ther investigation more examples will be identified, but Th(IV) represents an important addition to the group, as the major tetravalent cation. Tributyl phosphate dissolves uranyl nitrate in essentially anhydrous condition,[14,15] and with two tributyl phosphates per uranyl nitrate, suggesting again coördination number 4, as against the normal 6.[6] Americium nitrate also interacts strongly with tributyl phosphate.[16]

If in this case also a lower coördination number obtains, there is room for speculation that in these three heavy elements the multiplicity of coördination numbers may be linked with the use of d-orbitals, as seems the case with most of the lighter elements enumerated above.

Of importance in these considerations is the relation of the group coördinated to the coördination number of the cation. With Co(II), for example, the lower coördination number is never achieved with nitrate as the anion, but represents the common state in organic solution with the halides. With Fe(III), the lower coördination number is again found with chloride in organic solution. The ability of tributyl phosphate similarly to influence the coördination number of the cation is established at least with Th(IV) and uranyl ions, and may be expected to extend to others also.

LEMONT, ILLINOIS

(15) H. A. C. McKay and T. V. Healy, *Rec. trav. chim.*, in press.

(16) K. A. Walsh, Nuclear Engineering and Science Congress, Cleveland, Ohio, December, 1955, paper 270.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MICHIGAN]

Heat Capacity and Thermodynamic Functions of Uranium(IV) Oxychloride and Uranium (IV) Oxybromide from 10 to 350°K.[1]

BY ELLIOTT GREENBERG AND EDGAR F. WESTRUM, JR.

RECEIVED MAY 10, 1956

Low temperature heat capacity measurements have been made on uranium(IV) oxychloride and uranium(IV) oxybromide, and the data have been used to calculate the entropy, enthalpy and free energy functions for these substances. At 298.16°K., the molal values of C_p, S° and $H^\circ - H_0^\circ$ are 22.72 ± 0.03 cal./deg., 33.06 ± 0.05 cal./deg., and 4586 ± 7 cal., respectively, for $UOCl_2$, and 23.42 ± 0.03 cal./deg., 37.66 ± 0.06 cal./deg., and 4989 ± 7 cal. for $UOBr_2$.

The present study was undertaken to supplement the available chemical thermodynamic data on the uranium oxyhalides and to investigate by calorimetric measurements the possible occurrence of low temperature magnetic transformations in uranium(IV) oxychloride and uranium(IV) oxybromide. The presence of such phenomena in UO_2[2-4] and UI_3[5] has already been demonstrated.

Experimental

Preparation of Uranium Dioxide.—Ammonium diuranate, $(NH_4)_2U_2O_7$, was precipitated from hot aqueous solution by treating uranyl nitrate with ammonium hydroxide. The precipitate was washed with hot water, filtered on a sintered-glass Büchner funnel, air-dried at 115°, and, after being ground, was ignited at 700° to U_3O_8. Subsequent reduction to uranium dioxide was achieved in a Vycor apparatus, using hydrogen purified over hot copper and dried over anhydrous magnesium perchlorate. Although most of the reduction took place below 800°, the reactor was maintained at 950–1000° for at least one hour. This procedure yielded a finely divided, brown powder containing 87.76 ± 0.08% uranium (theoretical, 88.15%), determined by ignition in air to U_3O_8.

Preparation of Uranium(IV) Oxychloride.—Anhydrous uranous oxychloride ($UOCl_2$) was prepared on the 200-g. scale by dissolving uranium dioxide in excess molten uranium tetrachloride by the reversible reaction $UO_2 + UCl_4 \rightleftarrows 2UOCl_2$. After the product was cooled and ground the excess UCl_4 was removed *in vacuo* at 450°. Under these conditions disproportionation of the uranous oxychloride is said to be negligible.[6] Uranium tetrachloride (about a 10% excess) prepared in the manner previously described,[7] was ground in an agate mortar with uranium dioxide and transferred to a covered porcelain crucible within a Vycor reactor. After evacuation, the reactor was filled with purified dry nitrogen, placed in a furnace preheated to 600°, and maintained at that temperature for about 40 minutes. After cooling, the reactor was unloaded in a dry box, and the fused product ground. The product was then reloaded into the reactor, heated to 600° under a nitrogen atmosphere for 20 minutes, cooled to 450°, and held at this temperature for 20 minutes while the reactor was evacuated to 10^{-5} mm. in order to permit excess UCl_4 to sublime from the crucible. Analyses by ignition in air to U_3O_8 indicated 72.73 and 72.90% uranium (theoretical, 73.26%); gravimetric determination of chlorine as silver chloride yielded 22.17 ± 0.03% (theoretical, 21.82%).

Since the starting materials in this preparation, essentially equimolar quantities of UCl_4 and UO_2, should yield the same over-all analysis as the product, gross analyses for uranium and chlorine are not sufficient in themselves as an indication of the purity of the product. It was necessary to demonstrate that no appreciable quantities of UCl_4 and/or UO_2 remained in the sample.

X-Ray diffraction analysis indicated that the major constituent and only detectable crystalline phase was $UOCl_2$. Attempts to determine any excess UCl_4, by sublimation from a small sample at 460° in high vacuum, resulted in some disproportionation of the $UOCl_2$, and hence permitted only the establishment of an upper limit of 5% for the UCl_4 content.

Determinations of the amount of UO_2 present in the sample were made by washing a weighed sample on a filtering crucible with 2 *N* HCl and weighing the residue. The results indicated only a negligible trace of UO_2 in the sample.

Since the heat capacity curve of uranium dioxide exhibits a λ-type maximum at 28.7°K.[2,4] with an electronic enthalpy contribution of about 25 cal. for the transition, any UO_2 present as an impurity phase would be expected to show up

---

(1) Adapted from a portion of the thesis of Elliott Greenberg, submitted to the Graduate School of the University of Michigan in partial fulfillment of the requirements of the Ph.D. degree. This work was supported in part by the U. S. Atomic Energy Commission, Division of Research, Sub-contract AT(11-1)-70, No. 5.

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

(3) A. Arrott and J. E. Goldman, *Phys. Rev.*, **99**, 1641 (1955).

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

(5) L. D. Roberts, D. E. Lavalle and R. A. Erickson, *ibid.*, **22**, 1145 (1954).

(6) Reported in J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, pp. 588–90.

(7) E. Greenberg and E. F. Westrum, Jr., THIS JOURNAL, **78**, 4526 (1956).

in the heat capacity measurements on $UOCl_2$. The complete absence of any such anomalous behavior in this region was taken as evidence that there was no appreciable quantity of UO_2 present in the calorimetric sample. Furthermore, the fortunate circumstance that the heat capacity of $UOCl_2$ lies between that of UO_2 and UCl_4 tends to minimize the effect of these substances should they be present as impurities.

Preparation of Uranium(IV) Oxybromide.—Uranous oxybromide was prepared on the 100-g. scale by the following reactions[8]:

$$3UO_2 + 2CS_2 \xrightarrow{900°} U_3O_2S_4 + 2CO_2$$

$$U_3O_2S_4 + 6Br_2 \xrightarrow{600°} 2UOBr_2 + UBr_4 + 2S_2Br_2$$

Nitrogen (passed over hot copper and then through a drying tube containing anhydrous calcium sulfate) functioned as a carrier gas for both the carbon disulfide and bromine. The carbon disulfide was passed through a drying tube containing activated silica gel, and anhydrous magnesium perchlorate was used to dry the bromine. The reactor was a 38 mm. diameter Vycor tube (about 1.2 meters long) with a 50-ml. bulb on the exit end to collect the liquid sulfur bromide that condenses out during the bromination reaction. The reaction tube was inclined slightly in order to facilitate collecting the sulfur bromide in the bulb.

The reactor was loaded with uranium dioxide in a 22 cm. long Vycor boat, and was flushed with hydrogen while being heated to 850°. At this temperature the hydrogen atmosphere was replaced by nitrogen, and at 900° the passage of carbon disulfide was begun. Approximately ten times the stoichiometric quantity of carbon disulfide was passed over the sample during a three-hour period. Then the reaction tube was flushed with nitrogen while the temperature was allowed to drop to 600°. Five times the stoichiometric quantity of bromine was then swept through the reactor over a five-hour period. During this time the reactor temperature was maintained at 600°, and the furnace occasionally advanced along the tube for a few minutes to prevent the sublimed UBr_4 from blocking the flow of gas through the reactor.

Following the bromination reaction the system was swept out with nitrogen while being cooled to room temperature. The sample was then transferred to a vacuum line for removal of possible volatile contaminants.

Analyses for uranium indicated 57.38 ± 0.1% (theoretical, 57.52%) and gravimetric determination of bromine, by precipitation with silver nitrate, indicated 38.57 ± 0.05% (theoretical, 38.62%).

All transfers and handling of hygroscopic materials were carried out in a dry box except for loading and unloading the reactor used in the preparation of $UOBr_2$. The latter operations were carried out very rapidly, using previously dried tubes as intermediate transfer vessels. Subsequent operations (described above) tended to minimize the effect of any moisture introduced into the system by these transfers.

Cryogenic Technique.—The calorimeter (laboratory designation W-9) and cryostat (Mark I) have been described in previous papers from this Laboratory.[7,9] Temperatures were determined with a platinum resistance thermometer (laboratory designation A-3) calibrated by the National Bureau of Standards against the International Temperature Scale over the range from the boiling point of oxygen to that of sulfur, and over the range 10 to 90°K. by comparison with thermometers calibrated on the scale of Hoge and Brickwedde.[10] The accuracy of the calorimeter was ascertained by measuring the heat capacity of a standard sample of benzoic acid. The heat capacity of the empty calorimeter has been determined on three separate occasions.

Results

The experimental values of the molal heat capacities are presented chronologically in Tables I and II in terms of the defined thermochemical calorie equal to 4.1840 absolute joules and an ice point of 273.16°K. Sample weights of 140.066 and 132.319 g. (*in vacuo*) and molecular weights of 324.98 and 413.90 for the oxychloride and oxybromide, respectively, were employed. These heat capacity values are believed to have a probable error of 0.1% above 25°K. and an uncertainty increasing to about 1% at 10°K. Additional measurements from 5 to 10°K. have been made on uranium oxychloride, but because of an experimental exigency these were of lower precision and have not been included in Table I. They do, however, serve to establish the absence of any significant thermal anomaly over this range. The heat capacity values have been corrected for slight differences in the amounts of solder and helium in the full and empty calorimeter and for the finite temperature increments used in the determinations. These temperature increments can generally be inferred from the mean temperatures of the two adjacent runs as given in Tables I and II.

TABLE I

MOLAL HEAT CAPACITY OF URANIUM(IV) OXYCHLORIDE (in cal./degree)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		84.07	12.33	289.98	22.55
11.66	0.807	90.57	13.06	300.23	22.72
13.06	1.011	97.91	13.79	310.68	22.96
		105.76	14.52	321.19	23.16
Series II		113.63	15.22	331.62	23.33
11.66	0.792	121.63	15.88	341.96	23.42
12.86	1.001	129.86	16.53		
14.03	1.170	138.18	17.10	Series III	
15.44	1.412	146.60	17.62	258.56	21.88
17.09	1.726	155.52	18.11	273.94	22.25
18.91	2.121	165.08	18.61	289.28	22.54
20.91	2.392	174.90	19.09	304.59	22.86
23.26	2.794	184.61	19.51	319.83	23.13
25.92	3.258	194.24	19.90	335.18	23.37
28.76	3.773	203.68	20.25	348.01	23.56
31.70	4.308	212.98	20.58	Series IV	
34.80	4.874	222.19	20.87	55.03	8.322
38.28	5.514	231.41	21.15	59.95	9.077
42.38	6.212	240.74	21.42	65.52	9.914
47.03	7.010	250.14	21.65		
66.11	10.00	259.86	21.89		
72.24	10.81	269.77	22.14		
78.05	11.59	279.77	22.34		

Smoothed values of the heat capacity were read from large scale heat capacity curves, and thermodynamic functions were computed at rounded temperatures by numerical quadrature. These values are given in Tables III and IV. Nuclear spin and isotope mixing effects are not included in the entropy and free energy functions. Although the absence of thermal anomalies was established to temperatures as low as 5°K., the present measurements do not, of course, eliminate the possibility of significant magnetic contributions at even lower temperatures. Heat capacity data on an isostructural diamagnetic oxychloride and on a similar oxybromide might permit a resolution of the magnetic and lattice contributions to the thermodynamic functions. Moreover, the trend of the magnetic susceptibilities at very low temperatures are also desiderata. In the absence of these data, the extrapolations below 10°K. were made with the Debye cubic limiting law in accord with the trend

---

[8] Reported in J. J. Katz and E. Rabinowitch, ref. 6, pp. 593–5.

[9] E. F. Westrum, Jr., and A. F. Beale, Jr., to be published.

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

TABLE II

MOLAL HEAT CAPACITY OF URANIUM(IV) OXYBROMIDE (in cal./degree)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
Series I		48.06	9.685	215.58	21.57
		52.89	10.60	224.94	21.83
5.09	0.041	58.67	11.57	234.37	22.09
6.00	0.066	65.18	12.55	243.89	22.32
7.02	0.122	71.65	13.37	253.48	22.54
8.18	0.237	77.81	14.09	263.03	22.74
9.50	0.421	84.01	14.77	272.49	22.89
10.83	0.620	90.36	15.37	282.20	23.09
12.16	0.833	97.74	15.98	292.40	23.30
13.33	1.066	105.53	16.58	303.27	23.48
14.46	1.308	113.45	17.12	314.29	23.72
15.68	1.582	121.32	17.64	324.95	23.89
17.33	1.976	129.29	18.12	335.50	24.08
19.08	2.420	135.15	18.44		
20.60	2.827	143.31	18.86	Series II	
22.30	3.293	152.11	19.28		
24.22	3.821	151.06	19.24	286.06	23.17
26.58	4.483	160.20	19.65	296.35	23.38
29.41	5.273	169.26	20.04	306.85	23.56
32.52	6.097	178.36	20.38	317.50	23.79
35.99	6.993	187.65	20.71	328.30	23.97
39.72	7.890	196.96	21.04	339.14	24.19
43.71	8.778	206.26	21.30		

TABLE III

MOLAL THERMODYNAMIC FUNCTIONS OF URANIUM(IV) OXYCHLORIDE

T, °K.	C_p, cal./deg.	$S°$, cal./deg.	$(H° - H_0°)$, cal.	$-(F° - H_0°)/T$, cal./deg.
10	0.558	0.186	1.40	0.047
15	1.338	0.537	5.94	0.141
20	2.234	1.046	14.91	0.301
25	3.096	1.637	28.26	0.507
30	3.998	2.281	45.98	0.748
35	4.911	2.965	68.24	1.015
40	5.814	3.681	95.08	1.304
45	6.662	4.414	126.25	1.608
50	7.510	5.161	161.70	1.927
60	9.087	6.672	244.81	2.592
70	10.54	8.184	343.11	3.282
80	11.83	9.677	455.08	3.989
90	12.97	11.138	579.2	4.703
100	13.99	12.558	714.1	5.417
110	14.92	13.936	858.8	6.129
120	15.76	15.271	1012.2	6.836
130	16.53	16.563	1173.7	7.535
140	17.21	17.813	1342.4	8.224
150	17.81	19.022	1517.6	8.905
160	18.34	20.189	1698.4	9.574
170	18.86	21.317	1884.4	10.233
180	19.32	22.408	2075.2	10.879
190	19.73	23.463	2270.5	11.513
200	20.12	24.485	2469.7	12.136
210	20.47	25.476	2672.7	12.749
220	20.80	26.435	2879.1	13.348
230	21.11	27.368	3088.6	13.939
240	21.39	28.272	3301.1	14.517
250	21.66	29.150	3516.4	15.085
260	21.91	30.004	3734.2	15.642
270	22.14	30.835	3954.4	16.189
280	22.36	31.645	4176.9	16.728
290	22.56	32.433	4401.5	17.255
300	22.76	33.201	4628.1	17.774
350	23.59	36.774	5787.7	20.238
273.16	22.21	31.094	4024.5	16.361
298.16	22.72	33.060	4586.3	17.678

TABLE IV

MOLAL THERMODYNAMIC FUNCTIONS OF URANIUM(IV) OXYBROMIDE

T, °K.	C_p, cal./deg.	$S°$, cal./deg.	$(H° - H_0°)$, cal.	$-(F° - H_0°)/T$, cal./deg.
10	0.472	0.158	1.18	0.040
15	1.427	0.516	5.77	0.132
20	2.664	1.090	15.90	0.295
25	4.039	1.832	32.65	0.526
30	5.432	2.692	56.35	0.814
35	6.740	3.628	86.80	1.148
40	7.954	4.609	123.59	1.519
45	9.052	5.610	166.14	1.918
50	10.07	6.618	213.98	2.338
60	11.78	8.609	323.46	3.218
70	13.18	10.534	448.54	4.126
80	14.34	12.371	586.3	5.043
90	15.32	14.119	734.7	5.955
100	16.16	15.778	892.2	6.856
110	16.90	17.352	1057.5	7.738
120	17.56	18.852	1229.8	8.603
130	18.16	20.281	1408.5	9.447
140	18.69	21.646	1592.8	10.269
150	19.19	22.953	1782.2	11.072
160	19.64	24.207	1976.4	11.855
170	20.06	25.411	2175.0	12.617
180	20.44	26.568	2377.5	13.360
190	20.79	27.682	2583.7	14.084
200	21.12	28.757	2793.2	14.791
210	21.42	29.795	3005.9	15.481
220	21.70	30.798	3221.5	16.155
230	21.97	31.769	3439.9	16.813
240	22.21	32.709	3660.8	17.456
250	22.44	33.620	3884.1	18.084
260	22.66	34.504	4109.6	18.698
270	22.87	35.364	4337.2	19.300
280	23.07	36.199	4566.9	19.889
290	23.26	37.012	4798.6	20.465
300	23.45	37.804	5032.1	21.030
350	24.32	41.485	6226.9	23.694
273.16	22.93	35.630	4409.6	19.487
298.16	23.42	37.659	4989.0	20.926

of the heat capacity data to 5°K. and the implied absence of magnetic transformations below this temperature. The presence of magnetic anomalies below 5°K. could result in additive entropy increments of a unit. Apart from these contingencies the estimated probable error in the entropy, heat content, and free energy functions is 0.1% above 100°K., but some of the tabulated values are given to one more figure than is justified by the estimated probable error in order to make the tables internally consistent.

Discussion

It is to be noted that the entropies of uranium oxychloride and uranium oxybromide obtained in this investigation are considerably lower than estimates previously reported.[6,8] Combining the new entropy values from this research with other data yields thermochemical values of interest. For example, the formation of uranium(IV) oxychloride from the elements may be written

$$U(c,\alpha) + {}^1/_2O_2(g) + Cl_2(g) = UOCl_2(c)$$

The standard entropies of $UOCl_2$ and of the elements involved,[11,12] when combined with the heat of formation of $UOCl_2$,[6,13] permit the calculation of molal values for the entropy and free energy of formation at 298.16°K.

$$\Delta S_f^\circ = -56.76 \pm 0.06 \text{ cal./deg.}$$
$$\Delta H_f^\circ = -261.7 \text{ kcal.}^{7,14}$$
$$\Delta F_f^\circ = -244.8 \text{ kcal.}$$

In a similar manner (with reference to liquid bromine as the standard state) we obtain the thermochemical values for the formation of a mole of uranium(IV) oxybromide at 298.16°K.

$$\Delta S_f^\circ = -35.3 \pm 0.4 \text{ cal./deg.}$$
$$\Delta H_f^\circ = -246.9 \pm 0.7 \text{ kcal.}^{9,14}$$
$$\Delta F_f^\circ = -236.4 \pm 0.7 \text{ kcal.}$$

Davidson and Streeter[14] studied the disproportionation of $UOCl_2$ to UO_2 and UCl_4 gas utilizing the effusion method, and Gregory[13] studied the analogous reaction for $UOBr_2$. Combination of the disproportionation data with values for the vaporization equilibrium of UCl_4[14,15] and UBr_4[16,17] allows the calculation of the enthalpy increments for the disproportionation reactions at 298.16°K. as 7 and

$$2UOCl_2(c) = UCl_4(c) + UO_2(c)$$
$$2UOBr_2(c) = UBr_4(c) + UO_2(c)$$

8 kcal., respectively.[13] These enthalpy increments, combined with the heats of formation of the oxyhalides determined by Barkelew[6,8,13] on rather impure samples, and the accurately known heats of formation of UCl_4[15] and UBr_4,[16] yield calculated values for the heat of formation of UO_2 which differ by about 14 kcal., suggesting that "either the equilibria data are in error or the calorimetrically determined heats of formation of $UOCl_2$ and $UOBr_2$ are greatly in error."[13] Huber, Holley and Meierkord[18] have determined the heat of formation of UO_2 by combustion of uranium metal. Using their value, together with the heats of formation of $UOCl_2$, UCl_4, $UOBr_2$ and UBr_4, one obtains ΔH°_{298} = 13 kcal. for the disproportionation of $UOCl_2$, and ΔH°_{298} = 23 kcal. for the $UOBr_2$ reaction. This again suggests the inconsistency of the equilibrium data.

Bozic and Gal[19] report that $UOCl_2$ is unstable, and on exposure to air is converted to UO_2Cl_2. During the course of this investigation, samples of $UOCl_2$ were frequently exposed to the air of a dry box, occasionally for several hours, but no evidence of the claimed oxidation was observed.

Acknowledgment.—The authors appreciate the financial assistance of the United States Atomic Energy Commission and the coöperation of John J. McBride in the measurements.

---

[11] Reported in J. J. Katz and E. Rabinowitch, ref. 6, p. 146.

[12] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

[13] Reported in L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, "Thermodynamic Properties and Equilibria at High Temperatures of Uranium Halides, Oxides, Nitrides and Carbides," U. S. Atomic Energy Commission, MDDC-1543, Oak Ridge, Tenn., 1945, pp. 46–9.

[14] Ref. 13, pp. 33–6.

[15] Reported in J. J. Katz and E. Rabinowitch, ref. 6, pp. 476–483.

[16] Ref. 15, pp. 527–9.

[17] Reported in L. Brewer, *et al.*, ref. 13, p. 40.

[18] E. J. Huber, Jr., C. E. Holley, Jr., and E. H. Meierkord, THIS JOURNAL, **74**, 3406 (1952).

[19] B. I. Bozic and O. Gal, *Z. anorg. allgem. Chem.*, **273**, 84 (1953).

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE UNIVERSITY OF IOWA]

Lower Oxides of Samarium and Europium. The Preparation and Crystal Structure of $SmO_{0.4-0.6}$, SmO and EuO[1]

BY H. A. EICK,[2] N. C. BAENZIGER AND L. EYRING

RECEIVED MAY 14, 1956

A lower oxide of samarium whose oxygen to samarium ratio varied between 0.4 and 0.6 was prepared. This compound has the face centered cubic zinc blende-type structure; the lattice parameter varies between 5.3698 ± 0.0006 and 5.3790 ± 0.0008 Å. The lattice parameter of SmO is 4.9883 ± 0.0003 Å. Previously reported variations in the lattice parameter of SmO are believed to be due to nitride–oxide mixtures. EuO has a NaCl-type structure with a lattice parameter of 5.1439 ± 0.0005 Å.

Introduction

Ellinger and Zachariasen[3] reported a phase which they believed to be SmO on some annealed samples of samarium metal and some metal preparations. They reported a lattice parameter varying from 5.015 to 5.050 ± 0.002 Å. No reason for the variation was known. An investigation was undertaken to examine the lower oxides of samarium, europium and ytterbium with the hope of explaining these systems. Part of this work is reported here.

Experimental Part

Materials.—Samarium and lanthanum metals and Sm_2O_3 were obtained from Ames Laboratories, Ames, Iowa, and were labeled as greater than 99.9% pure. Europium ses-

---

[1] The data presented here were included in a dissertation submitted by H. A. Eick to the Graduate College of the State University of Iowa in partial fulfillment of the requirements for the Ph.D. degree. The work was supported in part by the Atomic Energy Commission Research Contracts Division.

[2] Allied Chemical and Dye Fellow, 1954–1955.

[3] F. H. Ellinger and W. H. Zachariasen, THIS JOURNAL, **75**, 5650 (1953).