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The Structure Theory of Water. II. The Thermodynamic Properties of Liquid Deuterium Oxide

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In the preceding paper[1] (Part I), a statistical thermodynamic theory was successfuly applied to liquid water, based on a two state model which consists of an ice-like structure (class I) and unbonded monomers (class II). The same treatment has been applied to liquid deuterium oxide, with the intention to explain the thermodynamic properties of the liquid and to test the applicability of the two state model.

In the calculation of the partition function (Part I), the two quantities, *viz.*, the energy difference between class I and class II, ε, and the free volume for the molecule in class II, v_f, were used as adjustable parameters. The values of the parameters were estimated to be 3 kcal/mol and 4.0×10^{-25} cm^3 respectively. They are in line with the thermodynamic properties of the liquid water. In the present calculation the same value for v_f has been used, since the dimension of the molecule and the dipolar interactions *etc.* of D_2O are practically the same as those of H_2O.[2]

For the magnitude of ε for D_2O a higher value is required than for H_2O, since the energy of sublimation for the former ($\Delta E^{D_2O}_{subl}$: 12.08 kcal/mol) is larger than that of the latter ($\Delta E^{H_2O}_{subl}$: 11.65 kcal/mol).[2] Considering that the van der Waals interactions between D_2O molecules may be nearly the same as those between H_2O molecules, the magnitude of ε for D_2O is estimated to be 3.4 kcal/mol.

$$\varepsilon_{D_2O} - \varepsilon_{H_2O} \fallingdotseq \Delta E^{D_2O}_{subl} - \Delta E^{H_2O}_{subl} \tag{1}$$

Concerning the frequencies which have been attributed to intermolecular vibrations of the molecules in class I, a tentative assignment has been made with reference to the data from the infrared and Raman spectroscopy[3,4] and also by taking into account the difference in the mass and the principal moments of inertia between D_2O and H_2O molecules.[5] The ratio of librational frequencies, and that of the principal moments of inertia between D_2O and H_2O are estimated to be 1.38, and 1.91 respectively, according to Swain and Bader.[5] The values for ν_i and A, B, C are given in Table 1.

TABLE 1. INTERMOLECULAR VIBRATIONAL FREQUENCIES AND PRINCIPAL MOMENTS OF INERTIA FOR D_2O

Frequency (cm^{-1})			
Translational vibration	Rotational vibration		
$\nu_1=\nu_2=\nu_3$	ν_4	ν_5	ν_6
170	340	470	540

Moment of inertia		
A	B	C
1.96×10^{-40}	3.67×10^{-40}	5.63×10^{-40}

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1) K. Arakawa and K. Sasaki, This Bulletin, **42**, 303 (1969).

2) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **41**, 680 (1964).

3) P. A. Giguére and K. B. Harvey, *Can. J. Chem.*, **34**, 798 (1956).

4) D. A. Draegert, N. W. B. Stone, B. Curnutte and D. Williams, *J. Opt. Soc. Am.*, **56**, 64 (1966).

5) G. Swain and R. F. Bader, *Tetrahedron*, **10**, 182 (1960).

Table 2. Thermodynamic variables

Temp. (°C)	A_{calc} (kcal/mol)	A_{obs} (kcal/mol)	E_{calc} (kcal/mol)	E_{obs} (kcal/mol)	S_{calc} (cal/deg·mol)	S_{obs} (cal/deg·mol)	$(C_v)_{calc}$ (cal/deg·mol)	$(C_v)_{obs}$ (cal/deg·mol)
4	−1.435	−1.58	3.205	3.04	16.74	16.6	28.88	20.5
10	−1.538	−1.68	3.374	3.15	17.34	17.1	27.64	20.3
20	−1.713	−1.85	3.633	3.36	18.23	17.8	26.64	20.1
30	−1.903	−2.03	3.883	3.57	19.08	18.4	23.17	19.9
40	−2.098	−2.22	4.103	3.77	19.80	19.1	21.05	19.7
50	−2.299	−2.42	4.307	3.97	20.44	19.7	18.94	19.4
60	−2.502	−2.62	4.478	4.17	20.95	20.4	17.26	19.1

Calculation of Thermodynamic Variables.

According to the statistical mechanical theory reported in Part I, calculations of thermodynamic variables for liquid D_2O have been made over the temperature range from 4—60°C, using the values of parameters described above. The calculated values of the Helmholtz energy, A, the internal energy, E, the entropy, S, and the specific heat at constant volume, C_v, are given in Table 2. The results calculated are compared with the experimental data for liquid D_2O and also with the results calculated by Némethy and Scheraga.[2] They are plotted against temperature in Figs. 1—4. The mole fraction x of hydrogen bonded portion is calculated and given in Table 3, together with the ratio,x_{D_2O}/x_{H_2O}.

Table 3. Fraction of hydrogen bonded portion, x

Temp. (°C)	x_{D_2O}	x_{D_2O}/x_{H_2O}*
4	0.514	1.03
10	0.479	1.03
20	0.427	1.03
30	0.378	1.03
40	0.336	1.03
50	0.298	1.02
60	0.268	1.02

* The values of x_{H_2O} are those calculated in Part I.

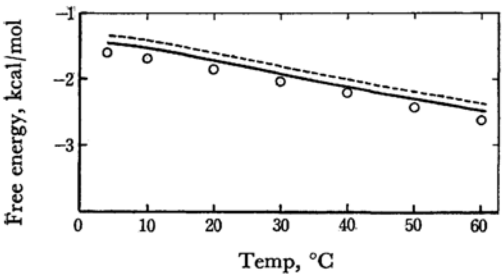

Fig. 1. Helmholtz energy, A, for liquid D_2O. Circle, observed: Solid ine, calculated; Dotted line, Némethy and Scherage[2]

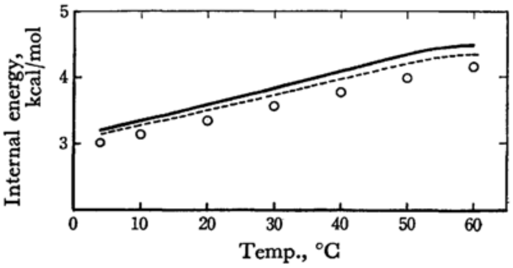

Fig. 2. Internal energy, E, for liquid D_2O. Circle, observed; Solid line, calculated; Dotted line, Némethy and Scheraga[2]

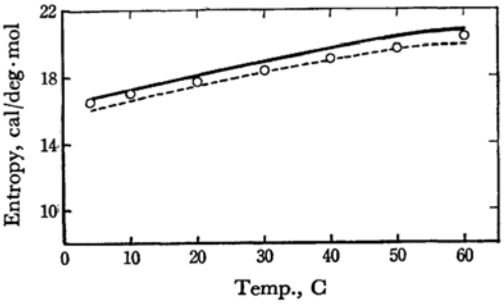

Fig. 3. Entropy, S, for liquid D_2O. Circle, observed; Solid line, calculated; Dotted line, Némethy and Scheraga[2]

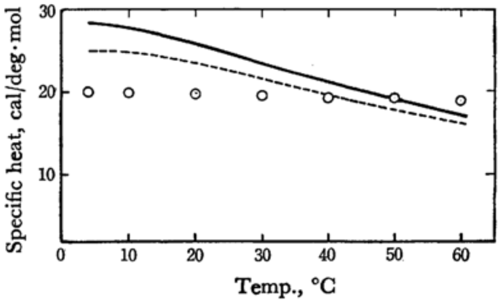

Fig. 4. Specific heat, C, for liquid D_2O. Circle, observed; Solid line, calculated; Dotted line, Némethy and Scheraga[2]

As seen in Figs. 1—4, the agreement between calculated and observed values for D_2O is fairly good, except that deviations are seen in the values of C_v. In the present calculation for D_2O, the parameters, ε, v_f, and ν_t have been fixed theoretically as compared with those for H_2O. Thus we might say that agreement is satisfactory.[2,6]

It seems reasonable from observed data[2] that in liquid D_2O the degree of hydrogen bonding is higher than for liquid H_2O. The ratio, x_{D_2O}/x_{H_2O} given in Table 3 is in line with this view.

We see that the thermodynamical behavior of liquid D_2O is described adequately by using the value of ε_{D_2O} which is larger than ε_{H_2O}. The results support the idea that the bond strength of O—D···O is stronger than that of O—H···O.

It is concluded that the two state theory for liquid water (Part I) gives an adequate representation of thermodynamical behaviors of liquid D_2O.

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6) M. R. Thomas and H. A. Scheraga, *J. Phys. Chem.*, **69**, 3722 (1965).