# Pressure and Temperature Dependence of Self-diffusion in Water

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The self-diffusion coefficient, $D$, for pure liquid water has been measured at temperatures between 275.2 and 498.2 K and at pressures up to 1.75 kbar† by the proton spin echo method. Our values of $D$ agree, where they overlap, with recently published data which, however, were measured mostly at low temperature and over rather narrow ranges of temperature.

The results are discussed in several ways. The Stokes–Einstein relation is found to be obeyed in the slipping boundary limit. The cubic cell model of Houghton accounts satisfactorily for the measured $D$ values, particularly at higher temperatures. A simple test of a hard-sphere model is found to give poor agreement at lower temperatures but a modified hard-sphere theory seems to be more satisfactory. The activation analysis at constant density shows that water behaves very differently from non-associated liquids. It also suggests that an increase in both temperature and pressure leads to an increase in the fraction of free unbonded water molecules.

A free-volume analysis has led to a modified Arrhenius equation which involves pressure-dependent terms. This semi-empirical equation describes the results within experimental error and predicts a glass temperature at 115 K which is in reasonable agreement with the values obtained by other methods.

There has recently been an increasing interest in the experimental determination of the self-diffusion coefficient, $D$, for compressed light[1–3] and heavy[4] water at various temperatures. Measurements of $D$ over a range of temperature and density will lead to a better understanding of both the diffusional behaviour of water imbedded in deep rocks and of some molecular transport properties of compressed heavy water such as the proton spin relaxation. However, all measurements of $D$ for $H_2O$ under pressure have so far been made[1–3,5–9] at moderate temperatures only up to 332.2 K. A detailed discussion of previous self-diffusion measurements for compressed water was recently presented by Woolf[2] and will not be repeated here. There also exist numerous measurements of $D$ for liquid water under its saturated vapour pressure (s.v.p.) but only a few covered wide temperature ranges.[10–12] The large spread of $D$ values at 298.2 K in the earlier measurements was caused by systematic errors as discussed by Mills[13a] and the best value[13b] is $2.299 \times 10^{-9}$ m$^2$ s$^{-1}$.

The present study of self-diffusion in compressed pure water was undertaken to compare our $D$ values measured by the proton spin echo method with those of tracer experiments by Woolf[2] at lower temperatures and to extend the experimental temperature range up to $\approx 500$ K. It seemed interesting to test the applicability of the Stokes–Einstein relations, the cubic cell model[14] and the hard-sphere model over the widest temperature range. Finally, since the shear viscosity of water at s.v.p. could be represented by a modified Arrhenius equation,[15] it was of interest to test the analogous equation for the self-diffusion of compressed water.

## EXPERIMENTAL

The self-diffusion measurements were made by the n.m.r. spin echo method,[16] using proton resonance on a 20.8 MHz pulsed spectrometer which was based on that described by Luszczyn-

† 1 bar $= 10^5$ N m$^{-2}$ $= 10^5$ Pa.

ski and Powles.[17] The 90°–$\tau$–90° pulse sequence was employed and the proton spin echo signals were amplified, diode detected and displayed on a storage oscilloscope or transient recorder. The receiver system was carefully calibrated and any non-linearity, due mainly to the diode characteristic, was allowed for in the echo signals. The steady magnetic field of 0.486 T was provided by a Mullard PM 208 permanent magnet with 127 mm pole face diameter and a 33.3 mm gap.

The basic high pressure apparatus used has been described by Powles and Gough.[18] Various modifications have since been made, particularly by installing more accurate pressure gauges and improving the radio frequency (r.f.) insert. The pressure system provides proton-free liquid $C_2Cl_4$ at a known pressure to the n.m.r. pressure vessel which is made of titanium 680 alloy and has o.d. = 22.2 mm and i.d. = 13.7 mm. The vessel is separated from the r.f. insert and contains a single r.f. coil of i.d. = 7 mm. A d.c. heating coil is wound non-inductively outside the basic vessel to control the sample temperature up to 580 K. To attain temperatures below ambient, cold nitrogen gas was passed through copper tubing soldered to a cylindrical copper jacket on the pressure vessel. The sample temperature was measured by means of a calibrated copper–constantan thermocouple, accurate to about 0.1 K and situated inside the pressure vessel close to the sample. During typical measurements the temperature was stable to $\pm 0.2$ K and pressure to better than $\pm 100$ bar.

The high pressure sample cell was made of Pyrex glass tubing and contained a mercury well separator, as described by Sawyer and Gale.[19] A modification, consisting of two pieces of a capillary tube one above and the other below the sample volume was made to produce a sample of well defined cylindrical symmetry. Pure water, which had been doubly distilled and de-ionized (electrical conductivity of 0.5 $\mu\Omega^{-1}$), was degassed and distilled into the sample cells, as described by Sawyer and Gale.[19]

The magnetic field gradient was produced by a pair of flat coaxial coils 31.2 mm apart, wound on a Tufnol former such that their fields oppose one another. Each coil consisted of 7 turns of copper wire and had a diameter of 36 mm. The field gradient, as calibrated from the spin echo envelope of a first-order Bessel function shape,[16] was typically $G = (30 \pm 0.3)$ mT m$^{-1}$ A$^{-1}$. With this value the self-diffusion coefficient measured for pure $C_6H_6$ at 298.2 K was $2.21 \times 10^{-9}$ m$^2$ s$^{-1}$ which agrees well with the value $2.215 \times 10^{-9}$ m$^2$ s$^{-1}$ obtained from tracer measurements extrapolated[20] to pure $C_6H_6$.

By varying the pulse separation $\tau$ in the 90°–$\tau$–180° pulse pairs at constant $G$, values of $D$ were derived graphically from the relation,[16]

$$A(2\tau) \propto \exp\left[-(2\tau/T_2) - (\tfrac{2}{3})\gamma^2 G^2 D\tau^3\right], \qquad (1)$$

where $A$ is the spin echo amplitude, $T_2$ the spin–spin relaxation time and $\gamma$ the nuclear gyromagnetic ratio. For protons in pure water and for $\tau > 1$ ms and $G > 10$ mT m$^{-1}$ the first term in the exponent of eqn (1) may be ignored, and a straight-line plot of $\ln A(2\tau)$ against $\tau^3$ has a slope of $-(\frac{2}{3})\gamma^2 G^2 D$ giving $D$.

## RESULTS

The measured pressure dependence of the self-diffusion coefficient, $D$, in liquid $H_2O$ is shown in fig. 1 as twelve isotherms ranging from 2 to 225 °C (275.2 to 498.2 K). The tracer diffusion measurements for THO in $H_2O$ at 308.2 K made by Woolf[2] are also shown for comparison. The general reproducibility of the results is estimated to be better than $\pm 5\%$. The random error in measuring $D$, caused by the scatter of points on a graph corresponding to relation (1), increases from $\approx 1.5\%$ at 298 K to 4% at 498 K. The smoothed values of $D$, taken from " best " lines through experimental points in fig. 1, are shown in table 1.

The results suggest that a broad maximum in $D$ occurs at pressures between 0.5 to 1 kbar for the three lowest isotherms 275.2, 283.2 and 298.2 K. The low temperature maxima in $D$ for $H_2O$ have also been observed by Hertz and Radle,[8] Kiselnik *et al.*,[9] Angell *et al.*[3] and Woolf,[2] and for self-diffusion in $D_2O$ by Wilbur *et al.*[4] and DeFries

TABLE 1.—SMOOTHED VALUES OF SELF-DIFFUSION $D$ (IN UNITS OF $10^{-9}$ m$^2$ s$^{-1}$) FOR COMPRESSED WATER

| pressure /$10^6$N m$^{-2}$ \ temperature /K | 275.2 | 283.2 | 298.2 | 323.2 | 343.2 | 363.2 | 383.2 | 403.2 | 423.2 | 448.2 | 473.2 | 498.2 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| s.v.p. | 1.17 | 1.43 | 2.30 | 3.89 | 5.61 | 7.42 | 9.81 | 12.8 | 15.7 | 19.6 | 23.8 | 28.0 |
| 100 | 1.18 | 1.45 | 2.31 | 3.90 | 5.60 | 7.40 | 9.78 | 12.7 | 15.6 | 19.4 | 23.5 | 27.8 |
| 300 | 1.20 | 1.49 | 2.34 | 3.92 | 5.55 | 7.28 | 9.66 | 12.5 | 15.3 | 19.0 | 22.8 | 27.1 |
| 500 | 1.20 | 1.50 | 2.37 | 3.95 | 5.50 | 7.20 | 9.57 | 12.3 | 15.1 | 18.7 | 22.2 | 26.5 |
| 700 | 1.18 | 1.48 | 2.39 | 3.95 | 5.44 | 7.09 | 9.44 | 12.2 | 14.9 | 18.3 | 21.6 | 25.9 |
| 900 | 1.17 | 1.46 | 2.39 | 3.94 | 5.40 | 6.97 | 9.38 | 12.0 | 14.7 | 18.0 | 21.0 | 25.3 |
| 1100 | 1.16 | 1.43 | 2.38 | 3.93 | 5.31 | 6.89 | 9.21 | 11.9 | 14.4 | 17.7 | 20.4 | 24.8 |
| 1300 | 1.15 | 1.41 | 2.36 | 3.89 | 5.28 | 6.79 | 9.13 | 11.8 | 14.2 | 17.4 | 19.8 | 24.1 |
| 1500 | 1.14 | 1.40 | 2.33 | 3.80 | 5.21 | 6.67 | 9.01 | 11.7 | 14.0 | 17.0 | 19.2 | 23.6 |
| 1700 | 1.13 | 1.39 | 2.30 | 3.74 | 5.15 | 6.59 | 8.92 | 11.6 | 13.8 | 16.7 | 18.6 | (22.9) |

and Jonas.[21] Our results for $H_2O$ agree qualitatively with the tracer data obtained at low temperatures by Woolf and collaborators[2,3] if the tracer results are extrapolated to pure $H_2O$.[2] The maxima in $D$ at low temperatures are consistent with the minima observed in shear viscosity[22] $\eta$ and maxima in the proton spin–lattice relaxation time $T_1$.[8,23,24] Woolf[2] discussed the correlation between the effects of pressure on the $\eta$ and $D$. He also[2] compared diffusion results for water under pressure obtained at 298.2 K by different investigators.

Because of the scarcity of high temperature $D$ measurements for water in the litera-

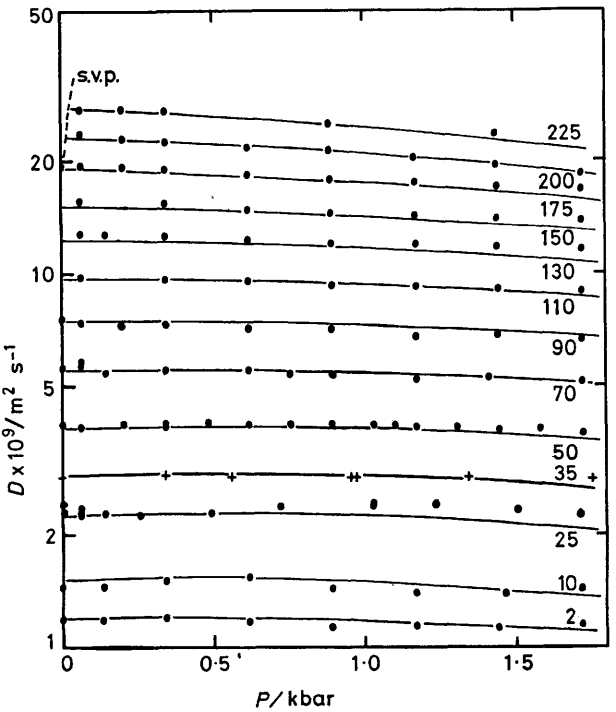


FIG. 1.—Self-diffusion coefficient for liquid $H_2O$ under pressure. ●, present measurements; +, results from ref. (2). The isotherms are indicated in °C. The solid curves are drawn according to eqn (12).

ture, we show in fig. 2 our interpolated $D$ values along the vapour pressure curve. To date only Hauser *et al.*[11] have reported measurements above 373 K and their values are somewhat smaller than ours at high temperature. From the wealth of the $D$ data below 373 K we include in fig. 2 the reliable values obtained by Mills,[13b] but we emphasize that the agreement with many results reported in recent years is good, *i.e.*, well within experimental errors. There is a gentle curvature in an Arrhenius log $D$ against $1/T$ plot particularly at lower temperatures, as studied by Mills.[13b]

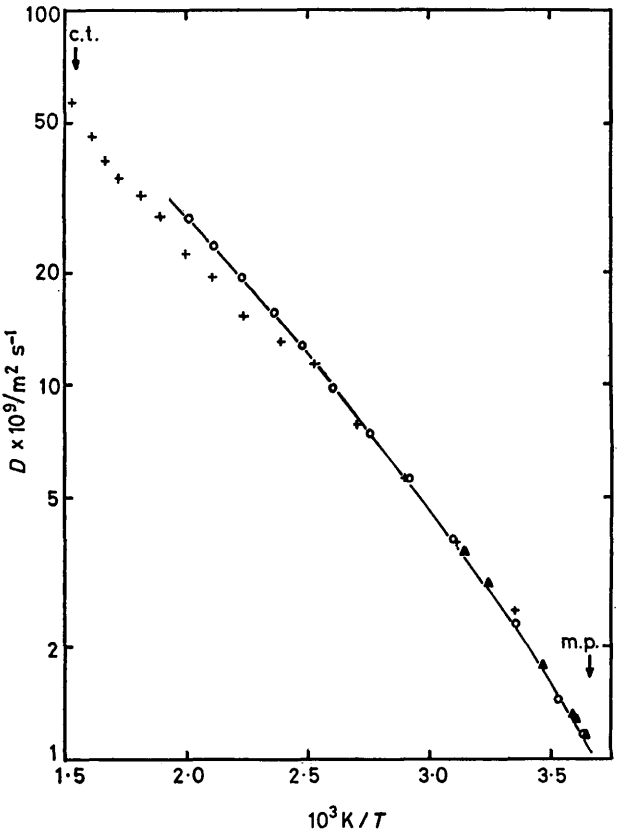


FIG. 2.—Self-diffusion coefficient plotted against reciprocal temperature for liquid $H_2O$ at s.v.p. ○, this work; ▲, ref. (13); +, ref. (11). c.t. indicates the critical temperature.

## DISCUSSION

### QUALITATIVE EXPLANATION OF MAXIMA IN $D$

We believe that the low temperature maxima in $D$ as a function of pressure arise from increased mobility of water molecules which can be explained by assuming that the open structure (hydrogen bonding) of water is distorted and disrupted by the initial application of pressure. This increases statistically the fraction of " free " or " unbonded " molecules participating in translational diffusion. However, the applied pressure also compresses the free molecules and tends to reduce their mobility. The balance between these two processes is such that at low temperature a maximum in $D$ is observed.

As the temperature increases, the ice-like structure of water is already appreciably destroyed by the thermal motion and no maximum in $D$ is observed.

## MODIFIED STOKES–EINSTEIN RELATION

The well known hydrodynamic relationship for a particle diffusing in a medium of viscosity $\eta$ is

$$D = \frac{kT}{C_s \pi a \eta}, \tag{2a}$$

where $k$ is the Boltzmann constant, $a$ the hydrodynamic radius and $C_s$ a numerical constant. When the diffusing particles are much larger than those of the medium (sticking boundary limit) $C_s = 6$ and eqn (2) becomes the familiar Stokes–Einstein relation. For diffusing particles of size approximately equal to those of the medium (slipping boundary limit) Sutherland's[25] modification of eqn (2) leads to $C_s = 4$. Thus for the self-diffusion coefficient one has the modified Stokes–Einstein relation

$$D = \frac{kT}{4\pi a \eta}. \tag{2b}$$

Assuming that $a$ for water is independent of pressure and temperature, one may write

$$\frac{D\eta}{T} = \lambda_s, \tag{3}$$

where $\lambda_s/(C_s \pi a)$ is a constant if eqn (2) is obeyed. Hausser *et al.*[11] reported that along the s.v.p. curve for water $\lambda_s$ is constant except close to the critical temperature.

Using our values of $D$ from table 1 and the literature viscosity data,[22,26] we find that at constant pressure $\lambda_s = (6.9 \pm 0.4) \times 10^{-15}$ N K$^{-1}$, *i.e.*, $\lambda_s$ is constant within the limits of the experimental error. The corresponding result calculated at constant volume is $\lambda_s = (6.9 \pm 0.3) \times 10^{-15}$ N K$^{-1}$, *i.e.*, more constant with no discernible trend. This result is in good agreement with that of Woolf but is lower by $\approx 14\%$ than the value reported by Kiselnik *et al.*[9] because of their correspondingly higher values of $D$. If we use for $H_2O$ $a = 1.38$ Å (which is more appropriate for ice but is close to a value used in machine simulation of liquid $H_2O$), we then deduce $C_s = 4.6 \pm 0.3$. This value is lose to the slipping boundary limit. To make $C_s = 4$ would require an increase in the value of $a$ from 1.38 to 1.58 Å. An estimate of $a$ for $H_2O$ from the van der Waals constant $b$ gives $a = 1.44$ Å, whereas an assumption of hexagonally close-packed spheres leads to $a = 1.74$ Å. We do not see the trend in $C_s$ from the slipping boundary limit to the sticking boundary limit with increasing temperature, as reported by Wilbur *et al.*[4] for $D_2O$.

## THE CUBIC CELL MODEL

Houghton[14] has developed for self-diffusion and viscous flow a simple cubic cell model based on the Navier–Stokes equation. He restricted interactions to nearest neighbours and considered the cell size equal to two molecular diameters. His expression for $D$ in liquids takes the form,

$$D = 194.3 \times 10^{-18} (T/\eta)(\rho/M)^{\frac{1}{3}} \text{ m}^2 \text{ s}^{-1}, \tag{4}$$

where $\rho$ is the density and $M$ the molar mass. The model was claimed[14] to give a good agreement with the measured $D$ values, particularly for non-associated liquids.

Using the reported data for viscosity[22,26] and density in eqn (5), we have calculated $D$ values for water at various temperatures and pressures under consideration. We find that the agreement with experiment is reasonably good particularly at high temperatures. The deviation of the calculated values of $D$ from the experimental ones varies from 15 to 3% as the temperature increases from 275 to 298 K. Note that in the cubic cell model for self-diffusion the molecular size is accounted for by the factor $(M/\rho)^{\frac{1}{3}}$ rather than by an explicit use of the molecular radius $a$. It seems appropriate to include density variation even in our ranges of pressure and temperature at which $D$ was measured.

## HARD-SPHERE MODELS

Another model involving density dependence of self-diffusion is a hard-sphere model. We first consider one of the simplest[27] of these theories which leads to the result

$$D\eta/\rho T = \text{constant}. \tag{5}$$

We have tested this expression for water and found that the mean value of $D\eta/\rho T$ increases from $6.3 \times 10^{-18}$ m$^4$ s$^{-2}$ K$^{-1}$ at 283 K to $8.2 \times 10^{-18}$ m$^4$ s$^{-2}$ K$^{-1}$ at 498 K which compares with the value of $8.24 \times 10^{-18}$ m$^4$ s$^{-2}$ K$^{-1}$ obtained from the original formula.[27] Moreover, the expression also decreases appreciably with increasing pressure along each of our isotherms as for water the product $D\eta$ alone is almost pressure independent.

Dymond[28,29] has combined the Enskog transport theory for a hard-sphere fluid with molecular dynamics to predict transport coefficients of liquids. This corrected Enskog theory has been successfully applied to a number of molecular liquids[29,30] including compressed water at low temperatures.[2] In Dymond's method the exact (molecular dynamics) hard-sphere coefficients of self-diffusion and shear viscosity are expressed in terms of the molar volume and used to obtain corrections to the Enskog expressions for a dense fluid. The corrected Enskog coefficients, $D_{ce}$ and $\eta_{ce}$, for a liquid can be expressed analytically (in SI units) by the following equations[29]

$$10^9 D_{ce} = \frac{7.292}{V_0^{\frac{1}{3}}} \left(\frac{T}{M}\right)^{\frac{1}{2}} . (V - 1.384V_0), \tag{6}$$

$$\frac{1}{10^3 \eta_{ce}} = \frac{45\,916}{V_0^{\frac{1}{3}}(MT)^{\frac{1}{2}}} (V - 1.384V_0), \tag{7}$$

where $M$ is the molar mass, $V$ is the molar volume of the liquid, $V_0 = N\sigma^3/2^{\frac{1}{2}}$ represents the volume of close packing of hard spheres with a diameter $\sigma$, and $N$ is the Avogadro number.

Eqn (6) and (7) show that if $V_0$ is independent of temperature, then both $D/T^{\frac{1}{2}}$ and $T^{\frac{1}{2}}/\eta$ should be proportional to $V$ and intersect the $V$ axis at a common point. The graphs (not shown) of $T^{\frac{1}{2}}/\eta$ and $D/T^{\frac{1}{2}}$ against V for water at the s.v.p., with the literature values of $\eta$ and our values of $D$, turn out to be curved, in contrast to many other molecular liquids,[30a] but they do intercept the $V$ axis at a common point. The fact that the $D/T^{\frac{1}{2}}$ graph is curved more than that of $T^{\frac{1}{2}}/\eta$ indicates that $V_0$ and hence $\sigma$ may be temperature dependent. This is indeed the case as seen in table 2 where the values of $\sigma$ for $H_2O$ at s.v.p. derived from eqn (7) decrease from 3.09 Å at 275 K to 2.65 Å at 498 K. This trend has been noticed at lower temperatures by Woolf.[2] A decrease of the hard-core molecular size with increasing temperature has also been found for other molecular liquids.[29,30] The $\sigma$ for water decreases also with increasing

TABLE 2.—CORRECTED ENSKOG THEORY FOR WATER. VALUES OF $\sigma$ AND $D_{ce}$ ARE CALCULATED FROM EQN (7) AND (6), RESPECTIVELY. VALUES OF $D_{ex}$ ARE TAKEN FROM TABLE 1.

| $T$/K | 298.2 | | 343.2 | | 423.2 | | 498.2 | |
|---|---|---|---|---|---|---|---|---|
| quantity / $P/10^5$ N m$^{-2}$ | $\sigma$/Å | $D_{ex}/D_{ce}$ | $\sigma$/Å | $D_{ex}/D_{ce}$ | $\sigma$/Å | $D_{ex}/D_{ce}$ | $\sigma$/Å | $D_{ex}/D_{ce}$ |
| s.v.p. | 3.05 | 0.996 | 2.97 | 0.939 | 2.80 | 0.921 | 2.65 | 0.870 |
| 500 | 3.03 | 1.02 | 2.95 | 0.933 | 2.79 | 0.930 | 2.64 | 0.880 |
| 900 | 3.02 | 1.06 | 2.94 | 0.929 | 2.78 | 0.940 | 2.64 | 0.873 |
| 1300 | 3.00 | 1.04 | 2.93 | 0.921 | 2.77 | 0.942 | 2.65 | 0.907 |
| 1700 | 2.99 | 1.01 | 2.92 | 0.914 | 2.77 | 0.949 | 2.65 | 0.907 |

pressure but this effect is becoming smaller as the temperature rises and disappears at $\approx$473 K in our pressure range.

The values of $\sigma$ deduced from eqn (7) are then substituted into eqn (6) and the values of $D_{ce}$ are calculated and compared with the experimental data, $D_{ex}$, in table 2. The agreement is within $\pm 10\%$ except at temperatures above 473 K where $D_{ce}$ exceeds $D_{ex}$ by as much as 15%.

The fact that both the modified Stokes–Einstein relation and the corrected Enskog theory are applicable to water is understandable, since eqn (6) and (7) give $D_{ce}\eta_{ce}\sigma/T = 2.11 \times 10^{-24}$ J K$^{-1}$, whereas eqn (2$a$) with $\sigma = 2a$ gives $D\eta\sigma/T = k/2\pi = 2.20 \times 10^{-24}$ J K$^{-1}$. However, for water the use of a constant $\sigma$ for $D$ in eqn (3) leads to a better agreement with experiment than that obtained for $D_{ce}$ in eqn (6) with the variable $\sigma$ from eqn (7).

## ACTIVATION ANALYSIS

For many liquids the behaviour of $D$ over wide temperature ranges can be described by the rate equation of the Arrhenius type

$$D = D_0 \exp(-E_D/RT), \tag{8}$$

where $R$ is the gas constant, $E_D$ is the experimental activation energy per mole, and $D_0$ is often called the frequency factor and is taken as practically independent of temperature. From thermodynamic considerations,[31] eqn (8) is an approximation valid only if the activation energy is not distinguishable from enthalpy and the exponential is dominant in the temperature variation.

Under the application of pressure $P$, eqn (8) is modified according to the Gibbs free energy definition to include the pressure term,

$$D = D_0 \exp[-(E_D + PV_D)/RT], \tag{9}$$

where $V_D$ is called the activation volume for diffusion. In the activation analysis of self-diffusion in compressed liquids two quantities based on eqn (9) are most useful: the apparent activation energy at constant volume (or density)

$$E_{DV} = -R[\partial \ln D/\partial(1/T)]_V, \tag{10}$$

and the apparent activation volume at constant temperature

$$V_D = -RT[\partial \ln D/\partial P]_T. \tag{11}$$

Another quantity, the activation energy at constant pressure $E_{DP}$, defined by an expression similar to eqn (10), appears for water[2] not to be much different from $E_{DV}$ and will not be considered here. As the shear viscosity $\eta$ obeys equations analogous to eqn (8) and (9) but with the positive sign in the exponent, one can define similar activation energy $E_{\eta V}$ and activation volume $V_\eta$ for viscosity.

In table 3 our values of $E_{DV}$ for water are compared with those of $E_{\eta V}$ deduced from the viscosity data.[22,26] The values of $E_{DV}$ were obtained from the slopes of the plots of ln $D$ against $10^3/T$ for several densities between $0.88 \times 10^3$ and $1.06 \times 10^3$ k g m$^{-3}$. There is an agreement within the experimental error ($\pm 5\%$) between our values of $E_{DV}$ and those of Woolf.[2] As seen in table 3, at low temperatures the activation energies for diffusion and viscosity agree within the limits of experimental error. However, with increasing temperature $E_{DV}$ is becoming appreciably greater than $E_{\eta V}$ and at 485 K the ratio $E_{DV}/E_{\eta V}$ is $\approx 2$. Hence at high temperature an appreciable percentage of low energy interactions between water molecules contributes to viscous flow but not to the rate of displacements of molecules from their temporary positions of equilibrium. We note the $E_{DV}$ decreases both with increasing density along all the isotherms and with increasing temperature. This behaviour of water contrasts with that of non-associated liquids such as benzene[32] and carbon tetrachloride[33] for which the opposite is true.

TABLE 3.—ACTIVATION ENERGIES (IN kJ mol$^{-1}$ AT CONSTANT DENSITY FOR SELF-DIFFUSION ($E_{DV}$) AND VISCOSITY ($E_{\eta V}$) OF WATER

| $T$/K → / $\rho/10^3$ kg m$^{-3}$ ↓ | 485 | | 423 | | 383 | | 343 | | 298 | | 278 | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $E_{DV}$ | $E_{\eta V}$ | $E_{DV}$ | $E_{\eta V}$ | $E_{DV}$ | $E_{\eta V}$ | $E_{DV}$ | $E_{\eta V}$ | $E_{DV}$ | $E_{\eta V}$ | $E_{DV}$ | $E_{\eta V}$ |
| 0.88 | 9.4 | 4.4 | | | | | | | | | | |
| 0.90 | 9.0 | 3.7 | | | | | | | | | | |
| 0.92 | 8.0 | 3.2 | 13.4 | 8.2 | | | | | | | | |
| 0.94 | 4.8 | 1.6 | 12.2 | 7.8 | | | | | | | | |
| 0.96 | | | 10.3 | 6.9 | 14.3 | 9.9 | | | | | | |
| 0.98 | | | 7.9 | 6.3 | 13.6 | 9.2 | | | | | | |
| 1.00 | | | | | 11.8 | 8.8 | 15.3 | 12.6 | 18.1 | 16.8 | 19.5 | 18.9 |
| 1.02 | | | | | 10.4 | 8.6 | 14.1 | 12.1 | 17.5 | | 19.1 | |
| 1.04 | | | | | | | 11.8 | 12.0 | 17.1 | 16.0 | 18.9 | |
| 1.05 | | | | | | | | | 16.9 | | 19.9 | |
| 1.06 | | | | | | | | | | | 19.9 | 16.5 |

Since $D$ varies rather little with pressure except at high temperatures, values of $V_D$ deduced from eqn (11) along the smoothed isotherms in fig. 1 are small and become zero at the low temperature maxima in $D$. For instance, at 283.2 K, $V_D$ varies from $-2.6$ cm$^3$ mol$^{-1}$ at 0.1 kbar to zero at 0.65 kbar and $+2.7$ cm$^3$ mol$^{-1}$ at 1.7 kbar which agrees with the Woolf[2] result; at 383.2 K, $V_D$ varies from 1.7 cm$^3$ mol$^{-1}$ at 0.1 kbar to 2.8 cm$^3$ mol$^{-1}$ at 1.7 kbar; at 473.2 K it varies from 5.5 cm$^3$ mol$^{-1}$ at 0.1 kbar to 11.1 cm$^3$ mol$^{-1}$ at 1.7 kbar. These results are in accord with the well known fact that the molecular association in water decreases with increasing temperature. In fact the value of 11.1 cm$^3$ mol$^{-1}$ at 473.2 K and 1.7 kbar is not so much smaller than that for a non-associated liquid, *e.g.*, benzene.[32] From the study of self-diffusion in compressed $D_2O$ Wilbur *et al.*[4] also concluded that at high temperature and high compression the dynamic behaviour of $D_2O$ resembles that of a normal molecular liquid.

## FREE VOLUME ANALYSIS

Cohen and Turnbull[34] considered translational diffusion to occur as a result of a redistribution of the free volume within a liquid rather than an activated process. They have obtained an expression for the self-diffusion coefficient which can be written in a form

$$D = AT^{\frac{1}{2}} \exp\{-B/[T - T_0(P)]\}, \tag{12}$$

where $T_0(P) = T_0 + C\Delta P$ for a pressure increment $\Delta P$, and $A$, $B$, $C$ are constants. $T_0$ is the temperature at which the free volume disappears and may be identified with the glass-transition temperature. Eqn (12), which may be thought of as a modified Arrhenius equation, has been used successfully by Miller[35] and Bernini *et al.*[15] to fit the viscosity data for liquid water over a wide temperature range.

In the free volume analysis of our measured values of $D$ for $H_2O$,[36] the data at each of our isobars have been computer-fitted to eqn (12) with $T_0$ as a variable parameter. A statistical measurement of the normal distribution about the fit was found to be a very sharp function of $T_0$. The use of pre-exponential factors $A$ and $AT$ gives a worse fit than that with $AT^{\frac{1}{2}}$. A plot of $\ln(DT^{\frac{1}{2}})$ against $10^3/[T - T_0(P)]$ for $T_0 = 108$ K and a pressure of 68 bar is linear. A full analysis, however, showed that $A$, $B$ and $T_0(P)$ in eqn (12) are pressure dependent. This pressure dependence is such that $\ln A$, $\ln B$ and $T_0(P)$ all become linear after an initial pressure increase of 0.2 kbar. An empirical equation was thus formed which describes our diffusion results for water within experimental error including those at low pressure. For the 117 data points the full equation is

$$D = 12.5 \times 10^{-9} \exp(-5.22 \times 10^{-4}P)T^{\frac{1}{2}} \exp\left[\frac{-925 \exp(-2.6 \times 10^{-4}P)}{T - (95 + 2.61 \times 10^{-2}P)}\right] \text{m}^2\,\text{s}^{-1}, \tag{13}$$

for $P$ in bar. This empirical equation was used to draw the isotherms shown in fig. 1.

From our diffusion results, $T_0$ for $H_2O$ at zero pressure is estimated to be 115 K. From viscosity results, $T_0$ for $H_2O$ has been estimated as 150 [35] and 146 K.[15] All these values are in reasonable agreement with the result of recent calorimetric studies[37] which suggest the existence of a glass-transition temperature of 135 K.

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