Copyright © 1966, by the author(s).
All rights reserved.

Permission to make digital or hard copies of all or part of this work for personal or classroom use is granted without fee provided that copies are not made or distributed for profit or commercial advantage and that copies bear this notice and the full citation on the first page. To copy otherwise, to republish, to post on servers or to redistribute to lists, requires prior specific permission.

STRUCTURE AND PROPERTIES OF LIQUID WATER

by

M. Orentlicher and P. O. Vogelhut

Memorandum No. ERL-M165

30 June 1966

ELECTRONICS RESEARCH LABORATORY

College of Engineering
University of California, Berkeley
94720

Manuscript submitted: 12 May 1966

The research reported herein was supported in part by the National Institutes of Health, Bioengineering Training Program PHS 1418 and in part by the Joint Services Electronics Program (U.S. Army, U.S. Navy, U.S. Air Force) under Grant AF-AFOSR-139-66.

NOMENCLATURE

Thermodynamic Terms

A	Helmholtz energy (molar)
A_1	Polar-liquid energy (molar)
E	Molar energy
N	Total molecules
p	Pressure
R	Gas constant
T	Absolute temperature
V	Total volume
v	Molar volume
ρ	Molar density
α	Coefficient of thermal expansion

Parameters of Water

b_c	Molar volume of hypothetical water lattice
E_H	Energy of hydrogen bond
a_1, a_2	Empirical parameters for polar-liquid energy
d	Empirical parameter for free volume

Other

g	Dipole correlation factor of Kirkwood
g_i	Degeneracy factor for i-bound molecule
i	Number of hydrogen bonds to a molecule
m	Dipole moment
n	Total number of hydrogen bonds
n_i	Number of i-bound molecules

Other- Cont'd

Q	Partition function for lattice with independent sites
q_i	Paritition function for i-bound molecule
r	Rate of a process
v_f	Free volume
y_i	Mole fraction of i-bound molecule
ϵ	Dielectric constant

Superscripts

0	Triple point
c	Critical point

STRUCTURE AND PROPERTIES OF LIQUID WATER

Abstract

The properties of liquid water are shown to be explicable in terms of a short-range tetrahedral structure. Conclusions regarding transport processes in liquid water are of biological importance.

INTRODUCTION

In this paper, conclusions regarding water structure are presented based on analyses of the dielectric, thermodynamic, spectroscopic, and transport properties of liquid water. These properties could be interpreted in terms of a short-range (nearest neighbor) tetrahedral structure which persists to temperatures beyond the normal boiling point.

The results also indicate that the amount of nonhydrogen-bound water is negligible at the triple point but rapidly increases to more than one fourth of the total molecules at 40°C. This result supports the view that unbound water dominates rate processes in biological systems.

In the first section of this paper, current theories about liquid water are briefly reviewed. The following sections deal with the properties listed above.

THEORY OF LIQUID WATER

Geometry and Energetics of Liquid Water

In order to understand the behavior of liquid water at equilibrium it is necessary to explore two primary areas. One is the statistical-geometric problem of describing the average configuration of the molecules composing the liquids. This problem has been most successfully attacked by Bernal[1, 2] and Pauling.[3] The second and more difficult problem is that of the energy of the water structure. This has been the subject of several papers by Coulson and his co-workers.[4]

The persistence of tetrahedral coordination in liquid water makes a lattice description of the liquid unusually apt. Bernal and Fowler[1] gave the first quantitative description of a water lattice. The parallels between the forms of ice and those of quartz caused them to seek a model for water in the high density, trydimite form of quartz. The study of clathrates now supplies new models for tetrahedrally coordinated structures. Pauling[3] describes the pentagonal dodecahedra that form the clathrate lattice. Bernal[2] adapts the ideas of Pauling and posits a "complicated arrangement" of "pentagonal rings" to describe the persistence of tetrahedral coordination in the liquid. He also states the belief that the H-bond system of water is almost intact at the triple point.

Coulson[4] gives estimates of the contributions to the energy per H-bond in ice. Recently, one of his students, Eisenberg,[5] made a more refined computation of the electrostatic term. In the following table, Eisenberg's figure replaces Coulson's original estimate. Otherwise, this is the same as Coulson's Table 33.[4]

TABLE 1

Estimated Energy Contribution per H-bond in Ice

A.	Electrostatic	4.2	
B.	Delocalization	8	
C.	Repulsive overlap	-8.4	
D.	Dispersion forces	3	
	Total	6.8	expt. 6. Kcal.

Not only will all these figures be different for liquid water, but the uncertainty about individual contributions for ice is quite high. A manageable apportionment of energy contributions for liquid water can be obtained by decreasing the number of categories to two, one short-range and one long-range. In this paper, the short-range contributions, B and C, are grouped together as the energy of a hydrogen bond, E_H. Table 1 indicates that this term is small, and we know it must be positive from the existence of the tetrahedrally coordinated structure. The long-range contribution is composed of A and D. It seems conservative to set A for liquid water at 3-4 Kcal, and estimates of D vary from 1 to 3 Kcal. Therefore, the long-range term must be in the range of 4-7 Kcal. per H-bond. But the total energy is 6, so the range of this term is limited to 4-6. We denote this term as the polar-liquid energy.

We can summarize the results of this review by describing liquid water as having a labile structure maintained by H-bonds of an energy 0-2 Kcal. The long-range interactions between molecules in this structure are the same as those present in any polar liquid and contribute 4-6 Kcal. per H-bond to the stabilization of the liquid.

Quantitative Descriptions of Water

There has been no adequate quantitative description of water to this time, but there does seem to be a line of development to which this paper belongs. The initial point is marked by the calculations of Nemethy and Scheraga[6] who computed the thermodynamic properties of liquid water from the partition function of a lattice that contained molecules with 0 to 4 H-bonds. Since their model was independent of volume, they were only able to deal with strictly thermal properties. Their success was quite respectable when one considers they used only two adjustable parameters. A critique of their work was made by Vand and Senior[7] who introduced a degeneracy factor for the various H-bonded species. We find that the introduction of this factor leads to a better description of liquid water than could be obtained if it were neglected.

The model for our calculations differs from that of the earlier work by considering the fluid as spanned by a single structure at any instant rather than filled by "clusters." Either model must be considered a heuristic device to facilitate quantitative formulations, rather than a geometrical description of the liquid.

PROPERTIES OF LIQUID WATER

Dielectric Constant

The dielectric constant of water serves to confirm our ideas of water as a structure. Water would have only a third of its measured dielectric constant if it behaved as a normal polar liquid. Non-associating polar liquids with considerably higher dipole moments than water can be accurately described by the continuum theory of Onsager.[8]

This theory predicts a value for the dielectric constant of about 35 at $0^{\circ}C$ when its true value is almost 90.

Some calculations of the dielectric constant were made in order to determine the nature of the water lattice. The first property required for such a calculation is the dipole moment, m, of a molecule in liquid water. Eisenberg[5] calculates a value of 2.59 D for the dipole moment in ice. A value of 2.51 D for the dipole moment of a molecule in liquid water is computed from continuum theory. The difference is small enough to encourage the use of Eisenberg's value for the liquid. At temperatures above $40^{\circ}C$, the increase in the volume of water causes a decrease in the dipole moment. This decrease can be handled adequately with continuum theory since its effect is small.

The structure of liquid water enters through a correlation factor, g, introduced by Kirkwood.[9] In ice, where the correlation is long range, the value of g is 2.91; while for correlation including only nearest neighbors, g is 2.34.[10] Our "labile structure" must include the nearest-neighbor correlations, but only some fraction of the longer-range terms. For simplicity, we set this fraction at zero, so g is 2.34.

At the triple point, these values of g and m predict a value of gm^2 of 1.57 D^2. An empirical fit of the Kirkwood equation to dielectric data of water[11] resulted in a value of $gm^2 = 1.55\ D^2$ at the triple point.

The dielectric constant of this water lattice is

$$\epsilon = 2.3 + 4.5\,(gm^2/3RT)\,((1-5\rho^0)/(1-5\rho))^2. \qquad (1)$$

If non-bonded molecules are not tetrahedrally coordinated in the water lattice, their contribution to the dielectric constant should be adequately described by continuum theory. This would cause the dielectric constant to be reduced by the following amount, where m_0

is the dipole moment given by continuum theory.

$$4.5\rho(y_0(gm^2-m_0^2)/3RT)((1-5\rho^0)/(1-5\rho))^2.$$

Both Eq. (1) and the result of deducting the above are compared to the experimental results of Akerlof and Oshry[12] in Fig. 1.* It is clear that the assumption of all molecules bound to the lattice is more accurate. But the accuracy of Eq. (1) decreases as the temperature increases. Since water behaves more like a normal liquid as the temperature increases past the boiling point, use of a lattice model is dubious at higher temperatures. The critical conditions for stability of the lattice will be examined after the thermodynamic properties of water are calculated.

These results imply that:

1. Water molecules are tetrahedrally oriented in the liquid, but the long-range order of ice is absent.

2. There are few, if any, freely rotating molecules at temperatures below the boiling point.

Partition Function of Liquid Water

To formulate a partition function for liquid water, we use a simple cell model. Consider a volume, V, containing N molecules. The volume is divided into N cells, each containing one molecule. The molecules may have zero to four bonds each, n_i molecules being the number with i bonds. When the correlations between "i" values for adjacent cells are neglected, it is simple to write the partition function for the liquid if the potential energy in each cell is known. We will assume the same constant potential in each cell, the polar-liquid energy previously discussed, and write the result in terms of the

---

* Calculation of the fraction non-bonded molecules, y_0, is given in a later section.

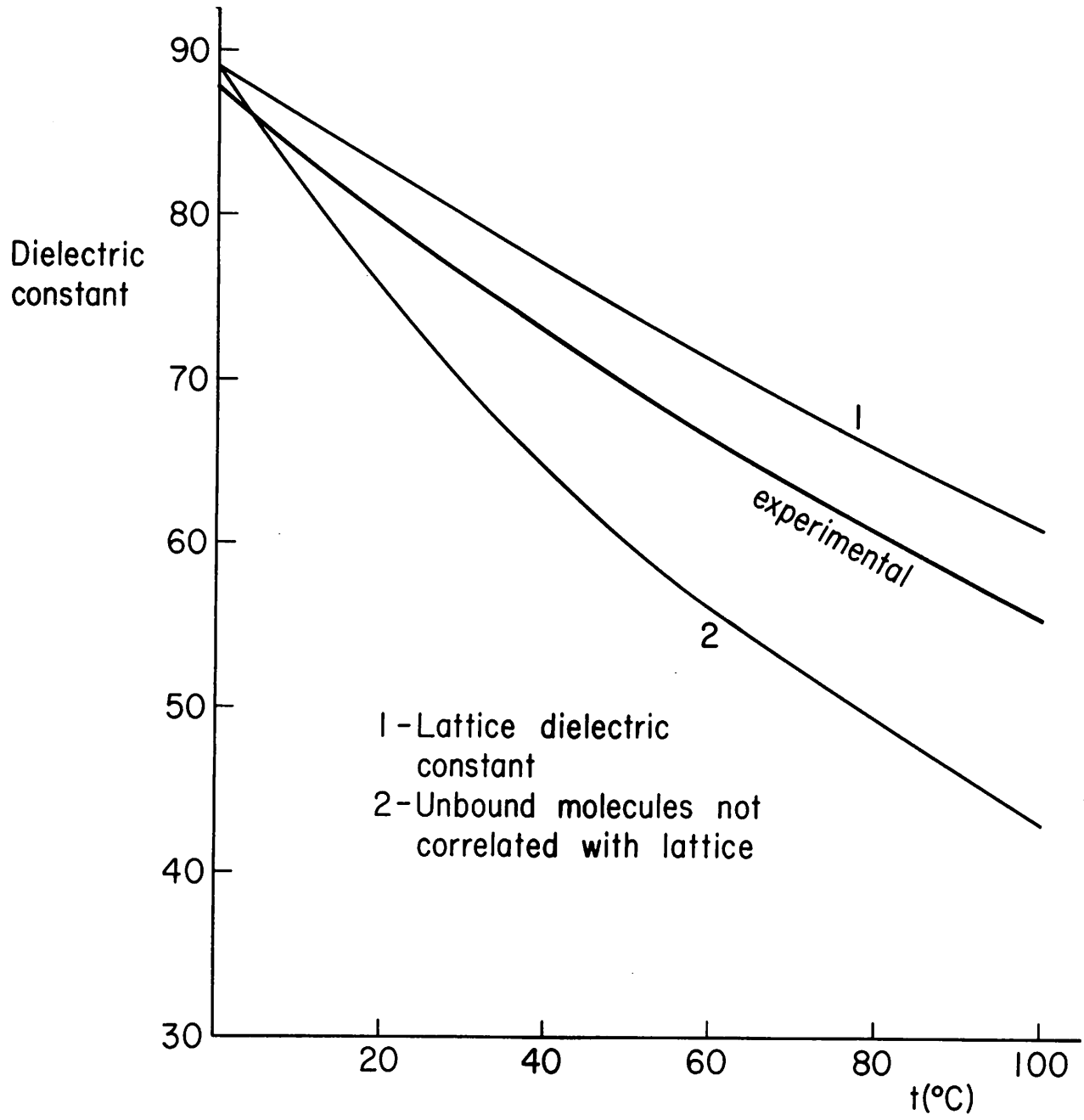

Fig. 1. Dielectric Constant of Liquid Water

Helmholtz energy, A. The polar energy is denoted by A_1.

$$-A/RT = -A_1/RT + nE_H/RT + \ln Q + 1 \tag{2}$$

$n = in_i/2$, number of H-bonds

$$Q = N! \prod_{1=0}^{4} [(g_i q_i)^{ni}/n_i !] .$$

The problem now divides into three parts: specify A_1, specify $g_i q_i$, find the n_i in terms of T, V, N, and the other parameters.

1. Polar Liquid Energy, A_1

In the absence of a theoretical value for this quantity, we specify a form with constants to be found empirically.

$$-A_1 = N a_1 \rho/(1-a_2 \rho) \tag{3}$$

The second constant a_2 is introduced to account for the effect of the lattice on the pair interactions. (A similar form appears in the continuum theory of polar liquids.)

2. Cell Partition Function

The g_i are those of Vand and Senior.[7] The q_i are single molecule partition functions for the motions of the molecule within its cell. For $i > 0$, the functions of Nemethy and Scheraga[6] are taken. These are functions of temperature only, $f_i(T)$.

For q_0 we use the same basic form as Nemethy and Scheraga but modify the content. $q_0 = v_f f_0(T)$.

We experimented with two formulations of f_0. Both leave the unbound molecule free to translate in its free volume, but the first did not allow free rotation while the second allowed all three degrees of free rotation. The latter could fit the volumetric properties of water only when all molecules were unbound. Since this contradicts both the

dielectric constant results and the spectroscopic data for water, we settled for no free rotations.

3. Distribution of Molecules, n_i

The n_i are obtained by maximizing the Helmholtz energy at constant T, V, and N. The result is given in terms of the fractions at each i, y_i.

$$i > 0, \quad y_i = g_i f_i(T) \exp\left(\frac{iE_H}{2RT}\right) / Q^*, \tag{4}$$

$$y_0 = g_0 f_0(T) v_f \exp(\Delta)/Q^*,$$

$$\Delta = \left(\frac{\partial \ln(v_f)}{\partial \ln(y_0)}\right)_{\rho, T}$$

$$Q^* = g_0 f_0(T) v_f \exp(\Delta) + F$$

$$F = \sum_{i=1}^{4} q_i f_i(T) \exp\left(\frac{iE_H}{2RT}\right) \tag{5}$$

Free Volume and Thermodynamic Functions of Water

It was necessary to specify the free volume, v_f, before the thermodynamic properties could be computed. Since an a priori value was not available, an approximation was employed. A more detailed model of water was constructed for computing an approximate v_f without using added adjustable parameters.

The water lattice becomes more irregular as the temperature rises. Due to this disruption, the specific volume of water, v, will differ from that of a perfect lattice, b_c. To the difference between v and b_c we added a term linear in y_0 to obtain the free volume.

$$v_f = v - b_c + y_0 d.$$

Floating constants were avoided by the restrictions that at the triple point both v_f and y_0 are zero. This could be rephrased anthropomorphically as follows: liquid water at the triple point, T^0, exists as a structure that squeezes out all free volume, and therefore has no unbound molecules.

The temperature dependence of b_c was needed to complete the specification of the free volume. For simplicity we take

$$b_c = b_c^0(1 + \alpha(T-T^0))$$

with α having the value of the thermal expansion coefficient of ice at the triple point. Neither the linear expression nor the choice of α can be expected to be accurate, but they can cause only relatively small errors in the thermodynamic property predictions.

These results allow us to write the thermodynamic properties of water as functions of T, V, N. From our definitions of A and A_1, it is clear that our zero for energy and entropy is an ideal tetrahedrally-coordinated lattice with no forces between molecules, at the absolute zero of temperature. This means that the energy of the "real" lattice at absolute zero is the heat of sublimation.

From Eq. (5),

$$\Delta = y_o d/v_f,$$

$$-A/NRT = a_1\rho/RT(1-a_2\rho) + \ln Q^* + 1 - y_0\Delta, \tag{6}$$

$$p/\rho RT = -a_1\rho/RT(1-a_2\rho)^2 + y_0/\rho v_f, \tag{7}$$

$$-E/N = a_1\rho/(1-a_2\rho) + y_0 \frac{d\ln f_0}{d(1/RT)} + (1-y_0)\frac{d\ln F}{d(1/RT)} + \Delta(b_c^0/d)\alpha RT^2 \tag{8}$$

An explicit equation for y_0 is obtained by combining Eqs. (4) and (7) with p = 0.

$$y_0 = (a_1/RT)\,[\,(v-b_c)/((v-a_2)^2 - a_1 d/RT)]\,. \qquad (9)$$

At this point we note three weak points in our model that prevent exact calculation of thermodynamic properties. These are:

1. Use of an ad hoc, constant coefficient of thermal expansion for the lattice,
2. Neglect of partial rotation of unbound molecules,
3. Neglect of possible free translation for dimers.

Prediction of Thermodynamic Properties

We have three adjustable parameters to fit to thermodynamic properties. These three parameters are fit as follows: E_H is fit to the triple point volume, a_1 is fit to the volume at 40°C, and a_2 is fit to the triple point energy. The parameters are listed in Table 2.

TABLE 2

Parameters of Liquid Water

b_c^0	18.01 cc/mole
α	$1.58 \times 10^{-4}/^{\circ}K$
d	0.29 cc/mole
E_H	1025.6 cal/mole
a_1	0.382×10^5 cal-cc/mole
a_2	13.33 cc/mole

There was a 0.01 cc/mole uncertainty in d which leads to a 2 percent uncertainty in E_H, and 1 and 3 percent uncertainties in a_1 and a_2, respectively. The polar energy per H-bond of a perfect lattice at the triple point volume is $1/2\, a_1/(v-a_2) = 4.1$ Kcal/mole.

Thus, our estimates of both the short-range and the long-range energies are confirmed.

In Fig. 2 we compare the experimental and predicted entropy, heat capacity, and volume up to the boiling point. The difference observable in the entropy is most likely due to our choice of α. But the high-temperature deviations may be caused by the factors mentioned in the preceding section.

Stability of the Water Lattice

From the conditions $(\frac{\partial p}{\partial v})_T = 0$, $(\frac{\partial^2 p}{\partial v^2})_T = 0$, the relation between the critical volume and the critical temperature of the water lattice is derived.

$$v^c = a_2 + 8a_1/9RT^c$$

The intersection of this equation with the experimental saturation curve for water gives the following critical parameters.

$$T^c = 617^oK,$$

$$v^c = 41 \text{ cc/mole}.$$

Comparison with Spectroscopic Data

Spectroscopic data give more direct access to the molecular domain. Unfortunately, interpretation is not simple, and the raw data always require processing which is somewhat subjective. Useful information has already been obtained about water structure from NMR as well as the IR and Raman spectra of the liquid.

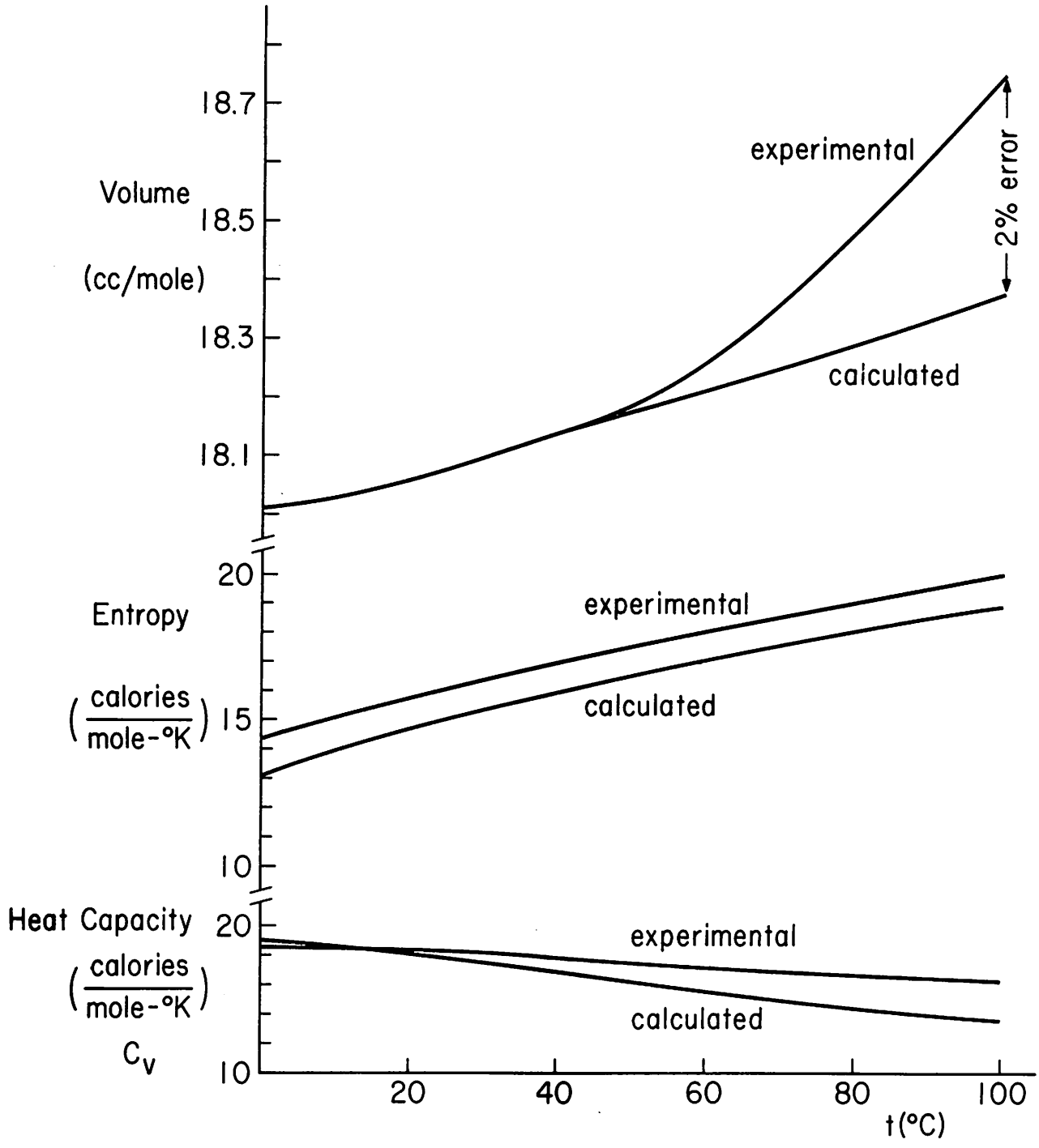

Fig. 2. Thermodynamic Properties of Liquid Water

In recent work on the Raman spectrum of water, Walrafen[13] describes liquid water as follows:

"On a time scale of 10^{-13} sec, liquid water appears to possess an intermolecular structure which involves tetrahedral hydrogen bonding. This structure is readily disrupted by increase of temperature. This disruption, which involves nearest-neighbor structure, is thought to produce a new species which engages in few or no hydrogen bonds.... ...The non-hydrogen-bonded molecules, then, would refer to molecules restrained by predominately noncovalent interactions...."

This picture is identical to that used in constructing our model. In Fig. 3 we show the temperature variation of y_0 predicted by our theory. It shows a rapid increase in unbound molecules near the triple point (0.01/C) which rate has fallen by more than half at 40°C and is about 0.001/C at the boiling point. Figure 3 also shows a comparison of the predicted fraction of unbroken H-bonds to those estimated from IR and Raman spectra. The agreement is satisfactory.

Another interesting spectroscopic investigation is described by Glasel.[14] From the NMR spectra of H_2O^{17} he shows that:

1. There was no O^{17} absorption from ice, only a vague absorption from water below 4°C, and a gradually sharper absorption as the temperature increased, and

2. Solid xenon hydrate gives a spectrum similar to that of water at a lower temperature, and the liquid solutions of xenon consistently have spectra similar to those of water at a lower temperature.

The first result seems to imply that the NMR response is from unbound H_2O and that the fraction of unbound molecules increases at first rapidly and then more gradually with increasing temperature. The second result reinforces our belief in the Pauling-Bernal model of liquid water.

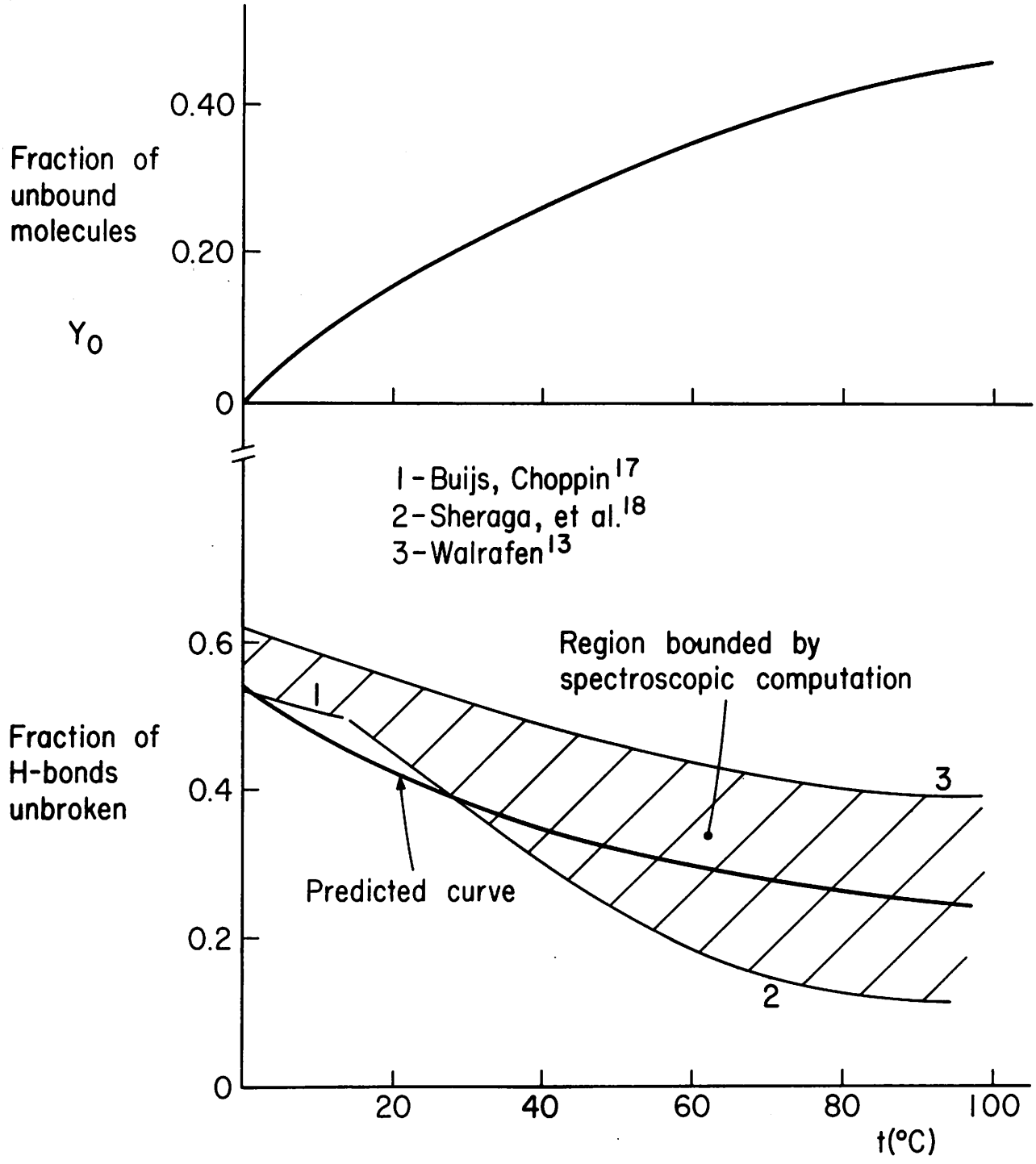

Fig. 3. Variation of Water Structure with Temperature

Rate Processes in Liquid Water

Our results allow certain qualitative statements about rate processes in water. First we note two important experimental facts.

1. Activation energies for rotational processes (proton transport, dielectric relaxation) are lower than for translational processes (viscosity, diffusion). At 0-20°C, $E_{rot} \simeq 3.$ Kcal/mole and $E_{trans} \simeq 5.$ Kcal/mole.

2. Activation energies for both types of processes decrease as the temperature increases.[15, 16] An apparent break in activation energy frequently occurs at around 40°C. For example, Glasel[14] found a "distinct break" in the activation energy for NMR relaxation at 30°C.

A possible source for this temperature dependence appears when we write the rate for any process as a sum over the five water states.

$$r = \sum_{i=0}^{4} y_i r_i$$

$$- E = \frac{d \ln r}{d\, 1/RT} = \frac{d \ln}{d\, 1/RT} \left(\sum_{i=0}^{4} y_i r_i \right) \tag{10}$$

If the dominant mode of transport is through one state, the apparent activation energy is,

$$- E = \left(\frac{d \ln y_i}{d\, 1/RT} \right) + \frac{d \ln r_i}{d\, 1/RT} \, . \tag{11}$$

Clearly, a transition from one mode to another will give the apparent break.

Both 0- and 1- bound molecules can rotate without breaking an H-bond, and the activation energy for a 1-bound molecule translation should only be about E_H or 1 Kcal/mole higher than that for an unbound

molecule. More highly bound molecules would have relaxation rates similar to those of ice, which are orders of magnitude lower than those of liquid water.

At low temperatures, y_1 is nearly independent of temperature, $\frac{d \ln y_1}{d 1/RT} \simeq 0.3$ Kcal/mole. Also, the number of 1-bound molecules with sufficient energy to break their H-bound is relatively large, $y_i \exp(-E_H/RT) \simeq 0.05$.

In contrast to this, y_0 is highly temperature dependent, $\frac{d \ln y_0}{d 1/RT} \simeq -10$ Kcal/mole at $t \leq 20^\circ C$, and $\frac{d \ln y_0}{d 1/RT} \simeq -3$ Kcal/mole at $40^\circ C$. The value of y_0 increases from 0 at the triple point to about 0.15 at $15^\circ C$ and 0.27 at $40^\circ C$.

From these numbers it is clear that the dominant mode for rate processes will be through 1-bound species below $20^\circ C$. Both 0- and 1-bound species will contribute between 20° and $40^\circ C$.

Above $40^\circ C$, y_0 becomes larger than y_1 and the temperature dependence of y_0 is comparable to that of rate processes in water, $-\frac{d \ln y_0}{d 1/RT} = 2\text{-}3$ Kcal/mole. Therefore, the dominant mode for rate processes at these temperatures is through the unbound water.

These conclusions are consistent with the hypothesis that the H_2O^{17} NMR signals detected by Glasel[14] were from unbound water molecules. They are also in general agreement with the conclusions of Horne and Johnson[16] on the role of unbound water in proton transport.

CONCLUSION

Our results indicate a highly labile structure for liquid water. That this structure can be readily perturbed is clearly shown by the variety of forms taken by clathrates and ice[2] as well as by NMR studies.[14] The reality of the structure in pure water is indicated by both our dielectric constant and our thermodynamic calculations.

From the thermodynamic properties of water we were able to estimate the fractions of water molecules with zero to four hydrogen bonds. The rarity of unbound molecules at temperatures below 20°C and their abundance at temperatures above 40°C seem to explain the temperature dependence of rate process activation energies. Also, the fact that the unbound molecules are not quite dominant at biological temperatures allows for control of the unbound fraction (and thereby rate processes) by biomolecule structures. This increases the interest of speculations by Horne and Johnson[16] on the role of unbound water in transport during muscle contraction.

Numerical results of importance are:

1. The short-range (H-bond) energy in water is 1 (Kcal/mole H-bond) and the polar-liquid energy is 4 (Kcal/mole H-bond) at the triple point,

2. The dipole moment of a water molecule at the triple point is the same as that in ice, 2.59 D.

REFERENCES

1. J. D. Bernal, R. H. Fowler, Trans. Far. Soc., 29, 148 (1933).
2. J. D. Bernal, Proc. Roy. Soc., A247, 421 (1958).
3. L. Pauling, The Nature of the Chemical Bond, Cornell, (1960).
4. C. A. Coulson, Valence, Oxford, (1961).
5. D. S. Eisenberg, Thesis, Oxford, (1964).
6. G. Nemethy, H. A. Scheraga, J. Chem. Phys., 36, 3382 (1962).
7. V. Vand, W. A. Senior, J. Chem. Phys., 43, 6 (1965).
8. C. J. F. Böttcher, Theory of Dielectric Polarization, Elsevier, (1952).
9. J. G. Kirkwood, J. Chem. Phys., 7, 911 (1939).
10. G. H. Haggis, J. B. Hasted, T. J. Buchanan, J. Chem. Phys., 20, 1452 (1952).
11. A. S. Quist, W. L. Marshall, J. Phys. Chem., 69, 3165 (1965).
12. G. C. Akerlof, H. I. Oshry, J. Am. Chem. Soc., 72, 2844, (1950).
13. G. E. Walrafen, J. Chem. Phys., 44, 1546 (1966).
14. J. A. Glasel, Proc. N. A. S., 55, 479 (1966).
15. K. Krynicki, Physica, 32, 167 (1966).
16. R. A. Horne, D. S. Johnson, Nature, 209, 82 (1966).
17. K. Buijs, G. R. Choppin, J. Chem. Phys., 39, 2035 (1963).
18. M. R. Thomas, H. A. Scheraga, E. E. Schrier, J. Chem. Phys., 69, 3722 (1965).