

A Discussion of the Expansivity and the Compressibility of Liquid Water

AASE HVIDT

Chemistry Laboratory III, H. C. Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

The expansivity, the compressibility and the internal pressure of water and other liquids at atmospheric pressure are compared. The anomalous behaviour of water is discussed on the basis of the assumption that structural equilibria exist in liquid water for which $\Delta H^\ominus \Delta V^\ominus < 0$. The discussion supports the conclusion that the structural transitions predominant in water at the lower temperatures are highly cooperative long-range interactions. It is tentatively suggested that the bulky low-energy state of water resembles "normal" liquids, but that the dense, high-energy state is atypical of liquids at atmospheric pressure.

In a recent paper¹ it is pointed out that a great many of the theories of liquid water presented with the years are essentially elaborations of the simple model of water proposed by Röntgen² nearly one hundred years ago. Röntgen suggested that liquid water is an "aggregate" of two molecular species. One is an "icelike" form which upon heating is converted to the other (less bulky) form. In Ref. 1 the model is described as two structural components of water in rapid equilibrium



B is a bulky ("icelike") form of a lower energy than the dense ("normal") form, D.

Experimental data on the variation of the enthalpy and the volume of water with temperature and pressure are discussed in Ref. 1 on the basis of the Röntgen model, and the discussion leads to the statement that "it is difficult to avoid the conclusion that the model is inadequate".¹

The present paper follows the lines of the approach suggested in Ref. 1, with only slight modifications. It is the aim of this sequel of the discussion to illustrate that available thermodynamic data on water are in accordance with the basic idea of Röntgen's model, that equilibria exist in liquid water, for which the changes in standard volume and enthalpy are of the opposite sign. The terms "icelike" and "normal" must, however, be used with care in attempts to characterize the two forms of water more closely.

EXPERIMENTAL DATA

Available experimental data on liquid water at atmospheric pressure are shown in Figs. 1–3. The (isobaric) thermal expansivity (the coefficient of thermal expansion), α , the (isothermal compress-

$$\alpha = V^{-1}(\partial V/\partial T)_P \quad (2)$$

ibility, κ , and the internal pressure, P_i , are plotted

$$\kappa = -V^{-1}(\partial V/\partial P)_T \quad (3)$$

$$P_i = (\partial U/\partial V)_T = T(\partial S/\partial V)_T - P \quad (4)$$

as functions of the temperature, see eqns. (2)–(4). Data on a few organic liquids are included in the figures for comparison with water.

Atypical features of water at atmospheric pressure, illustrated in Figs. 1–3, are

1. The thermal expansivity is below the normal range, and *negative* at temperatures below 4 °C.

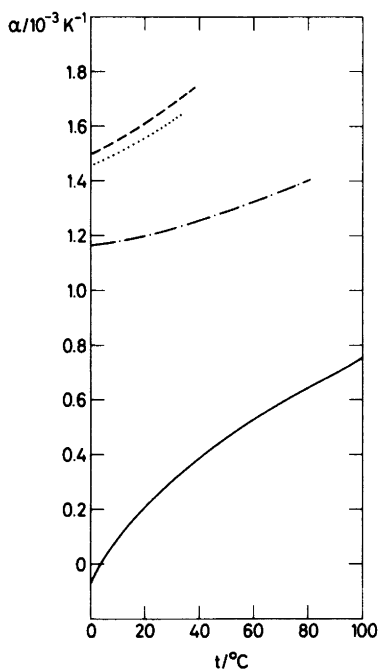


Fig. 1. Available data on the thermal expansivity at atmospheric pressure of water³ —, benzene⁴ ---, n-pentane⁴ ..., and diethyl ether⁴ -.-.

2. The compressibility is unusually low, and decreases with increasing temperature ($\partial\kappa/\partial T < 0$) at temperatures below 40 °C.

3. The internal pressure increases with increasing temperature from negative values below 4 °C to values above the normal range at temperatures above 60 °C.

The internal pressure of liquids at atmospheric pressure is normally about 300×10^6 Pa (i.e. $P_i \gg P \approx 0.1 \times 10^6$ Pa), slightly decreasing with increasing temperature. The negative values of P_i observed for water reflect the phenomenon that what keeps water molecules together in liquid water below 4 °C is not an energetic cohesion between the molecules ($\partial U/\partial V < 0$), but a positive entropic contribution to the free energy upon expansion ($-T(\partial S/\partial V) > 0$).

In the following, this anomalous behaviour of liquid water is tentatively discussed on the basis of the assumption that structural equilibria like (1) exist in liquid water, for which $\Delta H^\ominus > 0$.

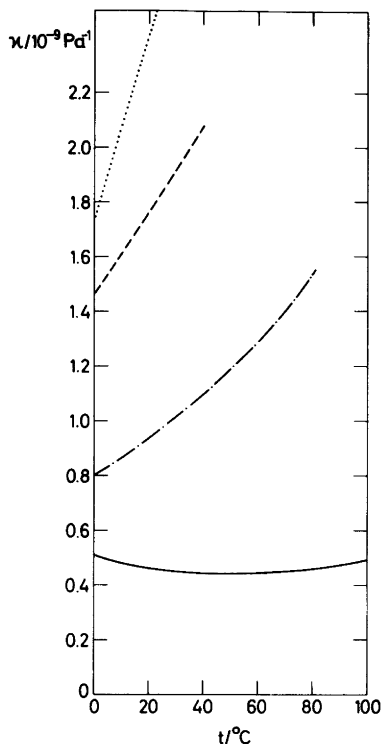
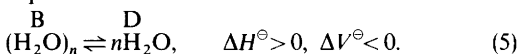


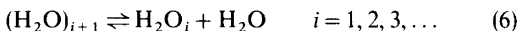
Fig. 2. Available data on the compressibility at atmospheric pressure of water³ —, benzene⁵ ---, n-pentane⁶ ..., and diethyl ether⁶ -.-.

THE MODEL

The equilibrium (1) is thought to be due to the ability of water molecules to associate through hydrogen bonding, and as such it is tentatively expressed as



The dissociation of a polymer of water to monomers does proceed through a series of reactions



but due to the kind of cooperation intrinsic to water association (in the sense that hydrogen bonding promotes hydrogen bonding) it is assumed that the distribution of i -mers in liquid water has a sufficiently sharp maximum (for $i = n$), that the formulation (5) is a reasonably good approximation of the reactions (6).

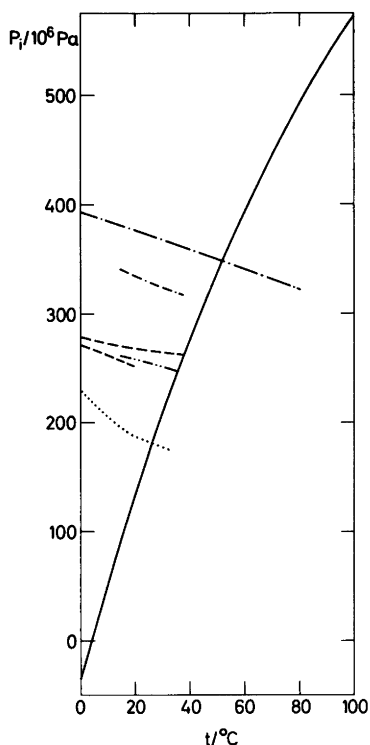


Fig. 3. The internal pressure $P_i = T\alpha/\kappa - P$ calculated on the basis of available data on water³ —, benzene^{4,6,7} ---, *n*-pentane^{4,6} ..., diethyl ether^{4,6,8} ----, heptane⁷ - · - ·, and acetone⁷ - - - - -.

In accordance with the procedure applied in Ref. 1 the molar volume and the molar enthalpy of water are expressed as

$$V = xV_D + (1-x)V_B = V_B + x\Delta V \quad (7)$$

and

$$H = xH_D + (1-x)H_B = H_B + x\Delta H \quad (8)$$

x is the fraction of water molecules present as monomers. $\Delta V = V_D - V_B$ (< 0), and $\Delta H = H_D - H_B$ (> 0) are the differences between the molar volume and the molar enthalpy, respectively, of water in the monomeric (dense) and in the associated (bulky) state. The relation between ΔV , ΔH and ΔV^\ominus , ΔH^\ominus of eqn. (5) is $\Delta V^\ominus = n\Delta V$ and $\Delta H^\ominus = n\Delta H$.

The temperature and the pressure dependence of the volume obtained from (7) and (8) are

$$\frac{\partial V}{\partial T} = x \underbrace{\frac{\partial V_D}{\partial T}}_{\text{static}} + (1-x) \underbrace{\frac{\partial V_B}{\partial T}}_{\text{relaxational}} + \Delta V \frac{\partial x}{\partial T} \quad (9)$$

and

$$\frac{\partial V}{\partial P} = x \underbrace{\frac{\partial V_D}{\partial P}}_{\text{static}} + (1-x) \underbrace{\frac{\partial V_B}{\partial P}}_{\text{relaxational}} + \Delta V \frac{\partial x}{\partial P} \quad (10)$$

The sum of the first two terms on the r.h.s. of these expressions (and of similar expressions following) is denoted the *static* contribution to the derivative, and the last term is denoted the *relaxational* contribution.

The equilibrium constant of (5) is

$$\frac{[\text{H}_2\text{O}]^n}{[(\text{H}_2\text{O})_n]} = K_c / (\text{mol dm}^{-3})^{n-1}$$

or

$$\frac{x^n}{(1-x)/n} = K_c V^{n-1} = K_x \quad (11)$$

In the following, the volume dependence of K_x is ignored and the subscript x of this constant is omitted, $K_x = K$.

It follows from (11) that

$$\frac{\partial \ln K}{\partial x} = \frac{n(1-x) + x}{x(1-x)} \quad (12)$$

so that the terms $\frac{\partial x}{\partial T}$ and $\frac{\partial x}{\partial P}$ in (9) and (10) may be expressed as

$$\frac{\partial x}{\partial T} = \frac{\partial x}{\partial \ln K} \frac{\partial \ln K}{\partial T} = \frac{x(1-x)}{n(1-x)+x} \cdot \frac{n\Delta H}{RT^2} = F(n,x) \frac{\Delta H}{RT^2} \quad (13)$$

and

$$\frac{\partial x}{\partial P} = \frac{\partial x}{\partial \ln K} \frac{\partial \ln K}{\partial P} = - \frac{x(1-x)}{n(1-x)+x} \cdot \frac{n\Delta V}{RT} = -F(n,x) \frac{\Delta V}{RT} \quad (14)$$

where $F(n,x) = nx(1-x)/[n(1-x)+x]$.

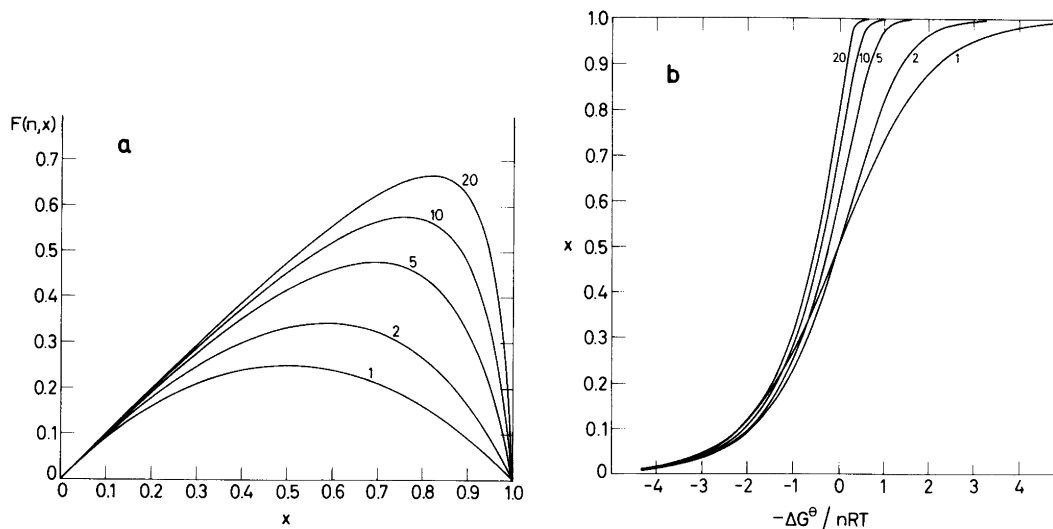


Fig. 4. *a.* $F(n,x) = nx(1-x)/[n(1-x)+x]$ calculated as a function of x for $n=1, 2, 5, 10$ and 20 . $F(n,x)$ enters the expressions (15) and (16) in the text. *b.* x as a function of $n^{-1} \ln K = -\Delta G^\ominus/nRT$, calculated according to eqn. (11) in the text for $n=1, 2, 5, 10$ and 20 . x is the fraction of water molecules present in the dense, monomeric state. ΔG^\ominus and n refer to eqn. (5). The values of n are indicated in the figure.

Expressions of the thermal expansivity, α , and the compressibility, κ , derived from eqns. (11)–(14), are

$$\alpha = \frac{1}{V} \frac{\partial V}{\partial T} = \frac{x}{V} \frac{\partial V_D}{\partial T} + \frac{(1-x)}{V} \frac{\partial V_B}{\partial T} +$$

$$F(n,x) \frac{\Delta V}{V} \frac{\Delta H}{RT^2} = \phi_D \alpha_D + \phi_B \alpha_B +$$

$$F(n,x) \frac{\Delta V}{V} \frac{\Delta H}{RT^2} \quad (15)$$

and

$$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P} = \phi_D \kappa_D + \phi_B \kappa_B + F(n,x) \frac{\Delta V}{V} \frac{\Delta V}{RT} \quad (16)$$

where $\phi_D = xV_D/V$ and $\phi_B = (1-x)V_B/V$ are the volume fractions of water in the monomeric and the associated state, respectively.

The function $F(n,x) = n \partial x / \partial \ln K$ as a function of x , and x as a function of $n^{-1} \ln K = -\Delta G^\ominus/nRT$, are shown in Fig. 4 for various values of n . Straight-forward calculations from (11) show that $F(n,x)$, or $\partial x / \partial (n^{-1} \ln K)$, exhibits a maximum ($F(n,x) = n/(1+n^2)$) for $x/(1-x) = n^2$, i.e. for $x = n^2/(1+n^2)$.

COMPARISON BETWEEN THE EXPERIMENTAL DATA AND THE MODEL

As already discussed by Röntgen² the negative expansivity of water below 4 °C is a strong indication that equilibria, for which $\Delta H^\ominus \Delta V^\ominus < 0$, play an important role in the volumetric behaviour of liquid water. Eqn. (5) is undoubtedly an oversimplification of the equilibria present in water, but this simple model may suffice as a starting point in a chemical-thermodynamic approach to the peculiar properties of water. The main purpose of the treatment suggested in this paper is to outline the possible influence of equilibria like (5) on the temperature dependence of the thermal expansivity and the compressibility of liquid water.

In eqn. (15) the thermal expansivity, α , is expressed as a sum of a static and a relaxational contribution. Experimental data on water (Fig. 1) indicate that at temperatures below 4 °C the (negative) relaxational contribution to α is numerically larger than the (positive) static one. The temperature dependence of α , however, suggests that the relaxational contribution vanishes rapidly with increasing temperature, such as is the case if, at 0 °C, $F(n,x)$ in eqn. (15) is about maximal (Fig. 4) or $\Delta G^\ominus/nRT$ of the equilibrium (5) is small and

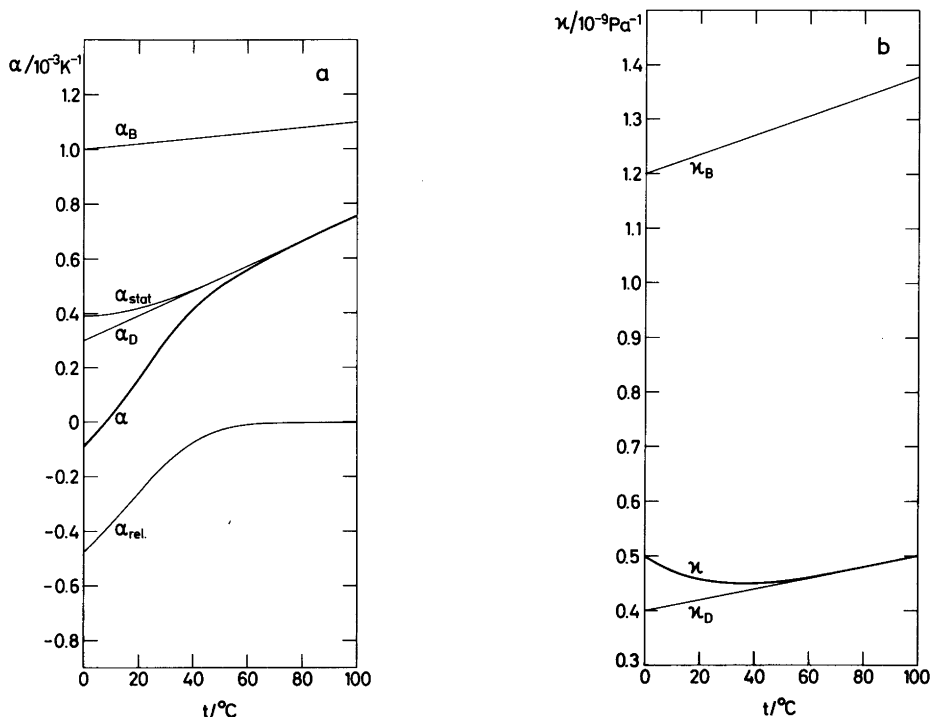


Fig. 5. The temperature dependence of the thermal expansivity (a) and the compressibility (b) of the water model calculated according to eqn. (15) and (16) for the following values of the thermodynamic quantities mentioned in the text: $\Delta H^\ominus = 75 \text{ kJ mol}^{-1}$, $\Delta S^\ominus = 300 \text{ J K}^{-1} \text{ mol}^{-1}$, $n = 15$, $\alpha_B = (1 + 10^{-3}t)10^{-3}\text{K}^{-1}$, $\alpha_D = 0.3(1 + 1.5 \times 10^{-2}t)10^{-3} \text{ K}^{-1}$, $\kappa_B = 1.2(1 + 1.5 \times 10^{-3}t) 10^{-9} \text{ Pa}^{-1}$, $\kappa_D = 0.4(1 + 2.5 \times 10^{-3}t) 10^{-9} \text{ Pa}^{-1}$. α_{stat} is the static contribution to the expansivity, $\alpha_{\text{stat}} = \phi_D\alpha_D + \phi_B\alpha_B$, and α_{rel} is the relaxational contribution, $\alpha_{\text{rel}} = F(n,x) \frac{\Delta H}{V} \frac{\Delta H}{RT^2}$ (see eqn. (15)). As it is explained in the text the relaxational contribution to the compressibility is vanishingly small.

negative, and if $\Delta H^\ominus = 50\text{--}100 \text{ kJ mol}^{-1}$, *e.g.* $\Delta H = 5\text{--}10 \text{ kJ mol}^{-1}$ and $n = 10$ (Fig. 5).

Fig. 5 illustrates the functions α and κ , calculated according to the eqns. (15) and (16) for the following values of the thermodynamic parameters of eqn. (5): $\Delta H^\ominus = 75 \text{ kJ mol}^{-1}$ ($n = 15$, $\Delta H = 5 \text{ kJ mol}^{-1}$), $\Delta S^\ominus = 300 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta V^\ominus = -30 \text{ cm}^3 \text{ mol}^{-1}$ ($\Delta V/V = -0.1$). For these values of the thermodynamic parameters x varies from 0.89 at 0°C to practically one at 100°C . The relaxational contribution to κ is vanishingly small ($F(n,x)(\Delta V)^2/VRT < 5 \times 10^{-12} \text{ Pa}^{-1}$ in eqn. (16)).

In the calculations illustrated in Fig. 5 it is assumed that the expansivity and the compressibility of water in the bulky state are within the normal range for liquids at atmospheric pressure, $\alpha_B = 10^{-3} \times$

$(1 + 10^3t)\text{K}^{-1}$ and $\kappa_B = 1.2 \times 10^{-9}(1 + 1.5 \times 10^{-3}t) \text{ Pa}^{-1}$, but the expansivity and the compressibility of water in the dense state are assumed to be smaller, and more strongly dependent on the temperature, $\alpha_D = 0.3 \times 10^{-3}(1 + 1.5 \times 10^{-2}t)\text{K}^{-1}$ and $\kappa_D = 0.4 \times 10^{-9}(1 + 2.5 \times 10^{-3}t) \text{ Pa}^{-1}$. Had it not been for the tradition, which dates back to Röntgen,² to call the bulky state of water "icelike" and the dense state "normal", these assumptions might not have seemed surprising. Bulky liquids are generally more compressible than dense ones, and flexible chains of associated water molecules do in many respects resemble the molecules present in normal liquids. The atypical liquid state of water is the dense, monomeric state; with respect to volume properties this state appears "solid-like", but with respect to

enthalpy or entropy it seems rather "gas-like".

A comparison between the calculated curves in Fig. 5 and the experimental curve in Figs. 1 and 2 shows a fairly good agreement between the calculated and the experimental data. No attempt has been made to estimate the values of the parameters of the model by a numerical fitting to the experimental data. The choice of values underlying the curves in Fig. 5 is based on a judgement in great outline of the data in Figs. 1–3, combined with the observation^{1,9} that at pressures above 5×10^8 Pa (5000 atm) the thermal expansivity of water at 25 °C is about "normal". For $\Delta V^\ominus = -30 \text{ cm}^3 \text{ mol}^{-1}$, we have $\partial \ln K / \partial P = -\Delta V^\ominus / RT \cong 10^{-8} \text{ Pa}^{-1}$, so an increase in pressure of 5×10^8 Pa, or more, will significantly perturb the equilibrium (5) in favour of the dense state. This dense state of liquid water apparently resembles other liquids elevated pressures.^{1,9}

The presence in liquid water of equilibria for which $\Delta S^\ominus = 300 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta V^\ominus = -30 \text{ cm}^3 \text{ mol}^{-1}$, i.e. $\Delta S^\ominus \Delta V^\ominus = -10 \text{ J K}^{-1} \text{ cm}^{-3} = -10^7 \text{ Pa K}^{-1}$ may counterbalance the positive value of $\partial S / \partial V \cong 10^6 \text{ Pa K}^{-1}$ which is common of liquids at 0 °C (see Fig. 3 and eqn. (4)), and thus explain the negative internal pressure of water at this temperature. The value of $\Delta H^\ominus = 75 \text{ kJ mol}^{-1}$ makes ΔG^\ominus slightly negative at 0 °C, and accounts for the temperature dependence of α and P_i .

The equilibria are assumed to be associations-dissociations of the water molecules through hydrogen bonding. Estimates of the strength of a hydrogen bond between water molecules are uncertain,¹⁰ but the above-mentioned values of ΔH^\ominus , ΔS^\ominus and ΔV^\ominus seem to show, that the structural transitions predominant in liquid water at the lower temperatures involve many hydrogen bonds ($n=15$ in eqn. (5)). In the primitive model of water here discussed it is implicitly assumed that n is independent of the temperature, and the presence of dimers, trimers etc. of water is ignored. There is all experimental evidence that lower associates of the molecules exist in liquid water,¹⁰ and they ought to be taken into account in more refined water models.^{11,12}

CONCLUSIONS

Experimental data on the expansivity and the compressibility of water indicate that the molecules in liquid water fluctuate between bulky low-energy states and dense high-energy states. The large changes in enthalpy, entropy and volume of the

fluctuations predominant at the lower temperatures suggest that the fluctuations are due to highly cooperative, long-range structural transitions of the water molecules. Judged from the experimental data considered, the bulky state of water resembles other liquids at atmospheric pressure, but the dense state is atypical.

REFERENCES

1. Kauzmann, W. In Alfsen, A. and Berteaud, A. J., Eds., *L'Eau et les Systèmes Biologiques*, Editions du Centre National de la Recherche Scientifique, 15, quai Anatole-France, 75700 Paris, (1976), p. 63.
2. Röntgen, W. C. *Annalen der Physik und Chemie, Neue Folge* 45, 281 (1892) 91.
3. Kell, G. S. *J. Chem. Eng. Data* 20 (1975) 97.
4. Landolt-Börnstein *Physikalisch-Chemische Tabellen II*, 5. Auflage (1923) 1232.
5. *Handbook of Chemistry and Physics* 55 (1974–1975) F-16.
6. Landolt-Börnstein *Physikalisch-Chemische Tabellen I*, 5. Auflage (1923) 97–100.
7. Westwater, W., Frantz, H. W. and Hildebrand, J. H. *Phys. Rev.* 31 (1928) 135.
8. Hildebrand, J. H. *Phys. Rev.* 34 (1929) 984.
9. Frank, H. S. *Science* 169 (1970) 635.
10. Eisenberg, D. and Kauzmann, W. *The Structure and Properties of Water*, Oxford Univ. Press, Oxford 1969.
11. Némethy, G. and Scheraga, H. A. *J. Chem. Phys.* 36 (1962) 3382.
12. Owicki, J. C. and Scheraga, H. A. *J. Am. Chem. Soc.* 99 (1977) 7403.

Received April 25, 1978.