Brewer's[1] compilation (−58.0 ± 0.5) and by 1.1 kcal./mole from that listed in the N. B. S. tables[2] (−58.4). These values were selected from data ranging from −57.1 to −59.9 kcal./mole.

The present value for cobaltous oxide is in good agreement with that listed by Brewer (−57.0 ± 0.5) and also with the N. B. S. listing (−57.2). These values were selected from data ranging from −54.5 to −57.6 kcal./mole.

The present heat of formation of nickelous oxide, together with entropy values listed by Kelley,[8] leads to $\Delta F^0_{298.16} = -50.6 \pm 0.1$ kcal./mole as the free energy of formation from the elements. The entropy of cobaltous oxide has not been determined. If it is assumed that this oxide has the same entropy of formation as nickelous oxide, then the free energy of formation becomes $\Delta F^0_{298.16} = -50.4$ kcal./mole.

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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Thermodynamic Properties of Thorium Tetrafluoride from 5 to 300°K. and the Magnetic Entropy of Uranium Tetrafluoride

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The heat capacity of thorium tetrafluoride was measured from 5 to 300°K., and the enthalpy, entropy and free energy were calculated from these data. At 298.16°K. the values of C_p, $H^0 - H_0^0$, and S^0 are 26.46 ± 0.03 cal. deg.$^{-1}$ mole^{-1}, 5113.8 ± 6 cal. mole^{-1}, and 33.953 ± 0.04 cal. deg.$^{-1}$ mole^{-1}, respectively. On the assumption that the heat capacity of thorium tetrafluoride is equal to the lattice heat capacity of uranium tetrafluoride, the magnetic entropy of uranium tetrafluoride was evaluated by subtracting the entropy of thorium tetrafluoride from the entropy of uranium tetrafluoride given by Brickwedde, Hoge and Scott. At 298.16°K. the value of the magnetic entropy obtained in this way, 2.17 cal. deg.$^{-1}$ mole^{-1}, is 0.87 cal. deg.$^{-1}$ mole^{-1} lower than the magnetic entropy of uranium dioxide, and this suggests that the extrapolation of the heat capacity of uranium tetrafluoride below 20°K. may be in error.

The measurements of the low temperature heat capacity of thorium tetrafluoride that are presented in this paper were made both to provide thermodynamic data which should be useful in thorium chemistry and to resolve the lattice and magnetic contributions to the heat capacity and entropy of uranium tetrafluoride.

It has been found that an anomaly or "hump" occurs in the heat capacity curve of uranium dioxide at 28.7°K.[2] and in that of neptunium dioxide at 25.3°K.[3] The anomalies are believed to be related to the magnetic behavior of these substances. However, there is no hump in the heat capacity curve of uranium tetrafluoride between 20 and 350°K.,[4] and the question arises as to whether the magnetic contribution is spread out over a wide range of temperature or whether it is concentrated in a hump in the heat capacity curve below 20°K. In the latter case the entropy obtained by extrapolating the heat capacity curve from 20 to 0°K. with a Debye function might be in error by 2 or 3 cal. deg.$^{-1}$ mole^{-1}.

Because the electronic structure of the Th^{+4} and F^- ions are of the rare gas type, with a $^1S_0$ ground state, so that thorium tetrafluoride is diamagnetic, the heat capacity of this compound depends only upon the lattice vibrations. Both thorium tetrafluoride and uranium tetrafluoride are monoclinic and isostructural with zirconium tetrafluoride, and the lattice dimensions of thorium tetrafluoride are only about 2.5% larger than those of uranium tetrafluoride.[5] In view of the small percentage difference in the atomic masses as well as in the lattice dimensions it seems reasonable to assume that the molal heat capacity of thorium tetrafluoride is very nearly equal to the lattice contribution to the molal heat capacity of uranium tetrafluoride, and hence that the molal entropy of thorium tetrafluoride is very nearly equal to the lattice contribution to the molal entropy of uranium tetrafluoride. The magnetic contribution to the heat capacity or entropy of uranium tetrafluoride can then be obtained by subtracting the lattice contribution, as given by the heat capacity or entropy of thorium tetrafluoride, from the total heat capacity or entropy of uranium tetrafluoride.

Thorium Tetrafluoride Sample.—The thorium tetrafluoride for this investigation was prepared by hydrofluorination of a pure sample of electrically fused thorium dioxide that had been used for the determination of the heat capacity of the latter substance.[6] The oxide charge was placed in a platinum boat, which was contained in a nickel reaction tube attached to a nickel vacuum line. Anhydrous, high purity, gaseous hydrogen fluoride was passed over the sample at 750° until constant weight was attained; this required a reaction time of 132 hours.

Weighing of the sample before and after hydrofluorination indicated that the amount of unconverted thorium dioxide was less than 0.13% by weight. Thorium determinations by gravimetric oxalate precipitation gave 75.40 and 75.26% (theoretical, 75.33%). Fluorine analysis by a method involving pyrohydrolysis in a platinum apparatus followed by titration with a standard base gave 24.6% fluorine (theoretical, 24.67%). The only significant amounts of impurities found by spectrochemical analysis of the thorium tetrafluoride were, in p.p.m.: 70 of Ca, 10 of Mg, less than 10 of K, 5

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(1) Department of Chemistry, University of Michigan, Ann Arbor, Mich.

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

(3) E. F. Westrum, Jr., J. B. Hatcher and D. W. Osborne, *ibid.*, **21**, 419 (1953).

(4) F. G. Brickwedde, H. J. Hoge and R. B. Scott, *ibid.*, **16**, 429 (1948).

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

(6) D. W. Osborne and E. F. Westrum, Jr., *J. Chem. Phys.*, **21**, 1884 (1953).

of Fe, Na and Ni, and less than 5 of Ag, Al, Be, Bi, Co, Cr, Cu, Li, Mn, Pb and Sn. From the analyses of the thorium dioxide starting material[6] the lanthanum content was known to be 40 p.p.m., and the sum of all the other rare earths was known to be less than 150 p.p.m.

The mass of the sample used in the calorimeter was 91.162 g. (*in vacuo*).

Apparatus.—The heat capacity determinations were made with the adiabatic calorimeter[6] and cryostat[3] previously described. The calorimeter contained 1 atm. 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[7] from 14 to 373°K. Below 14°K. the scale was obtained by fitting the equation[7] $R = A + BT^2 + CT^5$ 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.

TABLE I

HEAT CAPACITY OF THORIUM TETRAFLUORIDE IN CAL. DEG.$^{-1}$ MOLE^{-1}

Molecular weight = 308.12, 0°C. = 273.16°K.

$\overline{T}$, °K.	C_p	$\overline{T}$, °K.	C_p	$\overline{T}$, °K.	C_p
5.54	0.016	44.02	5.303	156.48	20.71
7.67	.044	48.54	6.210	166.57	21.44
9.31	.086	53.48	7.192	176.73	22.08
10.86	.146	59.02	8.270	186.96	22.67
12.47	.236	59.42	8.345	197.04	23.18
14.12	.365	65.42	9.481	206.90	23.65
15.98	.534	71.92	10.63	216.84	24.06
18.02	.756	79.31	11.89	227.16	24.47
20.07	1.014	87.48	13.20	237.60	24.83
22.14	1.303	96.65	14.50	247.88	25.18
24.21	1.614	106.08	15.73	258.06	25.48
26.59	2.001	115.58	16.87	268.18	25.77
29.43	2.489	125.48	17.96	278.25	26.02
32.62	3.078	135.92	18.99	288.25	26.25
36.06	3.735	146.33	19.92	298.17	26.46
39.79	4.470				

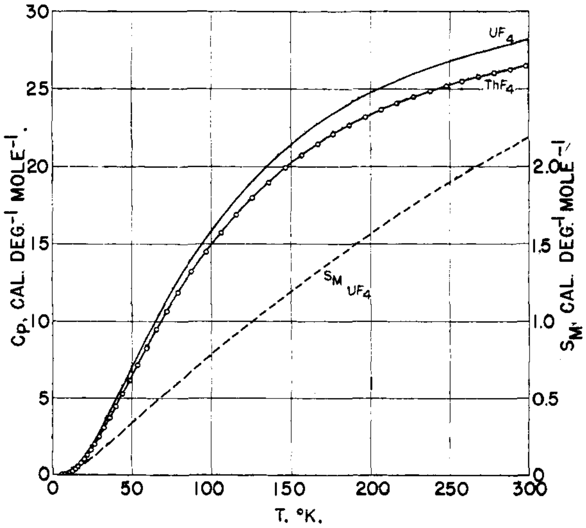

Fig. 1.—Molal heat capacities of ThF$_4$ and UF$_4$, and the magnetic entropy (S_M) of UF$_4$.

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.

Experimental Results.—The experimental values of the molal heat capacity of thorium tetrafluoride are given in Table I and are plotted in Fig. 1. A small correction for curvature (less than 0.002 cal. deg.$^{-1}$ mole^{-1} below 30°K. and less than 0.05% above 30°K.) has been applied. The results are expressed in terms of the defined thermochemical calorie, which is equal to 4.1840 absolute joules.

The molal heat capacity and the thermodynamic functions derived from the heat capacity are listed at rounded temperatures in Table II. These heat capacity values were read from a smooth curve through the experimental points, and they are estimated to have a probable error of 0.1% above 25°K., 1% at 14°K. and 5% at 5°K. The heat capacity was extrapolated below 5.54°K. with a Debye function. The effect of nuclear spin is not

TABLE II

THERMODYNAMIC PROPERTIES OF THORIUM TETRAFLUORIDE

T, °K.	C_p, cal. deg.$^{-1}$ mole^{-1}	$S°$, cal. deg.$^{-1}$ mole^{-1}	$H° - H_0^0$, cal. mole^{-1}	$-\frac{F° - H_0^0}{T}$, cal. deg.$^{-1}$ mole^{-1}
5	0.012	0.004	0.015	0.001
10	.109	.033	0.25	.008
15	.442	.131	1.52	.030
20	1.005	.329	5.05	.077
25	1.739	.630	11.85	.156
30	2.593	1.021	22.64	.266
40	4.511	2.026	58.02	.576
50	6.499	3.245	113.02	.985
60	8.455	4.604	187.88	1.473
70	10.29	6.047	281.70	2.023
80	12.00	7.534	393.26	2.618
90	13.56	9.039	521.21	3.248
100	14.96	10.541	663.9	3.902
110	16.22	12.027	819.9	4.573
120	17.37	13.488	987.8	5.256
130	18.41	14.920	1166.8	5.945
140	19.36	16.320	1355.7	6.636
150	20.22	17.686	1553.7	7.328
160	20.99	19.015	1759.7	8.017
170	21.66	20.308	1973.0	8.702
180	22.28	21.564	2192.8	9.382
190	22.83	22.783	2418.3	10.055
200	23.33	23.967	2649.2	10.721
210	23.78	25.117	2884.7	11.380
220	24.19	26.232	3124.6	12.029
230	24.57	27.317	3368.4	12.672
240	24.92	28.369	3615.9	13.303
250	25.24	29.393	3866.7	13.926
260	25.54	30.389	4120.7	14.540
270	25.81	31.358	4377.5	15.145
280	26.06	32.302	4636.8	15.742
290	26.29	33.220	4898.6	16.328
300	26.50	34.115	5162.5	16.907
298.16	26.46	33.953	5113.8	16.802
	±0.08	±0.04	±6	±0.02

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

included in the entropy and free energy function. The estimated probable error in the entropy, heat content and free energy function is 0.1% above 100°K., but in order to make the table internally consistent some of the values are given to one more figure than is justified by the estimated probable error.

Magnetic Entropy of Uranium Tetrafluoride.—The heat capacity of uranium tetrafluoride as determined by Brickwedde, Hoge and Scott[4] from 20 to 350°K. has been included in Fig. 1 for comparison with that of thorium tetrafluoride. The heat capacity of thorium tetrafluoride, as discussed above, is considered to be a good approximation for the contribution of the lattice vibrations to the heat capacity of uranium tetrafluoride. At all temperatures the heat capacity of uranium tetrafluoride is greater than that of thorium tetrafluoride, the difference presumably being the magnetic contribution.

The magnetic entropy of uranium tetrafluoride, which is also shown in Fig. 1, was obtained by subtracting the entropy of thorium tetrafluoride from the total entropy of uranium tetrafluoride[4] at the same temperature. Although there is no hump in the heat capacity curve of uranium tetrafluoride down to 20°K., there is an appreciable magnetic contribution to the entropy, increasing with temperature and amounting to 2.17 cal. deg.$^{-1}$ mole^{-1} at 298.16°K. This is very nearly equal to the spin-only value for the magnetic entropy at high temperatures, $R \ln (2S + 1) = R \ln 3 = 2.18$ cal. deg.$^{-1}$ mole^{-1}, but at higher temperatures the magnetic entropy exceeds the spin-only value.

The entropy calculations for uranium tetrafluoride involve an extrapolation of the heat capacity curve from 20 to 0°K., and there is, of course, a possibility that the extrapolation may be incorrect. In connection with this possibility it should be noted that the magnetic entropies of uranium dioxide and neptunium dioxide exceed the spin-only values by 0.86 and 0.85 cal. deg.$^{-1}$ mole^{-1}, respectively, at 298.16°K. The lower value for the magnetic entropy of uranium tetrafluoride suggests that there may be an anomaly in the heat capacity curve below 20°K. that causes the entropy to be greater than the tabulated values.[4] It therefore seems advisable to measure the heat capacity of uranium tetrafluoride below 20°K., and this work is now in progress.

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LEMONT, ILLINOIS

[CONTRIBUTION OF THE INTERNATIONAL NICKEL COMPANY'S MULTIPLE FELLOWSHIP, MELLON INSTITUTE]

Composition of Basic Nickel Carbonates

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Basic nickel carbonates were formed at constant *p*H and room temperature by the addition of standard nickel chloride and potassium hydroxide solutions to a reaction medium containing a 10-fold excess of potassium carbonates. The composition of the precipitates may be expressed $Ni(OH)_2 \cdot 3$ to $4NiCO_3$ in the *p*H range 8 to 10.5; above *p*H 10.5 the ratio of carbonate to hydroxide in the precipitate decreases rapidly. Essentially no chloride is absorbed by the precipitate. A previously developed method of precipitation at constant *p*H was adapted to permit calculation of the composition of the precipitate directly from buret readings.

Introduction

Basic nickel carbonates are frequently used as catalyst intermediates. Rather minor changes in preparative procedure have been known to influence the behavior of the ultimate reduced nickel catalyst. Fundamental data were sought as a step in the elucidation of problems connected with catalyst preparation. More specifically the objective was to determine the influence of *p*H of the reaction medium on the composition of the basic nickel carbonates formed. Previously a volumetric method was described for determining the composition of basic metal salts such as basic sulfates, nitrates, chlorides formed at constant *p*H.[1] This method had the advantage of avoiding possible changes in precipitate composition as a result of the washing and drying process required to prepare the materials for elemental chemical analysis. Briefly the composition of basic salts, formed at constant *p*H by the addition of standard alkali and metal salt solutions to an alkaline reaction medium, has been shown to be calculable from buret readings. The alkali added to maintain constant *p*H is an immediate measure of the hydroxide content of the precipitate.

With some modification of method, the composition of basic metal carbonates formed at constant *p*H by the addition of standard metal salt and alkali solutions to an alkaline reaction medium containing an excess of total carbonate is also calculable from buret readings. In the latter case, the calculation is slightly more complicated since the alkali added must not only compensate for hydroxide ion consumed by the precipitate but also must neutralize the acid hydrogen which may have been associated with carbonate ion consumed by the precipitate. It is assumed that precipitates are formed only by reaction of metal ions with carbonate ions, CO_3^{-2}, and that consumption of these ions by the precipitate is accompanied by equilibrium shifts tending to restore the relative concentrations among the various carbonate species. For example, if a

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[1] J. T. Carriel and W. J. Singley, Jr., THIS JOURNAL, **75**, 778 (1953).