is formed in the rate-determining step are characterized by abnormally high activation energies and entropies and an explanation of this effect has been suggested.[2a] There is no indication that the kinetics of the present reaction follow this pattern.

3. If the initial step involved a one-equivalent change, *i.e.*

$$\mathrm{U(IV)} + \mathrm{Tl(III)} \longrightarrow \mathrm{U(V)} + \mathrm{Tl(II)} \qquad (13)$$

some contribution to the reaction would be expected from a chain mechanism similar to that observed in the oxidation of U(IV) by O_2, *i.e.*

$$\mathrm{U(IV)} + \mathrm{Tl(II)} \longrightarrow \mathrm{U(V)} + \mathrm{Tl(I)} \qquad (14)$$

$$\mathrm{U(V)} + \mathrm{Tl(III)} \longrightarrow \mathrm{U(VI)} + \mathrm{Tl(II)} \qquad (15)$$

The kinetics of the reaction and, in particular, the insensitiveness of the rate to ions such as Cu^{2+}, suggest that this is not the case. An alternative interpretation, consistent with this observation, is that reaction 13 occurs initially but that the U(V) and Tl(II) ions formed react with each other (to form the products U(VI) and Tl(I)) in a shorter time than that required for them to diffuse out of their "solvent cage" and react with other species. In view of the practical difficulty of distinguishing this from a single two-equivalent change, Westheimer,[13] in a discussion of one- and two-electron reactions, has included processes of this type in the latter classification.

The conclusion that the oxidation of U(IV) by Tl(III) occurs through a two-equivalent mechanism is in line with Higginson and Marshall's[14] generalizations and appears to be applicable also to reactions of Tl(III) with other two-equivalent reductants.[2] The question of whether this and related reactions proceed through actual electron transfer between reactants or through group transfer mechanisms (*e.g.*, transfer of oxygen atoms) remains open.

VANCOUVER, CANADA

[CONTRIBUTION FROM THE ARGONNE NATIONAL LABORATORY]

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

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The heat capacity of β-UH_3 has been measured from 5 to 350°K. in an adiabatic calorimeter. The enthalpy and entropy at 298.15°K. calculated from the data are 2155 cal. mole^{-1} and 15.24 cal. deg.$^{-1}$ mole^{-1}, respectively. The entropy and free energy of formation for UH_3 at 298.15°K. as well as the heat of formation at absolute zero were calculated from these data and the previously determined heat of formation and have the values −43.60 cal. deg.$^{-1}$ mole^{-1}, −17,353 cal. mole^{-1} and −27,945 cal. mole^{-1}. It was found that the calculated and observed dissociation pressures are not in agreement. The discrepancy is believed due to a particle size effect in the dissociation pressure measurements or to the heat of transition from α-UH_3 to β-UH_3. An anomaly is observed in the heat capacity which arises from the transition from the ferromagnetic to the paramagnetic state. The maximum in the heat capacity is 10.72 cal. deg.$^{-1}$ mole^{-1} and occurs at 170.7 ± 0.5°K. It was estimated that 1.01 cal. deg.$^{-1}$ mole^{-1} is the entropy change in the transition which is less than $R \ln 2 = 1.38$ cal. deg.$^{-1}$ mole^{-1} expected from the Heisenberg theory of ferromagnetism.

Introduction

Measurements of the low temperature heat capacity of uranium hydride were undertaken to complement studies of the dissociation pressure[3,4] and the determination of the heat of formation[5] which have been reported previously. Neither heat capacity nor experimental entropy values for this compound have been published heretofore. Our interest in these measurements was increased by the discovery that UH_3 is ferromagnetic below 173°K.[6,7]

Two allotropic forms of uranium hydride are known. The β-phase, which is the one usually formed by the reaction between uranium and hydrogen, is cubic with a_0 = 6.63 kX. and with eight atoms of uranium per unit cell arranged as in α-tungsten, *i.e.*, $2U_I$ at (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$) and $6U_{II}$ at ±($^1/_4$, 0, $^1/_2$).[8] Each U_I atom is surrounded by twelve hydrogen atoms at the corners of an icosahedron of symmetry T_h, and each U_{II} atom is surrounded by twelve hydrogens in sets of three, each set forming a face of a different icosahedron. All of the U–H distances are equal to 2.32 Å.[9]

The α-form is also cubic, with a_0 = 4.153 kX. and with two molecules per unit cell.[10,11] The two uranium atoms are equivalent and occupy the positions (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$), and there are six hydrogen atoms at ±($^1/_4$, 0, $^1/_2$). Each uranium atom is surrounded by twelve hydrogen atoms at 2.32 Å., the same distance as in the β-form. The X-ray density of α-UH_3 is 11.11 g./cc., whereas that of β-UH_3 is 10.92. Small quantities of α-UH_3 have been formed on a uranium cathode by electrolysis of a perchloric acid solution or of a sodium carbonate solution below 20°. Mixtures of α-UH_3 and β-UH_3 containing up to 52% α have been pre-

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 16 to 21, 1956.

(3) F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns and A. H. Daane, *Nucleonics*, **4**, 4 (1949).

(4) H. Flotow and B. M. Abraham, AECD-3074, Jan. 5, 1951; also unpublished results.

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

(6) (a) W. Trzebiatowski, A. Sliwa and B. Stalinski, *Roczniki Chem.*, **26**, 110 (1952); (b) **28**, 12 (1954).

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

(8) R. E. Rundle, THIS JOURNAL, **69**, 1719 (1947).

(9) R. E. Rundle, *ibid.*, **73**, 4172 (1951).

(10) R. Caillat, H. Coriou and P. Perio, *Compt. rend.*, **237**, 812 (1953).

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pared by the reaction of uranium and hydrogen at −80°.[11]

This article presents a determination of the heat capacity of the β-form of UH_3 from 5 to 350°K. and the entropy and other thermodynamic functions derived from these data. The relation between the dissociation pressure measurements and the thermal measurements is discussed, and some comments are made concerning the magnetic measurements as they relate to the heat capacity measurements.

Experimental

Uranium Hydride Sample.—The uranium hydride sample was a fine powder prepared by the direct reaction of high-purity uranium metal and hydrogen above 200°. Under these conditions the β-phase is formed. The hydrogen was obtained by the thermal decomposition of another sample of uranium hydride. The uranium metal was prepared by the Metallurgical Division of this Laboratory[12] by the electrolysis of UF_4 in a fused mixture of KCl and LiCl. The crystals obtained in this process were vacuum cast into billets and then swaged into rods of 3 mm. diameter. The rods were annealed *in vacuo*, and after removal of any surface oxide with nitric acid, they were washed with water and alcohol, dried *in vacuo* and loaded into a calorimeter in a dry-box with an atmosphere of pure helium. The heat capacity of the uranium metal was measured between 6 and 352°K.,[13] and then the uranium was converted to the hydride in a vacuum line. The operations of transferring the hydride from the reaction vessel to the calorimeter and soldering shut the calorimeter were carried out in the helium dry-box to avoid oxidation. The mass of the sample was 94.6194 g. In addition to the UH_3 the calorimeter contained 1.11×10^{-5} mole of helium.

Chemical and spectroscopic analyses of the uranium billets showed the presence of the following elements in parts per million: C, 18; N, 5; O, 15; Al, 5; Cr, 2; Cu, 1; Fe, 2; Mg, 1; Si, 12. When the sample was removed from the calorimeter, it was assayed by measuring the volumes of hydrogen released by the thermal decomposition of weighed portions; 99.6 ± 0.1% of the amount calculated from the formula UH_3 was found. It also was analyzed for oxygen by the method of Smiley[14] and was found to contain 0.06 ± 0.01% by weight. No α-phase was detected in an X-ray examination of the sample (limit of detection 4% alpha in beta).

Apparatus and Technique.—The cryostat and the adiabatic method of operation have been described before.[15] The gold plated calorimeter was similar to one previously used,[16] except that it contained no copper vanes but had a thin-walled Monel tube, 6 mm. in diameter, in the lid for loading the sample. The sample was poured into the calorimeter through the tube which then was closed by soldering on a small brass cap.

Temperatures were determined with a capsule-type platinum resistance thermometer (Laboratory designation A-1) contained in a central well in the calorimeter. It was calibrated on the temperature scale of the National Bureau of Standards[17] from 14 to 373°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, to the resistance at 14°K. and to dR/dT at 14°K. A slight correction was applied to the calibration to make the ice point equal to 273.15°K. It is believed that the scale agrees with the thermodynamic scale within 0.1° from 4–14°K., within 0.03° from 14–90°K., and within 0.05° from 90–373°K.

Results and Discussion

Heat Capacity Results.—The experimental values of the heat capacity, expressed in terms of the thermochemical calorie, defined equal to 4.1840 joules, are presented in Table I in chronological sequence. The temperature intervals can be estimated from the differences between the successive mean temperatures. Smaller temperature intervals were used in Series III to VI in order to establish the shape of the heat capacity curve in the region of the anomaly near 171°K. All of the values in Table I, except one in Series I near the anomaly, have been corrected for the finite temperature intervals by adding $-(d^2C_p/dT^2)(\Delta T)^2/24$ to the measured mean heat capacity. A small correction was made for the difference in the amount of helium in the measurements on the empty and on the full calorimeter, but no correction was needed for solder or grease changes because the amounts were adjusted to be the same in all the measurements.

TABLE I

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

Mol. wt. = 241.09; 0°C. = 273.15°K.

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		199.31	8.627	165.91	10.18
7.30	0.092	209.17	8.831	167.79	10.37
9.54	.118	218.64	9.079	169.64	10.62
11.38	.160	228.00	9.343	171.48	10.55
13.26	.217	237.91	9.651	173.37	9.502
15.24	.305	248.03	9.983	175.34	8.944
17.22	.414	257.70	10.31	177.35	8.695
19.13	.549	267.36	10.65	179.37	8.583
21.04	.708	277.20	11.00	181.40	8.520
23.05	.898	287.09	11.36	183.43	8.486
25.32	1.131	297.06	11.73	185.45	8.475
27.95	1.420	307.28	12.12	Series IV	
30.86	1.748	317.40	12.50	168.95	10.55
34.03	2.109	327.14	12.86	169.45	10.59
37.61	2.501	336.88	13.23	169.96	10.67
41.57	2.908	346.94	13.59	170.49	10.71
45.84	3.309	Series II		171.03	10.69
50.56	3.718	6.13	0.076	171.57	10.51
55.62	4.101	8.15	.098	172.12	10.14
61.30	4.496	10.17	.131	Series V	
67.49	4.875	12.16	.182	187.86	8.499
74.65	5.256	14.15	.254	189.92	8.500
82.65	5.664	16.17	.350	191.98	8.525
91.26	6.060	18.18	.478	Series VI	
100.80	6.455	20.17	.633	168.23	10.43
111.19	6.903	22.15	.810	168.77	10.49
121.54	7.371	24.12	1.005	169.31	10.55
131.94	7.875	26.41	1.250	169.85	10.65
142.20	8.433	29.08	1.544	170.39	10.70
151.18	8.990	31.99	1.879	170.92	10.73
160.37	9.669	Series III		171.46	10.51
170.13	10.18[a]	160.14	9.645	172.00	10.19
180.00	8.571	162.09	9.817	172.55	9.888
189.80	8.496	164.01	9.995		

[a] This value was not corrected for the finite temperature increment (9.36°) and is lower than the true heat capacity at 170.13°K.

No correction has been made for the fact that the UH_3 assayed 99.6%. Although the most likely impurity is uranium dioxide, no evidence for its presence could be found in the heat capacity measurements near 28.7°K., where pure uranium di-

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(13) H. E. Flotow and H. R. Lohr, unpublished.

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

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

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

oxide has an anomaly in its heat capacity.[18] If a correction is applied to the observed heat capacity values on the basis of 0.4% UO_2 and additivity of the heat capacities, and a smooth curve is then drawn through all the points, the curve misses the corrected point at 27.95°K. in Series I by 0.8%, and the corrected point at 29.08°K. in Series II by 0.9%. Since the precision of the individual determinations is approximately 0.1% near 29°K., these deviations indicate either that the oxygen is not present in the form of UO_2 or that the UO_2 is too dilute for the coöperative phenomenon that gives rise to the anomaly to occur.

The heat capacities read from large-scale smooth curves through the experimental points are given in Table II at selected temperatures. The heat capacity values in both Tables I and II are considered to have a probable error of 5% at 5°K., 1% at 14°K., and 0.2% above 30°K., except for the runs in Series IV and VI, which had temperature rises of only 0.5°. For the latter the estimated probable error is 0.3%.

Thermodynamic Functions.—The thermodynamic functions calculated from the heat capacity are shown in Table II at selected temperatures. The entropy $S°$ was obtained by numerical integration of $\int C_p \, d \ln T$, and the increment in heat content or enthalpy, $H° - H_0°$, was obtained by numerical integration of $\int C_p \, dT$ between 0°K. and the temperature of interest. The C_p values for both integrations were read from the large-scale smooth curves mentioned above. The free energy function, $(F° - H_0°)/T$, was calculated from the relation $(F° - H_0°)/T = (H° - H_0°)/T - S°$, where $F°$ is the standard Gibbs free energy function.

It is expected that at sufficiently low temperatures the heat capacity of UH_3 should be given by

$$C_p = \gamma T + aT^3 \qquad (1)$$

where the T^3 term is the lattice contribution, and the linear term is the electronic contribution. The magnetic contribution probably is small compared to the other terms at temperatures far below the Curie temperature and is consequently not considered. Equation (2) was found to fit the heat capacity from 10 to 15°K. to ±2%

$$C_p = 0.0078T + 0.000050T^3 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (2)$$

and was used to extrapolate from 10 to 0°K.

Below 10°K. there are appreciable deviations of the observed heat capacities from equation 2, which probably arise from desorption of helium. It is believed that the surface area of the particles of UH_3 was so large that the heat of desorption of helium contributed significantly to the observed heat capacities near the critical temperature of helium (5.2°K.).

Although equation 2 is useful for the extrapolations needed to calculate the thermodynamic functions, the values for the coefficients should not be regarded as well-established. The coefficient of the linear term, 7.8×10^{-3}, is much larger than the corresponding coefficient for uranium metal,[19] 2.6×10^{-3}, and measurements to lower temperatures are needed to establish its value.

TABLE II

THERMODYNAMIC PROPERTIES OF β-URANIUM HYDRIDE AT SELECTED TEMPERATURES

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	$S°$, cal. deg.$^{-1}$ mole^{-1}	$H° - H_0°$, cal. mole^{-1}	$-\left(\frac{F° - H_0°}{T}\right)$ cal. deg.$^{-1}$ mole^{-1}
10	0.128	0.095	0.52	0.043
15	.292	.173	1.51	.072
20	.619	.298	3.71	.112
25	1.097	.485	7.95	.167
30	1.651	.734	14.81	.240
35	2.218	1.031	24.49	.331
40	2.751	1.362	36.93	.439
45	3.233	1.715	51.91	.561
50	3.667	2.078	69.18	.694
60	4.410	2.815	109.69	.987
70	5.016	3.541	156.91	1.299
80	5.532	4.246	209.70	1.625
90	6.002	4.925	267.41	1.954
100	6.426	5.579	329.56	2.283
110	6.850	6.211	395.93	2.612
120	7.299	6.827	466.66	2.938
130	7.778	7.429	542.02	3.260
140	8.307	8.025	622.41	3.579
150	8.905	8.618	708.43	3.895
160	9.636	9.215	800.99	4.209
170	10.67	9.828	902.10	4.522
170.7	10.72[a]	9.872	909.59	4.543
180	8.564	10.362	995.41	4.832
190	8.499	10.821	1080.4	5.135
200	8.638	11.260	1166.0	5.430
210	8.850	11.687	1253.4	5.718
220	9.116	12.104	1343.2	5.999
230	9.403	12.516	1435.8	6.273
240	9.719	12.923	1531.4	6.542
250	10.05	13.326	1630.2	6.805
260	10.39	13.727	1732.4	7.064
270	10.74	14.125	1838.1	7.317
280	11.10	14.523	1947.3	7.568
290	11.47	14.919	2060.1	7.815
300	11.84	15.314	2176.7	8.058
310	12.22	15.708	2297.0	8.298
320	12.60	16.102	2421.1	8.536
330	12.97	16.496	2549.0	8.772
340	13.34	16.888	2680.5	9.004
350	13.70	17.280	2815.8	9.235
273.15	10.85	14.25	1872	7.40
298.15	11.78	15.24	2155	8.01
	±0.02	±0.03	±4	±0.02

[a] Maximum.

The values in Table II may be combined with thermal data in the literature to obtain the entropy and free energy of formation at 298.15°K. and the heat of formation at 0°K. Abraham and Flotow[5] have measured the heat of formation of UH_3 from uranium metal and hydrogen gas at 25°. The reaction product was a mixture of approximately 25% α- and 75% β-UH_3. Assuming that the heat of transition is negligible, they reported $\Delta H_f°_{298.15} = -30{,}352$ cal. mole^{-1} for the reaction

$$U(\alpha) + 3/2H_2(g) = UH_3(\beta) \qquad (3)$$

Jones, Gordon and Long[18] have measured the heat capacity of bulk uranium metal from 15 to 300°K.

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

[19] P. L. Smith and N. M. Wolcott, "Conference de Physique des Basses Temperatures," Paris, 2–8 Sept., 1955, Annexe 1955-3, Supplement au Bulletin de l'Institut International du Froid, pp. 283–286.

and have calculated that the entropy at 25° is 12.03 ± 0.03 cal. deg.$^{-1}$ mole^{-1}. From their heat capacity data we calculate that $H^\circ_{298.15} - H_0^\circ$ is 1526 ± 3 cal. mole^{-1}. The measurements of Flotow and Lohr from 6 to 352°K.[13] and of Smith and Wolcott from 1.2 to 20°K.[19] on bulk uranium metal lead to an entropy of 12.00 ± 0.02 cal. deg.$^{-1}$ mole^{-1} at 25° and $H^\circ_{298.15} - \mathrm{H}_0^\circ = 1521 \pm 2$ cal. mole^{-1}, in excellent agreement with the results of Jones, Gordon and Long. We have arbitrarily chosen to use the measurements of Jones, Gordon and Long for the calculations in this paper. The thermodynamic properties of normal hydrogen gas were taken from the tables of Woolley, Scott and Brickwedde.[20] However, R ln 4 was subtracted from the tabulated values of the entropy and of the free energy function of normal hydrogen to exclude the contribution of the nuclear spins.

For reaction 3 we obtain these values

$$\Delta S_f{}^\circ{}_{298.15} = -\ 43.60 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

$$\Delta F_f{}^\circ{}_{298.15} = -17{,}353 \text{ cal. mole}^{-1}$$

$$\Delta H_{f0}{}^\circ = -27.945 \text{ cal. mole}^{-1}$$

Dissociation Pressure.—It is of interest to use the available thermodynamic data to calculate the dissociation pressure of UH_3 in the temperature range 580 to 717°K. and to compare the calculations with the measurements of Spedding, *et al.*,[3] and of Flotow and Abraham.[4] No comparison will be made with the measurements which have been made above 717°K. by a number of other investigators,[21–23] because extrapolation of the heat capacity of UH_3 to the higher temperature becomes too uncertain.

In addition to the data given above it is necessary to have the free energy function, $-(F^\circ - H_0^\circ)/T$ for uranium, hydrogen and uranium hydride up to 717°K. For uranium the free energy function was obtained from the increments in enthalpy and entropy above 25°, tabulated by K. K. Kelley,[24] and for normal hydrogen it was taken from the tables of Woolley, Scott and Brickwedde.[20] However, in order to obtain this function for UH_3, it is necessary to extrapolate the heat capacity above 350°K., the limit of the heat capacity measurements. Two methods of extrapolation were used which should bracket the correct heat capacity at constant pressure. One was a linear extrapolation of the heat capacity by means of the equation

$$C_p = 0.715 + 0.0371T \text{ cal. deg.}^{-1} \text{ mole}^{-1} \qquad (4)$$

which fits the data between 280 and 350°K. within the precision of the measurements. This equation probably gives too high a heat capacity at high temperatures. The other method was to equate C_p to a Debye heat capacity function with 12 degrees of freedom and a characteristic temperature of 1238°. This function approaches $12R$ at high temperatures and is probably too low.

The Gibbs free energy functions were combined with the $\Delta H_{f0}{}^\circ$ given above to obtain $\Delta F_f{}^\circ/T$ for reaction 3 at several temperatures of interest, and then the dissociation pressures were calculated from the relation

$$\frac{\Delta F_f{}^\circ}{T} = \frac{3}{2} R \ln p_{\text{atm}} \qquad (5)$$

The results are given in Table III, where they are compared with the experimental values of Spedding, *et al.*[3] (in the column labeled Ames) and with pressures obtained from equation 6 (in the column labeled ANL).

TABLE III

COMPARISON OF EXPERIMENTAL AND CALCULATED DISSOCIATION PRESSURES OF β-UH_3

	Obsd. p, mm.		Calcd. p, mm.	
T, °K.	Ames[3]	ANL[4]	Linear extrap.	Debye extrap.
580	32.8	31.6	47.5	48.1
630	134	134	191	197
717	1010	1034	1342	1440

$$\log p_{\text{mm}} = -\frac{4600}{T} + 9.430 \qquad (6)$$

This equation represents the measurements of Flotow and Abraham[4] from 573 to 694°K. It can be seen that the two methods of calculating the dissociation pressure, which should bracket the correct value, agree fairly well with each other, but that they differ significantly from the observed pressures.

Since the results of the calculation are insensitive to the temperature variation of the heat capacity, the disagreement between the calculated and observed pressures probably lies in the value of $\Delta H^\circ{}_{f0}$ used for making the calculations. If the preceding calculation is reversed to evaluate $\Delta H_f(298.15)$, one obtains the average value −31,006 ± 23 cal. mole^{-1} from the linear extrapolation and −31,082 ± 27 cal. mole^{-1} from the Debye extrapolation instead of the calorimetric value, −30,352 ± 30 cal. mole^{-1}. The difference of 700 cal. between the calorimetric and the calculated heat of formation at 298.15°K. is over an order of magnitude greater than the estimated error in the former. Further, the various determinations of the dissociation pressures combined with the two methods of extrapolation yield essentially a constant value for the heat of formation at 298.15°K. It appears, therefore, that the 700 cal. difference between the experimental and the calculated value is significant.

There are two plausible explanations for the 700 cal. discrepancy which will be discussed in turn. The first of these is the state of the uranium metal entering into the reactions. As Giauque has pointed out in the case of MgO,[25] the state of subdivision here made a difference of 888 cal. mole^{-1} in the heat of reaction with H_2O to form $Mg(OH)_2$. Using the results of Torgeson and Sahama,[26] Giauque calculated that the equilibrium pressure of H_2O over macrocrystalline $Mg(OH)_2$–MgO was 130% greater than that observed by Giauque and Archibald[27] over microcrystalline material. A

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

[21] T. R. P. Gibb, Jr., J. J. McSharry and H. W. Kruschwitz, Jr., THIS JOURNAL, **74**, 6203 (1952).

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[23] G. G. Libowitz and T. R. P. Gibb, Jr., *J. Phys. Chem.*, **61**, 793 (1957).

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

[25] W. F. Giauque, THIS JOURNAL, **71**, 3192 (1949).

[26] D. R. Torgeson and Th. G. Sahama, *ibid.*, **70**, 2156 (1948).

[27] W. F. Giauque and R. C. Archibald, *ibid.*, **59**, 561 (1937).

similar situation may exist in the dissociation pressure measurements with UH_3. The microcrystalline uranium resulting from the dissociation will have, due to the large surface, a larger value for $H°_0$ than macrocrystalline uranium; consequently $|\Delta H°_{f0}|$ will be greater than that formed from macrocrystalline uranium. The uranium used for the calorimetric measurements was formed by decomposing UH_3 at 270°. To assure complete decomposition the heating at this temperature was continued for several hours after H_2 evolution ceased. As a consequence, the uranium may have sintered and grown in particle size and may have become macrocrystalline in character. The 700 cal. difference possibly reflects the different state of subdivision of the uranium used in the two experiments from which the heat of formation was evaluated.

It is also worth pointing out at this time that the state of subdivision of the uranium can explain in a thermodynamically consistent fashion the hysteresis observed in making dissociation pressure measurements from the formation side as well as the dip in the plateau near the H/U ratio of 2.9 observed by Spedding.[3] The state of subdivision of the UH_3 is not considered since it has not been observed to sinter under the experimental conditions of preparation whereas uranium has been observed to sinter.

The second possible explanation can arise from the heat of transition of α-UH_3 to β-UH_3. The final product in the calorimetric determination by Abraham and Flotow[5] was found to contain approximately 25% α-UH_3. A heat of transition of approximately 3000 cal. mole^{-1} could account for the 700 cal. discrepancy between the calculated and the observed values for the heat of formation. With the present data it is not possible to evaluate the extent of either cause, the state of subdivision of the uranium or the alpha-beta transition.

The Ferromagnetic Transition.—The experimental values of the heat capacity are plotted in Fig. 1 to illustrate the position and shape of the ferromagnetic anomaly. We have taken the Curie temperature, T_c, to be 170.7 ± 0.5°K., at which point the heat capacity has a maximum value, 10.72 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, Shull and Rundle[7] have shown by neutron diffraction measurements that the ordering in UH_3 is ferromagnetic with all the atoms having approximately the same orientation and moment. These measurements as well as measurements of the magnetization as a function of field and temperature[28-30] 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 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 7.[31]

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

Here $\theta = T/(2\pi T_c)$. A plot of C_p, the experimental heat capacity, minus C_m was then made up to 85°K., and this curve was extrapolated to join smoothly with the experimental C_p curve somewhat above the Curie temperature, as shown by the dotted curve in Fig. 1. The magnetic entropy calculated from the difference between the two curves had the value 1.01 cal. deg.$^{-1}$ mole^{-1}.

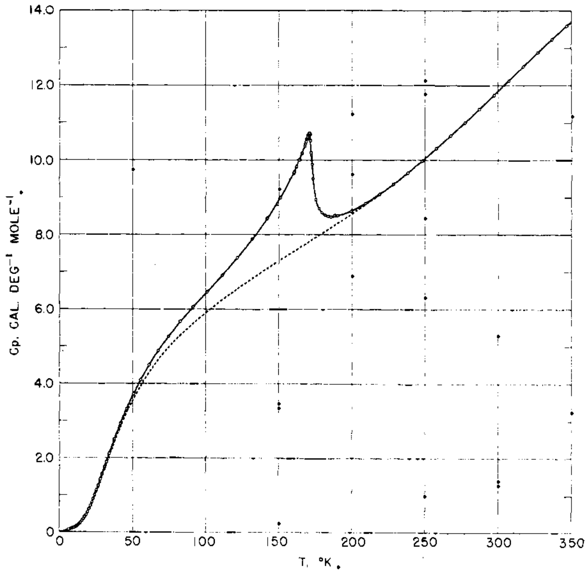

Fig. 1.—Molal heat capacity of β-UH_3.

The disagreement between the expected theoretical value, $R \ln 2$, and the calculated value, 1.01, is not at all unusual for ferromagnetics. It may arise from the persistence of long-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[32] permits any value of the entropy up to $R \ln 2$ to be obtained.

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