/T}). \qquad (2)$$

The apparent activation energies are: in D_2O, for process I, $E_I = 10.2 \pm 0.3$ kcal mole^{-1} and for process II (dominant at high temperature), $E_{II} = 3.30 \pm 0.05$ kcal mole^{-1} and in $H_2{}^{17}O$, for process I, $E_I = 9.2 \pm 0.5$ kcal mole^{-1} and for process II, $E_{II} = 3.28 \pm 0.06$ kcal mole^{-1}. (All $\pm$ values, unless otherwise specified, represent the 95% confidence level.) The relative magnitude of these activation energies suggests that process II is that involving the isotropic rotational diffusion of unbonded water molecules, whereas process I is associated with the breaking of hydrogen bonds. The derivation of correlation times and additional thermodynamic parameters for the two processes are considered in detail. Implications of the results with respect to the nature of the relaxing species and the structure in the liquid are discussed.

EXPERIMENTAL

The water samples for the deuteron measurements were prepared from conductivity-grade D_2O (enriched to 99.8% in deuterium). The $H_2{}^{17}O$ samples were prepared from Yeda Research and Development Company water enriched to 26.94% in oxygen-17. Individual samples were prepared by further multiple distillation on a vacuum line and were sealed after gas removal by the usual freeze–pump–thaw technique. Both quartz and pyrex sample tubes were used in D_2O. Only quartz sample tubes were used for $H_2{}^{17}O$. All glassware was boiled in hydrochloric acid for several hours before rinsing with conductivity water and drying, although the deuteron relaxation behavior did not indicate the sensitivity to trace impurities noted in the case of oxygen-17.[11]

The deuteron spin–lattice relaxation times T_1 were measured using an NMR Specialties Co. spin-echo spectrometer operating at 9.21 MHz. The oxygen-17 measurements were made at 8.133 MHz. The pulse sequence used was 180°–τ–90°. For the oxygen-17 measurements a multiple scan technique was used to improve signal to noise with a Fabri-Tek 1074 Instrument Computer as the signal storage unit.

Temperature of the sample in the probe was maintained by a flowing liquid coolant. To maximize the control of sample temperature and to minimize the thermal gradient problem, the sample tubes were kept short and held in place with a thin glass rod. Temperatures were measured using a thermocouple attached to the wall of the sample tube. Temperature control was approximately ±0.2° up to 100°C and then deteriorated gradually to ±0.5° at 180°C.

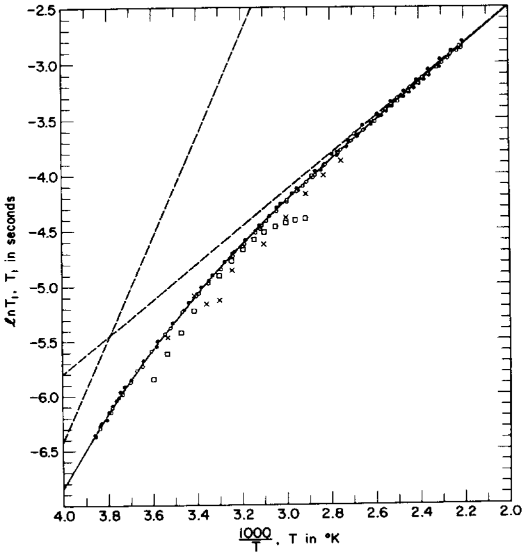

FIG. 2. Experimental data, $H_2{}^{17}O$, ⊙, ●. Solid line, Eq. (2). Dashed lines, process I and II contributions, Eq. (2), constants from Table II. ⊡, Glasel[13]; ×, Garrett, Denison, and Rabideau.[14]

TABLE I. Least squares parameters for temperature dependence of $T_1(D_2O)$ T_1 in seconds and T in degrees Kelvin.

	Eq. (2)	Eq. (3)	Eq. (4)
a	$(1.7\pm1.0)10^{-8}$	86.5 ± 4.0	$(6.0\pm0.4)10^{2}$
b	$(5.15\pm0.14)10^{3}$ [a]	-11.8 ± 0.6 [c]	$-100.\pm7.$ [e]
c	$(7.0\pm0.5)10^{-3}$	$(-6.1\pm0.2)10^{3}$ [d]	$(-2.06\pm0.12)10^{4}$ [f]
d	$(1.66\pm0.03)10^{3}$ [b]	···	0.13 ± 0.01 [g]
σ_{T_1}/T_1	2.13%	5.12%	2.73%

[a] $E_1=10.2$ kcal/mole.

[b] $E_2=3.30$ kcal/mole.

[c] $\Delta C_p^*=-25.4$ cal/deg·mole.

[d] $\Delta H_{(0°)}^*=12.1$ kcal/mole.

[e] $\Delta C_{p(0°)}^*=-200$ cal/deg·mole.

[f] $\Delta H_{(0°)}^*=41$ kcal/mole.

[g] $\Delta C_{p(298°)}^*=-45$ cal/deg·mole.

RESULTS

The experimental results for D_2O are shown in Fig. 1. Each black dot represents the mean observed T_1 at the measured temperature. The experimental uncertainty in the determination of T_1 was estimated to be 2%–3%, which was checked very well by a 2.1% standard deviation value obtained from the least squares fit. Comparison of our results with those of Woessner[6] (see Fig. 1) indicates that although the agreement between the two sets of data is within experimental error at low temperature, there is an increasing difference with increasing temperature. At 100°C, our T_1 value is approximately 15% lower than that reported by Woessner. Although we cannot state the exact reason for this discrepancy, we believe it may be associated with thermal differentials which are difficult to control with a gas-flow cryostat. Measurements on different samples of D_2O over a period of two years have yielded identical results within our experimental uncertainty.

The experimental results for oxygen-17 are shown in Fig. 2. The open and closed circles represent two separate samples. Each circle represents the mean observed T_1 at the measured temperature. The experimental uncertainty in the determination of T_1 was estimated to be ±2%. As a result of the improved measuring technique, the data show considerably less scatter than that reported in our earlier communication.[11] Within the experimental uncertainties of the two sets of data, however, the results are in agreement. The present results confirm the previously reported differences between our data[11] and that reported by Glasel[13] and by Garrett *et al.*[14]

TREATMENT OF THE DATA

In developing equations for the mathematical representation of the experimental data, it is of particular interest to consider forms that are susceptible to interpretation in terms of possible physical processes. For example, in an earlier communication[11] it was found that the temperature dependence of the available oxygen-17 relaxation data for water could be reproduced by an equation of the form

$$\ln T_1=a+b\ln T+c/T. \tag{3}$$

This form of the rate equation has been used by Conway[15] for the treatment of dielectric relaxation in water. According to Conway,[15] the constant c in Eq. (3) is identified with $-\Delta H_0^*/R$, where ΔH_0^* is the heat of activation at absolute zero (if water remained liquid down to this temperature). The constant b in Eq. (3) is then equal to $(\Delta C_p^*+R)/R$, where ΔC_p^* is defined as the difference in heat capacity between molecules in the activated state and those in the initial state of the relaxation process. Further, an explanation of the ΔC_p^* term could be given in terms of a distribution of activation energies among a number of harmonic oscillators[16] and hence related to the model of liquid water behaving as a continuum of oscillators of different frequencies.[17] It was found, however, that, although Eq. (3) adequately represented the available data for the dielectric oxygen-17 and deuteron relaxation in water, the ΔC_p term was considerably larger for processes involving relaxation in D_2O than in H_2O, a result inconsistent with the relative half-widths observed for the coupled or uncoupled OD(OH) stretching band in the two media.[18] It was also noted that application of Eq. (3) to calculate deuteron T_1 values at higher temperature (>100°C) indicated an increasingly non-Arrhenius temperature behavior, again contrary to experimental observation.[12] A further test of Eq. (3) was made using the present data. The derived values for the constants obtained from the D_2O data are given in Table I. The least squares calculations were made assuming a constant percentage error in all T_1 values. A plot of the data revealed significant deviations from the experimental points at both high and low temperatures. A significant improvement in the goodness of fit (σ_{T_1}/T_1) is obtained with the equation

$$\ln T_1=a+b\ln T+c/T+dT, \tag{4}$$

i.e., by considering that ΔC_p^* varies with temperature $(\Delta C_p^*=\Delta C_{p_0}^*+2dRT)$. The values of the parameters for Eq. (4) are given in Table I. We note immediately that the introduction of the additional parameter required to fit the data results in markedly altered values of the ΔH_0^* and ΔC_p^* parameters. We particularly note that the value of ΔH_0^* is much larger than the measured activation energy for the proton T_1

TABLE II. Least-squares parameters of Eq. (6) (95% level).

Constant	D_2O	$H_2{}^{17}O$
b_5	3.8644[a]	8.1861[b]
b_1, ΔS_I^*, e.u. mole^{-1}	28.5±1.0	24.6±1.5
b_2, ΔH_I^*, kcal mole^{-1}	9.3±0.3	8.0±0.4
b_3, ΔS_{II}^*, e.u. mole^{-1}	3.6±0.1	3.9±0.2
b_4, ΔH_{II}^*, kcal mole^{-1}	2.50±0.06	2.43±0.08
σ_{T_1}/T_1	2.20%	1.82%

[a] Quadrupole coupling constant =258.6 kHz and $\eta=0.1$.

[b] Quadrupole coupling constant =7.85 MHz and $\eta=0.94$.

process in ice ($E=14.1\pm0.1$ kcal),[19] a result for which we can find no plausible physical explanation. We therefore consider that the present results confirms our opinion that Eq. (3) [and Eq. (4)] is simply an empirical equation suitable for representing the experimental data over a limited temperature range.

The approach to Arrhenius behavior for the temperature coefficient of $\ln T_1$ at high temperature suggested that an examination of the temperature coefficient for the residual contribution to $\ln T_1$ should be made after correction for the high-temperature contribution. A graphical analysis showed that the temperature dependence of $\ln T_1$ could be represented as the sum of two contributions (see Figs. 1 and 2) corresponding to the two processes indicated in Eq. (2), with apparent activation energies, $E_I=bR$ and $E_{II}=dR$. Values of the parameters for Eq. (2) obtained by a computer least squares calculation using the D_2O data are given in Table I. The comparable constants for the oxygen-17 results are $a=(6.0\pm5.4)\times10^{-6}$ sec^{-1}, $b=(4.61\pm0.23)\times10^3$ °K, $c=0.447\pm0.034$ sec^{-1}, and $d=1650\pm33$°K. (All ± values represent the statistical 95% confidence level.) These yield apparent activation energies of $E_I=bR=9.2\pm0.5$ kcal mole^{-1} and $E_{II}=dR=3.28\pm0.06$ kcal mole^{-1}. The goodness of fit, σ_{T_1}/T_1, was found to be 1.78%, somewhat better than for the D_2O data.

Before we consider the interpretation of the results, we consider the derivation of further thermodynamic parameters from the data. If we use transition rate theory,[20] where

$$1/\tau=k'=(kT/h)\exp(-\Delta F^*/RT), \qquad (5)$$

we can rewrite Eq. (2) in the form

$$\ln(1/T_1)_{\text{obs}} =b_5-\ln T+\ln[\exp(-b_1/R)\exp(b_2/RT) + \exp(-b_3/R)\exp(b_4/RT)], \qquad (6)$$

where

$$b_5=\ln Q_1'h/k \qquad (7)$$

and

$$Q_1'=[(3/40)(2I+3)/I^2(2I-1)] \times[(1+\tfrac{1}{3}\eta^2)(e^2qQ/\hbar^2)]. \qquad (8)$$

The apparent enthalpies of activation for the two processes are then $\Delta H_I^*=b_2$ and $\Delta H_{II}^*=b_4$ and the corresponding entropies are $\Delta S_I^*=b_1$ and $\Delta S_{II}^*=b_3$. Calculation of the constants of Eq. (6) requires values for the asymmetry parameter η, and the quadrupole coupling constant e^2qQ/h for the relaxing species. The choice of coupling constant and asymmetry parameter only affects the derived value of the entropy terms. If another choice is made leading to a different value of Q', i.e., Q_2', then, if b_1^0 and b_3^0 are the values of the entropy term obtained assuming $Q_1'=Q_2'$, the entropy terms for $Q_1'\neq Q_2'$ will be

$$b_{1,3}=b_{1,3}^0+R\ln Q_2'/Q_1' \qquad (9)$$

or

$$b_{1,3}=b_{1,3}^0+2R\ln\left(\frac{(e^2qQ/h)_2}{(e^2qQ/h)_1}\right). \qquad (10)$$

The least squares values of the constants of Eq. (6) are given in Table II. The derivation of the particular values used for the quadrupole coupling constants are discussed later in the text. An uncertainty of ±30 kHz in the deuteron quadrupole coupling constant or ±1 MHz in the oxygen-17 quadrupole coupling constant corresponds to an uncertainty in the entropy terms of Table II of ±0.49 e.u. mole^{-1}. The reported value for the oxygen-17 asymmetry parameter for $H_2{}^{17}O$ (gas) is $\eta=0.75\pm0.01$ and for $H_2{}^{17}O$ (ice) is $\eta=0.935\pm0.01$.[21,22] We have arbitrarily used a value of $\eta=0.94$ in our calculations. The difference in asymmetry parameter between the gas- and solid-state values corresponds to a difference in entropy of 0.17 e.u. mole^{-1}, small enough to be ignored in the present instance.

The choice of the quadrupole coupling constant or asymmetry parameter in no way affects the goodness of fit (given by σ_{T_1}/T_1) of Eq. (6) to the data. However, it is interesting to note that the transition state rate theory actually gives a slightly poorer fit than the simpler Arrhenius case represented by Eq. (2), viz., 2.20% vs 2.13% for the D_2O data and 1.82% vs 1.78% for the oxygen-17 data.

INTERPRETATION OF THE DATA

Consideration of various possible structures that have been suggested as components of liquid water indicate a number of processes that could provide mechanisms for molecular reorientation in the liquid. Several of these have been discussed in some detail by Eisenberg and Kauzmann.[1] As a preliminary to further discussion, we have summarized in Table III the kinetic parameters calculated from various experimental data for relaxation of water molecules in various structural environments. These data were obtained using the Arrhenius equation in the form[20]

$$k=1/\tau =(ekT/h)\exp(\Delta S_c^*/R)\exp(E/RT), \qquad (11)$$

where the frequency factor is $A\equiv(ekT/h)\exp(\Delta S_c/R)$.

TABLE III. Energies and entropies of activation for relaxation processes involving water molecules ($T=273.15°K$).

Relaxation process	Relaxing species, medium	Arrhenius frequency factor, A (sec^{-1})	Experimental activation energy, E (kcal $mole^{-1}$)	Entropy of activation $\Delta S_c^{\pm}$, (e.u.)	Reference
Dielectric	D_2O in ice Ih	1.30×10^{15}	13.4	8.8	d
Dielectric	H_2O in ice Ih	1.89×10^{15}	13.2	9.5	d
Dielectric	H_2O in ice III	1.06×10^{16}	11.6	13.0	e
T_1	$H_2{}^{17}O$(l) Process I	1.07×10^{18}	9.2	26.7	
	$H_2{}^{17}O$(l) Process II	1.42×10^{14}	3.3	4.4	
T_1	D_2O(l) Process I	4.54×10^{19}	10.2	29.6	
	D_2O(l) Process II	1.12×10^{14}	3.3	3.8	
T_1	D_2O in CH_3NO_2(l)	1.06×10^{14}	2.3	3.8	f
Dielectric	H_2O, in Type I clathrate[a]	0.91×10^{13}	6.7	1.2	g, h
Dielectric	H_2O in Type II clathrate[b]	3.18×10^{14}	8.7	6.0	i, j
Dielectric	THF in Type II clathrate[b]	1.58×10^{12}	0.5	−4.5	j
Dielectric	THF(l)	2.52×10^{13}	2.5	1.0	k
Dielectric	H_2O in Type II clathrate[c]	1.38×10^{16}	10.2	13.5	Ref. 49

[a] Ethylene oxide (C_2H_4O)·hydrate, EOH.

[b] Tetrahydrofuran [$(CH_3)_2CO$]·hydrate, THF.

[c] Ethanol (C_2H_5OH)·hydrate, EH.

[d] R. P. Auty and R. H. Cole, J. Chem. Phys. **20**, 1309 (1952).

[e] G. J. Wilson, R. K. Chan, D. W. Davidson, and E. Whalley, J. Chem. Phys. **43**, 2384 (1965).

[f] J. C. Hindman, A. Svirmickas, and M. Wood, J. Phys. Chem. **72**, 4188 (1968).

[g] M. von Stackelberg and B. Meuthen, Z. Elektrochem. **62**, 130 (1958).

[h] D. W. Davidson and G. J. Wilson, Can. J. Chem. **41**, 1424 (1963).

[i] M. von Stackelberg and H. R. Muller, Z. Elektrochem. **58**, 25 (1954).

[j] M. Davies and K. Williams, Trans. Faraday Soc. **64**, 529 (1968).

[k] R. S. Holland and C. P. Smyth, J. Chem. Phys. **45**, 2799 (1966).

For consistency in the derivation of ΔS_c^*, T was set equal to 273.15°K.

We can immediately note that our analysis of the data in terms of two Arrhenius processes is formally equivalent to the assumption of two states for the water molecules in the liquid. Furthermore, the magnitude of the activation energy for process I indicates that this process is associated with the breaking of hydrogen bonds. Similar considerations suggest that process II could involve the rotational relaxation of single water molecules (cf. Table III, D_2O in CH_3NO_2). The question to be resolved is whether process I is associated with a kinetic or equilibrium process. If the former, the process might be related to the "flickering cluster" mechanism of Frank and Wen,[23] where the formation and dissolution of hydrogen-bonded clusters is considered to be a "cooperative process" arising as a result of thermal fluctuations. The structure of the liquid is characterized by these clusters of icelike material surrounded by, and alternating roles with, disordered fluid.[23] The dielectric relaxation time is considered to be the lifetime of the clusters. If the latter, the process might be related to the mechanism of dielectric relaxation in ice.[24,25] In ice small concentrations of orientational defects (D and L) are formed as a result of thermal agitation in the liquid. Reorientation of a molecule at an orientational defect is presumed to occur rapidly and to involve a relatively small activation energy. The dielectric relaxation time is then related to the concentration of defect sites and the reorientation rate of a molecule at the defect site.

Before we consider how these mechanisms can be differentiated, we must rule out a third possibility, i.e., that the non-Arrhenius behavior of the experimental T_1's can be explained in terms of the anisotropic rotation. As indicated earlier, if this were the case, additional correlation times would be introduced and the relation between the relaxation time and these correlation times would involve factors dependent on the angular relation between the principal symmetry

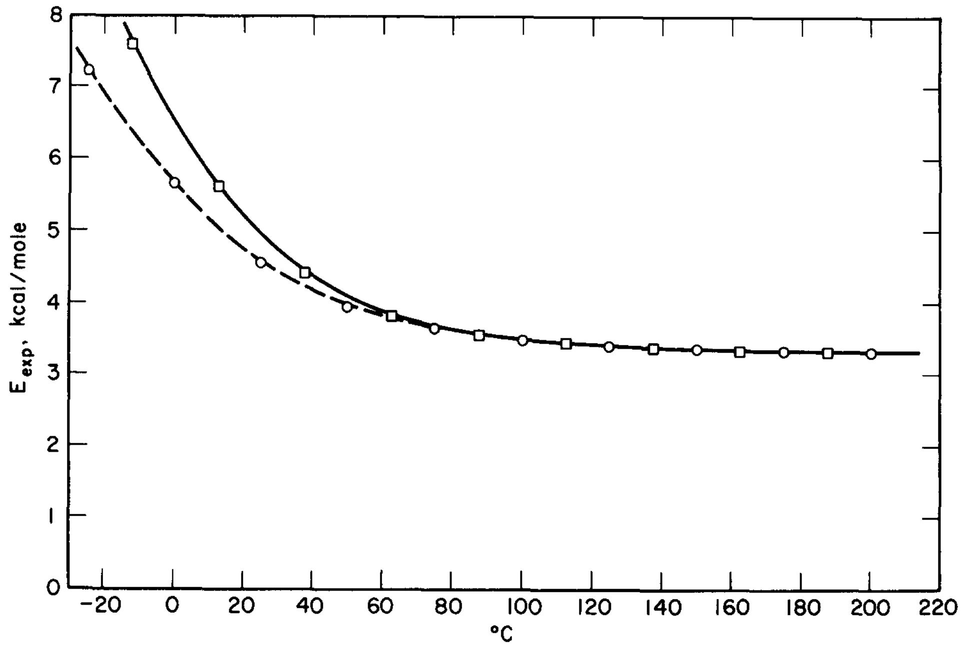

FIG. 3. Plot of apparent activation energies, E_{exp}, [Eq. (13)] vs temperature for D_2O, ⊡, and $H_2{}^{17}O$, ⊙.

axis of the tensor of interest relative to the rotation axis.[6–10] In this case the expression for the temperature dependence of the relaxation time will be a sum of Arrhenius terms with pre-exponential factors which include the appropriate angular terms, i.e.,[9,10]

$$1/T_1=A'Q'[m(\theta)\exp(E_{\perp}/RT)+n(\theta)\exp(E_{\parallel}/RT)], \tag{12}$$

where $m(\theta)$ and $n(\theta)$ are the angular terms with θ the angle between the rotational axis and the principal symmetry axis of the appropriate tensor. $E_{\perp}$ and $E_{\parallel}$ are the activation energies for the indicated rotational diffusive motions relative to the rotational axis. Where the rotational motion is restricted, e.g., by hydrogen-bond formation or strong dipole–dipole forces, $E_{\perp}$ and $E_{\parallel}$ will differ, with $E_{\perp}>E_{\parallel}$. Anisotropic rotation will therefore be reflected in differences in the apparent activation energies for relaxation of geometrically non-equivalent quadrupolar nuclei in the same molecule.[9,10] In Fig. 3 we have plotted the apparent Arrhenius activation energies

$$E_{\text{exp}}=RT^2(d\ln T_1/dT) \tag{13}$$

obtained from our deuteron and oxygen-17 data as a function of temperature. In each case the $(d\ln T_1/dT)$ values were calculated from the least squares parameters obtained with Eq. (2). The results clearly indicate that the rotational motion for the water molecules relaxing in process II (high-temperature path) is isotropic and thus rule out the possibility that anisotropic rotation is a factor in the relaxation process.

Returning to the question of how the equilibrium and kinetic mechanisms can be differentiated, we note that both mechanisms can be formally treated starting with a two-phase model and examining the effect on the relaxation rate with different relative rates of exchange and molecular rotation,[26,27] We write the equilibrium

$$D_2O\ (\text{``lattice''})\underset{k_3}{\overset{k_4}{\rightleftharpoons}}D_2O\ (\text{``free''}), \tag{14}$$

$$K=k_4/k_3$$
$$=[D_2O\ (\text{``free''})]/[D_2O\ (\text{``lattice''})], \tag{15}$$

$$C=1/(1+K)\ \text{concentration of ``lattice'' water}, \tag{16}$$

$$1-C=K/(1+K)\ \text{concentration of ``free'' water}, \tag{17}$$

and k_1 is the rotation rate of a "free" water molecule and k_2 is the rotation rate of a "lattice" water molecule. The two limiting cases to be considered are then: (1) the case where the chemical or phase exchange is fast relative to the rotation rate(s), and (2) the case where the chemical exchange is slow relative to the rotational rate of the "free" water molecule, i.e., the relaxation rate is limited by the rate of breaking hydrogen bonds.

Fast Exchange: k_3 and $k_4 \gg k_1$ and k_2. This case has been fully treated by Anderson and Fryer[27] with the result:

$$1/T_1=Q'[(1+K)/(k_1K+k_2)], \tag{18}$$

and if $k_2 \ll k_1K$, which is a reasonable assumption,

$$1/T_1=Q'(1/k_1+1/k_1K). \tag{19}$$

TABLE IV. Literature values of ΔH and ΔS related to the equilibrium H_2O ("lattice")$\rightleftharpoons$$H_2O$ ("free").

Author	Type observation	ΔH (kcal mole^{-1})	ΔS (e.u. mole^{-1})
Walrafen[29]	ν_T, Raman	$5._6$	~19
Stevenson[30]	uv	6.3_4	8.03
Marchi and Eyring[33]	Model, thermodynamics	6.9	17.3
Davis and Litovitz[32]	Model, thermodynamics	2.78	9.57
Davis and Bradley[31]	Model, (D_2O) thermodynamics	2.92	9.66
Nemethy and Scheraga[34]	Model, thermodynamics	2.7	9.5

Utilizing transition rate theory and converting K to the ΔF or free energy form,

$$-\ln T_1=\ln(Q'h/kT)+\ln[\exp(\Delta F_1^*+\Delta F)/RT+\exp(\Delta F_1^*/RT)], \quad (20)$$

which is formally equivalent to Eq. (6). Since ΔF must become more negative with increasing temperature, there is no ambiguity in matching the b terms of Eq. (6) with the appropriate enthalpy and entropy terms of Eq. (20).

We note that the assumption—$k_2 \ll k_1$ is based on the premise that the Debye–Stokes equation for the rotational correlation time,

$$\tau_r=4\pi\eta a^3/3kT, \quad (21)$$

where η = viscosity and a is a molecular radius—should be obeyed at least approximately. Hence even for a relatively small aggregate of molecules, a("lattice") > a("free") and $k_2 \ll k_1$. Further, if the relaxation were controlled by rotation of clusters of molecules since we would expect a distribution of cluster sizes, we would also expect a distribution of dielectric correlation times, contrary to fact. An alternative possibility is that the motion involves rotation of a molecule bound in a lattice site. In this case we expect the energy barrier for rotation to be appreciably larger than for unbonded molecules since hydrogen bonds must be broken in the rotation process and since, in general, we expect the relaxation rate to be correlated with the magnitude of the intermolecular forces,[28] we also expect the correlation time for the rotation of the hydrogen-bonded molecules to be appreciably longer than for the unbonded molecules.

If the relaxation were controlled by molecular motion of molecules in hydrogen-bonded lattice sites, i.e., $k_2 \gg k_1 K$,

$$1/T_1=Q'[1/k_2+K/k_2]. \quad (22)$$

Although Eq. (22) is a double exponential, it obviously cannot be used to represent the data since it would require a temperature coefficient of the wrong sign for the equilibrium constant, K. We will consider further the question of whether lattice modes can contribute to the relaxation later in the text.

Slow Exchange: k_1 or $k_2 \gg k_3$ and k_4. Anderson and Fryer[27] treated the case for k_1 and $k_2 \gg k_3$ and k_4 but a more general result is needed here because, as noted in the previous section, k_2 could be negligibly small. The more general T_1 equation is found to be

$$1/T_1=Q'\{[K/(1+K)](1/k_1)+[1/(1+K)][1/(k_2+k_4)]+k_3/(k_1-k_2)(k_2+k_4)\}, \quad (23)$$

which for $k_1 \gg k_2$ reduces to

$$1/T_1=Q'\{[K/(1+K)](1/k_1)+[1/(1+K)][1/(k_2+k_4)]+k_3/k_1(k_2+k_4)\}. \quad (24)$$

After introduction of the enthalpy and entropy terms, Eq. (24) contains eight adjustable parameters. This is certainly too much to expect from the present data. Meaningful interpretation can be obtained only if the relative magnitudes of k_2 and k_4 allow limiting forms of the general equation to be used. The subcases are then, if $k_2 \ll k_4$,

$$\frac{1}{T_1}=Q'\left(\frac{K/k_1+1/k_4}{1+K}+\frac{1}{Kk_1}\right), \quad (25)$$

and if $k_2 \gg k_3$ and k_4 and K not $\ll 1$,

$$\frac{1}{T_1}=Q'\frac{K/k_1+1/k_2}{1+K}, \quad (26)$$

which is equivalent to the Anderson and Fryer result.[27]

For $K \ll 1$

$$1/T_1=Q'/k_2. \quad (27)$$

TABLE V. Least squares tests of Eq. (25) and (26).[a]

	Eq. (25)		Eq. (26)	
	ΔH^* (kcal mole^{-1})	ΔS^* (e.u. mole^{-1})	ΔH^* (kcal mole^{-1})	ΔS^* (e.u. mole^{-1})
k_1	5.7±0.2	16.0±0.9	3.2±0.1	4.8±0.2
k_2	···	···	7.4±0.2	19.9±0.8
k_3	−3.0±0.1	−15.0±0.2	···	···
k_4	0.0±0.1	−5.4±0.2	···	···
σ_{T_1}/T_1	2.31%		2.46%	

[a] Thermodynamic quantities of Davis and Bradley[31] used for D_2O ("lattice")$\rightleftharpoons D_2O$ ("free").

Equation (26) can be considered the limiting equation for slow exchange and two rotational processes. Neither Eq. (25) nor (26) is a double exponential of the form indicated by Eq. (2) [or (6)] except in the limiting situations where $K \gg 1$ [Eqs. (25) and (26)] or $K \ll 1$ [Eq. (25) only]. For intermediate K values both cases can approximate the behavior of Eq. (2). Final decision between Eq. (25) or (26) and Eq. (19) requires additional thermodynamic and kinetic considerations.

THE RELAXATION MECHANISM

As a first step in resolving the question of which mechanism gives the best fit to our data, it is convenient to consider current estimates on the temperature dependence and extent of hydrogen bonding in water. In Table IV we give representative data from the literature for the thermodynamics of equilibrium (14).

The values of ΔH and ΔS obtained from Eq. (20) and the Table II parameters for the oxygen-17 data are, respectively, 5.6 kcal and 20.7 e.u.-mole^{-1}, which are close to the Walrafen[29] and Marchi and Eyring[30] results. We expect the thermodynamics of the rotational k_1 process should be similar to those for the rotation of a monomeric water molecule in an organic solvent. The corresponding quantities in Table II and Eq. (20) are b_3 and b_4. Comparison with the Ref. 19 entry of Table III again indicates good agreement.

Thus it is apparent that, in so far as the thermodynamics are concerned, our data could be interpreted in terms of the mechanism involving a rapid equilibrium and a relatively slow reorientation rate of the "free" water molecules [Eqs. (19) and (20)]. The question then is, is this equally true for the mechanism where the relaxation is limited by the chemical rate process k_4? Tests were made by least squares fits to our data with Eqs. (25) and (26) (after conversion to the enthalpy and entropy form), assuming ΔH and ΔS for equilibrium (14) to be known (cf. Table IV) and constant throughout the range of our measurements. Thus, as with Eq. (20), four-parameter fits to the data were made. A summary of the results obtained with the Davis and Bradley[31] D_2O values is given in Table V. These are typical results which were confirmed with our $H_2{}^{17}O$ data and the other entries of Table IV. In all cases the conclusions were the same and lead to the rejection of Eqs. (25) and (26) on thermodynamic and kinetic grounds.

Considering first the Eq. (25) case, it is necessary, because of the basic assumption made in the derivation of the equation, that both the k_1/k_3 and k_1/k_4 ratios exceed one. Using the oxygen-17 data for testing, it is found that this failed in all cases for k_1/k_3 at temperatures lower than 277°K. For two sets of data (Refs. 29 and 32) it also failed for k_1/k_4 at temperatures lower than 260°K. A more striking thermodynamic violation is the negative value for ΔH_3^* found in all cases, where a positive value would be expected for a normal kinetic reaction. Further, the calculations yield small (data, Ref. 33) or negative (data, Refs. 29–32,34) ΔS_4^* values where a large positive entropy of activation would be expected for a process which presumably involves either the rupture or significant weakening of the

TABLE VI. Comparison of correlation times for rate processes I and II [Eq. (26)], calculated using literature values for thermodynamics of the equilibrium H_2O ("lattice")$\rightleftharpoons H_2O$ ("free"), with dielectric relaxation times.[a–e]

T (°C)	$\tau_{\rm diel}$ ($\times 10^{12}$ sec)		Correlation times, $\tau\times 10^{12}$ sec f	g	h	i
0	18.20	τ_1	14.37	3.49	4812.	4.84
		τ_2	4.95	5.78	2.63	5.15
50	4.78	τ_1	3.39	1.33	353.5	1.74
		τ_2	1.02	1.19	0.255	0.76

[a] Reference 48.

[b] E. H. Grant, T. J. Buchanan, and H. F. Cook, J. Chem. Phys. **26,** 156 (1957).

[c] J. B. Hasted and S. H. M. ElSabah, Trans. Faraday Soc. **49,** 1003 (1953).

[d] J. A. Saxton, Proc. Roy. Soc. (London) **A213,** 473 (1952).

[e] R. W. Rampola, R. C. Miller, and C. P. Smyth, J. Chem. Phys. **30,** 566 (1959).

[f] Thermodynamic data, Ref. 30.

[g] Thermodynamic data, Ref. 29.

[h] Thermodynamic data, Ref. 33.

[i] Thermodynamic data, Ref. 32.

hydrogen bonds in the activated state formed from the "lattice" structure. Precisely similar results were obtained by making a least squares fit of both the D_2O and $H_2{}^{17}O$ data to Eq. (25), allowing all of the parameters (six) to be optimized. It is interesting to note that the enthalpy and entropy values associated with the equilibrium and "monomer" rotation obtained in this calculation are essentially the same as those given in Table VIII.

The important test for Eq. (26) is the k_1/k_2 ratio, which, because of the basic assumption made in the derivation of the equation, must always be greater than one. All of the calculations yield the result that at some temperature within the range of our experimental data $k_2>k_1$. It is also worth noting that Eq. (26) invariably gave a poorer fit to the data than either Eq. (25) or (20). We also find (see Table VI): (a) For three of the sets of equilibrium data[29,30,32] the calculated correlation times are of the same order of magnitude for the two processes and we should therefore see two dielectric relaxation times,[35,36] contrary to fact. (b) For the fourth set,[33] $k_2\gg k_1$ at all temperatures and the correlation time τ_1 for rotation of the "free" species is orders of magnitude larger than expected for rotation of a monomeric water molecule (e.g. at 0°C. $\tau_1=4.8\times10^{-9}$ sec vs $\tau\sim10^{-12}$ sec for monomer rotation, see Table III). (c) There is no correlation between the calculated τ_1 and τ_2 values and the dielectric relaxation time, assuming either a rotational diffusion process with $\tau\propto\tau_{\text{diel}}/3$ or a jump diffusion with $\tau=\tau_{\text{diel}}$.[37,38]

Since an examination of Eq. (23) shows that we could also derive Eq. (26) on the assumption that $k_2\gg k_1$, k_3, and k_4, we return at this point to consider whether k_2 in the present case reflects lattice mode contributions to the relaxation. In particular, we consider the possibility that the librational modes, which are reflected in the broad absorption in the infrared and Raman in the 300–900-cm^{-1} region, provide the mechanism for the T_1 relaxation in the hydrogen-bonded lattice. To obtain a correlation time associated with such motions, we have made use of the observations of Wall[39] on the broadening of the O–H and O–D Raman stretching bands in HDO. The Fourier transform of a depolarized Raman band yields the detailed time dependence of a rotational correlation function whose integral is the correlation time for the intramolecular quadrupole or dipole–dipole rotational motions.[40] Wall's analysis showed that the correlation function associated with the broadening of the stretching bands decays to zero in the order of 2.5×10^{-13} sec. He found no evidence for diffusional relaxation at long times and concluded that the breadth of the vibrational bands are determined by the local structure. Integration of his correlation function yields a correlation time of approximately 0.6×10^{-13} sec for the O–H band and 0.9×10^{-13} sec for the O–D band. The decay of the correlation function is not exponential. This observation indicates that the motion associated with the relaxation is not Brownian rotational diffusion but involves reorientation through large angles.[41] This suggests a jump-diffusion mechanism for the T_1 relaxation.[42,43] We have just noted, however, that the dielectric and quadrupole relaxation cannot be reconciled on the assumption of a jump-diffusion process. The experimental results suggest that the lattice modes occur at too high a frequency to make a contribution to the measured T_1. It would be of obvious interest to make a further study of the temperature dependence of the T_1 contribution arising from these lattice modes, particularly since there is evidence for a non-Debye process in the dielectric relaxation at far-infrared frequencies.[36]

To gain additional insight into the processes associated with the two terms in our rate expression [Eq. (2)], we write the equation in the form

$$\begin{aligned}1/T_1&=1/T_1'+1/T_1''\\&=Q'(\tau_Q'+\tau_Q'')\end{aligned}\tag{28}$$

and define an apparent correlation time $\tau_{Q(\text{app})}$ as

$$\tau_{Q(\text{app})}=\tau_Q'+\tau_Q''.\tag{29}$$

We note that experimental observations[31–34] show that dielectric relaxation involves, within very narrow limits, a single correlation time at the frequencies of immediate interest. If the dielectric relaxation involves isotropic rotational diffusion, then the rotational correlation time [Eq. (1)] is related to the dielectric correlation time by

$$3\tau_r=\tau_{\text{diel}}f(\epsilon,\epsilon_\infty),\tag{30}$$

where $f(\epsilon,\epsilon_\infty)$ is the internal field correction.[44,45] Anticipating the conclusions of our discussion, we proceed on the premise that the dielectric correlation time is a direct measure of the rotational correlation time for the quadrupole relaxation and calculate the quadrupole coupling constant for the deuteron (or oxygen-17) in the relaxing molecule from the equation

$$(e^2qQ/h)^2=6\epsilon/[\pi^2(1+\tfrac{1}{3}\eta^2)(2\epsilon+\epsilon_\infty)\tau_{\text{diel}}T_1].\tag{31}$$

Static dielectric constant or permittivity ϵ for D_2O was calculated from 5 to 60°C from the empirical equation derived by Malmberg.[46] For H_2O the dielectric data were obtained from Malmberg and Maryott.[47] Values of τ_{diel} for D_2O over this temperature range have been measured by Collie *et al.*,[48] who also found ϵ_∞ to be the same for D_2O and H_2O. Thus ϵ_∞ was set at 4.55 at 20°C, and the other values were calculated by assuming the distortion polarization to be temperature independent.[45] Interpolated smooth curve values of T_1 were obtained from Eq. (2) and Table I. The results for the D_2O data are illustrated graphically in Fig. 4. The mean calculated detuerium value (258.6 kHz) is intermediate between the directly measured gas (307.91 kHz) and solid (214.8 kHz) values.[4,5] Similarly, the oxygen-17 quadrupole coupling constant is found to be 7.85 MHz, also intermediate between the value in the

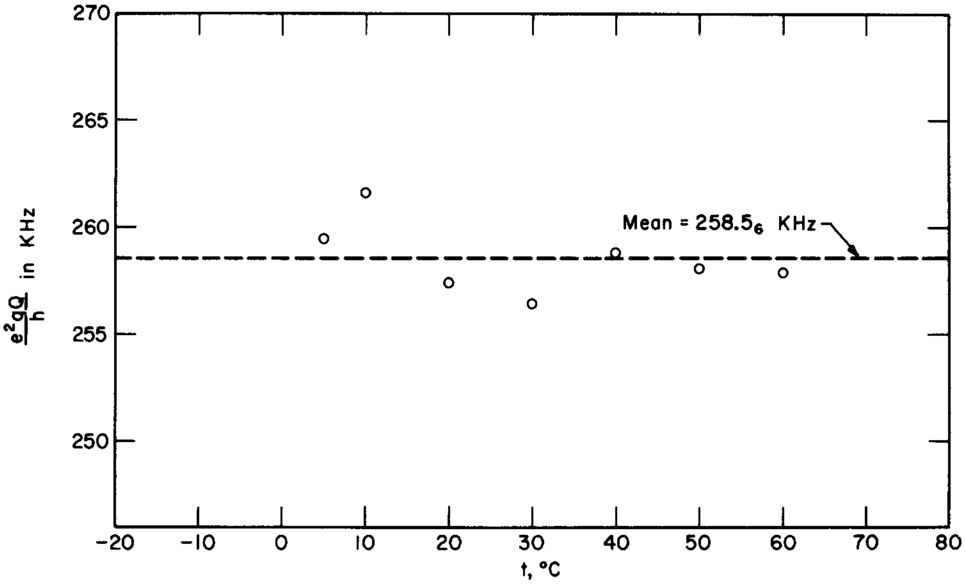

FIG. 4. Quadrupole coupling constant calculated for relaxing species in D_2O [Eq. (31)] vs temperature.

gas[4] (10.17±0.07 MHz) and in the solid[5] (6.66±0.1 MHz). In the limited range of the available data, there is no evidence for temperature dependence of the quadrupole coupling constants.

The mean value of the deuteron quadrupole coupling constant obtained in Fig. 4 was then used to derive values of τ_Q' and τ_Q'' presented in Table VII. Clearly, both τ_Q' and τ_Q'' cannot represent true rotational correlation times. If this were the case, we should readily see two dielectric processes since both the deuteron and oxygen-17 data yield relative correlation times varying in the same manner with temperature and, as is obvious from the discussion of anisotropic rotation, this would require that both processes be reflected in the dielectric relaxation. It is further apparent that the dielectric correlation time does not vary with temperature in the manner that would be required if τ_Q' were the rotational correlation time. Further, there is an obviously increasing correlation between τ_r and τ_Q'' as the temperature increases indicating that at higher temperatures τ_r becomes equal to τ_Q''. We would therefore conclude that process I can be treated as an equilibrium process. In accord with this we then find that $\tau_{Q(\mathrm{app})}$ equals τ_r when $\tau_{Q(\mathrm{app})}$ is calculated using the quadrupole coupling constant calculated for the relaxing species from Eq. (31) (last column, Table VII).

At this point we can note that our conclusions with respect to the nature of processes I and II would not have been affected if we had made these calculations starting with any arbitrary choice of quadrupole coupling constants between the solid state and gas-phase values for either of the two processes. The use of a value for the relaxing species calculated from Eq. (31) merely simplified the comparison between the experimental rotational correlation time obtained from the dielectric data and the apparent rotational correlation time calculated from the T_1 data.

Based on the conclusions of this section, final least squares values for the entropy and enthalpy for the equilibrium [Eq. (14)] and for the rotational rate process of a "free" water molecule (k_1) have been calculated from the data given in Table II. The results are summarized in Table VIII. A slight excess of significant figures has been retained for calculating purposes.

WATER AND ICE

At this point we should like to consider more closely the possible relationship between the mechanism for relaxation in water and in ice or in the clathrates. The latter two are lumped together on the premise that the mechanisms of relaxation is presumed to be the same in both, i.e., to involve rotation of water molecules at lattice defect sites. The clathrates do differ from the ices in that, in many cases, there are at least two readily resolved dielectric dispersion regions. The lower-frequency process represents the dipole relaxation of the host (ice) lattice molecules and the second, high-frequency dispersion is associated with the rotational relaxation of the guest molecules. An exception appears to be the clathrate of ethanol[49] where the second high-frequency dispersion is not observed. This has been explained on the basis that, in contrast to the other systems, the interstitial ethanol molecules are hydrogen bonded to the water lattice.

In order to more clearly illustrate the similarities between the relaxation process in water and in ice, we consider the formal relationship between the two. The relaxation process in ice can be written as follows:

TABLE VII. Temperature dependency of various correlation times (D_2O).

t (°C)	τ_{diel} ($\times 10^{12}$ sec)	τ_r ($\times 10^{12}$ sec)	τ_Q' ($\times 10^{12}$ sec)	τ_Q'' ($\times 10^{12}$ sec)	$\tau_{Q(\text{app})}$ ($\times 10^{12}$ sec)
5	20.39	4.65	1.93_5	2.76_5	4.70
20	12.26	2.80	0.75_0	2.03_8	2.79
40	7.22	1.65	0.24_4	1.41_9	1.66
60	4.90	1.13	0.091	1.03_2	1.12

First an equilibrium leading to the formation of the D and L defects is maintained;

$$2N = \mathrm{D} + \mathrm{L} \tag{32}$$

with

$$K_d = c_{\mathrm{D}} c_{\mathrm{L}} / c_{\mathrm{N}}, \tag{33}$$

where c_{D} = concentration of D defects = c_{L} = concentration of L defects = c and c_{N} = concentration of normal bonds. For one mole of bonds,

$$c = (K_d)^{1/2} / [1 + 2(K_d)^{1/2}] \tag{34}$$

and

$$c_{\mathrm{N}} = 1/[1 + 2(K_d)^{1/2}].$$

With rotation occurring only at the defect sites and with $k_{\mathrm{D}} = k_{\mathrm{L}} = k$ = rotation rate of a defect water molecule,

$$T_1 = (1/Q')\{2(K_d)^{1/2}(k)/[1 + 2(K_d)^{1/2}]\} \tag{35}$$

which is exactly the same as Eq. (19) with

$$2(K_d)^{1/2} = K. \tag{36}$$

Precisely similar equations will result if it is assumed that the relaxation involves an interstitial molecule associated with a defect site. This modification in the model for the relaxation mechanism in ice was suggested by Haas[25] to account for the mass transport properties. We then have the equality

$$\begin{aligned} \text{conc "free" water} &= K/(1+K) \\ &= \text{conc defects} \\ &= 2c \\ &= 2(K_d)^{1/2}/[1 + 2(2K_d)^{1/2}]. \end{aligned} \tag{37}$$

TABLE VIII. Thermodynamic values (95% level) for the equilibrium and rate derived processes involved in the deuteron and oxygen-17 relaxations in water [Eqs. (6), (20)].

Constant	$H_2{}^{17}O$	D_2O
e^2qQ/h (MHz)	7.85	0.2586
ΔH (kcal mole^{-1})	5.6 ± 0.3	6.8 ± 0.2
ΔS (e.u. mole^{-1})	20.7 ± 1.4	24.8 ± 0.9
ΔH_1^* (kcal mole^{-1})	2.43 ± 0.08	2.50 ± 0.06
ΔS_1^* (e.u. mole^{-1})	3.87 ± 0.17	3.64 ± 0.15
σ_{T_1}/T_1	1.82%	2.20%

A comparison of Eqs. (19) and (35) shows that the mechanism of relaxation can be the same in both cases. On the other hand, the limiting conditions are obviously different in the two cases. It is of interest to consider why, if the liquid is extensively hydrogen bonded, there should be such an abrupt change in the relaxation rate at the ice-water transition. It appears unlikely that any significant part of this difference in behavior can be attributed to the actual rotational process. Although no direct measurement of the activation energy or entropy has been made for a molecule rotating at a defect site, Bjerrum[24] estimated the activation energy to be ~2.5 kcal. This is of the same order as we have estimated for the rotational process in water; hence we consider that it would be reasonable to use the water values for the energy and entropy as approximations for ice (Table III). If we look at the data in Table III, we further note that the lower activation energy for process I would be expected from the observation that there is a trend toward lower activation energies in the high-pressure ices (and the clathrates) associated with weaker hydrogen bonds in these phases. On the other hand, even when the activation energy is quite low, as in the clathrate lattices in Table III, the relaxation rate is still several orders of magnitude lower than in water. The difference in the behavior of water and either ice or the clathrates is obviously connected with the large entropy value associated with the equilibrium process in water. The large entropy term has the effect of shifting the equilibrium so that, whereas in ice the concentration of defect sites is very low, in water at higher temperatures essentially all water molecules are "defect" molecules.

The large entropy factor indicates that in the transformation from the ice structure to water there is a marked rearrangement in the hydrogen-bonded structure. Looking at the data in Table III would indicate that, whatever the nature of this change, it is not similar to that involved in the formation of the clathrate lattice.

THE RELAXING SPECIES

Both the values calculated for the quadrupole coupling constants [Eq. (31)] and the activation data given in Table III constitute evidence that the relaxing molecules are not in any sense free or only slightly restricted rotors, i.e., where[50]

$$\tau_r = \tau_Q = \tfrac{1}{2}(\pi I/3kT)^{1/2} = 0.5\times 10^{-13}\ \text{sec at } 25°\text{C}, \qquad (38)$$

where I is the mean moment of inertia of the D_2O molecule. Further, if we examine the data for the highly polar guest molecules, e.g., acetone, tetrahydrofuran, and ethylene oxide (Table III), we find that the correlation times are short and there is obviously very little restriction of the rotational motion. In fact a comparison of the data for tetrahydrofuran in a clathrate lattice and in the pure liquid or in benzophenone solution[51] shows that the rotational rate for the THF is faster in the clathrate and involves an appreciably lower activation energy. Precisely the opposite behavior is observed with respect to monomeric water molecules in an organic solvent and in the pure liquid where the activation energy for the rotational motion of a water molecule in the pure liquid is found to be 0.5–1 kcal larger than in the solvent. This difference in behavior is a strong argument against the water molecules involved in the rotational process in water being "nonhydrophilic" molecules in a clathrate lattice.

DISCUSSION

At this point we wish to summarize the conclusions that have been drawn from the present measurements on the T_1 relaxation in D_2O and $H_2{}^{17}O$. We then wish to discuss the degree to which these are consistent with other data related to models for water structure, species present in the liquid, the relaxation process and molecular motion in the liquid.

We have found that the temperature dependence of the T_1 relaxation can be expressed as the sum of two Arrhenius terms, and we have concluded that one of the terms in the rate expression is due to relxation by a Brownian isotropic rotational diffusion process. No evidence was found for either an anisotropic rotational motion or other rotational motion that involves correlation time of the order of magnitude associated with the dielectric relaxation. It was further shown that the relaxation is not controlled by a chemical rate process. The data have therefore been interpreted in terms of an equilibrium between a hydrogen-bonded "lattice" and "free" or "defect" molecules which relax by rotational diffusion. The model for the T_1 process is therefore formally a "two-state" or "mixture" model.[52] Enthalpies and entropies have been derived from the data for both the equilibrium and the rotation process. Quadrupole coupling constants for the relaxing species were calculated using a rotational correlation time calculated from the dielectric relaxation time. Values intermediate between those for molecules in the solid and gas phase were found for both the ^2H and ^{17}O. This observation, coupled with the fact that the activation enthalpy for the rotational motion is 0.5–1 kcal larger than for the rotational relaxation of a water molecule in a noninteracting organic solvent, has been interpreted to indicate that the "defect" water molecules are not "gaslike" or freely rotating monomeric molecules. The inference that there are still appreciable intermolecular forces operative between the water molecules in the "defect" state is in general agreement with a variety of other observations. One example is provided by Stevenson's[30] studies on the vacuum uv spectra, and the vibration–rotational spectrum in the 1.8–2.0-μ region from which he concluded that the concentration of "gaslike" water molecules in liquid water is very low. Particularly pertinent results have been obtained from studies on the O–D stretching frequency. Walrafen[53] indicated that the temperature behavior of the Raman band for this frequency could be interpreted in terms of an equilibrium between two kinds of O–D groups which change in relative concentration with temperature. The component presumed to be associated with the "monomer" species has a broad band centered at 2643 cm^{-1}, 84 cm^{-1} below the vapor frequency and approximately 40 cm^{-1} lower than projected for water in a solvent with a dipole moment of 1.85 D.[54] Further, Franck and Roth[55] have observed that even at 400°C, it is necessary for the density to fall below 0.1 g/cm^3 before the existence of "gaslike" free water molecules is clearly demonstrated by the appearance of rotational structure in the spectrum.

We have noted that the thermodynamic parameters associated with the equilibrium differ significantly from values derived by many authors for two state models of the water structure. On the other hand, there is an obvious close correlation between the values obtained in this research and those calculated by Walrafen[29] from experimental observations on the 175-cm^{-1} Raman band, the band ascribed to hindered translational motion associated with the stretching of the $O{-}H\cdots O$ bond. According to Walrafen[29] all of the known intermolecular Raman bands of water, i.e., the bond-bending, stretching, and librational bands, show the same rapid decrease in intensity with rising temperature, indicating in agreement with our data a very rapid decrease in the concentration of "icelike" species with increasing temperature. Both the thermodynamics and the spectral observations are at variance with the idea that the "icelike" hydrogen-bonded structure persists up to high temperatures.[12,56] The thermodynamics are also incompatible with those required for various clathrate and interstitial models of the water structure.[57–61] We have also noted that the activation parameters associated with the rotational motion are not compatible with the idea that the relaxing molecules are essentially free rotors in a clathrate or interstitial site.

An important question is the degree to which our interpretation of the T_1 relaxation can be reconciled with ideas about the relaxation processes in water derived from other experimental observations, particularly slow neutron scattering and ultrasonic absorption.

As a prelimary to considering these data, we can recall that Litovitz and McDuffie[62] proposed, as a result of experimental studies on several associated liquids, that if groups or regions of appreciable order exist in the liquid, then the dielectric relaxation is closely related to the structural breakup of these groups. In particular, they propose that if the structural breakup is the rate determining step in the dielectric process, then the polarization changes do not proceed exponentially in time and a distribution of relaxation times results. Clearly, the existence of the single dielectric relaxation time in water is in accord with our conclusion that the reorientation process leading to the T_1 (and dielectric) relaxation is not determined by a rate process associated with the breakup of the hydrogen bonded lattice.

The ideas of Litovitz and McDuffie[62] have been further developed by Pinnow, Candau, and Litovitz.[63] They propose that the correlation time for structural (or volume) relaxation at constant pressure, $\tau_{v,p}$, plays the fundamental role in determining the transport properties in the liquid. They suggest that where $\tau_{\text{diel}}/\tau_{v,p}\gg 1$, the simple diffusional model, with $\tau_{\text{rot}}=\tau_{\text{diel}}/3$, holds. Alternatively, where $\tau_{\text{diel}}/\tau_{v,p}$ is of the order of unity, the reorientation is by a jump diffusion. Direct measurement of the structural relaxation time $\tau_{v,p}$ in water is not possible because of experimental limitations of the conventional ultrasonic techniques. An indriect determination has, however, been obtained from ultrasonic measurements on water–glycerol mixtures.[64] We shall refer to the results of these measurements a little later in the discussion.

A study of the inelastic scattering of neutrons provides another approach for estimating the structural relaxation time. The idea that relaxation in water involves a jump diffusion has been largely suggested by such studies.[65–68] These investigations have shown that the motion of the molecules at short times cannot be described by a simple diffusion model. It has been suggested that the diffusion process is delayed by a time τ_0 of the order of 10^{-12} sec and then diffuses by a jump process in a time $\tau_j\ll\tau_0$. At times shorter than the delay time, the liquid behaves as though it were in a quasicrystalline state. It has been further suggested that the time τ_0 is a measure of the lifetime of the hydrogen bond between adjacent molecules.[69] This conclusion was based on the observation that the activation energy for the diffusion process, which is controlled by τ_0, has a value of approximately 3 ± 1 kcal mole^{-1},[69] of the order of magnitude associated with that required to break a hydrogen bond.

The experimental measurements of Slie *et al.*[64] yield values for the structural relaxation time $\tau_{v,p}$ of 4.3×10^{-12} sec at 0°C and 2.0×10^{-12} sec at 25°C. Since these values are appreciably shorter than the dielectric relaxation times, the conditions are presumably satisfied for dielectric relaxation by a simple rotational diffusion process. Davis *et al.*[70] have concluded from this observation that dipole rotations do not occur when the molecules are hydrogen bonded (i.e., are in a quasicrystalline state). They further suggest that since $\tau_{p,v}$ is considerably shorter than τ_{diel}, the structure must break up and reform several times before the dipole is reoriented. This interpretation is similar to that given for the neutron data and implies that the structural relaxation time is a measure of the lifetime of the hydrogen bond in the lattice. A different explanation is suggested by a comparison of the structural relaxation times with the correlation times for the rotational motion in the T_1 (and dielectric) process. The rotational correlation times, i.e., $\tau_r\equiv1/Q'T_1$, obtained from our data are, respectively, 4.2×10^{-12} sec at 0°C and 2.0×10^{-12} sec at 25°C. The identity of these two sets of correlation times indicates that the rate involved is that for the structural (rotational) relaxation of "defect" molecules and not of hydrogen-bonded "lattice" molecules.

The neutron data can be interpreted similarly. Two observations are pertinent in this connection. The first is that the activation energy for the T_1 rotational process is 3.3 kcal, within the experimental uncertainty the same as that found for the diffusion process from the neutron data.[69] The most pertinent observations, however, relative to the present research are those of Sakamoto *et al.*[71] These authors made a Fourier transform of their neutron linewidth data to obtain the time dependence of the mean square displacement of a proton. They find that at 25°C the experimental mean square displacement is adequately described by continuous diffusion at times longer than approximately 3×10^{-12} sec. At 75°C continuous diffusion appears to begin at about 1×10^{-12} sec. As pointed out by Larsson,[68] these limiting times are comparable to the residence times τ_0 derived from the application of the jump-diffusion model to the experimental neutron data. They also correspond to the residence times used in the jump-diffusion model for the T_1 process.[42,43] On the other hand, these "residence" times are remarkably close to the rotational correlation times for the T_1 process, approximately 2.0×10^{-12} sec at 25°C and 0.7×10^{-12} sec at 75°C, where we have concluded from a comparison of the T_1 and dielectric data that we have a classical rotational diffusion. The preceding observations suggest that the ultrasonic, neutron, T_1, and dielectric data may be interpretable on a common basis. Since vibratory modes are permitted at frequencies greater than $1/\tau_r$ and these can persist until the molecules acquire the activation energy necessary to pass over the energy barrier for rotation, it would appear permissable to speak of quasilattice behavior at times shorter than the rotational correlation time. It thus appears to the authors completely unnecessary to assume a jump process in order to explain the data.

---

[*] Based on work performed under the auspices of the U.S. Atomic Energy Commission.

[1] D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford U. P., New York, 1969).

[2] Cf. H. Shimizu, J. Chem. Phys. **40**, 754 (1964).

[3] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford U. P., London, 1961), p. 314.

[4] H. Bluyssen, J. Verhoeven, and A. Dymanus, Phys. Letters **A25**, 214 (1967).

[5] P. Waldstein, S. W. Rabideau, and J. A. Jackson, J. Chem. Phys. **41**, 3407 (1964).

[6] D. E. Woessner, J. Chem. Phys. **40**, 2341 (1964).

[7] W. T. Huntress, Jr., J. Chem. Phys. **48**, 3524 (1968).

[8] D. E. Woessner, J. Chem. Phys. **36**, 1 (1962).

[9] T. E. Bopp, J. Chem. Phys. **47**, 3621 (1967).

[10] W. T. Huntress, Jr., J. Phys. Chem. **73**, 103 (1969).

[11] J. C. Hindman, A. Svirmickas, and M. Wood, J. Phys. Chem. **74**, 1266 (1970).

[12] J. G. Powles, M. Rhodes, and J. H. Strange, Mol. Phys. **11**, 515 (1966).

[13] J. A. Glasel, Proc. Natl. Acad. Sci. U.S. **58**, 27 (1967).

[14] B. B. Garrett, A. B. Denison, and S. W. Rabideau, J. Phys. Chem. **71**, 2606 (1967).

[15] B. E. Conway, Can. J. Chem. **37**, 613 (1959).

[16] Cf. E. A. Moelwyn-Hughes, *Physical Chemistry* (Pergamon, New York, 1961), p. 1246.

[17] J. Schiffer and D. F. Hornig, J. Chem. Phys. **49**, 4150 (1968).

[18] T. T. Wall and D. F. Hornig, J. Chem. Phys. **43**, 2079 (1965).

[19] D. E. Barnaal and I. J. Lowe, J. Chem. Phys. **48**, 4614 (1968).

[20] S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941), Chap. IV.

[21] J. Verhoeven, A. Dymanus, and H. Bluyssen, J. Chem. Phys. **50**, 3330 (1969).

[22] H. W. Spiess, B. B. Garrett, R. K. Sheline, and S. W. Rabideau, J. Chem. Phys. **51**, 1201 (1969).

[23] H. S. Frank and W. Y. Wen, Discussions Faraday Soc. **24**, 133 (1957); H. S. Frank, Proc. Roy. Soc. (London) **A247**, 481 (1958).

[24] N. Bjerrum, Kgl. Danske Videnskab. Mat.-Fys. Medd **27**, 1 (1951); Science **115**, 385 (1952).

[25] C. Haas, Phys. Letters **3**, 126 (1962).

[26] J. E. Anderson, J. Chem. Phys. **47**, 4879 (1967).

[27] J. E. Anderson, and P. A. Fryer, J. Chem. Phys. **50**, 3784 (1969).

[28] Cf. A. Bondi, J. Am. Chem. Soc. **88**, 2131 (1960).

[29] G. E. Walrafen, J. Chem. Phys. **44**, 1547 (1966).

[30] R. P. Marchi and H. Eyring, J. Phys. Chem. **68**, 221 (1964).

[31] C. M. Davis, Jr. and D. L. Bradley, J. Chem. Phys. **45**, 2461 (1966).

[32] C. M. Davis, Jr. and T. A. Litovitz, J. Chem. Phys. **42**, 2563 (1965).

[33] D. P. Stevenson, J. Phys. Chem. **69**, 2145 (1965).

[34] G. Nemethy and H. A. Scheraga, J. Chem. Phys. **36**, 3382 (1962).

[35] R. Pottel and O. Lossen, Ber. Bunsenges. Physik Chem. **71**, 135 (1967).

[36] J. E. Chamberlain, G. W. Chantry, H. A. Gebbie, N. W. B. Stone, T. B. Taylor, and G. Wyllie, Nature **210**, 790 (1966).

[37] K. A. Valiev and A. Sh. Agishev. Opt. Spectrosc. **16**, 477 (1964).

[38] E. N. Ivanov, Sov. Phys. JETP **18**, 1041 (1964).

[39] T. T. Wall, J. Chem. Phys. **51**, 113 (1969).

[40] R. G. Gordon, J. Chem. Phys. **42**, 3658 (1965).

[41] R. G. Gordon, J. Chem. Phys. **43**, 1307 (1965).

[42] P. K. Sharma and S. K. Joshi, Phys. Rev. **132**, 1431 (1963).

[43] P. K. Sharma and R. P. Gupta, Phys. Rev. **138**, A1045 (1965).

[44] J. G. Powles, J. Chem. Phys. **21**, 633 (1953).

[45] N. E. Hill, W. E. Vaughan, A. H. Price, M. Davies, *Dielectric Properties and Molecular Behavior* (Van Nostrand-Reinhold, Ltd., London, 1969), pp. 271–273, 297–298.

[46] C. G. Malmberg, J. Res. Natl. Bur. Std. (U.S.) **60**, 609 (1958).

[47] C. G. Malmberg and A. A. Maryott, J. Res. Natl. Bur. Std. (U.S.) **56**, 1 (1956).

[48] C. H. Collie, J. B. Hasted, D. M. Ritson, Proc. Phys. Soc. (London) **60**, 145 (1948).

[49] A. D. Potts and D. W. Davidson, J. Phys. Chem. **69**, 996 (1965).

[50] W. B. Moniz, W. A. Steele, and J. A. Dixon, J. Chem. Phys. **38**, 2418, (1963).

[51] H. Kilp, S. K. Garg, and C. P. Smyth, J. Chem. Phys. **45**, 2799 (1966).

[52] See D. Eisenberg and W. Kauzman, Ref. 1, Chaps. 4 and 5 for discussion of such models and appropriate references.

[53] G. E. Walrafen, J. Chem. Phys. **48**, 244 (1968).

[54] K. A. Hartman, Jr., J. Phys. Chem. **70**, 270 (1966).

[55] E. U. Franck and K. Roth, Discussions Faraday Soc. **43**, 108 (1967).

[56] A. H. Narten, M. D. Danford, and H. A. Levy, Discussions Faraday Soc. **43**, 97 (1967).

[57] L. Pauling, in *Hydrogen Bonding*, edited by L. Hadzi (Pergamon, London 1959), p. 1.

[58] O. Ya. Samoilov, Zh. Fiz. Khim. **20**, 1411 (1946).

[59] E. Forslind, Acta. Polytech. Scand. **115**, 9 (1952).

[60] M. D. Danford and H. A. Levy, J. Am. Chem. Soc. **84**, 3965 (1962).

[61] H. S. Frank and A. S. Quist, J. Chem. Phys. **34**, 604 (1961).

[62] T. A. Litovitz and G. McDuffie, J. Chem. Phys. **39**, 729 (1963).

[63] D. A. Pinnow, S. J. Candau, and T. A. Litovitz, J. Chem. Phys. **49**, 347 (1968).

[64] W. M. Slie, A. R. Donfor, Jr., and T. A. Litovitz, J. Chem. Phys. **44**, 3712 (1966).

[65] D. J. Hughes, H. Palevsky, W. Kley, and E. Tunkelo, Phys. Rev. **119**, 872 (1960).

[66] K. S. Singwi and A. Sjolander, Phys. Rev. **119**, 863 (1960).

[67] K. E. Larsson and U. Dahborg, J. Nucl. Energy A/B **16**, 81 (1962).

[68] For a review and additional references see K. E. Larsson, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic, London, 1965), Chap. 8.

[69] K. E. Larsson and U. Dahlborg, Physica **30**, 1561 (1964).

[70] C. M. Davis, Jr. and J. Jarzynski, *Advances in Molecular Relaxation Processes* (Elsevier, Amsterdam, 1967), Vol. 1, p. 155.

[71] M. Sakamoto, B. N. Brockhouse, R. G. Johnson, and N. K. Pope, J. Phys. Soc. Japan, **17**, Suppl. B-II, 370 (1962).