

Heat Capacities at High Temperatures of Uranium, Uranium Trichloride, and Uranium Tetrachloride

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The enthalpies referred to 0° C of uranium in the range 0° to 900° C, of uranium trichloride in the range 0° to 725° C, and of uranium tetrachloride in the range 0° to 425° C, have been determined using the "drop" method with an ice calorimeter. Derived values of entropy referred to 0° C and specific heat are given. The samples were of high purity. Two first-order transformations of uranium were observed and the heats of transition calculated from the experimental data. No evidence of first- or second-order transitions in the chlorides was found.

I. Introduction

This research was undertaken as a part of a program sponsored by the Manhattan District, U. S. Army Corps of Engineers. A portion of the information given in this paper will appear in Division VIII of the Manhattan Project Technical Series. The following report has been declassified by the Atomic Energy Commission.

II. Method and Apparatus

The method and apparatus have been described previously.^{1,2} In brief, the method consisted in heating the sample in a furnace to a known temperature and dropping it into an ice calorimeter that measured the heat evolved in cooling the sample to 0° C. The calorimeter was calibrated electrically. The sample was sealed in a Nichrome-5 capsule having a screw cap and gold gasket. The heat capacity of the empty capsule and the heat lost by the container during the drop were accounted for by "blank" experiments made with the empty capsule. The temperature of the sample in the furnace was measured by a platinum-platinum-rhodium thermocouple that had been calibrated at the National Bureau of Standards.

¹ D. C. Ginnings and R. J. Corruccini, J. Research N. B. S. **38**, 583 (1947) RP1796.

² D. C. Ginnings and R. J. Corruccini, J. Research N. B. S. **38**, 593 (1947) RP1797.

III. Materials

1. Uranium

The uranium sample, furnished by H. E. Cleaves of the National Bureau of Standards, was in the form of rods having a diameter of $\frac{1}{8}$ in. A spectroscopic analysis of a clean sample of uranium taken from the same batch showed impurities of 0.03 percent to 0.04 percent, including carbon, 0.015 percent; hydrogen, 0.0005 percent; nitrogen, 0.003 percent; and oxygen, 0.002 percent. These impurities were the most significant in computing the correction for impurity to be applied to the enthalpy.

2. Uranium Trichloride

The uranium trichloride sample was obtained from E. C. Evers of Brown University and was of the highest obtainable purity. It was prepared from sublimed uranium tetrachloride by reduction with hydrogen and was received in the form of a crystalline powder in a sealed glass bottle, which was kept in a desiccator. The following chemical analysis was received with the sample: U+Cl=99.97 percent; atom ratio Cl/U=3.001; material insoluble in water=0.13 percent, calculated as UO₂. A portion of the sample was transferred to the Nichrome capsule in a drybox containing P₂O₅, helium was admitted and the

capsule was sealed. At the time of the transfer, another portion of the sample was taken for further analysis. The analysis (performed under the direction of J. J. Tregoning of the National Bureau of Standards) gave $U+Cl=99.50$ percent, atom ratio $Cl/U=2.999$, material insoluble in water=0.55 percent, calculated as UO_2 . A spectrographic analysis performed at the same time indicated a total of about 0.08 percent miscellaneous metal impurities (mainly Ca, 0.01 %; Fe, 0.013 %; Mg, 0.01 %; Na, 0.02 %; and Si, 0.006 %) and confirmed the belief that the principal metallic constituent of the water-insoluble material was uranium.

3. Uranium Tetrachloride

The uranium tetrachloride was distilled in Pyrex in vacuum from a sample bearing the analysis, $U+Cl=99.50$ percent, atom ratio $U/Cl=3.997$. A small amount of reddish solid that was more volatile than the uranium tetrachloride was discarded in this process, as well as nonvolatile products such as UO_2 . (The UO_2 would result from contamination of the sample with water, followed by hydrolysis.) Uranium tetrachloride is extremely hygroscopic. At the close of the distillation, the receiver was sealed. It was next opened in a drybox containing P_2O_5 , the sample pulverized with a steel rod, and a portion transferred to the Nichrome capsule, helium was admitted and the capsule was immediately sealed. Samples taken before and after the filling of the capsule gave essentially identical chemical analyses averaging $U+Cl=99.97$ percent, atom ratio $Cl/U=4.003$. A spectrographic analysis made at the same time indicated the presence of 0.1 percent of miscellaneous metals (mainly Fe, 0.05 percent; Na, 0.02 percent; Ca, 0.01 percent; Mg, 0.01 percent; Al, 0.005 percent) and 0.1 to 1 percent of Ni. At the completion of the experimental work, the sample was removed from the capsule in the drybox and again analyzed, giving $U+Cl=99.64$ percent, atom ratio $Cl/U=4.023$.

IV. Results

Table 1 gives the results of the individual experiments. The "apparent" calibration factor³ of the ice calorimeter was taken as 64.638 calories per gram of mercury (1 cal=4.1833 int joule). In

columns 2 and 3 are given the masses of mercury after small corrections have been applied for buoyancy, heat leak, change in level of mercury meniscus, variation in capsule weight, and variation in the amounts of gas and gold contained in the capsule. As these corrections are in most cases so small as to be barely significant, they are not listed separately. They are approximately the same as in a previous report.⁴ The masses at a given temperature are listed in the order in which the experiments were performed, although this is not true of the order in the table as a whole.

1. Uranium

The first series of experiments extended up to $756.7^\circ C$, and was made with a sample of uranium that had been pickled in nitric acid to remove the surface film of oxide. The air in the capsule was replaced with helium before sealing. It was found in experiments at $790^\circ C$ that the uranium was attacking the Nichrome capsule. A second series of experiments in the range 723.9° to $898.6^\circ C$ was then made with a portion of the sample on which a thin protective film of oxide had been formed. In addition, the bottom of the capsule was covered with a layer of BeO (about 1 g) in order to reduce the contact between the uranium and the capsule. There was no evidence of attack with these precautions. The BeO was kept in the capsule during the blank experiments of the second series.

TABLE 1.—Results of individual experiments

Temperature $^\circ C$	Mass of Mercury			$(H-H_o^\circ c)$		
	Blank experi- ments	Experi- ments with sample	Net	Obs- erved ^a	Calcu- lated ^b	Observed minus calculated
URANIUM, SERIES A (58.7768-GRAM SAMPLE) ^c						
110.6 -----	g 1.4825 e 1.4909 1.4798 1.4823 1.4820	g d 4.3441 4.3425 4.3477 4.3450	g	cal g^{-1} 2.8635	cal g^{-1} 3.1421	cal g^{-1} 3.1419
200.8 -----	g 2.7659 2.7671 2.7658 2.7646	g d 8.1192 8.1258 8.1249 8.1242	g	cal g^{-1} 5.3583	cal g^{-1} 5.8797	cal g^{-1} 5.8812
300.9 -----	g 4.2401 4.2392 4.2404	g d 12.5696 12.5730 12.5763 12.5743 12.5723	g	cal g^{-1} 8.3336	cal g^{-1} 9.1445	cal g^{-1} 9.1437

See footnotes at end of table.

^a See footnote 1.

^b See footnote 2.

TABLE 1.—Results of individual experiments—Continued

Temperature	Mass of Mercury			(H-H _{0°C})			
	Blank experiments	Experiments with sample	Net	Observed ^a	Calculated ^b	Observed minus calculated	
URANIUM, SERIES A (58.7768-GRAM SAMPLE) ^c—Continued							
426.8	{ 6.1709 6.1731 6.1787	{ 18.6040 18.6098 d 18.6128 f 18.5993	12.4317	13.6413	13.6392	+.02	
579.2	{ 8.6187 8.6193 d 8.6243	{ 26.6812 26.6837 26.6782	18.0612	19.8186	19.8196	-.01	
637.9	g (9.619)	f 30.1245	20.506	22.501	22.501	.00	
657.2	g (9.956)	31.3063	21.350	23.427	23.428	.00	
676.5	g (10.293)	35.0466	24.754	27.163	27.160	+.01	
700.2	g (10.714)	36.3865	25.673	28.171	28.170	.00	
723.9	{ 11.1386 11.1420 11.1336	{ 37.7187 37.7279	26.5852	29.1719	29.1801	-.03	
756.7	b (11.727)	39.5975	27.871	30.583	30.578	+.02	
URANIUM, SERIES B (40.4032-GRAM SAMPLE) ^c							
723.9	{ 15.6009 15.6041	{ d 33.9078 33.8997	18.2999	29.172	29.180	-0.03	
789.2	17.2651	40.2712	23.0061	36.674	36.652	+.06	
807.7	17.7361	41.1632	23.4271	37.345	37.363	-.05	
853.4	d 18.9062	43.4475	24.5321	39.106	39.119	-.03	
898.6	18.9184	20.0762	45.7132	25.6370	40.866	40.856	+.02
URANIUM TRICHLORIDE (16.4069-GRAM SAMPLE) ^c							
50.3	{ 0.6995 .7003 .7002 .6996	{ 1.6051 1.6061 1.6066	0.9060	3.5633	3.5644	-0.03	
110.5	1.5633	3.5626					
209.7	1.5614	3.5625	1.9999	7.8636	7.8649	-.02	
300.9	1.5626	3.5619					
426.7	2.9156	6.5816					
498.9	2.9154	6.5786	3.6631	14.4012	14.3870	+.10	
597.0	2.9175	6.5777					
676.4	4.4770	10.0081					
723.8	4.4751	10.0114	5.5326	21.7466	21.7539	-.03	
	4.4792	10.0097					
	6.5116	14.4529					
	6.5181	14.4511					
	6.5142	14.4517	j 7.9358	31.1895	31.2041	-.05	
	d 6.5168	i 14.4329					
	6.5160	i 14.4314					
	6.5156	i 14.4329					
	6.5205	g (7.719)	i 17.0490	j 9.353	36.761	36.747	+.04
	9.0976	9.0968	20.0554	10.9601	43.076	43.035	+.09
	9.0885	9.0923	20.0555				
	9.0918	9.0918	20.0497				
	10.8650	10.8650	23.8144				
	10.8546	10.8546	23.8248	12.9594	50.933	50.991	-.11
	10.8563	10.8563	23.8148				
	11.7580	11.7580	25.7606	j 14.0155	55.084	55.053	+.06
	11.7650	11.7650	25.7451				
			25.7422				

See footnotes at end of table.

Uranium Heat Capacities

TABLE 1.—Results of individual experiments—Continued

Temperature	Mass of Mercury			(H-H _{0°C})			
	Blank experiments	Experiments with sample	Net	Observed ^a	Calculated ^b	Observed minus calculated	
URANIUM TETRACHLORIDE (16.8451 GRAM SAMPLE) ^c							
50.3	{ 0.7059 .7051 .7080	{ 1.7081 1.7102 1.7106 e 3.8083		1.0033	3.8333	3.8333	0.00
110.5	{ 1.5792 1.5763 1.5780	{ d 3.8197 d 3.8223 3.8179 3.8191		2.2415	8.5641	8.5635	+.01
200.7	{ 2.9393 2.9445 2.9457	{ 7.0878 7.0909 7.0922 7.0908		4.1465	15.8425	15.8443	-.01
211.3	g (3.107)	{ 7.4860 7.4876		4.380	16.733	16.714	+.11
221.8	g (3.270)	{ 7.8796 7.8839		4.612	17.620	17.578	+.23
300.9	{ 4.5173 d 4.5180	{ d 10.8522 10.8463		6.3324	24.194	24.193	.00
374.2	{ 4.5188 5.7009	{ 10.8533 13.6842		7.9781	30.482	30.483	.00
426.7	{ 5.7092 d 5.7036	{ d 13.6808 13.6826		9.1826	35.084	35.083	.00

^a Corrected for impurity.^b In the cases of α -uranium and UCl_3 , these data were obtained by interpolation in the smoothed tables of enthalpy before rounding off and with allowance for curvature. In the cases of β and γ -uranium and UCl_4 , these values were calculated from equations that were fitted to the observed data. See text.^c Corrected for buoyancy.^d Weighted less due to unsteady heat leak.^e Discarded according to Chauvenet criterion.^f These experiments followed experiments at temperatures above the first transition.^g Interpolated.^h Extrapolated.ⁱ These experiments followed those at 723.8° C, and are considered to be affected by corrosion of the capsule by the UCl_3 , at that temperature.^j Corrected for effect of corrosion of the capsule. See text.

The second series gave a result at 723.9° C that was 0.14 percent higher than that obtained in the first series. This difference could have been caused by only one part in 10,000 (by weight) of oxygen, present as U_3O_8 . Accordingly, the difference was attributed to the oxide film on the sample used in the second series and all results obtained in this series were corrected by -0.14 percent. In addition, an estimated correction of -0.21 percent for the impurities shown in the spectrographic analysis was applied to all results with uranium.

TABLE 2.—Enthalpy, specific heat, and entropy at even temperature intervals ($1 \text{ cal} = 4.1833 \text{ int } j$; $0^\circ\text{C} = 273.16^\circ\text{K}$)—

t	$H - H_0^\circ\text{C}$	C_p	$S - S_0^\circ\text{C}$
URANIUM			
($^\circ\text{C}$)	cal g^{-1}	$\text{cal g}^{-1} \text{ deg}^{-1}\text{C}$	$\text{cal g}^{-1} \text{ deg}^{-1}\text{K}$
0	0	0.0275	0
50	1.393	.0283	.00469
100	2.831	.02919	.008819
150	4.317	.03022	.012552
200	5.856	.03135	.015988
250	7.453	.03257	.019197
300	9.113	.03388	.022228
350	10.841	.03529	.025119
400	12.642	.03681	.027900
450	14.521	.03846	.030595
500	16.486	.04031	.033226
550	18.552	.04253	.035819
600	20.750	.04521	.038403
650	23.080	.04818	.041001
668 (α)	23.965	.0193	.04194
[Transition]	$\Delta H = 2.83$		$\Delta S = 0.00301$
668 (β)	26.797	.04262	0.04495
700	28.161	.04262	.04637
750	30.292	.04262	.04851
774 (β)	31.316	.04262	.04950
[Transition]	$\Delta H = 45.5$		$\Delta S = 0.00454$
774 (γ)	36.067	.03843	.05404
800	37.067	.03843	.05498
850	38.989	.03843	.05673
900	40.910	.03843	.05840
URANIUM TRICHLORIDE			
0	0	0.0706	0
50	3.543	.07112	.01191
100	7.112	.07167	.02218
150	10.709	.07224	.03123
200	14.336	.07284	.03933
250	17.995	.07348	.04667
300	21.687	.07416	.05340
350	25.414	.07489	.05963
400	29.178	.07568	.06544
450	32.982	.07655	.07089
500	36.832	.07755	.07604
550	40.738	.07877	.08094
600	44.716	.08036	.08564
650	48.790	.08256	.09018
700	52.994	.08573	.09160
725	55.173	.08774	.09680
URANIUM TETRACHLORIDE			
0	0	0.0748	0
50	3.810	.07745	.01280
100	7.730	.07923	.02408
150	11.726	.08056	.03412
200	15.787	.08189	.04319
250	19.916	.08329	.05149
300	24.116	.08473	.05916
350	28.389	.08617	.06630
400	32.734	.08762	.07301
425	34.933	.08834	.07622

The two transitions of uranium were clear-cut with no evidence of pretransition effects. No attempt was made to determine closely the tem-

peratures of the transitions. For the purpose of calculating the heats of transition, the values 668° and 774°C were used for the transition temperatures. These were estimated from measurements by Dahl and Van Dusen⁵ of the variation of electrical resistance of uranium with temperature and may be in error by a few degrees.

The results at temperatures below the first transition cannot be closely represented by a simple equation. Enthalpies at even temperature intervals were obtained by graphical interpolation and smoothed by adjustment of differences. The specific heat, C_p , and entropy referred to 0°C , $S - S_0^\circ\text{C}$, were derived graphically from the enthalpies in this temperature range. The results are given in table 2.

At temperatures above the first transition but below the second, the observed values of enthalpy in calories per gram, referred to the α -form at 0°C , are represented within 0.03 percent by the equation (fitted by the method of least squares)

$$H - H_0^\circ\text{C} = -1.675 + 0.04262t \text{ (}\beta\text{-form)}$$

where t is in deg C. Correspondingly,

$$C_p = 0.04262 \text{ (}\beta\text{-form)}$$

$$S - S_0^\circ\text{C} = \int_{668}^T [C_p(\beta)/T] dT + [S_{(\beta)668^\circ} - S_{(\alpha)0^\circ\text{C}}] \text{ (}\beta\text{-form)}$$

$$S - S_0^\circ\text{C} = 0.098144 \log_{10} T - 0.24690 \text{ (}\beta\text{-form),}$$

where T is in degrees Kelrin, taking 0°C as 273.16°K .

At temperatures above the second transition, the observed values of enthalpy referred to the α -form are represented within 0.06 percent by the equation (least squares)

$$H - H_0^\circ\text{C} = 6.326 + 0.03843t \text{ (}\gamma\text{-form)}$$

Correspondingly, $C_p = 0.03843$ (γ-form)

$$S - S_0^\circ\text{C} = \int_{774}^T [C_p(\gamma)/T] dT + [S_{(\gamma)774^\circ} - S_{(\alpha)0^\circ\text{C}}] \text{ (}\gamma\text{-form)}$$

$$S - S_0^\circ\text{C} = 0.088481 \log_{10} T - 0.21318 \text{ (}\gamma\text{-form).}$$

Values calculated for even temperature intervals from the above equations are given in table 2.

The regularity of the data for the β and γ forms would seem to indicate that the two transformations were reversible under the experimental con-

⁵Andrew I. Dahl and Milton S. VanDusen, J. Research NBS **39**, 53 (1947) RP1813.

ditions. Certain experiments in the α range (noted in table 1) that were performed after the sample had been heated above the first transition show no significant abnormality.

It may be interesting to note that both the β and γ forms have not only constant values of C_p , but also have constant values of temperature coefficient of electrical resistance.⁶ Also, the difference between the values of C_p for the two forms is 1.00 calories per degree-gram atom, which, within experimental error, is the value of $R/2$, where R is the universal gas constant. In the absence of complete information as to the crystal structures of the two forms, it is not possible to ascribe significance to the latter fact.

2. Uranium Trichloride

As it was expected that the capsule would be attacked to a slight extent by the UCl_3 , the effect of this upon the enthalpy was tested by making a group of three experiments at 426.7°C at the beginning and a similar group at the end of the series of experiments with the sample. The average of the results of the final group was 0.14 percent lower than the average of the first group. No consistent variation was noted within either group alone, the maximum deviation from the mean of a group being 0.007 percent. On the other hand the results of the three experiments at 723.8°C showed a definite downward trend with the order performed over a range of 0.07 percent. It was assumed, therefore, that corrosion of the capsule at the higher temperatures had indeed affected the results. As there was no clear-cut evidence of a trend with time in the experiments at 579.0° and 676.4°C , it was assumed that all the corrosion had occurred during the experiments at 723.8°C . With some arbitrariness, the mass of mercury that would have been obtained in an experiment at 723.8°C in the absence of corrosion was taken to be 0.14 percent higher than the last result in the group at that temperature. The result at 498.9°C which was the only other one obtained following the experiments at 723.8°C was also corrected by +0.14 percent. At the close of the experiments, after removal of the sample from the capsule, it was found that the latter had lost 17.1 mg, or 0.2 percent, of its mass as a result of the corrosion.

The correction for the impurities in the sample at the start of the experiments was somewhat uncertain because of the inconsistency of the two chemical analyses, the uncertainty as to the state of chemical combination of the spectrographically determined impurities, and the fact that the most probable forms (oxides or chlorides) of the latter have specific heats about three times that of UCl_3 , which magnifies their effect upon the results. Fortunately, UO_2 has nearly the same specific heat (within 20 percent) as UCl_3 , which reduces the uncertainty resulting from the variance in the amount of water-insoluble material found in the sample. Making reasonable assumptions with regard to the spectrographically determined impurities and employing the enthalpy data of Moore and Kelly⁷ for UO_2 , led to a total correction for impurities that ranged from -0.17 percent at 50.3°C to -0.24 percent at and above 426.7°C .

A smooth curve was drawn through a plot of $(H-H_0{}^\circ\text{C})_{obs}/t$ versus t , values were read off at even temperature intervals and smoothed by adjustment of differences. The specific heat, $C_p=(\partial H/\partial T)_p$, was calculated from the smoothed values of enthalpy by the method of Rutledge⁸ and $S-S_0{}^\circ\text{c}=\int_0^t (C_p/T)dt$ was calculated by using Simpson's Rule.

The results are given in table 2.

3. Uranium Tetrachloride

The effect of possible reaction between the capsule and UCl_4 was tested by making a pair of experiments at 200.7°C early in the series of experiments with sample and a similar pair at the end of the series. The average of the second pair was only 2.1 mg, or 0.03 percent higher than the average of the first pair, which is as good agreement as could have been expected had the experiments been performed at the same time. Accordingly, no correction for corrosion of the capsule was applied. At the close of the series of experiments it was found that the capsule had lost 6.8 mg owing to corrosion, or only about one-third as much as for the UCl_3 .

The correction for the impurities in the sample was subject to the same difficulties as for UCl_3 . In addition, the chemical analyses were discordant in that they appeared to indicate a loss of 0.32 per-

⁶ See footnote 5.

⁷ G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. **69**, 2105 (1947).

⁸ G. Rutledge, Phys. Rev. **40**, 262 (1932).

cent of uranium between the first and second analyses, the percentage of Cl remaining constant. Actually, there is every reason to believe that no detectable change in the sample occurred. The only reasonable alteration of the sample to expect would have been the loss of Cl (as HCl resulting from moisture absorption and hydrolysis) rather than the loss of uranium. Making reasonable assumptions with regard to the impurities led to a correction of -0.43 percent.

The mean specific heat, $(H-H_{0^\circ C})_{obs}/t$, was found to be practically a linear function of temperature above $200^\circ C$. The following equation was fitted by trial and error (gram basis):

$$H-H_{0^\circ C} = 0.07605t + 1.446 \times 10^{-5}t^2 - 0.00122t \times 10^{-0.00516t-0.0000278t^2}.$$

Correspondingly,

$$C_p = 0.07605 + 2.891 \times 10^{-5}t - 0.00122[1 - 2.3(0.00516t + 0.0000556t^2)] \times 10^{-0.00516t-0.0000278t^2}.$$

Values were calculated from these equations at even temperature intervals and the entropy, $S-S_{0^\circ C}$, obtained by Simpson's rule. The results are given in table 2.

V. Discussion

1. Accuracy

The instrumental error is about the same as in some previous measurements, where a more detailed discussion is given.⁹ The error involved in measuring the temperature of the sample in the furnace contributes the major part of this uncertainty to which a value of about 0.2 percent may be assigned. In addition, the corrections for impurity have uncertainties of perhaps one-half their own magnitudes or 0.1 percent in the cases of uranium and UCl_3 and 0.2 percent for UCl_4 . Taking all errors into account, the authors believe the corrected and smoothed enthalpies to be within 0.2 to 0.3 percent of the true values, except for the values at $50^\circ C$. At and below this temperature, the relative instrumental error is larger.

The specific heat and entropy possess a small additional uncertainty resulting from the fact that the derivative of a quantity can never be known as accurately as the quantity itself in the absence of

a rigid mathematical formulation. This uncertainty becomes larger at the ends of the experimental ranges of the data, except for the high-temperature end of the uranium and UCl_4 data, where linear representation of the enthalpy makes accurate differentiation possible. The heats of transition are accurate to perhaps 1 percent.

2. Comparison with other work

In none of the five known investigations presenting data comparable to those of this report was a correction applied for impurities, although only one of these authors¹⁰ claimed to have a sample that was pure within analytical error. The heat capacities of uranium and its compounds are exceptionally sensitive to the presence of impurities, because the specific heats of the latter are usually several times as large as that of the pure uranium or uranium compound. As the samples used in the present investigation were of high purity, and as a correction was applied in each case to account for the presence of impurity, it was to be expected that the results of the other investigations, with the exception noted, would be the higher, calorimetric errors being left out of account.

In order to permit a condensed presentation of the data for comparison purposes, values of C_p and $(H-H_{0^\circ C})/t$ in calories per degree-mole divided by the number of atoms per molecule are given in figure 1 for all three substances.

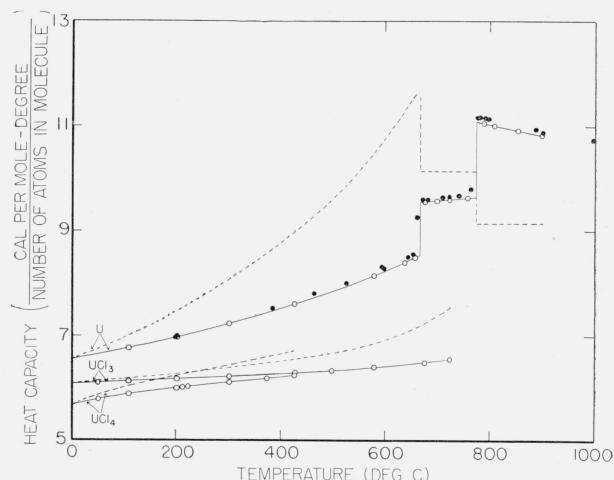


FIGURE 1. True and mean heat capacities.

$H-H_{0^\circ C}/t$: ○, NBS (observed); —, NBS (smoothed); ●, Moore and Kelley. C_p : -----, NBS (derived).

¹⁰ C. Zimmerman, Liebigs Ann. Chem. **216**, 14 (1883).

⁹ See footnote 2.

(a) Uranium

The specific heat of a sample of unstated purity has been determined from low temperatures up to 27° C by E. A. Long, W. M. Jones, and J. Gordon¹¹ in the laboratory of W. F. Giauque at the University of California. Their values are lower than those of this investigation, the difference decreasing from 1.0 percent at 27° C to 0.3 percent at 0° C. These authors appear to claim an accuracy of 0.2 percent in this range. The specific-heat curve from the present investigation, if extrapolated downward, would become tangent to the above authors' results at about -30° C.

The enthalpy (referred to 25° C) of a 99.71-percent-pure sample has been measured at temperatures up to 1,000° C by Moore and Kelley.¹² These data were converted to the same basis as the enthalpy data of this paper by addition of the quantity, $H_{25^\circ\text{C}} - H_{0^\circ\text{C}} = 0.688 \text{ cal g}^{-1}$, taken from the report of Long, Jones, and Gordon.¹³ The converted enthalpy data of Moore and Kelley were found to average 0.8 percent higher than those of the present investigation. The comparison is shown in figure 1, where the enthalpies have been converted to mean specific heats, $(H - H_{0^\circ\text{C}})/t$, in order to give a representation that is more sensitive to the small differences between the two sets of data. For the β -form, the data of Moore and Kelley give $C_p = 0.04360 \text{ cal g}^{-1} \text{ deg}^{-1} \text{ C}$, that is, 2.3 percent higher than the value in this investigation. For the γ -form, Moore and Kelley's results give $C_p = 0.03822 \text{ cal g}^{-1} \text{ deg}^{-1} \text{ C}$, which is 0.5 percent lower than the value in this investigation. Comparison of the values of C_p for the α -form is not as informative, as Moore and Kelley's values must be obtained from an equation for the enthalpy that does not represent the data as closely as did the equations given by them for the higher forms.

The mean specific heat between 0° and 98.7° C was measured by Zimmerman,¹⁴ who obtained 0.0277 cal g⁻¹ deg⁻¹ C as the mean of three experiments covering a spread of 1.5 percent. His sample reportedly was 100.0 percent pure. Blumecke¹⁵ later disputed the interpretation of the data

in these experiments and calculated the result to be 0.0280. These values are, respectively, 2 percent and 1 percent below the result of this investigation.

(b) Uranium Trichloride

The specific heat of a sample of unknown purity has been determined from low temperatures to 107° C by W. J. Ferguson and J. L. Prather¹⁶ at the National Bureau of Standards. They give $C_p = 0.0713 \text{ cal g}^{-1} \text{ deg}^{-1} \text{ C}$ at 0° C, which is 1 percent higher than the result of the present investigation. They report $C_p = 103 \text{ cal mole}^{-1} \text{ deg}^{-1} \text{ C}$ (equivalent to 0.0715 cal g⁻¹ deg⁻¹ C) for all temperatures from 17° to 107° C. This result is identical with those of this investigation from 53° to 107° C within the uncertainty of the number 103, or 0.5 percent. Correspondingly, the mean specific heat between 0° and 100° C is calculated to be 0.07147 cal g⁻¹ deg⁻¹ C, or 0.5 percent higher than the result of this investigation.

(c) Uranium Tetrachloride

The specific heat of a sample of unspecified purity has been determined from low temperatures to 82° C by W. J. Ferguson, J. L. Prather, and R. B. Scott.¹⁷ Their results above 0°C are 0.3 to 0.6 percent higher than those of this investigation.

The experiments at 211.3° and 221.8° C in this investigation were performed with the intent of disclosing the second-order transition reported found at 211° by N. W. Gregory.¹⁸ Such a transition would appear as a sudden change in slope of the plot of mean specific heat versus temperature. The deviations of the results at these temperatures from the function chosen to represent the data were, indeed, much larger than for the other results (see table 1). However, in view of the facts that only two experiments with the sample were made at each of these temperatures, and that values for blank experiments were obtained by interpolation rather than by direct measurement, it appears that the deviations (0.11 and 0.23 percent, respectively) of these results from the curve are not significantly greater than experimental error would allow. It can only be concluded that if this transition exists, it is quite small and occurs above 222°C for a pure sample.

¹¹ Classified report submitted to the Manhattan District, U. S. Army Corps of Engineers.

¹² See footnote 7.

¹³ See footnote 11.

¹⁴ See footnote 10.

¹⁵ A. Blumecke, Ann. Physik, (III) 24, 263 (1885).

¹⁶ Classified report submitted to the Manhattan District, U. S. Army Corps of Engineers.

¹⁷ See footnote 16.

¹⁸ See footnote 16.

VI. Summary

The enthalpies of uranium, UCl_3 and UCl_4 at high temperatures have been determined. Values of specific heat and entropy have been derived. Values of the heats of transition of two first-order

transformations in uranium are given. No evidence was found of first- or second-order transitions in UCl_3 or UCl_4 .

WASHINGTON, May 23, 1947.