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Isobaric heat capacity and structure of water and heavy water in the liquid state

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Abstract

The isobaric heat capacity of liquid H_2O, C_p, as a function of temperature, decreases between 0° and about 35°C and then increases up to 100°C. Analogous behaviour is shown by liquid D_2O. A statistical thermodynamic model has been applied to the experimental heat capacity data. The behaviour is explained by assuming that an equilibrium $A + B = AB$ is established between clusters A and AB of water of different composition. The total heat capacity is considered as the sum of three terms $C_p = (1 - \alpha)C_{p,0,AB} + \alpha C_{p,0,A} + \Delta C_{p,app}$. The term $\Delta C_{p,app}$ depends explicitly on the reaction enthalpy. In H_2O, the enthalpy $\Delta H = -1.84\,kJ\,mol^{-1}$ for the dissociation reaction and the heat capacity $C_{p,B} = 47.8\,J\,K^{-1}\,mol^{-1}$ for free water molecules are calculated. Analogous calculations performed for D_2O yield the enthalpy, $\Delta H = -1.64\,kJ\,mol^{-1}$ and the heat capacity, $C_{p,B} = 49.18\,J\,K^{-1}\,mol^{-1}$.

Keywords: Isobaric heat capacity; Heavy water, D_2O; Statistical thermodynamic model; Water

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1. Introduction

Liquid water shows peculiar properties very distinct from those of many other liquids [1], e.g., the high dielectric constant, the high heat capacity, and the high heat of vaporization. Further peculiar properties are the viscosity, which is low, and density, which is higher in the liquid than in the solid state. Because of these properties, liquid water plays an important role in most biological processes. The dielectric constant of liquid water is one of the highest known and explains the high solubility in water of

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ionic substances, because of the weakening effect on inter-ion attraction. The high heat capacity of liquid water is one of the main factors that come into play in the regulation of the body temperature in homeothermal animals or in the protection of plants from the damaging effects of temperature fluctuations. The high heat capacity of liquid water prevents superheating in man and some other perspiring (sweating) animals. The specific properties of water, however, make the liquid very difficult to study by simple application of treatments and models working for other liquids.

The best reference structural model for the study of liquid water is the structure of ice at ordinary pressure. The knowledge of the crystal structure of ice has been the starting point for characterization both of the assembly of water molecules and of single water molecules, even by means of quantum mechanical calculations. It has been established that the bond length is $O–H = 0.957\,Å$ and the H–O–H bond angle is $104°31'$ in accordance with a nearly tetrahedral arrangement. The electrons can be represented by a charge density cloud presenting beyond the normal density along the bond also lobes encompassing the *lone-pairs* which extend above and below the H–O–H plane and point backward relative to the hydrogens. The whole structure can be represented as a distorted tetrahedron where two vertices are occupied by H and two by *lone-pairs*. The dipole moment is 1.83 D and the quadrupole moment is -5.6×10^{-26} e.s.u.

The fact that melting point, boiling point and critical temperature are so high in comparison with those of the isoelectronic species Ne and CH_4 is attributed to the water dipoles (and higher multipoles) and also to the hydrogen bonds between water molecules. The hydrogen bond is an interaction involving a proton of one molecule and a *lone-pair* of another. The existence on each water molecule of two protons and two *lone-pairs* in an approximately tetrahedral arrangement produces the formation of a channel delimited by hydrogen bonds in the tetrahedral structure of ice. In this structure, the distances O–O are equal ($O–O = 2.76\,Å$) and the O–O–O angles are approximately tetrahedral. The protons lie almost exactly along the O–O line, each being about 1.0 Å from oxygen. On the whole, the structure of ice turns out to be rather rich in empty space, which explains the lower density of ice than that of liquid water.

2. Structural models for liquid water

The tetrahedral coordination characterizing the structure of ice is inefficient at completely filling the space available [2]. The fact that the liquid water formed when ice melts is denser than ice itself can be considered in terms of a liquid structure in which every void space is modified either by filling it (partially or completely) or by reducing it to the variable dimensions of bond-bending. Several different models have been proposed to explain the behaviour of liquid water; each assumes a different degree of polymerization, a different percentage of hydrogen bonds and a different type of *ice-like* structure with the possibility that non-bonded water molecules be located in the empty space at the centre of groups of molecules packed in a tetrahedral arrangement.

The peculiar properties of liquid water have been explained on the basis of the existence of two distinguishable species at equilibrium [3–9]. By assuming that water is formed from a mixture of the two distinct species, one voluminous and of low energy and another one dense and highly energetic, it is possible to calculate the aforementioned properties of liquid water. In such models, water should be regarded as a mixture [10].

A completely different proposal concerning ice melting has been put forward by Bernal and Fowler [11]. These authors assume that the hydrogen bond can be bent although not broken. They think that ice melting is a collapse of the crystal giving rise to a "uniform" structure characterized by a statistical average degree of bond bending which can be altered by variations of temperature and pressure. A mechanical–statistical discussion of a model bond-bending has been given by Pople [12]. A development of the "uniform" view has been the introduction of casuality. Examples are the concept of intrinsic disorder as typical of the liquid state as discussed by Bernal [13] and that of casual channel as discussed by Ben-Naim and Stillinger [14].

A third possible process proposed to interpret the increase of the density at the melting point is that proposed by Samoilov [15] and then independently by Frosind [16] and by Danford and Levy [17]. According to this theory, the structure of ice undergoes relatively minor changes, with interstitial molecules entering the empty space included in the structure. A variation of this theme is that proposed by Pauling [18] who thought that the structure of liquid water should resemble that of a hydrated clathrate rather than that of ice.

The most popular model is that of Némethy and Scheraga [8]. Typical of this mixture model is the 'flickering cluster' idea of Frank and Wien [18]; these clusters are short-lived aggregates produced by cooperative processes of formation and breaking of hydrogen bonds. Some water molecules enter as interstitial between the clusters. The statistical calculation of Némethy and Scheraga sums all the energy interactions, extended to all the species. These equations produce values of internal energy, free energy, entropy, molar volume and heat capacity of liquid water. Increasing the temperature reduces the average size of the clusters and increases the number of free molecules. The possible existence of the interstitial free molecules is under debate. Spectroscopic studies [19–21] by IR and IR-Raman in connection with the spectroscopic properties of heavy water has shown isosbestic points that would be in favour of the existence of different species in equilibrium with one another. Symons [22], again on the basis of IR experiments, proposes the existence among the species in equilibrium of some molecules which form three hydrogen bonds instead of four. These molecules are distinguished into $(OH)_{free}$ and $(LP)_{free}$ depending whether the fourth tetrahedral position not forming a hydrogen bond is an OH group or a lone-pair.

The computer simulations of aqueous solutions started with the purpose of understanding at the atomic and molecular level important signals and dynamics of biomolecular systems [23]. A critical component is given by the intermolecular potential functions which represent the energetics of water–water and water–solute interactions. Several potential functions for dimeric water have been developed [24–26].

3. Statistical thermodynamic model

The structural models proposed for liquid water H_2O and heavy water D_2O have been examined in order to establish their possible conformity with the conclusions reached by applying to the system 'water', the statistical model employed to study protonation and solubility equilibria [27–32]. In particular, the statistical model is suitable for describing the dependence upon the temperature of the experimental heat capacity data of liquid water. The isobaric heat capacity of liquid H_2O, C_p as a function of temperature, decreases between 0° and about 35°C and then increases up to 100°C (Fig. 1) [33]. Analogous behaviour is shown by liquid D_2O (Fig. 2) [34].

The thermodynamic statistical model for solutions considers the system where a reaction takes place as a *reacting* ensemble (re) represented by a reaction (grand canonical) partition function. The *reacting* ensembles are those in which definite enthalpy differences, ΔH_i, exist between levels i (quantization of enthalpy). Each level corresponds to one definite species. Within each level, the enthalpy differences between

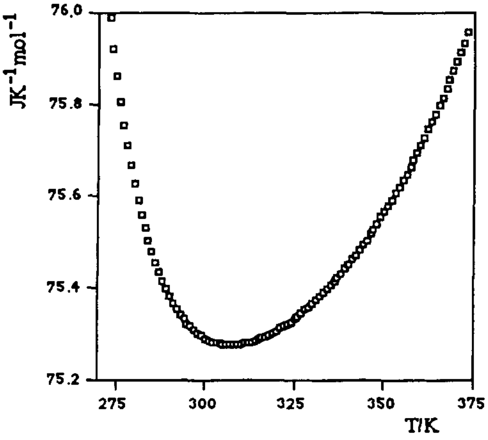

Fig. 1. Molar isobaric heat capacity of liquid water.

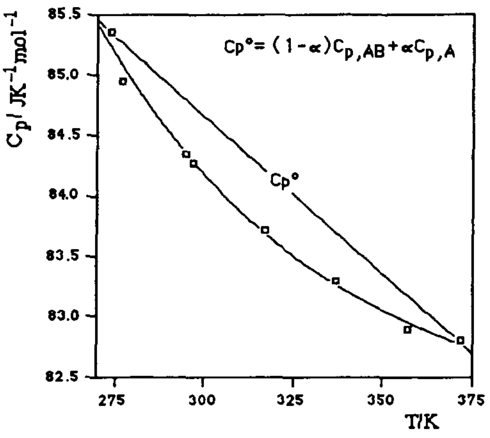

Fig. 2. Molar isobaric heat capacity of liquid heavy water.

sublevels j, $\Delta H_{j,i}$ are much less than ΔH_i. The distributions among sublevels j corresponding to each component are defined as *non-reacting* ensembles (nre).

The reaction excess partition function, $Z_{B/A}$ is related to the process of binding of a ligand B to the receptor A and evaluates the increment of probability of state of the solution by means of the dilution extent of the ligand upon binding. The higher the affinity of the ligand for the receptor, the higher is the dilution of the ligand itself. The value of $Z_{B/A}$ can be represented in the *Probability Space* [28], where free-energy probability $\exp(-\Delta G/RT)$, enthalpy probability $\exp(-\Delta H/RT)$ and entropy probability $\exp(-\Delta S/R)$ can also be represented. In the same space, the experimental quantity 'dilution' or that indirectly related to the experiment as 'affinity constant' can be also reported. The total probability of state can be represented by the total partition function, Ξ, whereby the relative dilution of the ligand as given by $Z_{B/A}$ is multiplied by the no-reaction partition functions ζ_A, ζ_{AB} of the other species taking part in the reaction.

By taking the logarithms of the quantities of the *Probability Space*, one moves to the *Thermodynamics Space* where free energy, enthalpy, and entropy can be represented. This space corresponds to the experimental domain of heat, chemical and electrochemical potential. By calculating the derivative with respect to temperature or dilution, one moves to the *Dispersion Space*, which is the domain of the experimental quantities 'heat capacity' or 'buffer capacity'. The dispersion corresponds to the second moment of the total probability function. In grand canonical ensembles, the buffer capacity is calculated as the second derivative with respect to the ligand concentration, $\partial^2 \ln Z_M/\partial(\ln[A])^2$ whereas the isobaric heat capacity is obtained as the second mixed derivative of concentration and temperature, $\partial^2 \ln Z_M/(\partial \ln[A]\partial \ln T)$.

The reaction taking part in liquid water can be written as

$$A + B = AB \tag{1}$$

where A, B, and AB are water molecules in different clusters or different species, for example $AB = (H_2O)_4$, $A = (H_2O)_3$, $B = (H_2O)$. The properties of this system can be represented in the *Probability Space* by means of the following partition functions referred to the corresponding ensemble

Probability Space

Ensemble	Partition function		
(re)	Total	$\Xi = \zeta_A \zeta_{AB}^{-1} Z_{B/A}$	(2)
(re)	Excess	$Z_{B/A}$	(3)
(nre)	No-reaction	ζ_A	(4)
(nre)	No-reaction	ζ_{AB}	(5)

By calculating the logarithms of the partition functions the following relationship is obtained for the formation reaction in the *Thermodynamics* (*Affinity*) *Space*

$$\ln\Xi = \ln\zeta_A - \ln\zeta_{AB} + \ln Z_{B/A} \tag{6}$$

By calculating the derivative of the partition function (with $d\ln[B] = d\ln[A] = -d\ln[AB]$) with respect to the dilution of the ligand, the following equation is obtained,

$$\partial\ln\Xi/\partial\ln[B] = \partial\ln\zeta_A/\partial\ln[A] + \partial\ln\zeta_{AB}/\partial\ln[AB] + \partial\ln Z_{B/A}/\partial\ln[B] \tag{7}$$

where one can note that each term is an entropy contribution

$$\partial \ln \Xi / \partial \ln[\mathrm{B}] = s_{\mathrm{A}}/R + s_{\mathrm{AB}}/R + \Delta s_{\mathrm{B/A}}/R = \Delta S/R \tag{8}$$

Distinction is made between capital letters (e.g. ΔS) which refer to molar quantities and small letters (e.g. s_{A}) which refer to partial or fractional quantities. The change of entropy is actually a change of relative dilution of the species A, AB, and B/A

$$\Delta S/R = (1-\alpha)_{\mathrm{AB}} + \alpha_{\mathrm{A}} + \alpha_{\mathrm{B/A}} \tag{9}$$

The derivative of entropy with respect to $\ln T$ (second moment) is actually the molar isobaric heat capacity

$$\partial(\Delta S/R)/\partial \ln T = C_p/R \tag{10}$$

A relationship analogous to Eq. (10) applies for species A

$$\partial(S_{\mathrm{A}}/R)/\partial \ln T = C_{p,\mathrm{A}}/R \tag{11}$$

The relationship between fractional and molar heat capacity can be calculated by assuming the principle of *thermal equivalent dilution* whereby the equivalent entropy change can be produced either by a change of temperature or dilution. Therefore any change of temperature $\mathrm{d}\ln T$ is equivalent to a change of dilution of each species multiplied by a factor that depends on the heat capacity of each species

$$(1/\alpha_{\mathrm{A}})\partial(s_{\mathrm{A}}/R)/\partial \ln T = C_{p,\mathrm{A}}/R \tag{12}$$

Therefore the derivative of the first entropy contribution in Eq. (8) is

$$\partial \alpha_{\mathrm{A}}/\partial \ln T = \alpha_{\mathrm{A}} C_{p,\mathrm{A}}/R \tag{13}$$

and analogously for the contribution of the species AB

$$\partial \alpha_{\mathrm{AB}}/\partial \ln T = (1-\alpha)_{\mathrm{AB}} C_{p,\mathrm{AB}} \tag{14}$$

The third entropy term, $\Delta C_{p,\mathrm{app}}/R$ or reaction apparent heat capacity is related to the reaction enthalpy by Eq. (15)

$$\Delta C_{p,\mathrm{app}}/R = \partial \alpha_{\mathrm{B/A}}/\partial \ln T \tag{15}$$

and as shown in a previous paper [30] ΔC_{app} can be obtained by the relationship for implicit functions

$$\{\partial \alpha_{\mathrm{B/A}}/\partial \ln T\}_{[\mathrm{B}]} = \{\partial \alpha/\partial \ln[\mathrm{B}]\}_T \{\partial \ln[\mathrm{B}]/\partial \ln T\}_\alpha \tag{16}$$

Therefore the apparent heat capacity is a buffer capacity function weighted for the heat produced in the reaction

$$\Delta C_{p,\mathrm{app}} = \{(1-\alpha)\alpha\}(-\Delta H/T + C_{p,\mathrm{B}}) \tag{17}$$

where further moments of ΔH and $C_{p,\mathrm{B}}$ have been omitted for the sake of simplicity. On the whole, the heat capacity of water can be calculated as the sum of three terms

$$C_p = (1-\alpha)C_{p,\mathrm{AB}} + \alpha C_{p,\mathrm{A}} + \{(1-\alpha)\alpha\}(-\Delta H/T + C_{p,\mathrm{B}}) \tag{18}$$

In water, H_2O, the isobaric heat capacity of the initial and final species is $C_{p,\mathrm{A}} \approx C_{p,\mathrm{AB}}$ and therefore the sum of the first two terms of Eq. (18) is expressed by the relationship

$$C_{p,0} = (1-\alpha)C_{p,\mathrm{AB}} + \alpha\, C_{p,\mathrm{A}} = 75.9861 - 0.031(T - T_0)/(T_1 - T_0) \tag{19}$$

with $T_0 = 273.15\,\mathrm{K}$ and $T_1 = 373.15\,\mathrm{K}$.

In heavy water, D_2O, the values of the heat capacities of A and AB are rather different ($C_{p,\mathrm{A}} \neq C_{p,\mathrm{AB}}$) and the contribution of the first two terms to the heat capacity is expressed by

$$C_{p,0} = (1-\alpha)C_{p,\mathrm{AB}} + \alpha C_{p,\mathrm{A}} = 85.35 - 2.55(T - T_0)/(T_1 - T_0) \tag{20}$$

where $T_0 = 276.97$ and $T_1 = 374.57\,\mathrm{K}$.

4. Isobaric heat capacity and reaction heat

The experimental data for isobaric heat capacity of liquid water (Table 1) have been taken from Ref. [33] and those for liquid heavy water (Table 2) from Ref. [34].

In order to calculate the contribution $\Delta C_{p,\mathrm{app}}$ to the isobaric heat capacity C_p produced by the reaction heat, the quantity $C_{p,0}$ calculated using Eq. (19) is subtracted from the observed heat capacity C_p. Then the function is calculated

$$Y = T\Delta C_{p,\mathrm{app}}/\{(1-\alpha)\alpha\} \tag{21}$$

where $\alpha = (T - T_0)/(T_1 - T_0)$.

Formally, the multiplication of $\Delta C_{p,\mathrm{app}}$ by T is equivalent to a change of axes in the *Thermodynamics Space* from $x(\Delta S/R)$ to $y\,(-\Delta H/RT)$. In fact,

$$T\partial\,(\Delta S/R)/\partial \ln T = \partial(\Delta S/R)/(1/T)^2\partial T = -\,\partial(\Delta S/R)/\partial(1/T)$$

Because of the equality between the enthalpy reaction factor $-\Delta H/RT$ and the corresponding equivalent entropy factor $\Delta S_H/R$ it is possible to write

$$-\,\partial(\Delta S/R)/\partial(1/T) = \partial - (\Delta H/RT)/\partial(1/T) = \Delta H/R$$

Therefore it is correct to extract information concerning enthalpy and reaction heat from the polynomial extension of the entropic derivative $\Delta C_{p,\mathrm{app}}$ multiplied by T.

This function (Eq. (21)) can be expanded to a polynomial

$$Y = a + b(T - T_0) + c(T - T_0)^2 + d(T - T_0)^3 + e(T - T_0)^4 \tag{22}$$

where $a = -\Delta H$, $b = C_{p,\mathrm{B}} + \partial(\Delta H)/\partial T$, $c = \partial(C_{p,\mathrm{B}})/\partial T + \partial^2(\Delta H)/\partial T^2$,

$d = \partial^2(C_{p,\mathrm{B}})/\partial T^2 + \partial^3(\Delta H)/\partial T^3$, $e = \partial^3 C_{p,\mathrm{B}})/\partial T^3 + \partial^4(\Delta H)/\partial T^4$.

The values of the coefficients of Eq. (22) for H_2O are $a = -1838.363$, $b = 47.76889$, $c = -0.8636959$, $d = 0.007416165$, $e = -0.00002544972$. The equation, the Y-function, is plotted in Fig. 3. By assuming that ΔH is constant (with $\partial(\Delta H)/\partial T = 0$ and so the higher derivatives are also equal to zero), one obtains for H_2O by considering the

Table 1
Isobaric Heat Capacity in liquid H_2O [33]

t° °C	T/K K	c_p J g^{-1}	C_p J mol^{-1}
0	273.15	4.2177	75.9861
1	274.15	4.2141	75.9212
2	275.15	4.2107	75.8600
3	276.15	4.2077	75.8059
4	277.15	4.2048	75.7537
5	278.15	4.2022	75.7068
6	279.15	4.1999	75.6654
7	280.15	4.1977	75.6258
8	281.15	4.1957	75.5897
9	282.15	4.1939	75.5573
10	283.15	4.1922	75.5267
11	284.15	4.1907	75.4997
12	285.15	4.1893	75.4744
13	286.15	4.188	75.4510
14	287.15	4.1869	75.4312
15	288.15	4.1858	75.4114
16	289.15	4.1849	75.3952
17	290.15	4.184	75.3789
18	291.15	4.1832	75.3645
19	292.15	4.1825	75.3519
20	293.15	4.1819	75.3411
21	294.15	4.1813	75.3303
22	295.15	4.1808	75.3213
23	296.15	4.1804	75.3141
24	297.15	4.1800	75.3069
25	298.15	4.1796	75.2997
26	299.15	4.1793	75.2943
27	300.15	4.1790	75.2889
28	301.15	4.1788	75.2853
29	302.15	4.1786	75.2818
30	303.15	4.1785	75.2799
31	304.15	4.1784	75.2781
32	305.15	4.1783	75.2763
33	306.15	4.1783	75.2763
34	307.15	4.1782	75.2745
35	308.15	4.1782	75.2745
36	309.15	4.1783	75.2763
37	310.15	4.1783	75.27626
38	311.15	4.1784	75.2781
39	312.15	4.1785	75.2799
40	313.15	4.1786	75.2817
41	314.15	4.1787	75.2835
42	315.15	4.1789	75.2871
43	316.15	4.1791	75.2907
44	317.15	4.1792	75.2925
45	318.15	4.1795	75.2979
46	319.15	4.1797	75.3015
47	320.15	4.1799	75.3051

Table 1 (*Continued*)

t° °C	T/K K	c_p J g^{-1}	C_p J mol^{-1}
48	321.15	4.1802	75.3105
49	322.15	4.1804	75.3141
50	323.15	4.1807	75.3195
51	324.15	4.181	75.3249
52	325.15	4.1814	75.3321
53	326.15	4.1817	75.3375
54	327.15	4.182	75.3429
55	328.15	4.1824	75.3501
56	329.15	4.1828	75.3573
57	330.15	4.1832	75.3645
58	331.15	4.1836	75.3718
59	332.15	4.184	75.3789
60	333.15	4.1844	75.3862
61	334.15	4.1849	75.3952
62	335.15	4.1853	75.4024
63	336.15	4.1858	75.4114
64	337.15	4.1863	75.4204
65	338.15	4.1868	75.4294
66	339.15	4.1874	75.4402
67	340.15	4.1879	75.4492
68	341.15	4.1885	75.4600
69	342.15	4.189	75.4690
70	343.15	4.1896	75.4798
71	344.15	4.1902	75.4906
72	345.15	4.1908	75.5015
73	346.15	4.1915	75.5141
74	347.15	4.1921	75.5249
75	348.15	4.1928	75.5375
76	349.15	4.1935	75.5501
77	350.15	4.1942	75.5627
78	351.15	4.1949	75.5753
79	352.15	4.1957	75.5897
80	353.15	4.1964	75.6023
81	354.15	4.1972	75.6168
82	355.15	4.198	75.6312
83	356.15	4.1988	75.6456
84	357.15	4.1997	75.6618
85	358.15	4.2005	75.6762
86	359.15	4.2014	75.6924
87	360.15	4.2023	75.7086
88	361.15	4.2032	75.7249
89	362.15	4.2042	75.7429
90	363.15	4.2051	75.7591
91	364.15	4.2061	75.7771
92	365.15	4.2071	75.7951
93	366.15	4.2081	75.8131
94	367.15	4.2092	75.8330
95	368.15	4.2103	75.8528
96	369.15	4.2114	75.8726

Table 1 (*Continued*)

t° °C	T/K K	c_p J g^{-1}	C_p J mol^{-1}
97	370.15	4.2125	75.8924
98	371.15	4.2136	75.9122
99	372.15	4.2148	75.9338
100	373.15	4.216	75.9555

Table 2
Isobaric Heat Capacity in liquid D_2O [34]

t° °C	T/K K	c_p J g^{-1}	C_p J mol^{-1}
3.82	276.97	4.261	85.35
6.85	280	4.241	84.94
25.00	298.15	4.211	84.35
26.85	300	4.207	84.27
46.85	320	4.180	83.72
66.85	340	4.159	83.30
86.85	360	4.138	82.89
101.42	374.57	4.134	82.80

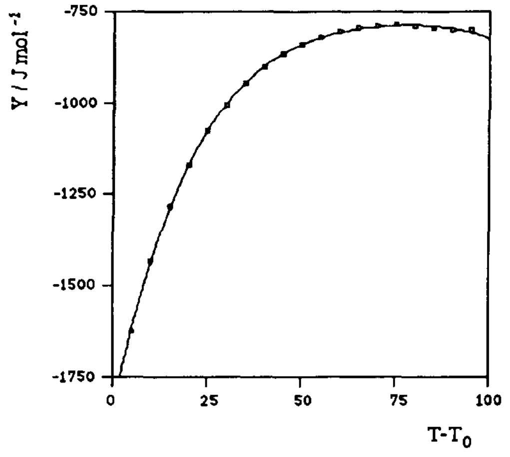

Fig. 3. Y-function for liquid water ($T_0 = 273.15$).

dissociation reaction,

$$-\Delta H = -1.84\,\mathrm{kJ\,mol^{-1}}, C_{p,\mathrm{B}} = 47.77\,\mathrm{J\,K^{-1}\,mol^{-1}},$$

$$\partial(C_{p,\mathrm{B}})/\partial T = -0.86\,\mathrm{J\,K^{-2}\,mol^{-1}}.$$

The higher derivatives of $C_{p,\mathrm{B}}$ are of minor relevance. The values of $\Delta C_{p,\mathrm{app}}$ are compared with those obtained from Eq. (22), $\Delta C_{p,\mathrm{calc}}$ in Table 3. The agreement is very good (Fig. 4).

Analogous calculations have been performed for heavy water D_2O. The original data have been fitted by an interpolation polynomial. Then the quantity $C_{p,0}$ from Eq. (20) has been subtracted from C_p values interpolated at selected temperatures (Table 4). The value of the heat capacity of species AB is $C_{p,\mathrm{AB}} = 85.35\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and that of species A is $C_{p,\mathrm{A}} = 82.80\,\mathrm{J\,K^{-1}\,mol^{-1}}$. The calculation of the Y-function (Fig. 5) leads to the coefficients: $a = -1642.775$, $b = 49.17889$, $c = -0.6730462$, $d = 0.0023740$, $e = 0.0000$. From the coefficients, one obtains for the dissociation reaction in D_2O, $-\Delta H = -1.64\,\mathrm{kJ\,mol^{-1}}$, $C_{p,\mathrm{B}} = 49.18\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $\partial(C_{p,\mathrm{B}})/\partial T = -0.67\,\mathrm{J\,K^{-2}\,mol^{-1}}$. The values of $\Delta C_{p,\mathrm{app}}$ and $\Delta C_{p,\mathrm{calc}}$ for D_2O are compared in Fig. 6.

5. Discussion

The trend of isobaric heat capacity of both water and heavy water with changing temperature can be interpreted on the assumption of the mixture model for these

Table 3
Observed $\Delta C_{p,\mathrm{app}}$ and calculated $\Delta C_{p,\mathrm{calc}}$ values of the reaction contribution to the heat capacity of liquid water

t° °C	$\Delta C_{p,\mathrm{app}}$ $\mathrm{J\,mol^{-1}}$	$\Delta C_{p,\mathrm{calc}}$ $\mathrm{J\,mol^{-1}}$
0	0	0
1	−0.065	−0.066
5	−0.278	−0.277
10	−0.456	−0.458
15	−0.570	−0.572
20	−0.639	−0.640
25	−0.679	−0.678
30	−0.697	−0.695
35	−0.701	−0.697
40	−0.692	−0.690
45	−0.674	−0.674
50	−0.651	−0.651
55	−0.619	−0.621
60	−0.581	−0.583
65	−0.536	−0.538
70	−0.484	−0.486
75	−0.425	−0.426
80	−0.359	−0.359
85	−0.283	−0.282
90	−0.199	−0.198
95	−0.104	−0.105
99	−0.020	−0.022
100	+0.001	0

$C_p^\circ = (1-\alpha)C_{p,\mathrm{AB}} + \alpha C_{p,\mathrm{A}} = C_{p,\mathrm{AB}} - 0.00031\,(T - T_0)/(T_1 - T_0)$.

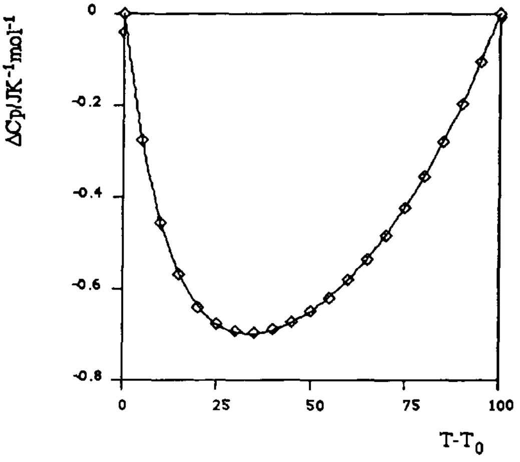

Fig. 4. Observed $\Delta C_{p,\mathrm{app}}$ (continuous curve) and calculated $\Delta C_{p,\mathrm{calc}}$ (empty points) contributions of the reaction heat to the heat capacity of liquid water ($T_0 = 273.15$).

Table 4
Observed $\Delta C_{p,\mathrm{app}}$ and calculated $\Delta C_{p,\mathrm{calc}}$ values of the reaction contribution to the heat capacity of heavy water

t° °C	$\Delta C_{p,\mathrm{app}}$ J mol^{-1}	$\Delta C_{p,\mathrm{calc}}$ J mol^{-1}
3.82	0	0
6.85	−0.171	−0.152
25.00	−0.488	−0.500
26.85	−0.494	−0.504
46.85	−0.470	−0.430
66.85	−0.411	−0.418
86.85	−0.295	−0.296
101.42	0.003	0

$C_p^\circ = (1-\alpha)C_{p,\mathrm{AB}} + \alpha C_{p,\mathrm{A}} = C_{p,\mathrm{AB}} - 2.55(T - T_0)/(T_1 - T_0)$.

liquids. The heat capacity at different temperatures is altered by the contribution of the reaction heat produced by the displacement of the equilibrium by the temperature. The reaction as written in Eq. (1) is an association reaction and is endothermic. The opposite dissociation reaction is exothermic. The dissociation increases on increasing the temperature and the heat released by the reaction is added to the heat supplied from outside. In fact, if we recall the definition of heat capacity as *the amount of heat supplied to system necessary to raise the temperature of one mole of substance by one degree centigrade*, it is evident that the quantity of heat needed in this case is less than the value $C_{p,0}$ expected for a mixture because one part of the heat is supplied from inside by the reaction itself. At 100°C the value of C_p is approaching $C_{p,0}$ because the reaction is near

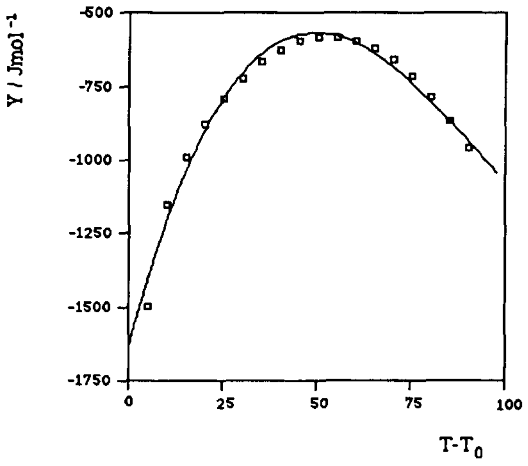

Fig. 5. Y-function for liquid heavy water ($T_0 = 276.97$).

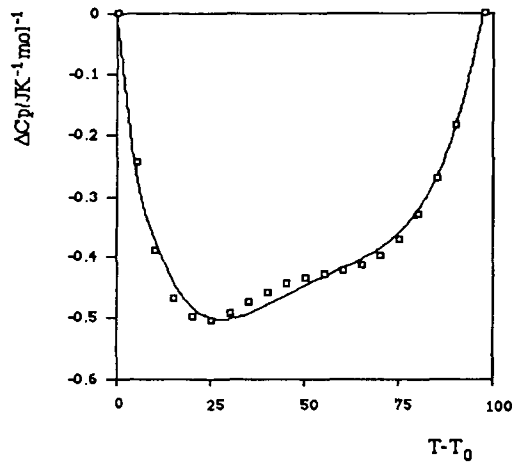

Fig. 6. Observed $\Delta C_{p,\mathrm{app}}$ (continuous curve) and calculated $\Delta C_{p,\mathrm{calc}}$ (empty points) contributions of the reaction heat to the heat capacity of liquid heavy water ($T_0 = 276.97$).

to completion and the amount of heat produced is tending to zero. The change of the isobaric heat capacity due to the reaction enthalpy is only a limited fraction (0.93%) of the whole heat capacity C_p, at 35°C.

No comparison can be made between the values of the enthalpy change calculated using the statistical thermodynamic model and the thermodynamic quantities obtained previously on the basis of the mixture model [10], because such values have been obtained by applying the so-called relaxation term which does not agree with the assumptions of the statistical model.

The accuracy and precision of the enthalpy obtained by the polynomial extension of the *Y*-function is related to the validity of the assumptions inherent to both mixture model and statistical thermodynamic model. The precision depends on the number of points and the precision of the experimental data. The data for H_2O are many and are given at each degree from 0°C to 100°C. The precision $\pm 0.05\,\mathrm{kJ\,mol^{-1}}$ for ΔH is acceptable and a precision $\pm 0.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for C_p is also acceptable. The data for D_2O are only few. Lower precision is expected and uncertainties of $\pm 0.5\,\mathrm{kJ\,mol^{-1}}$ for ΔH and $\pm 5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ for C_p are reasonable.

The absolute value of ΔH indicates that the difference of energy of the reaction is very small. The difference could be attributed to an average energy of three strong hydrogen bonds in comparison to four weak hydrogen bonds. The triplet of hydrogen bonds is more stable than the quartet of four hydrogen bonds. The hydrogen bonds of the triplet are stronger and shorter than those of the quartet because the constrictions are less in the former than in the latter. Thus the equilibrium of Eq. (1) conforms to the hypothesis of the mixture model [10] which assumes that there are two distinct species in liquid water, one voluminous with small energetic interactions and another one dense and more tightly bound (Fig. 7).

The difference in enthalpy in D_2O is almost the same as in H_2O. The deuterium bond is stronger than the hydrogen bond but the difference between the triplet and quartet of bonds in the deuterium compound, D_2O is almost the same as in the hydrogen compound, H_2O.

The isobaric heat capacity of free water (B) is $C_{p,\mathrm{B}} = 47.8\,\mathrm{J\,K^{-1}\,mol^{-1}}$ which is smaller than the heat capacity $C_{p,\mathrm{AB}} \approx C_{p,\mathrm{A}} = 76\,\mathrm{J\,K^{-1}\,mol^{-1}}$ of the other species. The isobaric heat capacity of free D_2O, $C_{p,\mathrm{B}} = 49.18\,\mathrm{J\,K^{-1}\,mol^{-1}}$ is approximately equal to that of water and again much lower than the heat capacity $C_{p,\mathrm{AB}} = 85.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ and $C_{p,\mathrm{A}} = 82.5\,\mathrm{J\,K^{-1}\,mol^{-1}}$ of the other species. Nothing can be said about the number of water units composing the species A and AB. The equilibrium of Eq. (1) is compatible with the assumptions $\mathrm{AB} = (H_2O)_4$, $\mathrm{A} = (H_2O)_3$, $\mathrm{B} = (H_2O)$ or $\mathrm{AB} = (H_2O)_5$, $\mathrm{A} = (H_2O)_4$, $\mathrm{B} = (H_2O)$, or $\mathrm{AB} = (H_2O)_9$, $\mathrm{A} = (H_2O)_8$, $\mathrm{B} = (H_2O)$.

The existence of the equilibrium Eq. (1) in liquid water is in agreement with the 'flickering cluster' model suggested by Frank and Wien [18] and accepted by Némethy and Scheraga [8]. At the same time, however, the dissociating water molecule B could

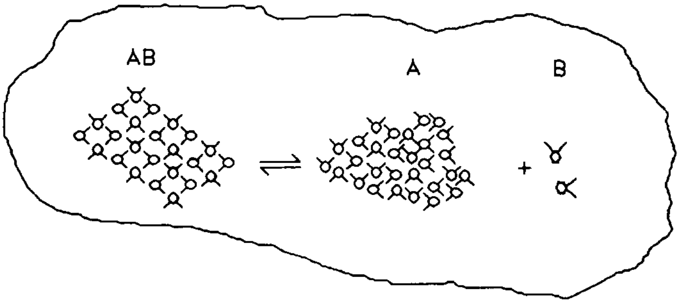

Fig. 7. Molecular picture of the equilibrium in liquid water.

be the interstitial molecule entering the empty space of the structure proposed by other authors [15–17].

The results confirm the validity of the statistical thermodynamic model for solutions [27–32]. The existence of the definite enthalpy change conforms to the assumption that in the system there is a difference between enthalpy levels, each level being associated with one species.

The analysis by the same statistical model of the solubility of noble gases in water as a function of the temperature [31] had reached conclusions which are consistent with the equilibrium found in pure water. The solubilization process of the gaseous atom is accompanied by release of free water molecules (similar to species B) to form a cavity in a cage of water molecules (similar to species AB or even A). The number of water molecules is strictly proportional to the size of the gas atom. Analogous mechanisms involving water molecules set free in the reaction can be invoked to explain the solubility of inert liquid and gases in water [32] and the protonation process of carboxylic acids [30].

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