

On the Correlation between Structure and Some Properties of Water

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Water is regarded as a mixture of an ice-like structure and a close-packed structure. This description is shown to make possible an approximate quantitative treatment of various properties of water. Such properties as heat of fusion, specific heat, magnetic susceptibility and X-ray diffraction data are found to be consistent with the theory developed. The directed forces responsible for association in water are probably rather weak. Applying the law of mass action, the bond energy is estimated to be within the range 1.3 to 2.6 kcal/mole. The larger part of the energy of vaporization is thus ascribed to forces which are only slightly dependent on orientation.

I. INTRODUCTION

The anomalous properties of water have frequently been treated by the introduction of a degree of association, defined by the average polymer $(\text{H}_2\text{O})_n$ in the liquid. The magnitude and the temperature dependence of n reported from different sources, vary within considerable limits, however, which may be due partly to an unprecise meaning of n . Many properties will depend upon whether the molecules associate in linear polymers, in rings or in some three-dimensional structure. In the first two cases the number of association bonds per molecule of H_2O will approach unity when n increases, whereas in the latter case it may be much larger. To overcome such difficulties the concept of a distribution of different polymers with different properties was introduced in some papers. Eucken¹ postulated water to be composed of four distinct molecules, H_2O , $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_4$, $(\text{H}_2\text{O})_8$. To each complex was attributed a specific volume and a dissociation energy consistent with the observed volume and thermal expansion of water. An objection could be raised, however, about Eucken's assumption that only some particular complexes should be stable.

The present point of view favours the interpretation of water as a distorted ice-like structure, with bonds constantly breaking and reforming and the association extending throughout the whole liquid. The major approach in this direction was started by the important work of Bernal and Fowler².

They assumed water to be composed of three structures. At low temperatures a dense quartz-like structure accounts for the high density compared with ice. At somewhat higher temperatures a tridymite-like structure (as in ice) is predominant. At even higher temperatures the usual closepacking of normal liquids prevails. As pointed out by Pople³, the evidence for the quartz-like structure is poor, however.

Later workers have suggested that a large number of the bonds in water is broken, which would explain a collapse of the ice structure on melting and heating. This explanation has recently been rejected by Lennard-Jones and Pople⁴. Using the value 4.5 kcal/mole estimated by Pauling⁵ for the hydrogen bond in ice, they argue that on thermodynamic grounds rather few bonds could be broken in water at room temperature. The structural changes were instead explained as a bending of the bonds, which of course would require less energy than their complete rupture.

II. THE RELATIONSHIP BETWEEN VOLUME AND BONDING IN WATER

A most striking evidence for the bonding in water is the temperature dependence of the volume. Obviously two effects counteract. The initial structure collapses, while the usual thermal expansion works in the other direction. Using this as a starting point, the following picture of water will be advanced as a hypothesis.

The water molecule, H_2O , is regarded as exerting on the surrounding molecules certain forces, which may be separated in two distinct parts. The first part gives rise to the major portion of the evaporation energy of water. It is assumed to be rather insensitive to the orientation of the molecule. If no other forces were present, water would behave as a normal liquid. In addition another field of force is effective, responsible for a tetrahedral orientation around the oxygen atom in the water molecule. This force is supposed to be markedly dependent on direction, and associated with a definite, comparatively small energy. Whenever this force is effective between two molecules, we shall refer to it as a bond.

A water molecule has four places available for bond formation. If all places are occupied by the neighbours, the structure will be that of ice,⁶ which for the sake of brevity will be called A. If no bonds exist, the structure will be that of the normal closepacked liquid, to be denoted by B in this paper.

The volume of water at higher temperatures can be shown to follow the empirical volume curves for a normal liquid quite closely, indicating that only few bonds are present. Below 170° C the observed volume of water diverges rapidly from the empirical curve. To obtain an idea about the number of bonds in water, the following assumption is introduced.

The volume of water at a given temperature will be altered if bonds are formed, the effect being proportional to the number of bonds. If two moles ($2N_{\text{Avogadro}}$) bonds per mole of water are formed, the volume will change to V_A which corresponds to the liquid A. Thus if x is the fraction of bonds (it is: the ratio of number of bonds to the possible total) and V is the observed volume of water, the following relationship is assumed:

$$V = V_B + x(V_A - V_B)$$

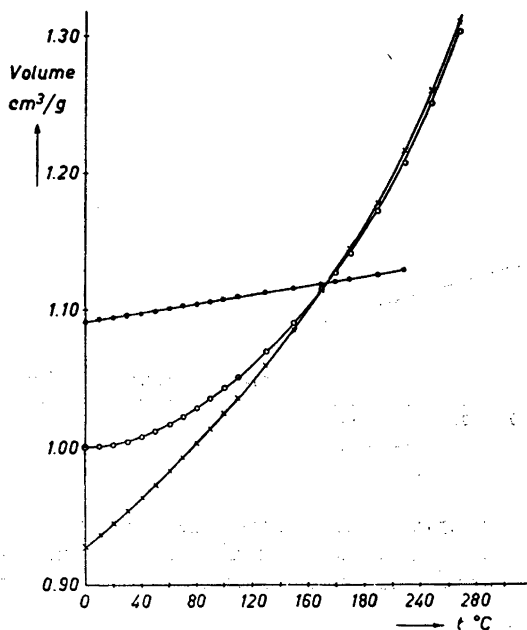


Fig. 1. ○ Volume (orthobaric) of water as a function of temperature, ● Volume, V_A , of ice extrapolated. × Volume, V_B , of hypothetical normal water.

This formula corresponds to the picture of x mole of liquid A being ideally mixed with $1-x$ mole of liquid B. In the temperature range from 0° to 150° C, where from 55 to 85 % of the bonds are broken, this approximation will probably hold.

Fig. 1 shows the volume of one g water as function of temperature. The volume of the same amount of liquid A is extrapolated from ice (data from Dorsey ⁷):

$$V_A = 1.0911 [1 + 0.000153 (T-273)]$$

The volume of one g of B, V_B , is determined according to Jacobson and Heedman ⁸. The critical temperature is taken as 374° C and the curve adjusted through the intersection of V_A and V , giving:

$$V_B = 0.7582 \left[1.546 - 0.546 \left(\frac{647-T}{647} \right)^{\frac{1}{2}} \right]^3$$

It is interesting to notice that the values for V_B correspond to a diameter of the B "molecule" of approximately 3.18 Å. (The estimate is based on the volume of B at 0° K, $0.7582 \text{ cm}^3 \cdot \text{g}^{-1}$ regarding the molecules as hexagonally closepacked).

The fraction of bonds as a function of temperature calculated from these equations is shown in Fig. 2. The extension of the curve above 150° C must

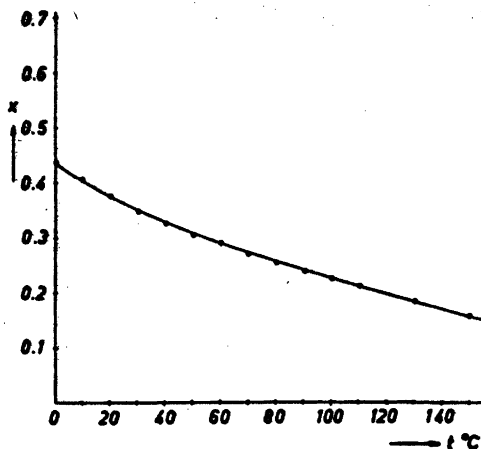


Fig. 2. Fraction of bonds in water as a function of temperature.

necessarily be rather uncertain. The curve itself is also to be regarded as approximate. Even if A and B mixes ideally, the volumes V_A and V_B are not known accurately, which causes an uncertainty in the determination of x .

III. THE MAGNETIC SUSCEPTIBILITY OF WATER

The specific susceptibility of water is likely to be dependent on the number of bonds by a simple relationship. Each bond alters the electron configuration of the molecule in a definite way and is assumed to reduce the susceptibility by a constant amount. As water is a diamagnetic substance, the increase in susceptibility with temperature is easily correlated with the bonding.

If $\chi_g \cdot 10^{-9}$ is the specific susceptibility at a given temperature, $2(1-x)$ the number of broken bonds at the same temperature we have:

$$\chi_g(\text{water}) = \chi_g(\text{ice}) + 2k(1-x)$$

where k is a constant, and corresponds to the rise in susceptibility due to the breaking of the total number of bonds.

For comparison with experiments we take $\chi_g(\text{water})$ at 0°C to be 719.0 and using our previous values for x , determine the value of k to be 17.5. The results are given in Table 1. The calculated values are tabulated in the second column, showing a fair agreement with the observed values in the third column. For ice the experimental value is taken from *Int. Crit. Tables*⁹. A somewhat larger value has been reported by Cabrera and Fahlenbrach¹⁰. The values for water are given by Auer¹¹. There is some spread between the values reported by the different authors, but according to Dorsey⁷ the experimental results of Auer are among the most reliable ones.

Table 1. The magnetic susceptibility of water.

Temp.	$\chi_g \cdot 10^{-9}$ c.g.s		State
$^{\circ}\text{C}$	calc.	obs.	
0	699.4	699.0	ice water
0	(719.0)		
1		718.96	
10	720.2	720.67	
20	721.2	721.83	
30	722.1	722.58	
40	722.9	723.12	
50	723.6	723.61	
60	724.0	724.06	
70	724.7	724.54	

IV. X-RAY DATA FOR WATER

The picture given for water in this paper is in agreement with X-ray diffraction experiments. Morgan and Warren¹² have determined the radial distribution function for liquid water at various temperatures from 1.5° C to 83° C. Between these temperatures they find that the maximum position of the first peak increases from 2.90 Å to 3.05 Å. This is a considerably larger temperature dependency than observed by normal liquids or crystalline solids. Thus the effect is unlikely to be due to an overall increase in the intermolecular bonds lengths.

A more likely explanation would be that the first distribution peak is caused by two different kinds of "molecules", A and B. The A-"molecules" have a diameter of 2.76 Å corresponding to the oxygen-oxygen distance in ice. The B-"molecules" have a diameter of approximately 3.18 Å as determined in the last part of section II. The two distances 2.76 Å and 3.18 Å are not resolved in the radial distribution curve owing to the large overlap of the two single contributions. The relative abundance of A and B will then determine the position of the first peak. A distance of 2.90 Å as observed in water just above the melting point, corresponds roughly to equal amounts of A and B, the distance increases when the amount of B rises.

A more quantitative treatment of the present X-ray data is questionable. The peak positions in the distribution function are quite reliable, but this does not hold for peak shapes and areas under the peak. The determination of the distribution curves introduces many sources of systematic errors which especially affects peak areas and shapes. A review of these errors has been given by Finbak¹³.

V. COMMENTS ON SOME OTHER PROPERTIES

Cross, Burnham and Leighton¹⁴ have studied the Raman spectrum of water. Their results are discussed on the basis of a broken-down ice structure for liquid water. They conclude that water appears to have an average coordination number in the temperature interval from 25° to 90° C of slightly more

than two. This would mean that about half the possible number of intermolecular bonds were broken, a result in rough agreement with ours.

Experimental data based on irreversible phenomena such as viscous flow, have been used to determine the number of intermolecular bonds in water. Owing to the complexity of these phenomena, the data seem rather unsuitable. Ewell and Eyring¹⁵ have determined the number of bonds from viscosity data. Their theory indicates the number of bonds to fall off more rapidly with temperature than the present work indicates. The ratio of energy of vaporization to activation energy of viscous flow increases with temperature. At 150° C the nearly normal value of unassociated polar liquids is attained.

Various authors apply measurements on the dielectric constant of water for a determination of the bonding^{3,16}. A similar procedure is not well adapted to the present theory, because the unbonded B "molecules" are also supposed to have energies which are slightly dependent on orientation.

VI. THE ENERGY OF THE BONDING IN WATER

The total energy change associated with the transition from liquid A to B consists mainly of two parts. The major contribution is due to the breaking of bonds. In addition an energy change of structural rearrangement is effective. The latter contribution depends upon the number of nearest neighbours in liquid B, and is probably of minor importance at room temperature.

If some reaction scheme for the transition from A to B is known, the energy of the transition could be computed from the previous values of x . The reaction can be represented by several different schemes, however. Three particular cases shall be considered:

- 1) All four bonds originating from a given A-"molecule" are fully coupled.
- 2) No coupling exists between the four bonds.
- 3) There is a certain coupling between two and two of the four bonds.

The two first cases 1) and 2) represent hypothetical limiting cases and limit the possible transition energies to within a certain interval. The latter case is intermediate, giving an intermediate energy.

1) If a complete coupling between the four bonds from a A-"molecule" exists, all bonds must break or reform simultaneously. This reaction scheme is pictured schematically for the central molecule in Fig. 3a. The corresponding equilibrium constant is given by:

$$K_1 = \frac{1-x}{x}$$

A plot of the logarithm of this equilibrium constant against the inverse of the absolute temperature is shown in Fig. 4 to be a straight line. Using the Van't Hoff's equation:

$$\frac{d \log K}{dT} = - \frac{Q}{R'T^2}$$

an energy of 2.0 kcal/mole is determined. (Q in this case can be approximated by the energy change, ΔE , as the volume work is negligible.) The corresponding entropy change is found to be 7.8 cal/mole·deg. If the energy of structural

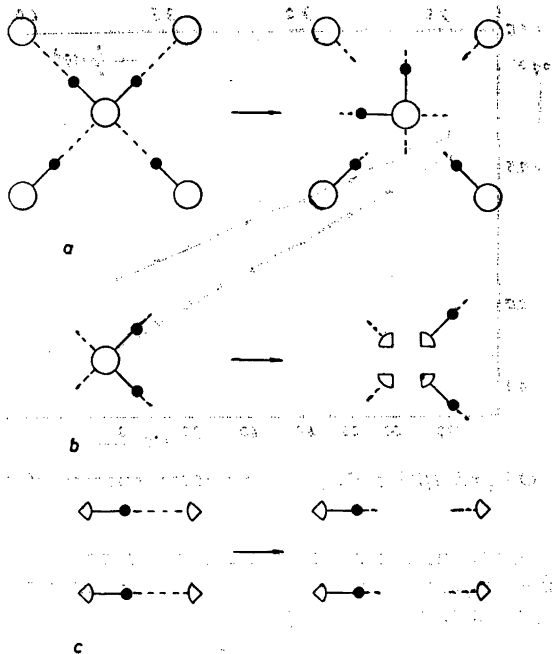


Fig. 3. \circ = Oxygen. \bullet = Hydrogen. ---- = Hydrogen bond or possibility for bond formation. \triangle = Hypothetical "subparticle". a) Reaction scheme when all bonds are coupled (case 1). b) Division into hypothetical "subparticles". c) Reaction scheme for uncoupled bonds (case 2).

change is neglected, the mean energy of each bond must be 1.0 kcal/mole, half of the determined ΔE .

2) If there is no coupling between the bonds, the breaking or reforming of a bond will occur irrespectively of any bonds existing in advance. All bonds would then be equivalent. To picture the corresponding reaction scheme, a B-"molecule" with four bonding possibilities is divided into four hypothetical "subparticles" as shown in Fig. 3b. Each subparticle contains one bonding possibility. This gives a reaction scheme for the transition $A \rightarrow B$ as shown in Fig. 3c. The equilibrium constant is in this case:

$$K_2 = \frac{(1-x)^4}{x^2}$$

A plot of $1/2 \log K_2$ against $1/T$ is given in Fig. 4. The straight line obtained, corresponds to an energy of 5.2 kcal/mole for the reaction $A \rightarrow B$, and 2.6 kcal for the breaking of one mole of bonds.

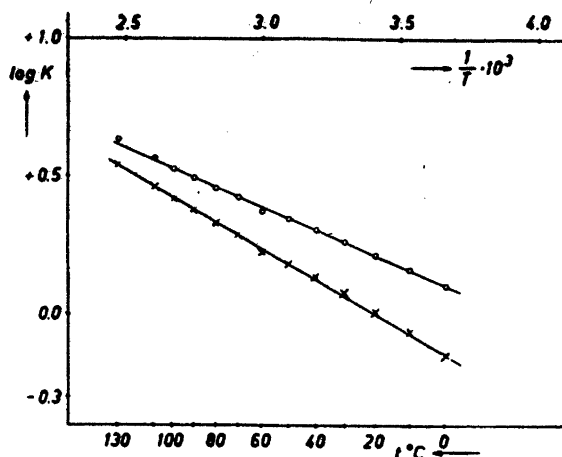


Fig. 4. $\log K_1$ (O) and $1/2 \log K_2$ (x) against the reciprocal of the absolute temperature.

3) If the bonds form and break in pairs, the reaction scheme will be analogous to the scheme just described. The equilibrium constant will be simply related to the previous constant by:

$$K_3 = \frac{(1-x)^2}{x} = K_2^{1/2}$$

As $\log K_3$ is equivalent to $1/2 \log K_2$ we also here get a straight line with an energy change 2.6 kcal/mole (and an entropy change of 8.9 cal/mole.deg.) The mean energy for one mole of bonds in this case is 1.3 kcal.

The obtained plots of $\log K$ against the reciprocal absolute temperature does not suffice for a decision between different possible reaction schemes. The functions are not sensitive enough within a limited temperature interval which is evident from Fig. 4. Other experimental evidence involving energy changes should be considered, for instance heat of fusion and specific heat of water.

The energy of the reaction $A \rightarrow B$ as computed from case 3), 2.6 kcal/mole, is found to be consistent with the heat of fusion on the assumption that a negligible amount of bonds are broken in ice. According to Fig. 2, 0.56 moles of liquid B will be formed on melting one mole of ice. This gives a calculated heat of fusion $0.56 \times 2.6 = 1.46$ kcal/mole which compares favourably with the observed value of 1.44 kcal/mole.

The reaction energy of 2.6 kcal/mole is also consistent with specific heat data. The specific heat at constant volume, C_V , shows an anomaly as it decreases by increasing temperatures. This is due to the break down of the A structure, (or breaking of bonds). The contribution to the specific heat of this break down is given by:

$$C_D = \Delta E \frac{dx}{dT}$$

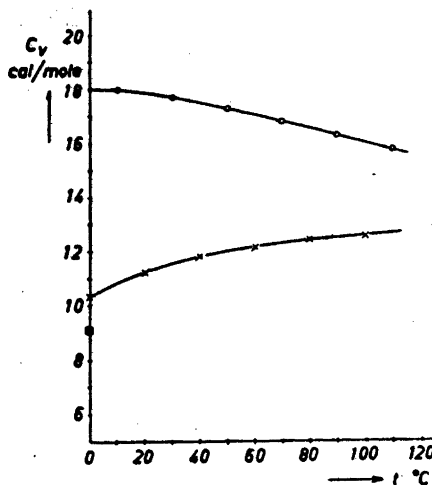


Fig. 5. O Molar specific heat at constant volume, C'_v , for water. x Specific heat C'_v when heat of dissociation is subtracted. [x] Specific heat of ice at 0° C.

where ΔE here is taken to be 2.6 kcal/mole. If this part of the specific heat is subtracted from the observed total, there remains a part:

$$C'_v = C_v - C_D$$

of the order of magnitude and with the temperature dependence to be expected if water were a normal liquid. C'_v (for one mole of water) as function of temperature is given in Fig. 5.

The agreement of these data does not prove the reaction scheme 3). If some bonds were broken in ice before melting, a larger bond energy than 1.3 kcal would be obtained from the heat of fusion. The bond energy is likely to be somewhere between 1.3 and 2.6 kcal. The correction for the energy of structural changes will perhaps increase the bond energy somewhat. Finbak¹⁷ and later others¹⁶ have used equations which incorporate the reaction scheme 2) given here.

The interaction between the molecules of ice is usually ascribed to hydrogen bonding. Various estimates of this hydrogen bond energy are to be found in the literature. The energy is commonly given as 5.8 kcal in water, half the sublimation energy of ice. Pauling⁵ subtracts one part due to what is called ordinary van der Waals' forces, leaving 4.5 kcal for the hydrogen bond. This division of the total interaction seems rather arbitrary, however. Cross, Burnham and Leighton¹⁴ have calculated the hydrogen bond energy from a simple Morse function model of the O—H O oscillator. They obtain energies from 1.6 to 2.8 kcal with different assumptions. From a more refined treatment they finally calculate 3.0 kcal for the hydrogen bond energy. The bond introduced in the present paper to explain the tetrahedral configuration in water could probably be compared with the hydrogen bond discussed by Cross, Burnham and Leighton¹⁴.

VII. DISCUSSION

The value 4.5 kcal/mole estimated by Pauling⁵ for the hydrogen bond, allows few bonds to be broken at moderate temperatures. Much experimental evidence, however, indicates extensive structural changes in water by heating. Lennard-Jones and Pople⁴ have tried to explain this by introducing a bending instead of breaking of the hydrogen bond. The picture given by them resembles the present to a certain extent. If the notion "bending of strong bonds" is substituted by "a breaking of weak bonds" the results would have some similarity. One would only have to impose on the treatment the condition that on reforming the broken bonds, the original configuration should be strongly preferred.

The idea of strong bonds connecting the water molecules seems to disagree with such properties as the rapid fall of viscosity with temperature, however. The general impression of the normal behaviour of water at moderately high temperatures indicates a smaller bonding energy than commonly accepted. This paper divides the total interaction between water molecules in a small energy responsible for tetrahedral orientation, and a larger energy not markedly dependent on orientation. A comparatively small energy of orientation seems adequate for a description of many properties of water.

The present picture of water is somewhat rough. When water is treated as an ideal mixture of liquid A and B, this could be only approximately true. The theories of water are not very advanced, however, and the introduction of such approximations at the present stage would thus be justified. Before any thorough treatment of water is attempted, a reliable general picture must be obtained. This paper indicates a possible approach which may perhaps be extended to other similar associated liquids.

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