Hydrogen Isotope Disproportionation and Fractionation Equilibria in H_2O-D_2O Solvent System. II.* Enthalpy of the Isotope Disproportionation Reaction between H_2O and D_2O

PIRKETTA SCHARLIN

Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku 50, Finland

The enthalpy of the isotope disproportionation reaction between H_2O and D_2O in liquid phase has been calculated from the results of calorimetric measurements. A value of 125.5(2) J mol^{-1} was obtained for $\Delta_r H^\ominus$ at 298.15 K and a value of 124.5(3) J mol^{-1} at 303.15 K. Molar excess enthalpies of H_2O-D_2O liquid mixtures are reported. The calculated $\Delta_r H^\ominus$ values are compared with earlier studies.

Many investigators involved in protium—deuterium studies in solution make use of the equilibrium $H_2O(l)+D_2O(l)=2$ HDO(l). Most of the studies of the thermodynamic properties of the disproportionation reaction between H_2O and D_2O are associated with the gas phase. The thermodynamic functions for the liquid phase reaction are usually calculated from the gas phase data and vapor pressure isotope effects. The equilibrium constant $K(HDO)^2$ of the isotope disproportionation reaction of water in liquid phase has been discussed in the previous paper.[1] As in the case of $K(HDO)^2$ there is quite a lot of discrepancy also in the values of $\Delta_r H^\ominus$ reported for the isotope disproportionation reaction of water.[2-8] The results of some investigations show a systematic trend in $\Delta_r H^\ominus$ with the deuterium content of water,[4,8] which would indicate excess thermodynamic properties of the H_2O-D_2O system or incorrect equilibrium constant $K(HDO)^2$ for the disproportionation reaction of water. According to some studies based on statistical mechanical calculations $\Delta_r H^\ominus$ is also strongly dependent on the temperature.[5,6] The aim of this work was to find out if the above mentioned dependence of $\Delta_r H^\ominus$ on the deuterium content of water exists and to check the temperature dependence of $\Delta_r H^\ominus$.

EXPERIMENTAL

The deuterium oxide used in the experiments was a product of Norsk Hydro-elektrisk Kvael-stofaktieselskab. Deuterium isotope mole fraction of D_2O was reported to be 0.998 and the commercial D_2O was used without further purification. The laboratory distilled protium oxide was purified by fractional distillation. It was found that the experiments in wich carbon dioxide was excluded from the waters gave heats identical to those obtained without precautions.

The equipment used in the measurements was an LKB 10700-2 Batch Microcalorimeter. The compartments of the reaction cell of the calorimeter were loaded with prethermostated H_2O and D_2O with the aid of long-headed polyethylene syringes. The syringes were weighed before and after the filling of the cell compartments. The corresponding compartments of the reference cell were filled with H_2O so that the volumes were as close as possible to the volumes in the reaction cell compartments. The technique used in the measurements has been described in Ref. 9. No heat from friction was observed and thus a correction run was not necessary. The areas below the reaction curve and calibration curve, representing the heat of reaction and calibration, respectively, were measured by a digital integrator.

* Part I. See Ref. 1.

Table 1. Molar excess enthalpies H_m^E of H_2O-D_2O liquid mixtures at 298.15 K.

$x(D;L_2O)^a$	$H_m^E/J\ mol^{-1}$	$x(D;L_2O)^a$	$H_m^E/J\ mol^{-1}$	$x(D;L_2O)^a$	$H_m^E/J\ mol^{-1}$
0.0731	8.41	0.403	29.8	0.608	30.7
0.0839	9.54	0.405	30.7	0.608	29.1
0.0890	10.3	0.408	30.0	0.675	27.6
0.0926	10.5	0.412	29.6	0.679	27.0
0.0975	11.0	0.412	30.1	0.684	26.9
0.101	11.6	0.416	29.3	0.690	25.7
0.102	11.6	0.429	30.1	0.692	25.7
0.117	13.2	0.473	31.0	0.695	25.4
0.125	13.9	0.479	30.2	0.695	25.7
0.139	14.9	0.481	30.8	0.696	26.4
0.176	17.5	0.486	31.7	0.699	25.5
0.182	18.2	0.487	31.6	0.701	25.9
0.190	19.0	0.495	32.6	0.782	20.9
0.191	18.8	0.498	31.4	0.789	21.2
0.192	19.3	0.499	31.4	0.797	19.8
0.194	19.0	0.502	30.4	0.798	20.0
0.195	19.5	0.503	30.1	0.800	19.3
0.199	19.3	0.505	31.9	0.802	19.5
0.203	19.6	0.505	31.4	0.806	18.9
0.223	21.2	0.505	31.1	0.809	19.0
0.290	25.2	0.507	31.1	0.819	18.1
0.296	26.1	0.507	31.5	0.821	17.7
0.300	25.3	0.513	31.2	0.884	12.9
0.302	26.1	0.513	31.9	0.893	12.3
0.303	26.0	0.530	30.1	0.893	12.2
0.312	25.9	0.585	29.2	0.894	12.1
0.314	27.5	0.588	30.0	0.899	11.4
0.319	27.0	0.590	30.0	0.900	11.6
0.325	27.5	0.598	29.4	0.903	11.0
0.336	27.5	0.603	29.8	0.907	10.9
0.393	29.9	0.605	28.7	0.923	8.73
0.396	29.8	0.605	29.1	0.923	9.18
0.399	30.2	0.607	28.7		

^{a} $x(D;L_2O)$ is the deuterium isotope mole fraction of water.

RESULTS AND DISCUSSION

The results of the calorimetric experiments are listed in Tables 1 and 2.

When the thermodynamic properties of H_2O-D_2O liquid mixtures are discussed it is customary to ascribe deviations from ideal mixture behaviour entirely to the isotope disproportionation reaction (1). Assuming the equilibrium mixture (1) to be an ideal mixture

$$H_2O\ (l)+D_2O\ (l)=2\ HDO\ (l) \qquad (1)$$

the value of $\Delta_rH^\ominus$ of reaction (1) can be calculated from the molar excess enthalpies of Tables 1 and 2. In the case of ideal mixture a relationship (2) exists between the enthalpy of reaction (1)

$$\Delta_rH^\ominus=\frac{2H_m^E}{x(HDO)} \qquad (2)$$

and the molar excess enthalpy of H_2O-D_2O liquid mixture. The mole fraction of HDO in the equilibrium mixtures (1) with different values of $x(D;L_2O)$, the deuterium isotope mole fraction of water, can be calculated from eqn. (3) which is derived from the equations given in the previous paper.[1]

Table 2. Molar excess enthalpies H_m^E of H_2O-D_2O liquid mixtures at 303.15 K.

$x(D;L_2O)$[a]	$H_m^E/J\ mol^{-1}$	$x(D;L_2O)$	$H_m^E/J\ mol^{-1}$	$x(D;L_2O)$	$H_m^E/J\ mol^{-1}$
0.0838	9.25	0.393	29.2	0.603	29.7
0.0929	10.8	0.393	30.0	0.604	29.5
0.0959	10.9	0.397	30.8	0.605	29.1
0.0965	10.7	0.398	30.2	0.606	28.9
0.0993	11.3	0.408	30.8	0.607	29.8
0.115	12.6	0.417	28.8	0.608	29.8
0.118	15.3	0.422	30.4	0.614	29.4
0.189	18.6	0.422	29.6	0.618	26.5
0.192	19.1	0.429	30.0	0.692	26.5
0.200	19.9	0.431	29.5	0.692	25.9
0.201	19.6	0.492	29.8	0.694	26.0
0.206	19.9	0.492	29.1	0.696	25.7
0.215	20.7	0.497	30.0	0.700	25.7
0.216	20.6	0.503	31.3	0.701	24.9
0.222	20.9	0.505	29.6	0.701	24.9
0.279	25.6	0.507	30.1	0.705	25.6
0.296	26.1	0.508	30.9	0.708	24.9
0.298	26.2	0.509	30.1	0.783	21.4
0.299	26.7	0.512	29.4	0.788	20.6
0.305	26.9	0.513	30.4	0.790	19.5
0.316	27.1	0.516	30.0	0.797	20.1
0.319	27.0	0.518	29.9	0.824	18.1
0.321	26.3	0.524	30.1	0.858	15.6
0.330	26.5	0.525	30.2	0.873	14.1
0.331	27.3	0.535	29.8	0.890	12.5
0.358	28.8	0.575	29.6	0.899	11.9
0.383	30.1	0.590	30.5	0.905	10.4
0.393	29.8	0.601	29.5		

[a] $x(D;L_2O)$ is the deuterium isotope mole fraction of water.

$$x(HDO)=$$

$$\frac{[F\{K(HDO)^2;\ x(D;L_2O)\}]^{1/2}-K(HDO)^2}{4-K(HDO)^2} \quad (3)$$

$$F\{K(HDO)^2;\ x(D;L_2O)\}=K(HDO)^4+$$
$$4K(HDO)^2[4-K(HDO)^2]x(D;L_2O)[1-x(D;L_2O)]$$

In the calculations a value of 3.76[1] was used for the equilibrium constant $K(HDO)^2$ of the isotope disproportionation reaction of water. The mean of the calculated $\Delta_r H^\ominus$ values is 125.2(2) J mol^{-1} at 298.15 K and 124.5(3) J mol^{-1} at 303.15 K. The values of $\Delta_r H^\ominus$ found in the literature are listed in Table 3. The values of $\Delta_r H^\ominus$ calculated from the excess enthalpy results of this work show no systematic variation with $x(D;L_2O)$. Thus they conform to the ideal behaviour of the isotopic water mixtures.

The Redlich-Kister equation, eqn. (4) was fitted to the molar excess enthalpies given in Tables 1 and 2. The parameters A_i with their standard errors are given in Table 4.

Table 3. Values of $\Delta_r H^\ominus$ reported for reaction $H_2O(l)+D_2O(l)=2\ HDO\ (l)$ at 298.15 K.

$\Delta_r H^\ominus/(J\ mol^{-1})$	Method[b]	Ref.
134	e	2
140(4)	e	3
130	e	4
139	t	6
131.8(6)	e	7
118(13)	e	8
120(20)	t	8
125.5(2)	e	This work

[b] Notations e and t mean experimental and theoretical value, respectively.

Table 4. Parameters A_i of the Redlich-Kister equation, eqn. (4).

T/K	$A_0/(J\ mol^{-1})$	$A_1/(J\ mol^{-1})$	$A_2/(J\ mol^{-1})$
298.15	123.9(2)	−0.5(5)	−0.8(9)
303.15	122.0(3)	−2.0(6)	6.1(12)

$$H_m^E = x(D;L_2O)[1-x(D;L_2O)] \times$$

$$\sum_{i=1}^{n} A_i[2x(D;L_2O)-1]^i \qquad (4)$$

Excess functions are used for expressing the deviation of observed behaviour of mixtures from that expected for ideal systems. For an ideal mixture the parameters A_i of the Redlich-Kister equation (4) are zero.[10] In the case of isotopic water mixtures the excess enthalpy is entirely due to the isotope disproportionation reaction of water. As seen in Table 4, the value of A_0 is approximately the same as the value of $\Delta_rH^\ominus$ for reaction (1), and the values of parameters A_1 and A_2 are quite close to zero. The corresponding parameters obtained by Fenby and Chand[8] are $A_0=130.9(14)$ J mol^{-1}, $A_1=6.5(35)$ J mol^{-1} and $A_2=-51.4(84)$ J mol^{-1}. Their value of A_2 differs markedly from zero and the values of $\Delta_rH^\ominus$ calculated from their excess enthalpy results show a remarkable variation with $x(D;L_2O)$ ranging from 93 J mol^{-1} and 104 J mol^{-1} for compositions of $x(D;L_2O)=0.1$ and $x(D;L_2O)=0.9$, respectively, to 132 J mol^{-1} for composition of $x(D;L_2O)=0.5$. The value of 118 J mol^{-1} for $\Delta_rH^\ominus$ reported in Table 3 represents the average of the $\Delta_rH^\ominus$ values obtained from H_m^E values at $x(D;L_2O)=0.1, 0.2,\ldots0.9$. Fenby and Chand used a value of 3.85[11] for the equilibrium constant $K(HDO)^2$. Their $\Delta_rH^\ominus$ values do not change remarkably if the value of 3.76 is used for $K(HDO)^2$ in the calculations.

The results of Skripov and Povyshev[4] also show a systematic trend in $\Delta_rH^\ominus$ with the deuterium content of water, as was reported by Duer and Bertrand.[7] The values of $\Delta_rH^\ominus$ range from 127 J mol^{-1} and 119 J mol^{-1} for compositions approaching pure H_2O and pure D_2O, respectively, to 130 J mol^{-1} for the equimolar mixture. It is the last value that is reported in Table 3. In their calculations Skripov and Povyshev obviously used for $K(HDO)^2$ a value of 3.27[12] which nowadays is considered to be too low. Use of

incorrect equilibrium constant causes the above mentioned trend in $\Delta_rH^\ominus$ but does not alone explain the low value of $\Delta_rH^\ominus$ when the composition of water approaches pure D_2O. If the value 3.76 is used for $K(HDO)^2$ instead of 3.27 the values of $\Delta_rH^\ominus$ obtained by Skripov and Povyshev will be 135 J mol^{-1} (Ref. 3 in Table 3) and 125 J mol^{-1} (Ref. 4 in Table 3).

It is evident that the variation of $\Delta_rH^\ominus$ with $x(D;L_2O)$ in both Skripov's and Fenby's works[4,8] results from some defect in the calorimeter when the heats of reaction are relatively small and do not indicate deviations from the ideal behaviour.

The value of $\Delta_rH^\ominus$ determined by Duer and Bertrand[7] has been obtained from the enthalpy of solution studies. They used a value of 3.8 for $K(HDO)^2$. No systematic trend with $x(D;L_2O)$ could be observed in the $\Delta_rH^\ominus$ values calculated from their results.

Narten[5] and Salomon[6] reported $\Delta_rH^\ominus$ at different temperatures. The values of $\Delta_rH^\ominus$ were obtained from theoretical calculations for the gas phase reaction using the vapor pressure relations for the liquid phase reaction. According to Salomon's calculations there is an increase of about 6 J mol^{-1} K^{-1} in the value of $\Delta_rH^\ominus$ between 273 K and 373 K. A temperature dependence of this magnitude seems strange since in practice the $\Delta_rH^\ominus$ has generally proved to be only weakly dependent on the temperature. Narten's calculations show a decrease of $\Delta_rH^\ominus$ with increasing temperature. In both studies the calculation of partition functions involves application of methods of classical statistical mechanics. There has been a lot of discrepancy between the conclusions drawn from different statistical mechanical studies. Also the vapor pressure isotope effect results used in the calculation of $\Delta_rH^\ominus$ for the liquid phase reaction differ from each other. Since Narten's and Salomon's studies additional anharmonicity corrections to the zero point energy have been published.[11] New investigations of vapor pressure isotope effects have also been made.[13] On the basis of these more recent investigations Fenby and Chand[8] calculated a theoretical value of 120(20) J mol^{-1} for $\Delta_rH^\ominus$ at 298.15 K.

Taking into account the uncertainties in the theoretical values of $\Delta_rH^\ominus$ the calculated temperature dependence does not seem to be very reliable. If the temperature dependence of $\Delta_rH^\ominus$, however, is of the magnitude calculated by

Salomon,[6] it should be revealed even by measurements made in a quite narrow temperature range. In this work the measurements for $\Delta_r H^\ominus$ were made at 298.15 K and 303.15 K. The $\Delta_r H^\ominus$ values calculated from the excess enthalpy results at both temperatures proved to be, within the experimental error, almost equal to each other.

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