from H_2SO_4 solution, because in concentrated H_2SO_4 the nitrate ion is converted to NO_2^+.

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COLUMBUS 10, OHIO

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

The Heat Capacity and Thermodynamic Functions of β-Uranium Deuteride from 5 to 350°K.[1,2]

BY BERNARD M. ABRAHAM, DARRELL W. OSBORNE, HOWARD E. FLOTOW AND ROBERT B. MARCUS

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The heat capacity of UD_3 has been measured in an adiabatic calorimeter from 5 to 350°K. The enthalpy and entropy at 298.15°K. calculated from the data are 2577 ± 5 cal. mole^{-1} and 17.20 ± 0.03 cal. deg.$^{-1}$ mole^{-1}, respectively. The entropy and free energy of formation for UD_3 at 298.15°K. as well as the heat of formation at the absolute zero were calculated from these data and the previously reported heat of formation and have the values -46.76 cal. deg.$^{-1}$ mole^{-1}, $-17{,}080$ cal. mole^{-1} and $-29{,}000$ cal. mole^{-1}. It was found that the calculated and observed dissociation pressures are not in agreement. A similar discrepancy was found for UH_3 and it was suggested that the source might be a particle size effect in the dissociation pressure measurements or the heat of transition of the α-form of UH_3 to the β-form. These heat capacity data were combined with the reported values for UH_3 to calculate the hydrogen and deuterium vibration frequencies in the compounds. An anomaly in the heat capacity was observed which arises from the transition from the ferromagnetic state to the paramagnetic state. The maximum in the heat capacity is 11.72 cal. deg.$^{-1}$ mole^{-1} and occurs at 167.6 ± 0.5°K. It was estimated that 1.19 cal. deg.$^{-1}$ mole^{-1} is the entropy change in the transition which is less than the expected value, $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1}, from the Heisenberg theory of ferromagnetism. Measurements of the magnetization of UD_3 do not appear to be in accord with the thermal measurements.

Introduction

Measurements of the heat capacity of β-UH_3 from 5 to 350°K. previously have been reported from this Laboratory.[3] In order to observe the effect of isotopic substitution on the thermodynamic properties as well as on the ferromagnetic transition similar measurements have been made on β-UD_3. We report here the heat capacity measurements on β-UD_3, the thermodynamic functions derived from the measurements and an analysis of the data from which the vibrational frequencies of H and D in the hydride molecule were calculated and also some conclusions regarding recently reported magnetic measurements on β-UD_3.

The structure of β-UD_3 is identical to that of β-UH_3. The unit cell has cubic symmetry and contains eight uranium atoms arranged as in α-tungsten, *i.e.*, $2U_I$ at (0,0,0) and $(^1/_2,{}^1/_2,{}^1/_2)$ and $6U_{II}$ at $\pm\,(^1/_4,0,{}^1/_2)$.[4] The lattice constant a_0 is equal to 6.62 kX units; all of the U–D distances are equal to 2.32 Å. as in β-UH_3. The density of β-UD_3 is equal to 11.11 g./cc. which is to be compared to 10.92 g./cc. for the density of β-UH_3.

The deuteride has been shown to be ferromagnetic but with a saturation moment of 0.98 Bohr magnetons per atom at 1.3°K. compared with 1.18 Bohr magnetons for UH_3.[5] Although the data are not presented by Henry, the statement was made: "The absolute moment of uranium deuteride seems to be less, for all equal conditions of temperature and magnetic field, than that of the hydride." Karchevskii, *et al.*,[6,7] have reported the Curie temperature of UH_3 as 182.0°K. and of UD_3 as 178.4°K., the former in close agreement with the value 181°K. given by Lin and Kaufmann.[8] Karchevskii[7] has in addition determined the magneto-caloric effect for both compounds and finds that the effect is 1.6 times greater for UH_3 at the Curie temperature than for UD_3. One might expect therefore to observe some difference between the heat capacity of β-UH_3 and β-UD_3 at low temperatures as a result of the smaller magnetic moment and smaller magneto-caloric effect for UD_3.

Experimental

The UD_3 sample was prepared from high purity uranium in the form of rods 3 mm. in diameter, made by the Metallurgy Division of this Laboratory.[9] Spectroscopic analysis of the uranium showed the presence of these various elements in p.p.m.: Al, 5; Cr, 1; Cu, 1; Fe, 2; Mg, 0.5; and Si, 10; all other elements were below the limits of spectroscopic detection. Chemical analysis showed 24 p.p.m. of carbon and less than 10 p.p.m. of nitrogen. After removal of a small amount of surface oxide with nitric acid, the uranium metal was placed in a reaction vessel attached to a vacuum line. It was converted to UD_3 by reaction at 190 to 200° with deuterium gas liberated from the thermal decomposition of another sample of UD_3. Under these conditions the β-phase is formed.

The operation of transferring the sample from the reaction vessel to the calorimeter and soldering it shut was performed in a dry-box under an atmosphere of purified helium. Two 1-gram portions were taken for analysis at the time the calorimeter was loaded. These were assayed by thermally decomposing the samples on a vacuum line and volumetrically determining the total gas evolved. The amount of gas collected corresponded to 99.65% of the theoretical for UD_3. The isotopic composition of the gas, determined mass spec-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Presented in part at the 133rd meeting of the Am. Chem. Soc., San Francisco, April 13–18, 1958.

[3] H. E. Flotow, H. R. Lohr, B. M. Abraham and D. W. Osborne, THIS JOURNAL, **81**, 3529 (1959).

[4] R. E. Rundle, *ibid.*, **73**, 4172 (1951).

[5] W. Henry, *Phys. Rev.*, **109**, 1976 (1958).

[6] A. I. Karchevskii, E. V. Artyushkov and L. I. Kikoin, *Zhur. Eksptl. i Teoret. Fiz.*, **36**, 636 (1959).

[7] A. I. Karchevskii, *ibid.*, **36**, 638 (1959).

[8] S. T. Lin and A. R. Kaufmann, *Phys. Rev.*, **102**, 640 (1956).

[9] B. Blumenthal and R. A. Noland, "Progress in Nuclear Energy," Vol. I, Pergamon Press, London and New York, 1956, Series V, pp. 62–80.

trometrically, was 99.67 atom % D and 0.33 atom % H. The mass of the sample used for the calorimetric measurements was 116.6883 g.

The measurements were made with the same apparatus used for β-UH_3 and for a number of other compounds measured and reported from this Laboratory.[10,11] Briefly, the calorimeter is of the adiabatic type. The temperature measurements were made with a platinum resistance thermometer which has been calibrated on the International Scale above 90°K. and on the scale of the National Bureau of Standards[12] between 14 and 90°K. Below 14°K. the scale was obtained by fitting the equation $R = A + BT^2 + CT^5$ to the resistance at the boiling point of helium, the resistance at 14°K. and dR/dT at 14°K. It is believed that the temperature scale agrees with the thermodynamic scale within 0.1° from 4 to 14°K., within 0.03° from 14 to 90°K., within 0.05° from 90 to 373°K.

Results

The experimental values of the heat capacity, expressed in terms of the thermochemical calorie, defined equal to 4.1840 joules, are presented in chronological sequence in Table I. The temperature differences can be estimated from the successive mean temperatures. Smaller temperature intervals were used in Series II in order to establish the shape of the heat capacity curve in the region of the anomaly, near 168°K. A small correction for the finite temperature increment has been applied to all values in Table I by adding $-(d^2C_p/dT^2)(\Delta T)^2/24$ to the measured mean heat capacity. Another small correction was made for the difference in the amount of helium in the measurements on the empty and on the full calorimeter. No correction was applied for the presence of 0.33 atom % H nor for the fact that the total amount of hydrogen isotopes evolved on thermal decomposition was only 99.65% of theoretical. The heat capacities of β-UD_3 are plotted in Fig. 1 together with those previously obtained for β-UH_3.[3]

TABLE I

HEAT CAPACITY OF β-URANIUM DEUTERIDE (IN CAL. DEG.$^{-1}$ MOLE^{-1})

Mol. wt. = 244.11; 0°C. = 273.15°K.

$\bar{T}$, °K.	C_p	$\bar{T}$, °K.	C_p	$\bar{T}$, °K.	C_p	$\bar{T}$, °K.	C_p
Series I							
5.95	0.080	72.09	5.141	239.15	12.80	170.35	11.29
7.72	.098	79.28	5.536	249.11	13.28	171.35	11.03
9.70	.127	87.08	5.954	259.20	13.77	172.36	10.81
11.64	.168	95.72	6.385	269.17	14.24	173.37	10.62
13.59	.231	105.25	6.888	278.99	14.69	174.92	10.45
15.55	.315	114.85	7.440	289.03	15.13	176.96	10.33
17.47	.424	124.45	8.048	299.21	15.58	178.97	10.29
19.45	.566	134.23	8.732	309.19	16.00	180.98	10.29
21.49	.738	143.96	9.490	319.05	16.41	Series III	
23.66	.946	154.21	10.39	328.93	16.81	6.23	0.082
25.94	1.183	161.98	11.18	338.89	17.20	8.17	.102
28.45	1.458	167.02	11.72	346.94	17.51	10.04	.129
31.23	1.771	172.16	10.85	Series II		11.98	.176
34.27	2.114	177.27	10.32	160.99	11.07	13.92	.243
37.68	2.485	182.25	10.31	163.00	11.29	15.91	.333
41.51	2.880	187.20	10 44	164.49	11.45	17.91	.453
45.61	3.268	192.18	10.62	165.47	11.57	19.90	.601
49.94	3.647	199.66	10.93	166.45	11.66	21.92	.778
54.76	4.029	209,48	11.37	167.42	11.72	24.07	.987
59.77	4.392	219.38	11.84	168.39	11.68	26.49	1.242
65.64	4.773	229.29	12.31	169.37	11.51	29.15	1.535

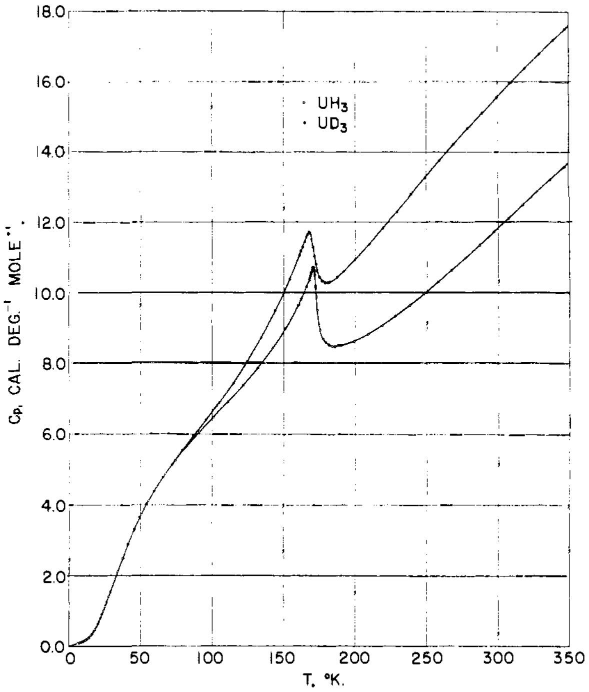

Fig. 1.—Heat capacity of UH_3 (top curve) and UD_3 (bottom curve) as a function of temperature.

The heat capacity values read from a smooth curve through the experimental points are given in Table II for selected temperatures; these values are considered to have a probable error of 0.2% above 30°K., 1% at 14°K. and 5% at 5°K. The same curve was used to obtain the heat capacity values for evaluating the thermodynamic functions given in Table II. The entropy S^0 was obtained by numerical integration of $\int C_p \, d \ln T$ and the increment in the enthalpy, $(H^0 - H_0^0)$, by numerical integration of $\int C_p \, dT$ between 0°K. and the temperature of interest. Below 8°K. the heat capacity was extrapolated by the equation

$$C_p = 0.0126T, \qquad (1)$$

which joins the experimental curve smoothly at 8°K. Below this temperature the experimental values were somewhat higher than equation 1, perhaps due to the desorption of helium gas.

The values in Table II may be combined with the thermal data in the literature to obtain the free energy and entropy of formation of UD_3 at 298.15°K. and the heat of formation at 0°K. Abraham and Flotow[13] have measured the heat of formation of UD_3 calorimetrically by the direct combination of uranium metal and deuterium gas at 25°. The reaction product was not analyzed but in the UH_3 experiment it was found that the product was 25% α-UH_3 and 75% β-UH_3; it was assumed, however, that the heat of transition α → β was negligible. Making the similar assumption for UD_3, they reported the value −31,021 cal. mole^{-1} for the heat of formation, $\Delta Hf^0_{298.15}$, for the reaction

$$U(\alpha) + 3/2D_2(g) = UD_3(\beta) \qquad (2)$$

Jones, Gordon and Long[14] have measured the heat capacity of bulk uranium metal from 15 to 300°K.

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[10] E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, *J. Chem. Phys.*, **21**, 419 (1953).

[11] D. W. Osborne and E. F. Westrum, Jr., *ibid.*, **21**, 1884 (1953).

[12] H. J. Hoge and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **22**, 351 (1939).

[13] B. M. Abraham and H. E. Flotow, THIS JOURNAL, **77**, 1446 (1955).

[14] W. M. Jones, J. Gordon and E. A. Long, *J. Chem. Phys.*, **20**, 695 (1952).

TABLE II

THERMODYNAMIC PROPERTIES OF β-URANIUM DEUTERIDE AT SELECTED TEMPERATURES

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	S^0 cal. deg.$^{-1}$ mole^{-1}	$H^0 - H_0^0$, cal. mole^{-1}	$-\left(\frac{F^0 - H_0^0}{T}\right)$ cal. deg.$^{-1}$ mole^{-1}
5	0.063	0.063	0.16	0.031
10	.131	.126	0.63	.063
15	.289	.204	1.63	.095
20	.610	.327	3.80	.137
25	1.083	.512	7.99	.192
30	1.631	.757	14.75	.265
35	2.194	1.051	24.32	.356
40	2.728	1.379	36.64	.463
45	3.212	1.729	51.51	.584
50	3.651	2.091	68.69	.717
60	4.408	2.825	109.09	1.007
70	5.024	3.553	156.36	1.319
80	5.576	4.260	209.37	1.643
90	6.100	4.947	267.80	1.971
100	6.605	5.616	331.30	2.303
110	7.154	6.271	400.06	2.634
120	7.758	6.919	474.59	2.964
130	8.424	7.566	555.46	3.293
140	9.169	8.217	643.37	3.621
150	10.01	8.877	739.18	3.949
160	10.96	9.553	843.94	4.278
167.6[a]	11.72	10.081	930.36	4.530
170	11.37	10.245	958.18	4.609
180	10.29	10.850	1063.9	4.939
190	10.53	11.412	1167.8	5.266
200	10.94	11.962	1275.1	5.586
210	11.40	12.507	1386.8	5.903
220	11.87	13.048	1503.1	6.216
230	12.34	13.586	1624.2	6.524
240	12.84	14.122	1750.1	6.830
250	13.32	14.655	1880.9	7.131
260	13.80	15.187	2016.5	7.431
270	14.27	15.717	2156.9	7.729
280	14.73	16.245	2301.9	8.024
290	15.18	16.769	2451.5	8.316
300	15.61	17.291	2605.4	8.606
310	16.03	17.810	2763.6	8.895
320	16.45	18.325	2926.0	9.181
330	16.85	18.837	3092.5	9.466
340	17.24	19.347	3262.9	9.750
350	17.63	19.852	3437.2	10.031
273.15	14.42	15.88	2202	7.82
298.15	15.53	17.20	2577	8.56
	±0.02	±0.03	±5	±0.02

[a] Maximum.

and calculated from their data that the entropy at 25° has the value 12.03 ± 0.03 cal. deg.$^{-1}$ mole^{-1}. From their data we calculate that $(H^0_{298.15} - H_0^0)$ has the value 1526 ± 3 cal. mole^{-1}. The thermodynamic properties of normal deuterium were taken from the tables of Woolley, Scott and Brickwedde[15]; however, $R \ln 9$ was subtracted from the tabulated values of the entropy and the free energy function to exclude the contribution from the nuclear spins. For reaction 2 we obtain these values

$$\Delta S_f{}^0{}_{298.15} = -46.76 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$
$$\Delta F_f{}^0{}_{298.15} = -17{,}080 \text{ cal. mole}^{-1}$$
$$\Delta H_{f0}{}^0 = -29{,}000 \text{ cal. mole}^{-1}$$

Dissociation Pressures.—The available thermodynamic data may be used to calculate the dissociation pressures of UD_3 in the temperature range 500–700°K. for a comparison with the experimental values[16] as was done with UH_3.[3] To obtain $\Delta F_f{}^0/T$ from which the dissociation pressures were calculated by the relation

$$\frac{\Delta F_f{}^0}{T} = \frac{3}{2} R \ln P_{\text{atm}} \qquad (3)$$

it is necessary to have the free energy function, $-(F^0 - H_0{}^0)/T$, for uranium, deuterium and UD_3 up to 700°K. in addition to $\Delta F_f{}^0{}_{298.15}$ and $\Delta H_{f_0}{}^0$. The free energy function for uranium was obtained from the increments in the enthalpy and entropy above 25° tabulated by K. K. Kelley,[17] and the function for normal deuterium was taken from the Woolley, Scott and Brickwedde tables.[15] However, in order to obtain this function for UD_3, it is necessary to extrapolate the heat capacity above 350°K., the temperature limit of the measurements. The experimental values between 250–350°K. were fitted to the equation

$$C_p = -2.18 + 0.0755T - 0.000054T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (4)$$

which reproduces the experimental values to better than 0.01 cal. deg.$^{-1}$ mole^{-1}. It was shown in ref. 3 that the calculated values for the dissociation pressures are insensitive to the method of extrapolating the heat capacity so that only equation 4 was used, and as before it was found that the calculated pressures were higher than the observed pressures. Recalculation of the heat of formation at 298.15°K. yielded a value of −31,757 cal. mole^{-1} instead of the calorimetric value of −31,021 cal. mole^{-1} a difference of approximately 700 cal. mole^{-1} as observed with UH_3.[3]

Hydrogen Vibration Frequencies.—It can be seen from Fig. 1 that below 90°K. the heat capacities of UH_3 and UD_3 are nearly the same and that above that temperature the heat capacity of UD_3 becomes appreciably higher. We have analyzed the heat capacity curves on the assumption that the difference arises solely from the effect of the isotopic mass on the hydrogen frequencies, except for a difference in the magnetic heat capacity near the Curie temperature. As a result of the much larger mass of the uranium atoms the optical modes can be considered, to very good approximation, to be vibrations of the individual H or D atoms in the field of stationary U atoms. The remaining vibrations, the acoustical modes, are chiefly vibrations of the uranium lattice. The contribution of the optical modes to the heat capacity should be well approximated by the sum of three Einstein functions. It is assumed that each of the three characteristic hydrogen frequencies in UH_3 is reduced in UD_3 by the ratio of the square root of the masses, or $(D/H)^{1/2} = \sqrt{2}$. The heat capacities of UH_3 and of UD_3 are then given by

$$C_p(UH_3)/3R = D + C_H/3R = D + \sum_{i=1}^{3} E(u_i) \qquad (5)$$

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[15] H. W. Woolley, R. B. Scott and F. G. Brickwedde, *J. Research Natl. Bur. Standards*, **41**, 379 (1948).

[16] F. H. Spedding, *et al.*, *Nucleonics*, **4**, No. 1, 4 (1949).

[17] K. K. Kelley, U. S. Bur. Mines Bull. 476, U. S. Government Printing Office, Washington, D. C., 1949.

$$C_p(UD_3)/3R = D + C_D/3R = D + \sum_{i=1}^{3} E(u_i/\sqrt{2}) \quad (6)$$

where C_H and C_D are the contributions of the hydrogen and deuterium vibrations, respectively, E is the Einstein heat capacity function, and $u_i = hc\bar{\nu}_i/kT$. D is a function of T representing the sum of the contribution of the uranium vibrations, the electronic contribution, and the magnetic part of the heat capacity, and this function is assumed to be the same for the two compounds, except near the Curie temperatures. The difference in the heat capacities is then

$$C_p(UD_3) - C_p(UH_3) = \sum_{i=1}^{3} \{E(u_i) - E(u_i/\sqrt{2})\} \quad (7)$$

A relation between the characteristic frequencies can be obtained from the difference in the zero point energies of UH_3 and UD_3. The heat of formation of UD_3 at absolute zero (*vide supra*) may be combined with the published value for UH_3[3] ($\Delta H_{f0}{}^0 = -27{,}945$ cal. mole^{-1}) and the zero point energy difference for hydrogen and deuterium[15] to obtain the difference in zero point energy between UH_3 and UD_3; *i.e.*

$$\Delta E_0{}^0(UH_3 - UD_3) = \Delta(\Delta H_{f0}{}^0) - (3/2)\Delta E_0{}^0(H_2 - D_2) = 3769 \text{ cal. mole}^{-1} \quad (8)$$

Since the uranium contributions to the zero point energy are assumed to be the same in both compounds then

$$\Delta E_0{}^0(UH_3 - UD_3) = (3/2)Nhc \sum_{i=1}^{3} \bar{\nu}_i(1 - 1/\sqrt{2}) \quad (9)$$

Equating (8) and (9) we find that the sum of the three hydrogen frequencies is 3001 cm.$^{-1}$.

Equation (7) was fitted to the difference between the experimental heat capacities from 250 to 350°K. subject to the condition that the sum of the hydrogen frequencies is 3001 cm.$^{-1}$. This temperature region was chosen because the magnetic contributions to the heat capacity, which is somewhat different for the two compounds, should be small there. It was found that a satisfactory fit is obtained with the three frequencies 810, 940, and 1251 cm.$^{-1}$ for UH_3 and $810/\sqrt{2}$, $940/\sqrt{2}$, and $1251/\sqrt{2}$ cm.$^{-1}$ for UD_3. When C_H or C_D calculated from these frequencies is subtracted from the experimental UH_3 or UD_3 heat capacity the total uranium contribution, $3RD$, is obtained. The curve so obtained from UD_3, designated as $3RD_D$ in Fig. 2, nearly coincides with that from UH_3, designated as $3RD_H$, from 0 to 350°K. except in the region 160 to 190°K. near the Curie temperatures. The deviations are 0.02 cal. deg.$^{-1}$ mole^{-1} or less up to 80°K., between 0.02 and 0.07 from 80 to 160°K., and 0.02 cal. deg.$^{-1}$ mole^{-1} or less from 190 to 350°K.

From measurements of exchange equilibria between UH_3 and HD, Bigeleisen and Kant[18] deduced that there must be at least two hydrogen frequencies in the range 400–1500 cm.$^{-1}$ which brackets the calculated frequencies presented here.

Ferromagnetic Transition.—The shape and position of the ferromagnetic anomaly can be seen in Figs. 1 and 2. We have taken the Curie temperature T_c for UD_3 to be 167.6 ± 0.5°K., at which point the heat capacity has a maximum value of 11.72 cal. deg.$^{-1}$ mole^{-1}. This is to be compared with T_c for UH_3 of 170.7°K.[3] and a heat capacity maximum of 10.72 cal. deg.$^{-1}$ mole^{-1}. However, when C_H and C_D are subtracted from the respective heat capacity values, the Curie temperature remains unchanged but the value at the maximum becomes 9.82 cal. deg.$^{-1}$ mole^{-1} for UD_3 and 10.26 cal. deg.$^{-1}$ mole^{-1} for UH_3.

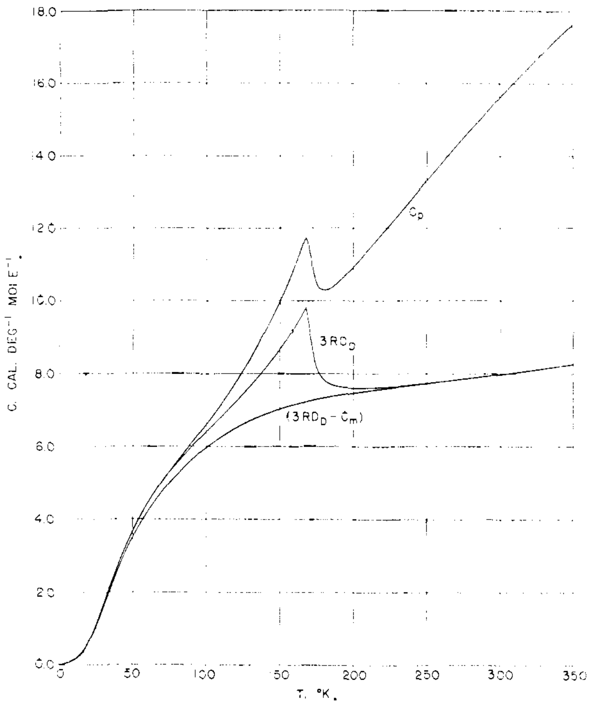

Fig. 2.—Comparison of experimental heat capacity of UD_3 with calculated total uranium contribution to the heat capacity, $3RD_D$, and with uranium contribution minus magnetic heat capacity, $3RD_D - C_m$.

The heat capacity data were used in the following manner to evaluate the contribution of the magnetic ordering process to the entropy. We assumed that up to $T_c/2$ the magnetic heat capacity C_m is given by equation 10[19]

$$C_m = 9.99\theta^{3/2} + 58.1\theta^{5/2} + 483\theta^{7/2} \text{ cal. deg.}^{-1}\text{mole}^{-1} \quad (10)$$

where $\theta = T/(2\pi T_c)$. A plot of $3RD_D$ minus C_m was prepared up to 85°K., and this curve was extrapolated to join smoothly with the curve $3RD_D$ above the Curie temperature as shown in Fig. 2. The magnetic entropy calculated from the difference between these two curves had the value 1.19 cal. deg.$^{-1}$ mole^{-1}, which is to be compared with the value of 1.18 cal. deg.$^{-1}$ mole^{-1} obtained for UH_3 in a similar fashion. The previously reported value[3] for the entropy change in the ferromagnetic transition of UH_3 was 1.01 cal. deg.$^{-1}$ mole^{-1}.

According to the Heisenberg model of ferromagnetism the entropy increase on going from a state of complete magnetic order to one of complete disorder would be R ln $(2S + 1)$. Wilkinson,

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[18] J. Bigeleisen and A. Kant, THIS JOURNAL, **76**, 5957 (1954).

[19] F. J. Dyson, *Phys. Rev.*, **102**, 1230 (1956).

Shull and Rundle[20] have shown by neutron diffraction measurements that the ordering in UH_3 or UD_3 is ferromagnetic with all the atoms having approximately the same orientation and moment. These measurements as well as the measurements of magnetization as a function of field and temperature[5,8,21] indicate that the magnetism arises from a single electron spin per molecule. One would expect, then, an entropy contribution of $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1} from the magnetic transition.

The disagreement between the expected theoretical value, $R \ln 2$, and the calculated values, 1.19 and 1.18, is not at all unusual for ferromagnetics. It may arise from the persistence of short range order above the Curie temperature, so that C_m does not vanish as we assumed. On the other hand it should be pointed out that Stoner's collective electron treatment[22] permits any value of the entropy up to $R \ln 2$ to be obtained.

In the temperature range 5–85°K. the experimental values of the heat capacity for UH_3 and UD_3 differ by at most 2% and the values of C_m are nearly identical as would be expected from the values of T_c. However Henry's measurements[5] of the magnetization of UH_3 and UD_3 as a function of temperature would imply a greater difference than actually has been observed. Further the values of $3RD_H$ and $3RD_D$ would indicate that even in the neighborhood of the Curie temperature the spontaneous magnetization and magnetic heat capacity of UH_3 and UD_3 are almost identical, which would lead one to expect similar values for the magneto-caloric effect in contradiction to the results reported by Karchevskii.[7] It would appear from this work that the thermal and magnetic measurements are in disagreement.

Acknowledgment.—We wish to thank Dr. T. Usui whose present address is Inst. of Phys. University of Tokyo, Tokyo, Japan, for many helpful discussions and for suggesting the method of analyzing the heat capacity data.

LEMONT, ILLINOIS

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(20) M. K. Wilkinson, C. G. Shull and R. E. Rundle, *Phys. Rev.*, **99**, 627 (1955), Abstract.

(21) D. M. Gruen, *J. Chem. Phys.*, **23**, 1708 (1955).

(22) E. C. Stoner, *J. phys. radium*, **12**, 372 (1951); *Proc. Roy. Soc.* (*London*), **A165**, 372 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE UNIVERSITY OF WASHINGTON]

The Heat of Sublimation and the Condensation Coefficient of Bromine

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From an effusion study, the heat of sublimation of bromine is found to be 10,680 ± 100 cal. mole^{-1} at 185°K. The condensation coefficient appears larger than 0.3.

The entropies of solid[1] and gaseous[2] bromine are well established; the heat of sublimation may be predicted from measured heats of vaporization (liquid) and fusion and heat capacities, but insufficient low temperature vapor pressure data for the solid have been reported to provide a good basis for an independent experimental determination. Several investigators, using either a direct manometric method or the measured quantity of vapor in a known volume, have reported vapor pressures for the solid close to its melting point.[3–5] Only one measurement in the low temperature range has been reported (Henglein, *et al.*, at 178°K., by the swinging quartz fiber method).

We have made an effusion study of the vapor pressure above solid bromine between 170 and 196°K. from which, together with calculated entropies, the heat of sublimation has been evaluated. The study also was designed to determine the magnitude of the condensation coefficient of solid bromine by comparison of effusion steady state pressures in various cells, as described in an earlier paper on iodine.[6]

Experimental Part

An effusion cell was constructed by rounding off the end of the inner part of a 20/35 ST Pyrex ball joint 4.3 cm. from the top of the ball. A piece of 0.001″ nickel foil was annealed and trimmed so as to overlap the inside opening uniformly by about one mm. With the foil in place a seal to the outer part of the joint was completed by lubrication with Spectrovac stopcock grease and clamping the two parts together. The joint was found leak-tight at room temperature and below; at the low temperatures of the vapor pressure measurements no perceptible reaction of bromine with the lubricant was observed.

Interchangeable foils with two different orifice sizes were prepared, giving the equivalent of two cells. A third all-glass cell, No. 5 described in the earlier paper on iodine,[6] also was used. Geometric characteristics of the cells are summarized in Table I.

TABLE I

Cell	Orifice area, $A_0 \times 10^3$ cm.^{2}	$A_0/A_s \times 10^4$ [a]	K [b]
2	3.58	2.85	0.96
3	28.2	22.4	.99
5	16.7	135	.98

[a] A_s cell cross-section area. [b] Orifice Clausing factor.[7]

Bromine was produced directly in the vacuum system by heating a sample of anhydrous copper(II) bromide (the sample could be isolated from the effusion system by a fluorocarbon lubricated stopcock). The released bromine was condensed directly in the effusion cell, entering through the orifice, by cooling the bottom with liquid nitrogen. The cell then was brought to the desired temperature for each vapor pressure measurement by immersing it in a Dewar flask filled with one of these described slush baths:

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