

RESEARCH PAPER RP1287

Part of Journal of Research of the National Bureau of Standards, Volume 24,
April 1940

HEAT AND FREE ENERGY OF FORMATION OF DEUTERIUM OXIDE*

By Frederick D. Rossini, John W. Knowlton, and Herrick L. Johnston¹

ABSTRACT

Calorimetric measurements of the ratio of the heat evolved in the formation of 1 mole of liquid deuterium oxide, from gaseous deuterium and ordinary oxygen, to the heat evolved in the formation of 1 mole of ordinary liquid water, from gaseous ordinary hydrogen and oxygen, yielded the value 1.03068 ± 0.00029 for 25° C and a constant pressure of 1 atmosphere.

Calorimetric measurements of the ratio of the heat of vaporization of 1 mole of deuterium oxide to that of 1 mole of ordinary water yielded the value 1.03145 ± 0.00075 for 25° C and zero pressure.

Combination of these with other data yielded the following thermodynamic values:

$D_2(g) + 1/2 O_2(g) = D_2O(liq)$, $\Delta H^\circ_{298.16} = -294,563 \pm 94$ int. j/mole ($-70,414.0 \pm 22.5$ cal/mole), $\Delta F^\circ_{298.16} = -243,470 \pm 100$ int. j/mole ($-58,200.5 \pm 23.9$ cal/mole);

$D_2O(liq) = D_2O(g)$, $\Delta H^\circ_{298.16} = 45,391 \pm 36$ int. j/mole ($10,850.5 \pm 8.6$ cal/mole), $\Delta F^\circ_{298.16} = 8,949 \pm 9$ int. j/mole ($2,139.2 \pm 2.2$ cal/mole);

$D_2(g) + 1/2 O_2(g) = D_2O(g)$, $\Delta H^\circ_{298.16} = -249,172 \pm 100$ int. j/mole ($-59,563.5 \pm 23.9$ cal/mole), $\Delta F^\circ_{298.16} = -234,521 \pm 100$ int. j/mole ($-56,061.2 \pm 23.9$ cal/mole), $\Delta H^\circ_0 = -246,231 \pm 100$ int. j/mole ($-58,860.5 \pm 23.9$ cal/mole);

$D_2(g) + H_2O(liq) = H_2(g) + D_2O(liq)$, $\Delta H^\circ_{298.16} = -8,770 \pm 83$ int. j/mole ($-2,096.4 \pm 19.8$ cal/mole), $\Delta F^\circ_{298.16} = -6,316 \pm 96$ int. j/mole ($-1,509.8 \pm 22.9$ cal/mole);

$D_2(g) + H_2O(g) = H_2(g) + D_2O(g)$, $\Delta H^\circ_{298.16} = -7,386 \pm 90$ int. j/mole ($-1,765.6 \pm 21.5$ cal/mole), $\Delta F^\circ_{298.16} = -5,966 \pm 90$ int. j/mole ($-1,426.1 \pm 21.5$ cal/mole), $\Delta H^\circ_0 = -7,337 \pm 90$ int. j/mole ($-1,753.9 \pm 21.5$ cal/mole);

$D_2O(liq)$, $S^\circ_{298.16} = 76.099 \pm 0.130$ int. j/degree mole (18.191 ± 0.031 cal/degree mole).

On the assumption that the bond energies in H_2 and D_2 are the same, and likewise in H_2O and D_2O , the difference in the zero-point energies of $H_2O(g)$ and $D_2O(g)$ was calculated to be $14,841 \pm 91$ int. j/mole ($3,548 \pm 22$ cal/mole, or $1,243.0 \pm 7.6$ wave numbers). The accord of this value with that recently calculated by Darling and Dennison from the vibrational-rotational spectra of deuterium oxide and protium oxide, $1,245.5 \pm 2.0$ wave numbers, indicates that, within the assigned limits of uncertainty, the respective bond energies are independent of the mass of the nucleus of the atom.

* Paper presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Cincinnati, Ohio, April 9-11, 1939.

¹ Professor of Chemistry, The Ohio State University, Columbus, Ohio.

CONTENTS

	Page
I. Introduction.....	370
II. Units, molecular weights, etc.....	370
III. Ratio of the heats of formation of deuterium oxide and ordinary water, in the liquid state at 25° C.....	371
1. Method and apparatus.....	371
2. Chemical procedure.....	371
3. Calorimetric procedure.....	372
4. Experimental results.....	374
IV. Ratio of the heats of vaporization of deuterium oxide and ordinary water, at 25° C.....	376
1. Method and apparatus.....	376
2. Chemical procedure.....	376
3. Calorimetric procedure.....	378
4. Experimental results.....	380
V. Comparison with previous experimental data.....	382
1. Heat of formation of liquid deuterium oxide.....	382
2. Heat of vaporization of deuterium oxide.....	382
VI. Thermodynamic calculations.....	383
1. Heat of formation of deuterium oxide at 25° C and 0° K.....	383
2. Free energy of formation of deuterium oxide at 25° C.....	383
3. Entropy of liquid deuterium oxide at 25° C.....	384
4. The reaction $D_2 + H_2O = H_2 + D_2O$	384
5. Zero-point energies.....	385
VII. Summary.....	386
VIII. References.....	388

I. INTRODUCTION

It has been generally established, both experimentally and theoretically, that the various isotopes of a given chemical element differ in those properties which are functions of the mass of the nucleus, but not in those properties which are functions of the distribution of electrons about the nucleus. The greatest difference in the properties of any two isotopes is exhibited by the isotopes of hydrogen, because of the relatively large difference in mass between protium and deuterium. This relatively great difference in properties has made possible the preparation of substantially pure deuterium in large amount. Since ordinary hydrogen, oxygen, and water are substances whose properties are well known, it appeared desirable to make a calorimetric comparison of the heats of formation of ordinary liquid water and of liquid deuterium oxide from their respective elements, and of their heats of vaporization, and by appropriate thermodynamic calculations to ascertain whether the theoretical expectations and the experimental observations agree within the limits of accuracy of present-day measurements.

This paper reports the calorimetric determination of the ratio of the heats of formation of ordinary liquid water and liquid deuterium oxide, and of their heats of vaporization, and presents the results of thermodynamic calculations giving the heat and free energy of formation of deuterium oxide in the liquid and gaseous states, the heat and free energy of the reaction $D_2 + H_2O = H_2 + D_2O$, and the difference in the zero-point energies of H_2O and D_2O .

II. UNITS, MOLECULAR WEIGHTS, ETC.

The unit of energy in this work is the international joule (int. j) based upon standards of electromotive force and resistance maintained at this Bureau. Conversion to the artificial or defined calorie was made with the relation $1 \text{ cal} = 4.1833 \text{ int. j}$. The absolute tempera-

ture of the ice point was taken as $0^{\circ}\text{C} = 273.16 \pm 0.02^{\circ}\text{K}$. The value of the gas constant per mole, R , was taken² as 8.3145 ± 0.0006 absolute j/degree, or 8.3128 ± 0.0008 int. j/degree, or 1.98714 ± 0.00019 cal/degree.

On the chemical scale, the molecular weights were taken as follows:³ H_2O , 18.0162; H_2^{18}O , 18.0158; $\text{H}^1\text{D}^1\text{O}$, 19.0221; D_2^{16}O , 20.0284 [1, 2, 3, 4].⁴

The uncertainties assigned to the various quantities dealt with in this paper were derived, where possible, by a method previously described [5]. In other cases, reasonable estimates of the uncertainties were made.

III. RATIO OF THE HEATS OF FORMATION OF DEUTERIUM OXIDE AND ORDINARY WATER, IN THE LIQUID STATE AT 25°C

1. METHOD AND APPARATUS

The calorimetric method used was the same as in the investigation on the heat of formation of ordinary water [6]. The reaction vessel, calorimeter, and other apparatus were also the same, except for the control of the temperature of the jacket of the calorimeter [7], the heating coil in the calorimeter [8], and the resistance thermometer and bridge [9], which had been replaced in later investigations.

2. CHEMICAL PROCEDURE

The oxygen and hydrogen, commercially prepared, were purified by passage through copper oxide and copper, respectively, each at about 600°C , Ascarite (a mixture of sodium hydroxide and asbestos), anhydrous magnesium perchlorate, and phosphorus pentoxide, in the order given.

The deuterium oxide used for preparing the gaseous deuterium for the experiments on the heat of formation has already been described [10]. The ratio of the density of the deuterium oxide to that of ordinary water at 27°C was 1.10771, and the purity was calculated to be 1.0000 ± 0.0003 mole fraction. The deuterium was prepared by passing the gaseous deuterium oxide through powdered magnesium at 480°C .⁵ The purity of the deuterium as it was finally obtained under pressure in a 1-liter brass bottle was determined from measurements of vapor pressures kindly made for the authors by F. G. Brickwedde and R. B. Scott, of the Cryogenic Laboratory of this Bureau. At a temperature of 20.333°K , the vapor pressures of normal hydrogen and of the prepared deuterium, each in the liquid state, were found to be 747.34 and 253.31 mm Hg, respectively. For this same temperature, the data of Brickwedde, Scott, and Taylor [12] and of Brickwedde and Scott [13] yield 250.68 and 429.68 mm Hg, respectively, for the vapor pressures of liquid normal D_2 and liquid H^1D . Assuming from the method of preparation that the impurity in the deuterium was in equilibrium⁶ with respect to the reaction $\text{H}_2(\text{g}) + \text{D}_2(\text{g}) = 2$

² The derivation of these values of the constants will be discussed in a later report by one of the authors (F. D. Rossini).

³ The chemical symbols have the following significance: H, naturally existing or normal hydrogen (consisting of 0.9998 H^1 and 0.0002 D); H^1 , protium; D, deuterium; H^2 , O, naturally existing or normal oxygen.

⁴ Figures in brackets indicate the literature references at the end of this paper.

⁵ See reference [11] for a detailed description of the method and apparatus.

⁶ The assumption most contrary to this, namely, that the impurity is present entirely as molecules of H_2^1 appears to be extremely unlikely. If the calculations were carried through on this basis, the resulting value for the heat of formation of deuterium oxide would differ from that actually calculated by about 1 part in 10,000.

H^1D (g) and that the value of the observed difference in vapor pressure between pure liquid D_2 and that used in this investigation was uncertain by 0.50 mm (or about 20 percent of itself), the impurity in the deuterium used was calculated to be 0.0147 ± 0.0028 mole fraction of H^1D and 0.00006 ± 0.00001 mole fraction of H_2 .

The amount of reaction in the calorimetric experiments was determined from the mass of water formed in the reaction, in the manner previously described,⁷ with the absorption tubes always filled with hydrogen at the times of weighing.

3. CALORIMETRIC PROCEDURE

The aim of the experimental part of this investigation was to determine as accurately as possible the ratio of the heats of formation of ordinary water and deuterium oxide, whence the value for the latter could be calculated from the value previously determined for ordinary water [6, 14, 15]. In principle, this was accomplished by determining the ratio of the masses of ordinary water and deuterium oxide whose formation produced identical rises of temperature in the same calorimeter system.

The method of reducing the actual experimental observations to this end was as follows: Let

ΔR_c = the corrected rise of temperature of the calorimeter system, expressed as the increase in resistance in ohms of the given platinum resistance thermometer at a mean temperature of 25°C , as measured on the given resistance bridge;

W = the mass of water in the given calorimeter system;

W_s = the mass of water in the "standard" calorimeter system (W will usually differ from W_s by not more than ± 10 g or $\pm 1/360$ of itself);

E_s = the energy equivalent, over a "standard" interval of temperature, of the "standard" calorimeter system, expressed as international joules per ohm increase in resistance of the given platinum resistance thermometer at a mean temperature of 25°C , as measured on the given resistance bridge;

E = the energy equivalent of the given calorimeter system containing W grams of water;

w = the mass of ordinary water formed as liquid in the reaction vessel;

w' = the mass of deuterium oxide formed as liquid in the reaction vessel;

q_{vap} = the heat of vaporization or that amount of water (ordinary or heavy) formed in the reaction but not remaining as liquid in the reaction vessel (this term corrects to the liquid state all the water formed in the reaction);

q_{gas} = the energy taken from the calorimeter by the inflowing gases;

q_{ign} = the energy added to the calorimeter by the ignition operation;

⁷ See p. 6 to 9 of reference [6].

c_w = the heat capacity of 1 g of ordinary water, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer;

c'_w = the heat capacity of 1 g of deuterium oxide, expressed as joules per ohm increase in resistance of the given platinum resistance thermometer;

m_{H_2O} = the mass of water formed in the reaction with ordinary hydrogen;

m_{D_2O} = the mass of deuterium oxide formed in the reaction with deuterium;

$(qf)_{H_2O}$ = the heat evolved, at 25° C and a constant pressure of 1 atmosphere, in the formation of 1 g of ordinary water in the liquid state from normal oxygen and hydrogen in the gaseous state; and

$(qf)_{D_2O}$ = the heat evolved, at 25° C and a constant pressure of 1 atmosphere, in the formation of 1 g of deuterium oxide in the liquid state from normal oxygen and deuterium in the gaseous state.

For the experiments with ordinary hydrogen, the following relations hold:

$$E = E_s + c_w(W - W_s + 1/2 w) \quad (1)$$

$$m_{H_2O}(qf)_{H_2O} = (\Delta R_c)E + q_{vap} + q_{gas} - q_{ign}. \quad (2)$$

Substituting for E in eq 2, and solving for $(qf)_{H_2O}/E_s$, which will be called A_{H_2O} , there is obtained

$$A_{H_2O} = (qf)_{H_2O}/E_s =$$

$$\frac{\Delta R_c}{m_{H_2O}} \left[1 + \frac{c_w(W - W_s + 1/2 w) + (q_{vap} + q_{gas} - q_{ign})/\Delta R_c}{E_s} \right]. \quad (3)$$

For the experiments with deuterium, the analogous equations are:

$$E = E_s + c_w(W - W_s) + c'_w(1/2 w') \quad (4)$$

$$m_{D_2O}(qf)_{D_2O} = (\Delta R_c)E + q_{vap} + q_{gas} - q_{ign} \quad (5)$$

$$A_{D_2O} = (qf)_{D_2O}/E_s =$$

$$\frac{\Delta R_c}{m_{D_2O}} \left[1 + \frac{c_w(W - W_s) + 1/2 c'_w w' + (q_{vap} + q_{gas} - q_{ign})/\Delta R_c}{E_s} \right]. \quad (6)$$

Then from eq 3 and 6

$$(qf)_{D_2O}/(qf)_{H_2O} = A_{D_2O}/A_{H_2O}. \quad (7)$$

If M_{H_2O} and M_{D_2O} are the molecular weights of H_2O and D_2O , respectively, then the ratio of the heats of formation, from gaseous oxygen and hydrogen or deuterium, of H_2O and D_2O in the liquid state

at 25° C and a constant pressure of 1 atmosphere, expressed in terms of the increment in heat content, ΔH , per mole, is

$$(\Delta Hf)_{D_2O}/(\Delta Hf)_{H_2O} = (A_{D_2O}/A_{H_2O})(M_{D_2O}/M_{H_2O}). \tag{8}$$

4. EXPERIMENTAL RESULTS

The data of the experiments with ordinary hydrogen and with the deuterium are given in tables 1 and 2, respectively, where the column headings are defined as above and on page 379. To the mean values of A_{H_2O} and $A_{(D_2O)^*}$ obtained from these experiments, uncertainties of 0.018 percent and 0.014 percent, respectively, were assigned, so that ⁸

$$A_{H_2O} = 0.103\ 508 \pm 0.000\ 019\ \text{ohm/g} \tag{9}$$

$$A_{(D_2O)^*} = 0.096\ 013 \pm 0.000\ 013\ \text{ohm/g}. \tag{10}$$

From these values, there is obtained the ratio

$$A_{(D_2O)^*}/A_{H_2O} = 0.927\ 59 \pm 0.000\ 21. \tag{11}$$

Neglecting the minute amount of H₂O, the molecular weight of the (D₂O)* is

$$20.0284 - (0.0147 \pm 0.0028)(20.0284 - 19.0221) = 20.0136 \pm 0.0028.$$

The ratio of the molecular weights is

$$M_{(D_2O)^*}/M_{H_2O} = 1.110\ 87 \pm 0.000\ 16. \tag{12}$$

And, by eq 8, 11, and 12

$$(\Delta Hf)_{(D_2O)^*}/(\Delta Hf)_{H_2O} = 1.030\ 43 \pm 0.000\ 28. \tag{13}$$

TABLE 1.—*Calorimetric data of the experiments on the heat of formation of ordinary water* ^{a, b}

Ex- per- iment num- ber ^c	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_0	<i>W</i>	<i>q</i> _{vap}	<i>q</i> _{gas}	<i>q</i> _{icn}	<i>m</i> _{H₂O}	<i>A</i> _{H₂O}	Deviation from mean
	<i>1/min</i>	<i>Ohms</i>	<i>Ohms</i>	<i>Ohms</i>	<i>g</i>	<i>Joules</i>	<i>Joules</i>	<i>Joules</i>	<i>g</i>	<i>Ohms/g</i>	<i>Ohms/g</i>
1.....	0.001 872	0.003 797	-0.000 120	0.300 460	3615.33	67.8	1.0	7.5	2.903 42	0.103 531	0.000 023
2.....	.001 905	.003 844	.000 022	.299 316	3623.11	67.1	1.6	7.5	2.896 70	.103 565	-.000 057
3.....	.001 894	.003 152	-.000 008	.251 031	3615.67	51.7	0.8	7.5	2.426 24	.103 497	-.000 011
4.....	.001 875	.003 098	.000 082	.250 485	3619.09	47.6	3.6	7.5	2.422 47	.103 526	-.000 016
5.....	.001 870	.003 123	.000 030	.250 633	3618.66	52.2	2.4	7.5	2.424 92	.103 480	-.000 028
6.....	.001 856	.003 048	.000 020	.250 217	3614.87	58.8	0.7	7.5	2.418 17	.103 504	-.000 004
7.....	.001 879	.003 183	-.000 018	.249 375	3609.63	53.2	3.2	7.5	2.406 66	.103 494	-.000 014
8.....	.001 874	.003 141	-.000 032	.247 892	3620.46	52.9	0.8	7.5	2.398 92	.103 507	-.000 001
9.....	.001 911	.003 123	.000 084	.248 798	3619.54	60.1	2.4	7.5	2.408 52	.103 469	-.000 039
Mean.....										0.103 508	-----
Standard deviation of the mean [5].....										±0.000009 ₀	-----

^a The results of 2 other experiments made in this series are not included, because their deviations from this mean were, respectively, about 6 and 8 times the normal deviation for such experiments.

^b See text on p. 372 for explanation of symbols.

⁸ The symbol (D₂O)* is used to denote the actual deuterium oxide, which, in the experiments on formation, was formed from deuterium that contained 0.0147 ± 0.0028 mole fraction of H²D and 0.000 06 ± 0.000 01 mole fraction of H₂ (see section III-2).

TABLE 2.—Calorimetric data of the experiments on the heat of formation of deuterium oxide ^a

Ex- per- iment num- ber	<i>k</i>	<i>K</i>	<i>U</i>	ΔR_c	<i>W</i>	<i>q_{vap}</i>	<i>q_{gas}</i>	<i>q_{ign}</i>	<i>m_{D₂O}</i>	<i>A_{(D₂O)*}</i>	Deviation from mean
	<i>l/min</i>	<i>Ohms</i>	<i>Ohms</i>	<i>Ohms</i>	<i>g</i>	<i>Joules</i>	<i>Joules</i>	<i>Joules</i>	<i>g</i>	<i>Ohms/g</i>	<i>Ohms/g</i>
1.....	0.001 916	0.004 081	-0.000 066	0.245 183	3619.61	53.3	2.5	7.5	2.556 57	0.096 034	+0.000 021
2.....	.001 877	.002 774	.000 070	.250 078	3621.70	57.2	1.2	7.5	2.610 41	.096 005	-.000 068
3.....	.001 891	.002 689	.000 052	.251 528	3620.47	45.7	2.9	7.5	2.623 57	.096 020	+-.000 007
4.....	.001 975	.002 845	.000 200	.248 997	3616.96	39.6	1.7	7.5	2.595 13	.095 987	-.000 026
5.....	.001 888	.002 813	.000 156	.250 733	3623.51	46.6	1.5	7.5	2.617 46	.096 018	+-.000 005
6.....	.001 886	.003 289	.000 048	.211 428	3619.94	49.0	1.0	7.5	2.205 59	.096 013	.000 000
Mean.....										0.096 013	-----
Standard deviation of the mean [5].....										±0.000006%	-----

^a See text on p. 372 for explanation of symbols.

With an approximate value for the difference in the heats of formation of D₂O and H¹DO, one can correct the value for (D₂O)* for the small amount of H¹DO in it and obtain a value for the heat of formation of pure D₂O. By the method discussed in section VI-5, it was calculated that, for the formation of liquid water from gaseous normal oxygen and the given hydrogen at 25° C,

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{H^1DO} = -4,700 \pm 900 \text{ int. j/mole.} \quad (14)$$

In a similar manner, it was calculated that

$$(\Delta Hf)_{H^1DO} - (\Delta Hf)_{H_2^1O} = -4,070 \pm 900 \text{ int. j/mole.} \quad (15)$$

The foregoing calculations were made by taking the heat of vaporization of liquid H¹DO at 25° C to be 44,700 ± 200 int. j/mole, the value of $H^\circ_{298.16} - H^\circ_0$ to be 8,519 ± 8 int. j/mole for H¹D(g) and 9,930 ± 12 int. j/mole for H¹DO(g), and the difference in the zero-point energies between H₂(g) and H¹D(g) and between H₂O(g) and H¹DO(g) to be 3,419 ± 12 and 7,400 ± 900 int. j/mole, respectively. The value for the heat of formation of liquid ordinary water, from gaseous normal hydrogen and oxygen, at 25° C, has already been reported [15] to be

$$(\Delta Hf)^\circ_{H_2O} = -285,795 \pm 40 \text{ int. j/mole.} \quad (16)$$

Taking account of the 0.0147 mole fraction of H¹DO in the D₂O, it was calculated that

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{(D_2O)^*} = -70 \pm 13 \text{ j/mole.} \quad (17)$$

Or, in terms of $(\Delta Hf)_{H_2O}$,

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{(D_2O)^*} = (0.000 25 \pm 0.000 05) (\Delta Hf)_{H_2O}. \quad (18)$$

Combination of eq 13 and 18 yields

$$(\Delta Hf)_{D_2O} = (1.030 68 \pm 0.000 29) (\Delta Hf)_{H_2O}, \text{ or} \quad (19)$$

$$(\Delta Hf)_{D_2O} - (\Delta Hf)_{H_2O} = -8,768 \pm 83 \text{ int. j/mole.} \quad (20)$$

Taking account, in a similar manner, of the 0.0004 mole fraction of H^1DO in H_2O , it was calculated that

$$(\Delta H_f)_{\text{H}_2^1\text{O}} - (\Delta H_f)_{\text{H}_2\text{O}} = 1.6 \pm 0.4 \text{ j/mole.} \quad (21)$$

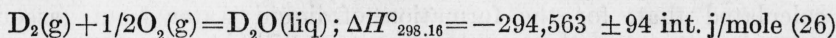
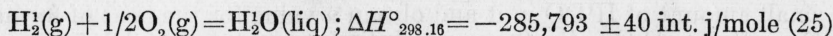
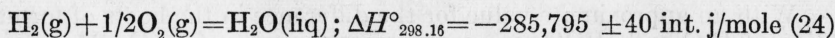
Or, in terms of $(\Delta H_f)_{\text{H}_2\text{O}}$,

$$(\Delta H_f)_{\text{H}_2^1\text{O}} = (0.999\,994 \pm 0.000\,002)(\Delta H_f)_{\text{H}_2\text{O}}. \quad (22)$$

Therefore,

$$(\Delta H_f)_{\text{D}_2\text{O}} = (1.030\,68_8 \pm 0.000\,29_0)(\Delta H_f)_{\text{H}_2^1\text{O}}. \quad (23)$$

Assuming the conversion from a real pressure of 1 atmosphere to the hypothetical standard state with fugacity equal to 1 atmosphere to be the same (-3.6 j/mole [15] for the formation of the different species of water, the following values were obtained:



IV. RATIO OF THE HEATS OF VAPORIZATION OF DEUTERIUM OXIDE AND ORDINARY WATER, AT 25° C

1. METHOD AND APPARATUS

The calorimetric method used in these experiments was substantially the same as that previously used in this laboratory to determine the change in internal energy of gases as a function of the pressure [33], in which experiments the change of state was from that of a gas at a high pressure (20 to 40 atmospheres) to that of a gas at a pressure of 1 atmosphere. In the experiments on vaporization, the change of state was from that of a liquid under its own vapor pressure to that of a gas at a low pressure (about 2 mm Hg).

The calorimetric apparatus for the experiments on the heat of vaporization was the same as for the experiments on the heat of formation, except that the reaction vessel (see fig. 2 of reference [6]) was replaced by the one shown in figure 1 of this paper.

2. CHEMICAL PROCEDURE

In the case of both the ordinary water and the deuterium oxide, all transfer of material was effected in the absence of air by distilling the material under its own vapor pressure at room or lower temperature. The experiments with ordinary water were performed first, followed by those with deuterium oxide. Before receiving deuterium oxide, the entire system, including vessels and connecting tubes, was twice flushed with the vapor of deuterium oxide and evacuated.

The deuterium oxide was removed from its sealed glass ampoule by placing the latter inside a second glass tube connected, as shown in

figure 1, to a receiving vessel; evacuating the entire system; placing liquid air around the tube containing the sealed glass ampoule; letting the latter break as a result of the expansion of the deuterium oxide on freezing; replacing the liquid air with water at room temperature; flushing and evacuating the system twice; placing a refrigerant at about -80°C (solid carbon dioxide in a mixture of carbon tetrachloride and chloroform) around the receiving bulb; and permitting the distillation to proceed at the vapor pressure of the deuterium oxide at room temperature. The deuterium oxide was then transferred in a similar manner to the reaction vessel.

For the experiments with ordinary water, distilled water from the Bureau's Chemistry Building supply line was used, with dissolved air removed by the distillation process described above.

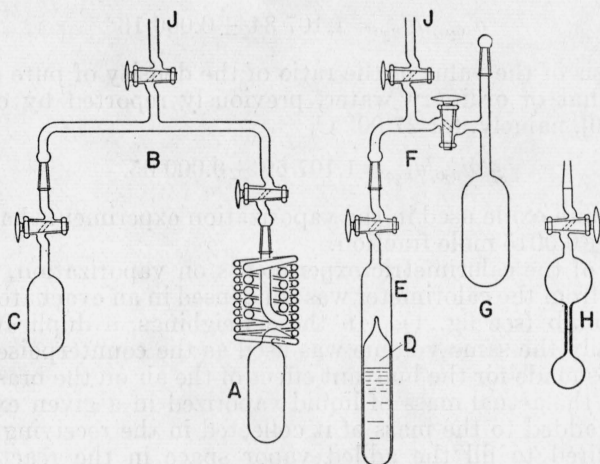


FIGURE 1.—Apparatus (glass) used in the experiments on vaporization.

A, calorimetric reaction vessel from which water is vaporized; B, connecting tube; C, receiving bulb; J, connection to vacuum pump; D, sealed ampoule containing original deuterium oxide; E, bulb in which the ampoule of deuterium oxide is broken; F, connecting tube; G, reservoir; H, picnometer for determining densities "in vacuo."

The deuterium oxide used in the experiments on vaporization was a lot of 25 g obtained commercially,⁹ which was sealed in a glass ampoule and labeled "99.9+ percent deuterium oxide." The purity of this material was determined at the conclusion of the experiments on vaporization by measuring at 27.00°C the ratio of the mass of it to the mass of ordinary water required to fill to a given mark the picnometer shown in figure 1. In the determination of the specific gravity of the deuterium oxide, the material was transferred entirely in the absence of air, by distillation at its own vapor pressure at room temperature, with the deuterium oxide and the ordinary water being at all times in contact only with their respective vapors. In weighing

⁹ This deuterium oxide was purchased from the Stuart Oxygen Co., San Francisco, Calif.

the pycnometer, a duplicate of it was used as a counterpoise, and correction was made for the buoyant effect of the air on the brass weights. If d is the density and m is the mass of liquid required to fill the pycnometer to the given volume, then¹⁰

$$d_{(D_2O)^*}/d_{H_2O} = m_{(D_2O)^*}/m_{H_2O} \quad (27)$$

To obtain the actual mass of liquid in the pycnometer, there was subtracted from the total mass of water (liquid plus vapor) in the pycnometer the mass of the water vapor in the space above the liquid. This correction amounted to 0.001 39 g for the ordinary water, and correspondingly to 0.001 35 g for the deuterium oxide. The total volume of the liquid in the pycnometer was near 16.8 ml. The measurements yielded, for 27.00° C, the value

$$d_{(D_2O)^*}/d_{H_2O} = 1.107\ 84 \pm 0.000\ 16 \quad (28)$$

On the basis of the value of the ratio of the density of pure deuterium oxide to that of ordinary water, previously reported by one of the authors [10], namely, for 27.00° C,

$$d_{D_2O}/d_{H_2O} = 1.107\ 69 \pm 0.000\ 05 \quad (29)$$

the deuterium oxide used in the vaporization experiments had a purity of 1.0000 ± 0.0015 mole fraction.

In each of the calorimetric experiments on vaporization, the liquid vaporized from the calorimeter was condensed in an evacuated weighed receiving bulb (see fig. 1). In these weighings, a duplicate bulb of substantially the same volume was used as the counterpoise, and correction was made for the buoyant effect of the air on the brass weights. To obtain the actual mass of liquid vaporized in a given experiment, there was added to the mass of it collected in the receiving bulb that mass required to fill the added vapor space in the reaction vessel caused by the removal of liquid from it. This added mass of water was calculated from the densities of the liquid and vapor phases at 25° C to be 0.000 02₃ g of vapor per gram of liquid for H₂O, and correspondingly to 0.000 02₀ g of vapor per gram of liquid for D₂O.

3. CALORIMETRIC PROCEDURE

In the calorimetric experiments, the water under investigation was vaporized from the calorimetric reaction vessel by lowering the vapor pressure of the water in the receiving bulb outside the calorimeter through control of its temperature. The pressure in the reaction vessel in the calorimeter was constant at the value water normally has at 25° C, namely, about 24 and 21 mm Hg for ordinary water and deuterium oxide, respectively. The temperature of the jacket of the calorimeter was maintained constant, and, during the actual vaporization of water, electric energy was given to the calorimeter at a rate that substantially balanced the rate of withdrawal of energy by vaporization. Having once determined approximately the electric power required, this was kept constant, and necessary slight variations in the rate of vaporization were effected by changing the effective

¹⁰ (D₂O)* represents the actual deuterium oxide used.

temperature of the receiving bulb through alteration of its depth of immersion in the refrigerant (solid carbon dioxide in a mixture of carbon tetrachloride and chloroform).

The times of the "fore," "reaction," and "after" periods in the calorimetric experiments were 20, 70, and 20 minutes, respectively, with the actual vaporization occurring in the first 60 minutes of the 70-minute "reaction" period. The substantially constant rate of input of energy to the calorimeter through stirring, etc., u , measured in ohms per minute, was taken as the average of the values calculated for this quantity from the observations of the "fore" and "after" periods. The value of the heat-leak constant, k , was taken as 0.00198/min. a value determined in other experiments with larger differences of temperature between the jacket and the calorimeter can.

During the reaction period, the energy removed from the calorimeter by the vaporization process, is

$$Q = (\text{electric energy}) - E(\Delta R - U - K), \quad (30)$$

where the electric energy is in int. j; E is the energy equivalent of the calorimeter system in int. j/ohm; ΔR is the increase in resistance, in ohms, of the platinum resistance thermometer during the reaction period; U is the product of u and the time of the reaction period; and K is the product of k , the time of the reaction period, and $(R_1 - R_c)_{\text{ave}}$, the average, with respect to time, of the difference in temperature between the jacket and the calorimeter expressed in ohms on the given platinum resistance thermometer.

If m is the mass of water vaporized, then the heat of vaporization of 1 g of water, from a liquid under its own vapor pressure to a gas issuing from the exit end of the calorimeter at the given pressure and velocity, is

$$l_v = Q/m, \quad (31)$$

where Q is given by eq 30.

To reduce the heat content of the gas to zero pressure with no directed kinetic energy, there must be added to the above value of l_v the increase in the heat content of the gas in going to zero pressure from the pressure at the exit end of the calorimeter, and there must be subtracted from it the amount of directed kinetic energy possessed by the gas as it issued from the calorimeter. For the former correction, the value of $(dH/dP)_T$ is taken to be the same, per mole, for both ordinary water vapor and deuterium oxide vapor, namely, 705 ± 35 j/atm mole [15]. This correction was calculated to be 0.10 and 0.09 j/g for ordinary water and deuterium oxide, respectively, under the given conditions. The pressure of the gas at the exit end of the calorimeter was calculated, from the known dimensions of the path of travel of the vapor and the total known pressure drop from the reservoir in the reaction vessel to the receiving vessel outside the calorimeter, to be 1.9₈ and 1.7₂ mm Hg for the ordinary water and the deuterium oxide, respectively. From the pressure, the cross-sectional area at the exit end of the calorimeter, and the known rate of with-

drawal of water from the reaction vessel, the directed kinetic energy was calculated to be 0.61 and 0.59 j/g for the ordinary water and the deuterium oxide, respectively.

4. EXPERIMENTAL RESULTS

The experimental data obtained on the vaporization of ordinary water are given in table 3 and those for deuterium oxide in table 4. The final over-all uncertainty of each value, obtained by including uncertainties in the small corrections to zero pressure and for directed kinetic energy equal to 100 percent of their own values, is given in the last line of each table.

TABLE 3.—*Calorimetric data on the heat of vaporization of ordinary water*^a

Experiment number	Electric energy	ΔR	U	K	Energy equivalent of calorimeter	Mass of H ₂ O	Average temperature	Heat of vaporization ^b at 25° C	Deviation from mean
	<i>Int. j</i>	<i>Ohms</i>	<i>Ohms</i>	<i>Ohms</i>	<i>Int. j/ohm</i>	<i>g</i>	<i>° C</i>	<i>Int. j/g</i>	<i>j/g</i>
1.....	22, 406.6	-0.004 158	0.000 762 2	0.000 691 6	147, 460	9.495 99	24.95	2446.11	2.07
2.....	22, 398.8	.002 690	.000 770 0	.000 189 9	147, 084	9.061 56	24.98	2443.20	-0.84
3.....	23, 123.0	-.001 864	.000 805 0	-.000 221 8	147, 609	9.608 57	25.02	2443.63	-.41
4.....	23, 141.6	.002 066	.000 798 0	-.000 140 0	147, 215	9.385 08	25.01	2443.21	-.83
Mean.....								2444.04	
Standard deviation of the mean [5].....								±0.70	
Uncertainty interval ^c [5].....								±1.52	

^a See text on p. 379 for explanation of symbols.

^b Corrected to 25.00° C (taking $dl/dT = -2.36$ j/g degree), to zero directed kinetic energy (-0.61 j/g), and to zero pressure (+0.10 j/g).

^c Including assumed uncertainties of 100 percent of the values of the corrections given in footnote b.

TABLE 4.—*Calorimetric data on the heat of vaporization of deuterium oxide*^a

Experiment number	Electric energy	ΔR	U	K	Energy equivalent of calorimeter	Mass of D ₂ O	Average temperature	Heat of vaporization ^b at 25° C	Deviation from mean
	<i>Int. j</i>	<i>Ohms</i>	<i>Ohms</i>	<i>Ohms</i>	<i>Int. j/ohm</i>	<i>g</i>	<i>° C</i>	<i>Int. j/g</i>	<i>j/g</i>
1.....	20, 161.0	-0.001 905	0.000 615 6	0.000 046 6	147, 429	9.052 67	25.01	2268.41	0.76
2.....	20, 148.6	.000 993	.000 574 0	.000 123 4	147, 064	8.861 84	25.00	2268.23	.58
3.....	19, 728.9	-.002 623	.000 503 2	-.000 177 3	147, 319	8.889 67	25.02	2267.72	.07
4.....	19, 705.8	.001 971	.000 406 0	.000 011 1	146, 962	8.592 79	25.01	2266.23	-1.42
Mean.....								2267.65	
Standard deviation of the mean [5].....								±0.50	
Uncertainty interval ^c [5].....								±1.17	

^a See text on p. 379 for explanation of symbols.

^b Corrected to 25.00° C (taking $dl/dT = -2.36$ j/g degree), to zero directed kinetic energy (-0.59 j/g), and to zero pressure (+0.09 j/g).

^c Including assumed uncertainties of 100 percent of the values of the corrections given in footnote b.

The value obtained from the present experiments for the heat of vaporization of ordinary water to zero pressure, namely, 2444.04 ± 1.52 int. j/g at 25° C, agrees, within the respective limits of uncer-

tainty, with the value obtained by converting the recent data of Osborne, Stimson, and Ginnings [34] (which were obtained at saturation pressure) to zero pressure, which value is 2442.63 ± 0.72 int. j/g at 25°C [15].

The calorimeter used in the present experiments on vaporization was not especially designed for measuring heats of vaporization (in particular, it was designed to transfer energy at the rate of 50 to 150 watts, whereas in the experiments on vaporization the rate of transfer of energy was less than 7 watts), and there is the possibility of the existence of some small unaccounted-for constant errors. Therefore, it is felt that, from the data of the present experiments on vaporization, there can be obtained a value for the ratio of the heats of vaporization of deuterium oxide and ordinary water that is more accurate than the value for either one separately, and that a "best" value for the difference in their heats of vaporization and for the heat of vaporization of deuterium oxide can be obtained by combining this ratio with the "best" value for the heat of vaporization of ordinary water, as obtained from the data of Osborne, Stimson, and Ginnings [34], plus a correction to zero pressure [15].

The present data yield for the ratio of the heat of vaporization of 1 g of ordinary water to that of 1 g of deuterium oxide, to zero pressure at 25°C , the value

$$l^\circ_{\text{H}_2\text{O}}/l^\circ_{\text{D}_2\text{O}} = 1.077\ 79 \pm 0.000\ 78. \quad (32)$$

Combination of this ratio with the ratio of the molecular weights of D_2O and H_2O ,

$$M_{\text{D}_2\text{O}}/M_{\text{H}_2\text{O}} = 1.111\ 69 \quad (33)$$

yields for the ratio of the molal heats of vaporization, to zero pressure at 25°C ,

$$L^\circ_{\text{D}_2\text{O}}/L^\circ_{\text{H}_2\text{O}} = 1.031\ 45 \pm 0.000\ 75. \quad (34)$$

For the heat of vaporization of ordinary water, the following "best" value has already been reported [15]:

$$\text{H}_2\text{O}(\text{liq}) = \text{H}_2\text{O}(\text{g}); \Delta H^\circ_{298.16} = 44,007 \pm 13 \text{ int. j/mole.} \quad (35)$$

Combination of eq 34 and 35 yields for the difference in the heats of vaporization of deuterium oxide and ordinary water at 25°C

$$L^\circ_{\text{D}_2\text{O}} - L^\circ_{\text{H}_2\text{O}} = 1,384 \pm 33 \text{ int. j/mole,} \quad (36)$$

and for the heat of vaporization of deuterium oxide to zero pressure at 25°C

$$\text{D}_2\text{O}(\text{liq}) = \text{D}_2\text{O}(\text{g}); \Delta H^\circ_{298.16} = 45,391 \pm 36 \text{ int. j/mole.} \quad (37)$$

The difference in the heats of vaporization of H_2O and H_2O would be expected to be quite negligible—of the order of 0.2 j/mole.

V. COMPARISON WITH PREVIOUS EXPERIMENTAL DATA

1. HEAT OF FORMATION OF LIQUID DEUTERIUM OXIDE

In 1935, Flood and Tronstad [28] reported the results of experiments on the determination of the ratio of the heat of formation of liquid deuterium oxide to that of ordinary water. The following is descriptive of their experimental work: In each experiment, they exploded about 18 cm³ (measured at 1 atmosphere) of "Knallgas" (D₂+1/2O₂ or H₂+1/2O₂); the volume of the explosion vessel was 100 cm³; the temperature rise was of the order of 3.9° C; about 5 percent of the water formed in the reaction remained as vapor in the explosion vessel, and this amount was corrected to the liquid state; the average temperature of the reaction was about 17° C; about 0.0005 mole of deuterium (or of ordinary hydrogen) was burned in each of the experiments. This last figure is to be compared with the approximately 0.13 mole of deuterium burned in each of the six experiments of the present investigation. For the ratio of the heat of formation of liquid deuterium oxide to that of liquid ordinary water, Flood and Tronstad reported 1.027 ± 0.003, without giving the numerical details of their work or the manner of estimating the uncertainty. Within its assigned limits of uncertainty, this value is in substantial accord with the value 1.030 68 ± 0.000 29 obtained in the present investigation (eq 19).

2. HEAT OF VAPORIZATION OF DEUTERIUM OXIDE

A value for the heat of vaporization of deuterium oxide may be deduced from the calorimetric measurements of Bartholomé and Clusius [17] on the heat of sublimation of deuterium oxide at 0° C and those of Long and Kemp [16] on the heat of fusion of deuterium oxide at 3.82° C, together with appropriate heat-capacity data for conversion to 25° C. The data to be combined are the following:

$$\text{D}_2\text{O}(c) = \text{D}_2\text{O}(g); \Delta H_{273.16}^\circ = 52,996 \pm 110 \text{ int. j/mole} \quad (38)$$

$$\text{D}_2\text{O}(c) = \text{D}_2\text{O}(liq); \Delta H_{276.98}^\circ = 6,279 \pm 15 \text{ int. j/mole} \quad (39)$$

$$\text{D}_2\text{O}(liq); H_{298.16}^\circ - H_{276.98}^\circ = 1,770 \pm 3 \text{ int. j/mole} \quad (40)$$

$$\text{D}_2\text{O}(c); H_{276.98}^\circ - H_{273.16}^\circ = 172 \pm 1 \text{ int. j/mole} \quad (41)$$

$$\text{D}_2\text{O}(g); H_{298.16}^\circ - H_{273.16}^\circ = 852 \pm 3 \text{ int. j/mole.} \quad (42)$$

The values for eq 39, 40, and 41 were calculated from the data of Long and Kemp [16], who measured the heat of fusion of deuterium oxide and its heat capacity in the liquid and solid states (see also references [30, 31, 32]). The value for eq 42 was calculated statistically, the vibrational energy contribution being found to be 20.8 j/mole. The value for eq 38 was calculated from the data of Bartholomé and Clusius [17], who measured the heat of sublimation of D₂O at 0° C in a Bunsen ice calorimeter. Their data yield 9.7604 g of mercury displaced for each gram of deuterium oxide sublimed, the total in three experiments being 12.5714 g of mercury displaced and 1.2880 g of deuterium oxide sublimed. Taking as the energy equivalent of the Bunsen ice calorimeter 271.10 int. j/g of mercury displaced [18], the data of Bartholomé and Clusius yield 52,996 int. j/mole for the heat of the reaction given by eq 38. Combination of eq 35, 38,

39, 40, 41, and 42 yields $1,620 \pm 112$ int. j/mole for the difference in the heats of vaporization of deuterium oxide and ordinary water at 25°C .

The data of Miles and Menzies [19], who measured the difference between the vapor pressures of deuterium oxide and of ordinary water as a function of the temperature over the range from 25° to 230°C , yield $1,324 \pm 135$ int. j/mole for the difference in the heats of vaporization at 25°C .

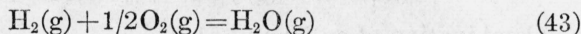
The less extensive data of Lewis and MacDonald [20] on the difference in the vapor pressures as a function of the temperature over the range from 20° to 110°C yield $1,140 \pm 150$ int. j/mole for the difference in the heats of vaporization.

The three values just given for the difference between the heats of vaporization of deuterium oxide and of ordinary water, namely, $1,620 \pm 112$, $1,324 \pm 135$, and $1,140 \pm 150$ int. j/mole, are to be compared with the value $1,384 \pm 33$ int. j/mole determined in the present investigation.

VI. THERMODYNAMIC CALCULATIONS

1. HEAT OF FORMATION OF DEUTERIUM OXIDE AT 25°C AND 0°K

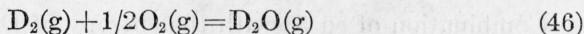
Values for the heat of formation of gaseous ordinary water at 25°C and 0°K have already been reported¹¹ [15]:



$$\Delta H_{298.16}^\circ = -241,788 \pm 42 \text{ int. j/mole} \quad (44)$$

$$\Delta H_0^\circ = -238,896 \pm 42 \text{ int. j/mole} \quad (45)$$

The corresponding values for deuterium oxide may be obtained by combining eq 20, 24, and 36 (or 26 and 37) and the values for $H_{298.16}^\circ - H_0^\circ$ given in table 5 for $\text{D}_2(\text{g})$, $\text{D}_2\text{O}(\text{g})$, and $\text{O}_2(\text{g})$:



$$\Delta H_{298.16}^\circ = -249,172 \pm 100 \text{ int. j/mole} \quad (47)$$

$$\Delta H_0^\circ = -246,231 \pm 100 \text{ int. j/mole} \quad (48)$$

2. FREE ENERGY OF FORMATION OF DEUTERIUM OXIDE AT 25°C

The entropies given in table 5 may be appropriately combined with the heat of formation to obtain the free energy of formation, according to the relation

$$\Delta F = \Delta H - T\Delta S. \quad (49)$$

In this way there was obtained

$$\underline{\text{D}_2(\text{g}) + 1/2\text{O}_2(\text{g}) = \text{D}_2\text{O}(\text{g}); \Delta F_{298.16}^\circ = -234,521 \pm 100 \text{ int. j/mole}} \quad (50)$$

¹¹ The values used in this paper for $\Delta F_{298.16}^\circ$ and ΔH_0° for the formation $\text{H}_2\text{O}(\text{g})$, according to eq 43, differ from those given in reference [15] by -9 and 4 j/mole, respectively, because of slight improvements in the accuracy of the values calculated by one of the authors [25] for $S_{298.16}^\circ$ and $H_{298.16}^\circ - H_0^\circ$ for $\text{H}_2\text{O}(\text{g})$. These changes are almost negligible, however, being only one-fifth and one-tenth, respectively, of the assigned uncertainties.

TABLE 5.—Summary of values of the entropy (not including nuclear spin) at 25° C, and of the heat content at 25° C referred to 0° K

Substance	$S^{\circ}_{298.16}$		$H^{\circ}_{298.16} - H^{\circ}_0$		Sources of data
	Int. j/deg mole	cal °/deg mole	Int j/mole	cal °/mole	
O ₂ (g).....	205.090 ±0.040	49.026 ±0.010	8563.6 ±3.0	2068.6 ±0.7	[15, 26]
H ₂ (g).....	130.644 ±0.020	31.230 ±0.005	8466.6 ±2.0	2023.9 ±0.5	[15, 25, 27]
H ₂ O (g).....	188.813 ±0.040	45.135 ±0.010	9901.3 ±3.0	2366.9 ±0.7	[15, 24]
H ₂ O (liq).....	70.081 ±0.080	16.752 ±0.019	-----	-----	[15]
D ₂ (g).....	144.914 ±0.040	34.641 ±0.010	8568.7 ±3.0	2048.3 ±0.7	° [25]
D ₂ O(g).....	198.322 ±0.040	47.408 ±0.010	9954.0 ±3.0	2379.5 ±0.7	[16]
D ₂ O(liq).....	76.099 ±0.130	18.191 ±0.031	-----	-----	(^b)

^a The calorie is defined as 4.1833 int. j.

^b See eq 54.

^c The values of the entropies (including nuclear spin) of D₂ and HD given in table 4 of reference [25] are recorded incorrectly for $T=298.1^{\circ}\text{K}$. The correct values are, respectively, 39.001 and 37.919. The entries for the other temperatures are correct (H. L. Johnston).

From the data of Miles and Menzies [19] (see also Lewis and MacDonald [20]), the vapor pressure of liquid deuterium oxide at 25° C may be taken as 3.15 ± 0.05 mm Hg less than that of ordinary water. With the vapor pressure of ordinary water taken as 0.031222 ± 0.000020 atmosphere at 25° C [21], the vapor pressure of liquid deuterium oxide at 25° C becomes 0.02708 ± 0.00007 atmosphere. Assuming $d(F_{ideal} - F_{real})/dP$ at 25° C to be the same for D₂O(g) as for H₂O(g), namely, 150 ± 40 j/atm mole [15], there is obtained

$$\text{D}_2\text{O}(\text{liq}) = \text{D}_2\text{O}(\text{g}); \Delta F^{\circ}_{298.16} = 8,949 \pm 9 \text{ int. j/mole.} \quad (51)$$

Combination of eq 50 and 51 yields

$$\text{D}_2(\text{g}) + 1/2\text{O}_2(\text{g}) = \text{D}_2\text{O}(\text{liq}); \Delta F^{\circ}_{298.16} = -243,470 \pm 100 \text{ int. j/mole.} \quad (52)$$

3. ENTROPY OF LIQUID DEUTERIUM OXIDE AT 25° C

Combination of eq 37, 49, and 51 yields

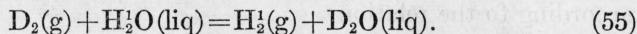
$$\text{D}_2\text{O}(\text{liq}) = \text{D}_2\text{O}(\text{g}); \Delta S^{\circ}_{298.16} = 122.223 \pm 0.124 \text{ int. j/degree mole.} \quad (53)$$

Combination of eq 53 with the entropy of D₂O(g) given in table 5 yields

$$\text{D}_2\text{O}(\text{liq}); S^{\circ}_{298.16} = 76.099 \pm 0.130 \text{ int. j/degree mole.} \quad (54)$$

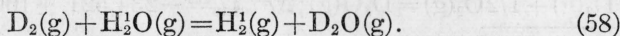
4. THE REACTION $\text{D}_2 + \text{H}_2\text{O} = \text{H}_2 + \text{D}_2\text{O}$

The data on the heats and free energies of formation of ordinary water and deuterium oxide were combined to give the following values for the isotopic exchange reaction:



$$\Delta H^{\circ}_{298.16} = -8,770 \pm 83 \text{ int. j/mole.} \quad (56)$$

$$\Delta F^{\circ}_{298.16} = -6,316 \pm 96 \text{ int. j/mole.} \quad (57)$$



$$\Delta H^{\circ}_{298.16} = -7,386 \pm 90 \text{ int. j/mole.} \quad (59)$$

$$\Delta F^{\circ}_{298.16} = -5,966 \pm 90 \text{ int. j/mole.} \quad (60)$$

$$\Delta H^{\circ}_0 = -7,337 \pm 90 \text{ int. j/mole.} \quad (61)$$

It should be noted that the above values are significantly different from those reported in the literature. For example, for the isotopic exchange reaction in the gaseous phase as given by eq 58, the calculations of Jones and Sherman [29] give

$$\Delta H_0^\circ = -1,488 \text{ cal/mole}; K_{298.16} = 7.088, \quad (62)$$

which values are to be compared with

$$\Delta H_0^\circ = -1,754 \pm 22 \text{ cal/mole}; K_{298.16} = 11.10 \pm 0.42 \quad (63)$$

from the present work.¹²

5. ZERO-POINT ENERGIES

If the energy of binding of atoms is the same for different isotopes of the same element, that is, dependent on the electron distribution about the nucleus but independent of the mass of the nucleus, then the differences in the heats of formation of D_2O and H_2O at $0^\circ K$, as given by eq 26, 28, 35, and 37, will be equal to the appropriate differences in the zero-point energies of the molecules concerned. If $(\Delta H_f^\circ)_{H_2O}$ and $(\Delta H_f^\circ)_{D_2O}$ represent, respectively, the heats of formation of H_2O and D_2O from their elements at $0^\circ K$, as given by the equations just cited, and ZPE represents the zero-point energy, then, on the assumption just mentioned,

$$(\Delta H_f^\circ)_{H_2O} - (\Delta H_f^\circ)_{D_2O} = [(ZPE)_{H_2O} - (ZPE)_{D_2O}] - [(ZPE)_{H_2} - (ZPE)_{D_2}]. \quad (64)$$

Values of the zero-point energies of H_2 and D_2 are accurately known from the spectroscopic data of Teal and MacWood [22], which are in substantial agreement with the data of Jeppeson [23]. Expressed in terms of wave numbers (in cm^{-1}) the zero-point energies of H_2 and D_2 are, respectively, 2171.3₅ and 1542.8₅, the difference being 628.5 wave numbers. Converted to international joules by means of the factor 11.940, these values become, respectively, 25,926, 18,422, and 7,504 int. j/mole. The uncertainty in the difference may be conservatively placed at ± 12 j/mole. Then

$$(ZPE)_{H_2} - (ZPE)_{D_2} = 7,504 \pm 12 \text{ int. j/mole.} \quad (65)$$

From eq 61,

$$(\Delta H_f^\circ)_{H_2O} - (\Delta H_f^\circ)_{D_2O} = 7,337 \pm 90 \text{ int. j/mole.} \quad (66)$$

Therefore, from eq 64, 65, and 66

$$\begin{aligned} (ZPE)_{H_2O} - (ZPE)_{D_2O} &= 14,841 \pm 91 \text{ int. j/mole} = \\ &= 3,548 \pm 22 \text{ cal/mole} = 1243.0 \pm 7.6 \text{ wave numbers.} \end{aligned} \quad (67)$$

An extensive analysis of the data on the vibrational-rotational spectra of the H_2O and D_2O molecules has just been completed by Darling and Dennison [35], who have developed a new theory of the water molecule in connection with the problem of expressing the

¹² K is defined by the relation $\Delta F^\circ = -RT \ln K$, and, for the isotopic exchange reaction under consideration, at pressures sufficiently low for the fugacity to be replaced by the partial pressure $K = (P_{D_2O} P_{H_2}) / (P_{H_2O} P_{D_2})$.

energies of the various levels of the molecule in terms of certain constants evaluated from their equation and the spectroscopic data. They find that, for those states where resonance may be neglected, of which the ground state is one, the energy, W , of a given level is given by the equation

$$W/hc = \omega_1(n_1 + 1/2) + \omega_2(n_2 + 1/2) + \omega_3(n_3 + 1/2) + X_{11}(n_1 + 1/2)^2 + X_{22}(n_2 + 1/2)^2 + X_{33}(n_3 + 1/2)^2 + X_{12}(n_1 + 1/2)(n_2 + 1/2) + X_{13}(n_1 + 1/2)(n_3 + 1/2) + X_{23}(n_2 + 1/2)(n_3 + 1/2), \quad (68)$$

where ω_1 , ω_2 , and ω_3 are the normal frequencies, n_1 , n_2 , and n_3 are the quantum numbers for the three different modes of vibration, and the X 's are the interaction coefficients. Darling and Dennison [35] obtain the following values for the constants, with the energy expressed in wave numbers:

	H ₂ O	D ₂ O
ω_1 -----	3825. 32	2758. 06
ω_2 -----	1653. 91	1210. 25
ω_3 -----	3935. 59	2883. 79
X_{11} -----	- 43. 89	- 22. 81
X_{22} -----	- 19. 50	- 10. 44
X_{33} -----	- 46. 37	- 24. 90
X_{12} -----	- 20. 02	- 10. 56
X_{13} -----	- 155. 06	- 81. 92
X_{23} -----	- 19. 81	- 10. 62

The zero-point energy of the molecule is given by eq 68 with $n_1 = n_2 = n_3 = 0$, as follows:

$$ZPE = 1/2(\omega_1 + \omega_2 + \omega_3) + 1/4(X_{11} + X_{22} + X_{33} + X_{12} + X_{13} + X_{23}). \quad (69)$$

On substitution of the constants in eq 69, Darling and Dennison obtain the following values for the zero-point energies:

$$(ZPE)_{\text{H}_2\text{O}} = 4631.25 \text{ wave numbers.} \quad (70)$$

$$(ZPE)_{\text{D}_2\text{O}} = 3385.74 \text{ wave numbers.} \quad (71)$$

$$(ZPE)_{\text{H}_2\text{O}} - (ZPE)_{\text{D}_2\text{O}} = 1245.51 \text{ wave numbers.} \quad (72)$$

Dennison, in a private communication to the authors, has placed an uncertainty of 2 wave numbers on the above value for the difference in the zero-point energies. The value 1245.5 ± 2.0 wave numbers is to be compared, therefore, with the value 1243.0 ± 7.6 wave numbers deduced from the data of the present investigation, and indicates that, within the accuracy with which calorimetric measurements and spectroscopic analyses can be made today, the energies of atomic linkages are independent of the mass of the nuclei of the atoms.

VII. SUMMARY

The various thermodynamic values calculated in this paper are summarized in table 6.

TABLE 6.—Summary of thermodynamic values

Reaction	$\Delta H_{298.15}^{\circ}$		$\Delta F_{298.15}^{\circ}$		$\Delta H_{\ddagger}^{\circ}$	
	Int. j/mole	cal/mole	Int. j/mole	cal/mole	Int. j/mole	cal/mole
$D_2(g) + 1/2 O_2(g) = D_2O(liq)$	-294,563 \pm 94	-70,414.0 \pm 22.5	-243,470 \pm 100	-58,200.5 \pm 23.9	-----	-----
$D_2(g) + 1/2 O_2(g) = D_2O(g)$	-249,172 \pm 100	-59,563.5 \pm 23.9	-234,521 \pm 100	-56,061.2 \pm 23.9	-246,231 \pm 100	-58,860.5 \pm 23.9
$D_2O(liq) = D_2O(g)$	45,391 \pm 36	10,850.5 \pm 8.6	8,949 \pm 9	2,139.2 \pm 2.2	-----	-----
$D_2(g) + H_2^{1/2}O(liq) = H_2^{1/2}(g) + D_2O(liq)$	-8,770 \pm 83	-2,096.4 \pm 19.8	-6,316 \pm 96	1,509.8 \pm 22.9	-----	-----
$D_2(g) + H_2^{1/2}O(g) = H_2^{1/2}(g) + D_2O(g)$	-7,386 \pm 90	-1,765.6 \pm 21.5	-5,966 \pm 90	1,426.1 \pm 21.5	-7,337 \pm 90	-1,753.9 \pm 21.5

* The calorie is defined as 4.1833 int. j.

The authors are greatly indebted to F. G. Brickwedde and R. B. Scott, of the Cryogenic Laboratory of this Bureau for analyzing, by measurement of vapor pressures, the deuterium used in the experiments on the heat of formation of liquid deuterium oxide.

VIII. REFERENCES

- [1] G. P. Baxter, M. Guichard, O. Hönigschmid, and R. Whytlaw-Gray, *J. Am. Chem. Soc.* **61**, 223 (1939).
- [2] F. W. Aston, *Nature* **137**, 357, 613 (1936); **139**, 922 (1937).
- [3] K. T. Bainbridge and E. B. Jordan, *Phys. Rev.* **51**, 384 (1937).
- [4] E. B. Jordan and K. T. Bainbridge, *Phys. Rev.* **51**, 385 (1937).
- [5] F. D. Rossini, and W. E. Deming, *J. Wash. Acad. Sci.* **29**, 416 (1939).
- [6] F. D. Rossini, *BS J. Research* **6**, 1 (1931) RP259.
- [7] F. D. Rossini, *BS J. Research* **9**, 679 (1932) RP499.
- [8] F. D. Rossini, *BS J. Research* **12**, 735 (1934) RP686.
- [9] F. D. Rossini and J. W. Knowlton, *J. Research NBS* **19**, 249 (1937) RP1024.
- [10] H. L. Johnston, *J. Am. Chem. Soc.* **61**, 878 (1939).
- [11] J. W. Knowlton and F. D. Rossini, *J. Research NBS* **19**, 605 (1937) RP1050.
- [12] F. G. Brickwedde, R. B. Scott, and H. S. Taylor, *J. Research NBS* **15**, 463 (1935) RP841.
- [13] F. G. Brickwedde and R. B. Scott, *Phys. Rev.* **55**, 672 (1939).
- [14] F. D. Rossini, *BS J. Research* **7**, 329 (1931) RP343.
- [15] F. D. Rossini, *J. Research NBS* **22**, 407 (1939) RP1192.
- [16] E. A. Long and J. D. Kemp, *J. Am. Chem. Soc.* **58**, 1829 (1936).
- [17] E. Bartholomé and K. Clusius, *Z. physik. Chem.* **B28**, 167 (1935).
- [18] F. D. Rossini. Unpublished calculations.
- [19] F. T. Miles and W. C. Menzies, *J. Am. Chem. Soc.* **58**, 1067 (1936).
- [20] G. N. Lewis and R. T. MacDonald, *J. Am. Chem. Soc.* **55**, 3057 (1933).
- [21] N. S. Osborne and C. H. Myers, *J. Research NBS* **13**, 1 (1934) RP691.
- [22] G. K. Teal and G. E. MacWood, *J. Chem. Phys.* **3**, 760 (1935).
- [23] C. R. Jeppesen, *Phys. Rev.* **49**, 797 (1936).
- [24] H. L. Johnston. Calculations to be published.
- [25] H. L. Johnston and E. A. Long, *J. Chem. Phys.* **2**, 389 (1934).
- [26] H. L. Johnston and M. L. Walker, *J. Am. Chem. Soc.* **55**, 172 (1933); **57**, 682 (1935).
- [27] W. F. Giauque, *J. Am. Chem. Soc.* **52**, 4816 (1930).
- [28] H. Flood and L. Tronstad, *Kgl. Norske Videnskab, Selskabs. Forh.* **8**, No. 40, 139-142 (1935).
- [29] T. Jones and A. Sherman, *J. Chem. Phys.* **5**, 375 (1937).
- [30] V. K. La Mer and W. N. Baker, *J. Am. Chem. Soc.* **56**, 2641 (1934).
- [31] L. Jacobs, *Trans. Faraday Soc.* **31**, 813 (1935).
- [32] R. S. Brown, W. H. Barnes, and O. Maass, *Canadian J. Research* **12B**, 699 (1935).
- [33] F. D. Rossini and M. Frandsen, *BS J. Research* **9**, 733 (1932) RP503.
- [34] N. S. Osborne, H. F. Stimson, and D. C. Ginnings, *J. Research NBS* **23**, 197 (1939) RP1228.
- [35] B. T. Darling and D. M. Dennison, *Phys. Rev.* **57**, 128 (1940).

WASHINGTON, November 28, 1939.