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THERMODYNAMIC PROPERTIES OF LIQUID H_2O AND D_2O AND THEIR MIXTURES

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ABSTRACT

The liquid and gas phase equilibria $H_2O + D_2O = 2HDO$ have been reinvestigated. By combining spectroscopic and vapor pressure data, fairly good agreement is found between the experimental and calculated enthalpy for the liquid phase reaction. It is found that the value of the equilibrium constant for the liquid phase reaction is very close to the geometric mean value of 4.0.

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SUMMARY

The thermodynamics of the two isotopic equilibria

$$H_2O_{(\ell)} + D_2O_{(\ell)} = 2HDO_{(\ell)} \qquad [1]$$

and

$$H_2O_{(g)} + D_2O_{(g)} = 2HDO_{(g)} \qquad [2]$$

have been studied with the object of obtaining more accurate values for the equilibrium constants. By using the experimental data for the vapor pressures of liquid H_2O, D_2O, and HDO, together with the spectroscopic gaseous data, the free energies and enthalpies of reactions [1] and [2] were calculated. The only accurate experimental data relating to either [1] or [2] is the heat of mixing of liquid H_2O and D_2O. The results of the present calculation give a value of 33.2 calories per mole for the heat of mixing which is close to the experimental value of 32 calories per mole.

INTRODUCTION

Many investigators involved in hydrogen-deuterium studies in solution either directly or indirectly make use of the equilibria

$$H_2O_{(\ell)} + D_2O_{(\ell)} = 2HDO_{(\ell)} \quad . \qquad [1]$$

Values for the equilibrium constant K(I) for reaction [1] have been measured directly (refs. 1-3), have been calculated by an indirect method (ref. 4), and have been calculated from spectroscopic data (refs. 1,5-8). Despite these many attempts to arrive at a value of K(I), there exist several discrepancies between calculated values, depending upon the source of the spectroscopic data (refs. 9,10), the method of calculation, and also between the experimental values and the geometric mean value of four obtained by Pyper and Long (ref. 4). In general, calculated values of K(I) based on Darling and Dennison's (DD) data (ref. 9) are higher than those based on the data of Benedict et. al. (ref. 10) (BGP). The experimental values tend to indicate higher values than those obtained from the BGP data, but they are somewhat smaller than those values obtained from the DD data. Weston (ref. 11) has recently discussed this problem and suggests that some accurate determination of K(II),

$$HD_{(g)} + H_2O_{(g)} = H_{2(g)} + HDO_{(g)} , \qquad [2]$$

would help resolve this problem. In this report, an additional criterion is suggested and investigated with the object of helping to resolve this problem. The additional criterion suggested here is the standard enthalpy of reaction [1], viz., $\Delta H^\circ(I)$ which is chosen as a valid criterion because it is the only quantity which can be easily and accurately measured experimentally. The measured value of $\Delta H^\circ(I)$ is 32 cal/mole (refs. 12,13).

METHOD

Since spectroscopic data for liquid species are not accurate enough to permit one to calculate K(I), the procedure used here, following Kirshenbaum's suggestion (ref. 7), is to relate reaction [1] to the gas phase equilibrium reaction:

$$H_2O_{(g)} + D_2O_{(g)} = 2HDO_{(g)} \qquad [3]$$

via the relation

$$K(I) = K(III) \frac{p^\circ_{H_2O} \cdot p^\circ_{D_2O}}{\left(p^\circ_{HDO}\right)^2} \qquad [4]$$

In Eq. [4], p° is the vapor pressure of the pure liquid indicated by the subscript. In terms of standard free energies, Eq. [4]

can be written as

$$\Delta G^\circ(\mathrm{I}) = \Delta G^\circ(\mathrm{III}) - RT\left\{2\ \ln\left(\frac{p^\circ_{H_2O}}{p^\circ_{DHO}}\right) - \ln\left(\frac{p^\circ_{H_2O}}{p^\circ_{D_2O}}\right)\right\} . \qquad [5]$$

Because HDO can exist only in a mixture of H_2O and D_2O, its vapor pressure cannot be measured directly. This problem has often been avoided by assuming that the rule of the geometric mean (ref. 14) is applicable; i.e.:

$$\left(p^\circ_{HDO}\right)^2 = \left(p^\circ_{H_2O}\right)\left(p^\circ_{D_2O}\right)$$

and hence that

$$\Delta G^\circ(\mathrm{I}) = \Delta G^\circ(\mathrm{III}) .$$

However, application of the rule of the geometric mean to the vapor pressures does not give acceptable $\Delta H^\circ(\mathrm{I})$ values. The vapor pressure ratio

$$\frac{p^\circ_{H_2O}}{p^\circ_{HDO}}$$

can be measured in dilute D-containing solutions by single-stage equilibrium experiments. Narten (ref. 8) has combined two sets of data (refs. 15,16) to arrive at the relation:

$$\ln\frac{p^\circ_{H_2O}}{p^\circ_{HDO}} = -0.033198 + \frac{11.6763}{T - 185.586} \qquad [6]$$

where T is temperature in degrees Kelvin. The experimental relation for

$$\frac{p^\circ_{H_2O}}{p^\circ_{D_2O}}$$

is given by Miles and Menzies (ref. 17) as

$$\log \frac{p^{\circ}_{H_2O}}{p^{\circ}_{D_2O}} = 16.9987 - \frac{268.843}{T} - 7.4972 \log T$$

$$+ 9.7611\times10^{-3}T \quad 4.4288\times10^{-6}T^{2} \quad . \qquad [7]$$

Another relationship obtained by Whalley (ref. 18) is that resulting from a least squares refinement of several sets of data and is

$$\log \frac{p^{\circ}_{H_2O}}{p^{\circ}_{D_2O}} = -0.030661 + \frac{9.14056}{75.753+t} \qquad [8]$$

where t is the temperature in degrees centigrade. Narten (ref. 8) used Eqs. [6] and [8] to evaluate the term in curly brackets in Eq. [5] and combined this with the free energy functions calculated by Friedman and Haar (ref. 19) and found $\Delta H^{\circ}(I) = 137$ cal/mole. Whalley (ref. 18) has pointed out that Eq. [8] gives acceptable results for temperatures above 100°C, but deviates significantly from the experimental relation [7] below this temperature. In the present calculations, the correct value of $\Delta H^{\circ}(I)$ was obtained only by using Eqs. [6] and [7].

To calculate K(I) values, the corresponding K(III) values are required. To calculate K(III) values, the spectroscopic data of BGP and DD [as quoted by Kirshenbaum (ref. 7)] were used. The familiar statistical mechanical procedures (ref. 20) were employed in the calculation. The translational partition function (p.f.) was calculated in the usual manner. Since there is no explicit formula for the rotational levels of an asymmetric top molecule, use was made of the approximate relation given by Herzberg (ref. 21):

$$q_r = \exp\left[\frac{(BC)^{1/2}hc}{4kT}\right]\left\{\frac{\pi}{ABC}\left(\frac{kT}{hc}\right)^{3}\right\}^{1/2}\left\{1+\frac{1}{12}\left(1-\frac{\sqrt{BC}}{A}\right)\frac{\sqrt{BC}\,hc}{kT}\right\} \qquad [9]$$

where A, B, and C are the effective rotational constants defined by

$$A = A_e - \sum \alpha_i^A \left(v_i + \frac{1}{2}\right)$$

$$B = B_e - \sum \alpha_i^B \left(v_i + \frac{1}{2}\right)$$

$$C = C_e - \sum \alpha_i^C \left(v_i + \frac{1}{2}\right) \quad . \qquad [10]$$

BGP have evaluated the nine molecular constants α_i for each isotope whereas DD have evaluated similar, but not equivalent, α_i' values. Herzberg (ref. 21) re-evaluated the DD α_i' values in terms of the α_i constants for H_2O only, and they are very similar to those reported by BGP. Hence the BGP α_i values have been used for HDO and D_2O in all the calculations presented in this report.

The vibrational p.f. was evaluated from the relation

$$q_v = \sum_i \exp - G(v_i)\frac{hc}{kT} \qquad [11]$$

where

$$G(v_i) = \sum_i \omega_i \left(v_i + \frac{1}{2}\right) + \sum_{i \leq j} x_{ij} \left(v_i + \frac{1}{2}\right)\left(v_j + \frac{1}{2}\right) \quad . \qquad [12]$$

In Eq. 12, the ω_i are the zero-order frequencies and the x_{ij} are the anharmonicities. Both the ω_i and x_{ij} values reported by BGP and DD differ slightly except for HDO where the difference is very large. The result is that the zero point energies for HDO vary accordingly as seen in Table I. The DD data indicate the only important states to be (0, 0, 0) and (0, 1, 0) and the BGP data show no important contributions to $G(v_i)$ beyond the second vibrational state. The calculations presented here, however, were carried out for all possible combinations of v_1, v_2, and v_3 up to the fourth vibrational state. The results were practically identical whether the first, second, third, or fourth vibrational states were considered. All these calculations were carried out on a Univac 1108 computer located at the NASA Manned Spacecraft Center, Houston, Texas. In all cases the effects due to nuclear spin have been ignored.

TABLE I

ZERO POINT ENERGIES* FOR ISOTOPIC WATERS

	H_2O	HDO	D_2O
Data of Dennison	4631.247	4018.585	3386.238
Data of Benedict	4634.253	4032.162	3388.687

*In cm^{-1}

RESULTS AND DISCUSSION

Table II gives the results of the calculations for the gaseous reaction [3]. Table III gives the data for the liquid phase reaction [1] obtained from the vapor pressure relations [6] and [7] and Eq. [5]. Table IV gives the results of a least squares fit to the relation

$$\Delta G°(I) = A + BT + CT^2 \quad .$$

The first entry in Table IV, which is one of the ERC results, is in very good agreement with the experimental $\Delta H°(I)$ value. Kirshenbaum's K(III) values also led to an acceptable value for the enthalpy. All calculations using the BGP data did not give very good $\Delta H°(I)$ values. It should be noted that the direct determination of K(I) by Friedman and Shiner (ref. 2) gives a very good value for $\Delta H°(I)$.

TABLE II

THERMODYNAMIC QUANTITIES FOR REACTION [3]

°C	Data of Dennison		Data of Benedict	
	K(III)	$\Delta H°(III)$*	K(III)	$\Delta H°(III)$*
0	3.985	56.62	3.409	118.10
25	4.019	54.61	3.471	116.06
50	4.047	52.41	3.524	113.82
75	4.071	50.05	3.568	111.41
80	4.075	49.56	3.576	110.90
100	4.083	48.561	3.592	109.89

*Units of ΔH are calories per mole.

TABLE III

THERMODYNAMIC QUANTITIES FOR REACTION [1]

°C	Data of Dennison		Data of Benedict	
	K(I)	ΔH°(I)*	K(I)	ΔH°(I)
0	4.010	15.33	3.432	59.82
25	4.010	33.15	3.463	94.54
50	4.035	67.76	3.522	129.19
75	4.086	106.51	3.582	167.98
80	4.094	114.95	3.593	176.43
100	4.108	132.60	3.614	194.10

*Units of ΔH are calories per mole.

TABLE IV

POWER SERIES CONSTANTS A, B, C FOR REACTION [1]

ΔH°(I)* at 298.15°K	A	B	C	Notes/ References
33.15	-174.32	-1.486	$-2.322\ 10^{-3}$	a
94.54	-113.15	-1.399	$-2.324\ 10^{-3}$	b
39.27	-173.61	-2.384	$-6.370\ 10^{-4}$	2(g)
21.06	-9.56	-2.613	$-3.146\ 10^{-4}$	6
36.09	-220.43	-1.052	$-2.877\ 10^{-4}$	7
65.81	-358.00	-2.506	$-4.101\ 10^{-3}$	2f
84.94	-98.79	-1.546	$-2.067\ 10^{-3}$	8
100.63	230.71	-3.977	$1.459\ 10^{-3}$	c
162.09	292.47	-3.894	$1.462\ 10^{-3}$	d
50.07	73.24	-3.051	$2.387\ 10^{-4}$	6(e)

*ΔH units are calories per mole.

a, c = results of present calculations using the DD data
b, d = results of present calculations using the BGP data
c, d, e = results based on Eqs. [5], [6], and [8]
g, f = ref. 2; experimental and theoretical data, respectively

All other entries were calculated from Eqs. [5] - [7].

The results of the present calculations can be extended to additional isotopic equilibria. To accomplish this, the p.f. ratio

$$\frac{q_{HDO}}{q_{H_2O}}$$

for the liquid species is needed. This ratio can be calculated from the relation:

$$\frac{q_{HDO}}{q_{H_2O}}_{\ell} = \left\{K(I)\left(\frac{q_{D_2O}}{q_{H_2O}}\right)_{\ell}\right\}^{1/2} \qquad [13]$$

where the ratio

$$\frac{q_{D_2O}}{q_{H_2O}}_{\ell}$$

has been calculated previously in the temperature range of interest (ref. 22).

Two important equilibria are

$$H_2O_{(g)} + HD_{(g)} = HDO_{(g)} + H_{2(g)} \qquad [14]$$

$$H_2O_{(\ell)} + HD_{(g)} = HDO_{(\ell)} + H_{2(g)} \qquad [15]$$

The p.f. ratio

$$\frac{q_{HD}}{q_{H_2}}$$

was obtained as a function of temperature from an NBS monograph (ref. 23), whereas the ratios for the water species were obtained from the present calculations resulting from the application of the DD data. K(14) and K(15) values are given in Table V as a function of temperature.

TABLE V

EQUILIBRIUM CONSTANTS K(14) AND K(15)

°C	0	25	50	75	80
K(14)	4.340	3.752	3.360	2.986	2.929
K(15)	4.780	4.000	3.449	3.049	3.982

CONCLUSIONS

The present work was performed with the intent of clarifying some of the existing uncertainties in the value of K(I) and the problems associated with its calculation. The ERC calculations agree very well with the measured quantity ΔH°(I) and with Pyper and Long's value at 25°C. The ERC results are also in fair agreement with the measurements of Friedman and Shiner (ref. 2) and hence lend support to the validity of the higher value of K(I).

Despite the fact that the BGP study (ref. 10) was much more extensive than the earlier one by Darling and Dennison (ref. 9), it gives very low K(I) values and very high ΔH°(I) values. The reason for this difference has been traced (refs. 4, 11) to differences in anharmonicity constants for HDO which results in significant differences between the zero-point energies for the gaseous molecules. Since the HDO spectrum, by necessity, contains equilibrium quantities of H_2O and D_2O, it is quite understandable that the frequencies and molecular constants for HDO are the least reliable (cf. discussions in references 4 and 11).

Darling and Dennison (ref. 9) did not observe the HDO spectrum but calculated the required molecular constants by the usual methods based on the H_2O and D_2O spectra. The direct summation of the vibration energies does not account for the present success in the calculated value for ΔH°(I) since this method has also been applied to the BGP data.

Weston (ref. 11) discussed the use of other equilibria which would aid in the choice between the more accurate spectroscopic data. For example, he cites the isotopic equilibria [14] for which the foregoing equilibrium constant has been calculated here. Weston gives two references (refs. 24,25) in which K(14) was indirectly estimated to be 3.41 and 3.54 at 25°C. These values are in good agreement with those values calculated using the BGP data (ref. 11) but are not in particularly good agreement with the ERC value of 3.75 based on the DD data. According to Kirshenbaum (ref. 7), however, Grosse (ref. 26) measured a value of 3.88 for K(14) at 25°C. Thus this important point needs further experimental confirmation.

While the present calculations give acceptable results, it should be pointed out that Wolfsberg (ref. 27) has questioned the use of Eq. [11], since he questions the usual assumption that the anharmonicity constants are invariant to isotopic substitution. If this is true, Eq. [11] cannot be used to calculate the zero-point energies.

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