posed that the structure of the liquid bromide and iodide is very similar to that of the chloride. On melting not only the long range order disappears but the coördination number of 8 in the crystals decreases to a coördination number in the liquid similar to that in cesium chloride, probably an average of 6.[19]

The above assumption should be checked by an examination of the entropy changes associated with the melting of cesium halides. An increase in the entropy of fusion of the bromide and iodide over that for the chloride would support this postulated coördination number decrease. The N.B.S. compilation[15] lists the heat of transition of cesium chloride as 1.8 kcal./mole. This corresponds to an entropy change of 2.4 e.u. at 469°. The entropy of fusion is given as 3.92 e.u at 645°. An estimate of 2 e.u. for this transition if it occurred at the melting point combined with the entropy of fusion of the face-centered cubic structure would result in an entropy of fusion of 5.9 e.u for simple cubic cesium chloride melting at 645°. Thus one might expect the entropy change associated with the melting of the bromide and iodide should be 5.8 to 6.0 e.u. since the melting points of all three salts are not greatly different. The N.B.S. compilation[15] gives a value of 1.9 e.u. for the entropy of fusion of cesium bromide and does not list a value for cesium iodide. Brewer[20] estimates 3 e.u. for both salts. The first of these two values appears to be inordinately low, and even the second one seems low in the light of this discussion. A direct experimental determination of the heat of fusion of these salts would, therefore, be of considerable interest. The most direct check, however, of the liquid salt structure proposed here will come from X-ray and neutron diffraction measurements of the radial distribution functions in the molten salts, which are in preparation at this Laboratory.

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(19) This prediction of a structure on the basis of comparing molar volumes recalls a similar prediction by K. Fajans and H. Grimm, *Z. Physik*, **2**, 304 (1920), of a structure for solid CsCl, CsBr, and CsI different from that of CsF, shortly thereafter verified by X-ray diffraction.

(20) Leo Brewer in "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," National Nuclear Energy Series, IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, p. 197.

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Heat Capacity of Uranium Tetrafluoride from 5 to 300°K.

BY DARRELL W. OSBORNE, EDGAR F. WESTRUM, JR., AND HAROLD R. LOHR

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The heat capacity of a pure sample of uranium tetrafluoride was determined from 5 to 300°K. and found to be at variance with measurements by Brickwedde, Hoge and Scott. The new data make possible a better evaluation of the magnetic entropy above 5°K. and suggest the probability of a thermal anomaly below 5°K. The values of C_p, $H^\circ - H^\circ_5$, and $S^\circ - S^\circ_5$ are 27.73 ± 0.03 cal. deg.$^{-1}$ mole^{-1}, 5389 ± 6 cal. mole^{-1}, and 36.13 ± 0.04 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.16°K.

Tentative values of the magnetic entropy of uranium tetrafluoride have been calculated[1] from previous heat capacity measurements on this substance in the temperature range 20 to 350°K.[2] The heat capacity of thorium tetrafluoride was taken to represent the lattice contribution to the heat capacity of uranium tetrafluoride. By comparing these values of the magnetic entropy of uranium tetrafluoride with those of neptunium dioxide and uranium dioxide it was concluded that an anomaly might well exist in the heat capacity of uranium tetrafluoride below 20°K. and thus invalidate the extrapolation made by Brickwedde, Hoge and Scott from 20 to 0°K. It was considered desirable, therefore, to extend the heat capacity measurements to lower temperatures in order to obtain more reliable thermodynamic functions for chemical thermodynamic purposes and in order to explore further the question of the magnetic behavior of this substance.

Uranium Tetrafluoride Samples.—Preliminary measurements were made from 5 to 300°K. on a sample of uranium tetrafluoride prepared by the Mallinckrodt Chemical Works. These heat capacity measurements were significantly higher than the values extrapolated by Brickwedde, Hoge and Scott[2] below 20°K. but were unaccountably lower near 300°K. Because of these discrepancies and because of the presence of 2% of uranyl fluoride in both the Mallinckrodt sample and the sample used by Brickwedde, Hoge and Scott, we prepared a purer sample for further measurements by twice subliming the Mallinckrodt sample in high vacuum. The platinum crucible containing the material to be sublimed was heated by a tantalum wire heater which fit into a re-entrant well in the center of the crucible. The crucible was surrounded by a cylindrical platinum radiation shield and rested on a base plate of Alsimag 222 ceramic, which in turn was supported by two tungsten rods serving also as electrical leads through a tungsten-glass seal. The heater was wound on a projection from the base plate. The sublimate crystallized on the inner surface of a bell-jar shaped platinum collector suspended directly above the crucible. Each sublimation required several hours at about 1100° and gave essentially 100% yield. After the first sublimation a small amount of oxygen was detected in the sample, perhaps because of adsorption of atmospheric water in the handling of the sublimate. After resublimation to remove the residual oxygen the sublimate was handled in an atmosphere of anhydrous nitrogen while it was being removed from the collector, broken up in a mortar, and loaded into the calorimeter. The mass of the sample used in the calorimeter was 123.417 g. (*in vacuo*).

Analyses of the purified sample indicated 75.83 ± 0.07% uranium by ignition to U_3O_8 (theoretical, 75.80%), 24.18 ± 0.06% fluorine by pyrohydrolysis and titration of the HF formed (theoretical, 24.20%), and 0.006 ± 0.003% oxygen by bromine trifluoride dissolution.[3] The oxygen content corresponds to 0.05% UO_2F_2. Spectrochemical analyses showed less than 0.002% each of Ag, Al, As, Be, Bi, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sn, Ta and Zr; less than 0.005% Ti, and less than 0.01%

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(1) H. R. Lohr, D. W. Osborne and E. F. Westrum, Jr., THIS JOURNAL, **76**, 3837 (1954).

(2) F. G. Brickwedde, H. J. Hoge and R. B. Scott, *J. Chem. Phys.*, **16**, 429 (1948).

(3) H. R. Hoekstra and J. J. Katz, *Anal. Chem.*, **25**, 1608 (1953).

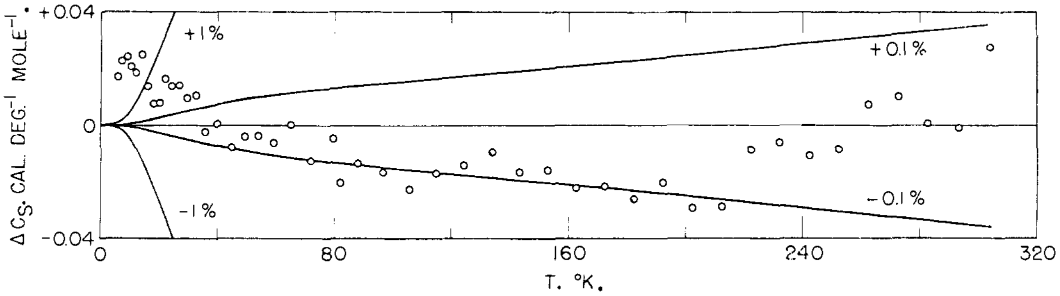

Fig. 1.—Deviations of our measurements of the heat capacity of benzoic acid from the NBS smoothed curve.[8]

Pt. Analyses for the presence of rare earth elements by a procedure involving extraction of the uranium into thenoyltrifluoroacetone and spectroscopic examination of the raffinate for the rare earths established that the total concentration of these elements was less than 15 parts per million.

Experimental Technique.—The adiabatic calorimeter, cryostat, and method of operation have been described previously.[4,5] The calorimeter was evacuated and filled with one atmosphere of helium at 300°K. to aid in the establishment of thermal equilibrium.

Temperatures were measured with a capsule-type platinum resistance thermometer (Laboratory designation A-1) contained in a re-entrant well in the calorimeter. A 160-ohm constantan heater was wound on a cylindrical copper tube surrounding the resistance thermometer. The thermometer was calibrated on the temperature scale of the National Bureau of Standards[6] from 14 to 373°K. Below 14°K. the scale was obtained by fitting the equation[6] $R = A + BT^2 + CT^5$ to the resistance at the boiling point of helium and to the resistance 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., and within 0.05° from 90 to 373°K.

The thermometer resistance and the power input were measured with a calibrated White double-potentiometer, calibrated resistances, and a calibrated standard cell. An electric timer operated by a calibrated tuning fork and amplifier was automatically started at the beginning of the heating period and stopped at the end.

Heat Capacity of a Standard Sample of Benzoic Acid.—In order to verify the over-all accuracy of our technique, measurements were made on the heat capacity of pure benzoic acid made available by the National Bureau of Standards in conjunction with the program of the Calorimetry Conference.[7] A sample of 22.226 g. (*in vacuo*) of benzoic acid was utilized. The heat capacities measured in our apparatus agree excellently with the values reported by the National Bureau of Standards.[8] The deviations of our individual experiments from the smoothed heat capacity curve obtained at the National Bureau of Standards are indicated in Fig. 1. Solid lines represent limits of ±0.1% and ±1%.

Heat Capacity of Pure Uranium Tetrafluoride.—The experimental values of the molal heat capacity of uranium tetrafluoride determined on the purified sample are given in Table I. Temperature increments of the individual determinations can usually be inferred from the adjacent mean temperatures. Small corrections have been made for the finite temperature increments and for the slight differences in the amounts of helium and solder in the measurements on the empty and on the full calorimeter. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 absolute joules. The ice point was taken to be 273.16°K., and the molecular weight of uranium tetrafluoride was taken as 314.07.

TABLE I

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

$\bar{T}$ (°K.)	C_p	$\bar{T}$ (°K.)	C_p	$\bar{T}$ (°K.)	C_p
5.26	0.264	41.13	5.095	165.59	22.53
6.26	.272	45.39	5.987	175.31	23.19
7.69	.274	49.92	6.939	184.84	23.76
9.38	.300	54.80	7.939	194.39	24.29
11.08	.355	60.11	9.008	204.20	24.78
12.71	.441	60.38	9.059	214.29	25.20
14.23	.549	66.31	10.22	224.48	25.64
15.73	.671	72.63	11.37	234.69	26.03
17.30	.822	79.57	12.59	244.92	26.37
18.95	1.014	86.96	13.84	255.00	26.67
20.80	1.258	95.22	15.08	264.94	26.96
22.94	1.574	104.44	16.36	274.75	27.21
25.36	1.968	114.06	17.59	284.43	27.43
27.97	2.430	123.95	18.75	294.11	27.64
30.69	2.946	134.43	19.87	303.79	27.84
33.73	3.558	145.14	20.89		
37.22	4.280	155.50	21.77		

The molal heat capacity at selected temperatures is presented in Table II. These values are considered to have a probable error of 0.1% above 25°K., 1% at 14°K., and 5% at 5°K.

TABLE II

HEAT CAPACITY OF URANIUM TETRAFLUORIDE AT ROUNDED TEMPERATURES (IN CAL. DEG.$^{-1}$ MOLE^{-1})

T (°K.)	C_p	T (°K.)	C_p	T (°K.)	C_p
5	0.268	100	15.76	220	25.47
10	0.317	110	17.09	230	25.85
15	0.608	120	18.30	240	26.21
20	1.149	130	19.41	250	26.53
25	1.908	140	20.42	260	26.83
30	2.811	150	21.31	270	27.09
40	4.863	160	22.12	273.16	27.17
50	6.955	170	22.84	280	27.33
60	8.980	180	23.48	290	27.55
70	10.90	190	24.05	298.16	27.73
80	12.67	200	24.58	300	27.76
90	14.30	210	25.05		

In Table III are given representative deviations of the heat capacity of the Mallinckrodt sample

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

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

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

(7) D. C. Ginnings and G. T. Furukawa, THIS JOURNAL, **75**, 522 (1953).

(8) G. T. Furukawa, R. E. McCoskey and G. J. King, *J. Research Natl. Bur. Standards*, **47**, 256 (1951).

from the heat capacity of the purified sample (Table II). Over most of the temperature range these deviations can be satisfactorily accounted for by the presence in the Mallinckrodt sample of 2% of uranyl fluoride, for which heat capacity data are available.[9] Corresponding deviations of the measurements of Brickwedde, Hoge and Scott at the National Bureau of Standards[2] are given in the last column of Table III. Above 100°K. the latter deviations have the wrong sign to be explained by the presence of uranyl fluoride or uranium dioxide in their sample, and above 270°K. the deviations are greater than their estimated uncertainty of 1%. The heat capacity values given in Table II are considered to be more accurate than those given by Brickwedde, Hoge and Scott because of the higher purity of the uranium tetrafluoride sample, the higher precision of the measurements, and the verification of the over-all accuracy by the results on benzoic acid.

TABLE III

DEVIATIONS OF OTHER HEAT CAPACITY DATA ON URANIUM TETRAFLUORIDE FROM VALUES IN TABLE II (IN CAL. DEG.$^{-1}$ MOLE^{-1})

T (°K.)	Mallinckrodt sample	BHS[2] data	T (°K.)	Mallinckrodt sample	BHS[2] data
20	0.032	0.013[a]	200	−0.06	0.12
50	.009	.030	250	− .06	.22
100	− .01	.00	300	− .03	.40
150	− .05	.05			

[a] The value given by BHS at 20°K. in their smooth table is apparently in error. The corrected extrapolation equation[10] was used here.

The heat capacity determinations on the purified sample from about 5 to 25°K. are plotted in Fig. 2. The extrapolation equation used by Brickwedde, Hoge and Scott is also shown.[10] It is seen that the experimental heat capacity in this region is considerably higher than predicted by the extrapolation equation. Indeed, the shape of the experimental curve suggests that there may be a hump in the curve below 5°K. Unfortunately it was not possible to make measurements below 5°K. with the present apparatus, because of the low sensitivity of the platinum resistance thermometer in that temperature region.

Thermodynamic Functions of Uranium Tetrafluoride.—Because of the uncertainty in any extrapolation of the heat capacity below 5°K. only the increments in the entropy and heat content from 5 to 298.16°K., calculated from the heat capacity of the purified sample, will be reported here. These are

$$S°_{298.16} - S°_5 = 36.13 \pm 0.04 \text{ cal. deg.}^{-1} \text{ mole}^{-1}$$

and

$$H°_{298.16} - H°_5 = 5389 \pm 6 \text{ cal. mole}^{-1}.$$

It seems reasonable to assume that the heat capacity of thorium tetrafluoride very nearly equals the lattice contribution to the heat capacity of uranium tetrafluoride, because (1) the two compounds are isostructural, with only about 2.5% difference in the lattice dimensions[11] and only 2.6% difference in the masses of the cations, and (2) the heat capacity of thorium tetrafluoride should depend solely upon the lattice vibrations, inasmuch as the electronic structures of the ions are like those of the rare gases. With this assumption the magnetic entropy of uranium tetrafluoride can be calculated by subtracting the entropy of thorium tetrafluoride (to represent the lattice contribution) from the total entropy of uranium tetrafluoride at the same temperature. At 298.16°K., where the entropy of thorium tetrafluoride[1] is 33.95 ± 0.04 cal. deg.$^{-1}$ mole^{-1}, the magnetic entropy of uranium tetrafluoride is thus calculated to be $S°_5$ + 2.18 cal. deg.$^{-1}$ mole^{-1}.

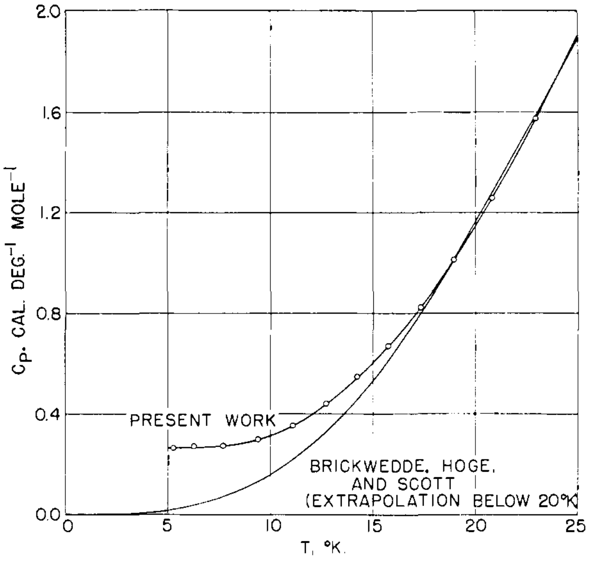

Fig. 2.—Heat capacity of uranium tetrafluoride below 25°K.

In order to obtain an accurate value for $S°_5$, the entropy of uranium tetrafluoride at 5°K., it will be necessary to make heat capacity measurements at lower temperatures, and another apparatus is being constructed for this purpose. However, an estimate may be made in the following manner. By analogy with uranium dioxide and neptunium dioxide it is expected that at 298.16°K. the magnetic entropy of uranium tetrafluoride should be about 0.9 cal. deg.$^{-1}$ mole^{-1} higher than the spin-only value of R ln 3, or a total of 3.0 cal. deg.$^{-1}$ mole^{-1}. Comparison with the result given in the preceding paragraph gives an estimated value of 0.8 cal. deg.$^{-1}$ mole^{-1} for $S°_5$. This estimate, as well as the shape of the heat capacity curve near 5°K., suggests that a thermal anomaly may exist below this temperature.

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(9) P. F. Wacker and R. K. Cheney, *J. Research Natl. Bur. Standards*, **39**, 317 (1947).

(10) The equation given in reference 2 contains a typographical error and should read $C = 3R[D(150/T) + 4.1 \times 10^{-6}T^3]$. The corrected equation agrees with the values tabulated, at 5, 10 and 15°K.

(11) W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).