

or reproducible ammonate could be isolated. In view of the heterogeneous character of the ammonation products together with the fact that the decomposition temperature of uranyl nitrate is 200°,¹² it seems unlikely that the thermal dehydration product is a single substance.

Uranyl nitrate 2-hydrate 3-ammonate was prepared as follows. Twenty-five grams of uranyl nitrate 6-hydrate was dissolved in 300 ml. of anhydrous ether and cooled in a Dry Ice-acetone-bath so long as crystals of ice continued to separate. The supernatant ether solution was decanted into a glass-stoppered flask, dried for twenty-five hours over 75 g. of anhydrous copper(II) sulfate, and filtered in an atmosphere of anhydrous nitrogen. Subsequent addition of anhydrous ammonia gas resulted in precipitation of a brilliant yellow solid which was dried *in vacuo* over barium oxide and thereafter maintained in an atmosphere of anhydrous ammonia gas at atmospheric pressure.

Anal. Calcd. for $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} \cdot 3\text{NH}_3$: U, 49.5; N, 8.7. Found: U, 49.7; N, 8.5.

Summary

1. Thorium(IV) nitrate 4-hydrate reacts with liquid ammonia at -33.5° to form ammonium nitrate and, probably, hydrated thorium(IV) oxide.

2. The ammonolysis of thorium(IV) sulfate by liquid ammonia at -33.5° yields ammonium sul-

(12) Lebeau, *Compt. rend.*, **152**, 439 (1911); **155**, 163 (1912).

fate and other products believed to be basic sulfates of thorium.

3. The solubilities of thorium(IV) iodate and thorium(IV) oxalate 2-hydrate in liquid ammonia at 25° have been measured. These salts are unreactive toward liquid ammonia at 25° and at -33.5° .

4. Uranium peroxide 2-hydrate does not react with liquid ammonia or with liquid ammonia solutions of ammonium bromide at -33.5° . The peroxide reacts with potassium amide to form potassium peruranate, but is only slowly reduced by solutions of potassium.

5. Uranyl nitrate 6- and 2-hydrates react with liquid ammonia at -33.5° to form ammonium diuranate, *e. g.*, $2\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} + 6\text{NH}_3 \rightarrow (\text{NH}_4)_2\text{U}_2\text{O}_7 + 4\text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$.

6. Uranium(III and IV) chlorides and bromides are ammonolyzed by liquid ammonia at -33.5° and the resulting ammonolysis products are not reduced to elemental uranium by solutions of potassium.

7. The preparation of uranyl nitrate 2-hydrate 3-ammonate is described.

AUSTIN, TEXAS

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High-Temperature Heat Contents of Some Zirconium-containing Substances¹

By J. P. COUGHLIN AND E. G. KING

Current interest in development of commercial means of producing ductile zirconium has emphasized the need for thermal data for zirconium and its simpler compounds. This paper reports high-temperature heat-content measurements of five zirconium-containing substances—the metal, oxide (ZrO_2), nitride (ZrN), silicate (ZrSiO_4), and chloride (ZrCl_4). No previous similar data are available for the nitride, silicate, and chloride. A previous study² of the metal had given reproducible results to about 900°K ., and there are available also results for the oxide² at three temperatures in the range 673 to 1073°K .

Experimental

Materials.—Zirconium, in the form of trimmings from rolled sheet, was furnished for this work by the Foote Mineral Company, through the courtesy of W. F. Luckenbach, Jr. The metal strips were sheared into small pieces and cleaned in turn with acetone, a magnet, 3 *N* hydrochloric acid, and distilled water.

Zirconium oxide was prepared by igniting at 1000° the chloride described below, thus taking advantage of the purification inherent in the chloride preparation process. The X-ray diffraction pattern showed only lines corresponding to the monoclinic variety of the oxide.

Zirconium nitride was prepared from a mixture of 94.8% zirconium nitride and 5.2% zirconium hydride obtained

from the Manhattan Project through Prof. John Chipman of Massachusetts Institute of Technology. The material was treated at 1250° in a stream of nitrogen and hydrogen of 3:1 ratio until analysis indicated 86.65% zirconium, after which it was further heated in vacuum at 1250° for 14 hours. Analysis of the final product by ignition to the oxide gave 86.75% zirconium (hafnium) (theor. 86.69% Zr).

The zirconium silicate was a portion of the natural zircon sand from Lincoln, California, used previously by Kelley³ in low-temperature heat-capacity measurements. The analysis reported by him was 66.3% ZrO_2 (HfO_2), 33.6% SiO_2 and 0.4% Fe_2O_3 .

Zirconium chloride was prepared by passing chlorine gas at 500° over an intimate mixture of 4 parts of Norblack (99.7% carbon) and 1 part of *p* zirconium oxide. The sublimed and condensed tetrachloride was resublimed at 300 to 350° , ground in a dry box, and stored in a sealed container. Analysis for zirconium (hafnium) by precipitation with ammonium hydroxide and ignition to the oxide gave 39.21% (theor. 39.14% Zr).

An estimation of the hafnium contents of these materials was made by the Chemical and Physical Section of the Salt Lake City Station of the Bureau of Mines, as follows: Zr, 2.15%; ZrO_2 , 1.25%; ZrN, 1.35%; ZrSiO_4 , 1.15%; and ZrCl_4 , 0.75%. Corrections for the hafnium contents were made on the assumption that corresponding hafnium and zirconium compounds have the same molal heat contents. These corrections increased the measured heat content values by the following amounts: Zr, 1.0%; ZrO_2 , 0.6%; ZrN, 0.7%; ZrSiO_4 , 0.6%; and ZrCl_4 , 0.35%.

(1) Article not copyrighted.

(2) Jaeger and Veenstra, *Rec. trav. chim.*, **53**, 917 (1934).

(3) Kelley, *This Journal*, **63**, 2750 (1941).

Measurements and Results

The measurements were made by the "dropping" method in apparatus^{4,5} previously described. Each sample was enclosed in a platinum-rhodium alloy capsule. The capsules holding the metal, the nitride, and the tetrachloride were sealed gas-tight by pinching shut and platinum-welding the necks, after having evacuated the pore space, and filled with helium. The necks of the capsules for the oxide and silicate were pinched shut. The heat contents of the empty capsules were known from previous calibration measurements. During the course of the measurements the platinum-rhodium furnace thermocouple was calibrated frequently at the melting point of pure gold and occasionally at the melting point of pure palladium.

The experimentally determined heat contents, expressed in defined calories⁶ (1 cal. = 4.1833 int. joules) per mole (*in vacuo*), are listed in Table I and shown graphically in Figs. 1 and 2. Molal weights are computed according to the 1947 International Atomic Weights.⁷

The results for zirconium metal average about 5% higher than the best values of Jaeger and Veenstra,² who obtained reproducible values only to about 900°K. In the present instance, reproducible values were obtained to 1370°K., beyond which point measurements were not possible because of deterioration of the platinum-rhodium alloy capsules. The transition region was found to lie between about 1110 and 1190°K., whereas the generally accepted transition point is near 1135°K. (The results labeled (*a*) in Table I are in the transition region.) The spread and especially the extension of the transition region beyond 1135°K. is considered as evidence that our sample contained some oxygen, nitrogen, or both. For this reason, the results for this substance are considered provisional, and it is hoped to repeat the measurements when better zirconium is available. Until such time, the present data have value, as they extend the temperature range of usable measured heat contents by about 470°. In constructing the table of smooth values (part of Table II), the true transition point has been taken as 1135°K. and the heat of transition evaluated as 920 cal. per mole.

No evidence of non-reproducibility or other difficulties were encountered with the zirconium oxide. A reversible and reproducible transition was found at 1478°K., with a heat absorption of 1420 cal. per mole. The transition was quite sharp, no pretransition phenomena being encountered at the 1459°K.-point in Table I. The two values labeled (*b*) in Table I, at 1470° and 1475°K., respectively, do show pretransition effects, but the temperatures are very near the transition point.

(4) Southard, *THIS JOURNAL*, **63**, 3142 (1941).

(5) Kelley, Naylor and Shomate, *Bur. Mines Tech. Paper*, 686 (1946).

(6) Mueller and Rossini, *Am. J. Phys.*, **12**, 1 (1944).

(7) Baxter, Guichard and Whytlaw-Gray, *THIS JOURNAL*, **69**, 731 (1947).

TABLE I

HIGH-TEMPERATURE HEAT CONTENTS

$T, ^\circ\text{K.}$	$H_T - H_{298.15}$ cal./mole	$T, ^\circ\text{K.}$	$H_T - H_{298.15}$ cal./mole
Zr (mol. wt. = 91.22)			
390.3	605	1124.7	6,160 ^a
477.5	1,195	1147.5	6,685 ^a
585.6	1,970	1165.8	7,115 ^a
694.6	2,775	1182.1	7,355 ^a
780.4	3,400	1208.3	7,620
877.3	4,140	1231.1	7,790
968.5	4,845	1253.0	7,940
1073.7	5,680	1294.0	8,260
1082.0	5,795	1335	8,530
1098.4	5,855	1371	8,925
1104.4	5,925		
ZrO ₂ (mol. wt. = 123.22)			
396.8	1,405	1176.5	14,990
439.4	2,095	1248.7	16,340
479.7	2,685	1273.2	16,800
480.1	2,720	1323	17,720
576.4	4,265	1379	18,750
576.9	4,280	1424	19,510
640.1	5,380	1431	19,780
673.4	5,925	1459	20,210
682.5	6,090	1470	21,340 ^b
781.8	7,820	1475	21,660 ^b
831.5	8,640	1481	22,130
852.8	9,040	1489	22,210
869.7	9,440	1495	22,230
878.2	9,550	1573	23,790
978.7	11,390	1635	24,870
1029.3	12,300	1715	26,250
1040.4	12,550	1776	27,420
1057.5	12,880	1835	28,350
1079.9	13,210	1841	28,520
ZrN (mol. wt. = 105.23)			
371.0	740	1076.8	9,190
476.5	1,875	1173.5	10,440
578.2	2,995	1272.8	11,720
674.8	4,155	1372	13,030
774.2	5,360	1474	14,340
874.2	6,605	1569	15,620
976.7	7,910	1672	16,960
1072.6	9,130		
ZrSiO ₄ (mol. wt. = 183.28)			
384.9	2,205	1033.4	23,420
470.4	4,620	1128.9	26,700
547.6	6,915	1231.9	30,490
597.1	8,480	1334	34,040
625.5	9,250	1442	38,020
694.9	11,720	1538	41,430
723.0	12,620	1637	44,960
754.5	13,650	1730	48,280
850.5	16,960	1820	51,810
936.8	19,960	1823	51,800
ZrCl ₄ (mol. wt. = 233.05)			
335.9	1,075	480.3	5,440
385.9	2,595	522.5	6,695
433.8	4,030	566.8	8,090

TABLE II
 HEAT CONTENTS (CAL./MOLE) AND ENTROPY INCREMENTS (CAL./DEG./MOLE) ABOVE 298.16°K.

T, °K.	Zr		ZrO ₂		ZrN		ZrSiO ₄		ZrCl ₄	
	H _T ^o - H _{298.16} ^o	S _T ^o - S _{298.16} ^o	H _T ^o - H _{298.16} ^o	S _T ^o - S _{298.16} ^o	H _T ^o - H _{298.16} ^o	S _T ^o - S _{298.16} ^o	H _T ^o - H _{298.16} ^o	S _T ^o - S _{298.16} ^o	H _T ^o - H _{298.16} ^o	S _T ^o - S _{298.16} ^o
350									1495	4.62
400	665	1.91	1,475	4.24	1,040	3.00	2,620	7.53	3005	8.65
450									4525	12.23
500	1350	3.44	3,050	7.75	2,120	5.40	5,460	13.86	6050	15.44
550									7580	18.36
600	2065	4.74	4,690	10.74	3,260	7.48	8,550	19.48		
700	2800	5.88	6,380	13.34	4,450	9.31	11,800	24.50		
800	3550	6.88	8,120	15.68	5,670	10.94	15,180	29.01		
900	4315	7.78	9,910	17.79	6,920	12.41	18,640	33.08		
1000	5095	8.60	11,730	19.70	8,190	13.75	22,140	36.77		
1100	5890	9.36	13,570	21.46	9,470	14.97	25,670	40.13		
1135	6170 ^a	9.61								
1135	7090 ^b	10.42								
1200	7560	10.82	15,420	23.07	10,760	16.10	29,220	43.22		
1300	8290	11.40	17,280	24.55	12,060	17.14	32,790	46.08		
1400	9015	11.94	19,150	25.94	13,370	18.11	36,380	48.74		
1478			20,620 ^a	26.96						
1478			22,040 ^b	27.92						
1500			22,430	28.18	14,690	19.02	39,990	51.23		
1600			24,210	29.33	16,020	19.88	43,630	53.58		
1700			25,990	30.41	17,360	20.69	47,290	55.80		
1800			27,770	31.43			50,980	57.91		

Jaeger and Veenstra² have reported heat-content values for zirconium oxide at three temperatures, 673, 903 and 1073°K. Comparison with present results shows their values to deviate by 0.0, -1.5 and -1.7%, respectively.

The data for the nitride, silicate and tetrachloride are regular and require no discussion. Values for the tetrachloride were not obtained above 567°

because of failure of the platinum-rhodium capsule which developed a pinhole just beyond this point.

Table II contains smooth values of heat-content and entropy increments above 298.16°K. at even 100° temperature intervals and at phase-change points. The entropy values have been calculated to match exactly the heat contents by the method described by Kelley.³

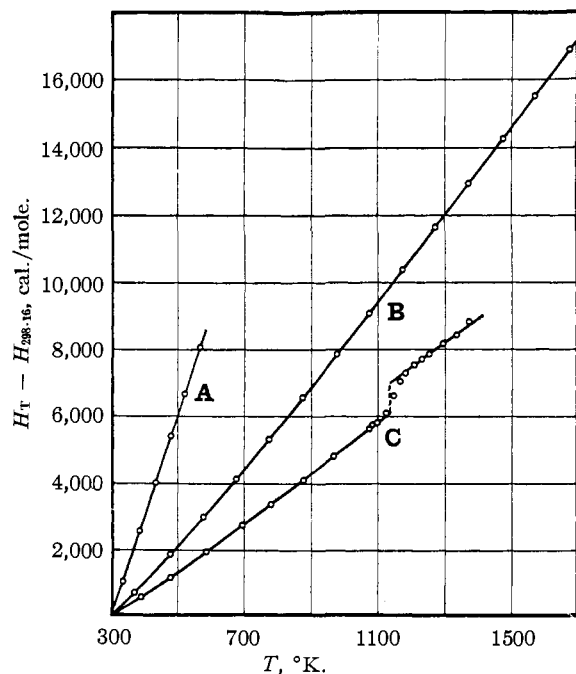


Fig. 1.—Heat contents: A, ZrCl₄; B, ZrN; C, Zr.

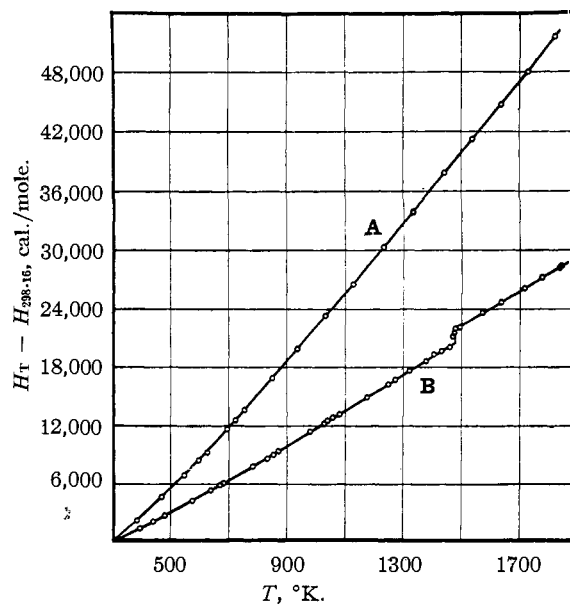


Fig. 2.—Heat contents: A, ZrSiO₄; B, ZrO₂.

(3) Kelley, *Bur. Mines Bulletin*, 476 (1949).

Molal heat-content equations were derived by the method of Shomate.⁹ Figures in parentheses give the temperature range of validity and the average degree of fit of the equation to the measured data.

$$\text{Zr}(\alpha): H_T - H_{298.16} = 6.83T + 0.56 \times 10^{-3}T^2 + 0.87 \times 10^6 T^{-1} - 2378; (298-1135^\circ\text{K.}, 0.2\%)$$

$$\text{Zr}(\beta): H_T - H_{298.16} = 7.27T - 1163 (1135-1400^\circ\text{K.}, 0.3\%)$$

$$\text{ZrO}_2(\alpha): H_T - H_{298.16} = 16.64T + 0.90 \times 10^{-3}T^2 + 3.36 \times 10^6 T^{-1} - 6168 (298-1478^\circ\text{K.}, 0.2\%)$$

$$\text{ZrO}_2(\beta): H_T - H_{298.16} = 17.80T - 4267 (1478-1850^\circ\text{K.}, 0.2\%)$$

$$\text{ZrN}(\text{c}): H_T - H_{298.16} = 11.10T + 0.84 \times 10^{-3}T^2 + 1.72 \times 10^6 T^{-1} - 3961 (298-1700^\circ\text{K.}, 0.4\%)$$

$$\text{ZrSiO}_4(\text{c}): H_T - H_{298.16} = 31.48T + 1.96 \times 10^{-3}T^2 + 8.08 \times 10^6 T^{-1} - 12,270 (298-1800^\circ\text{K.}, 0.7\%)$$

$$\text{ZrCl}_4(\text{c}): H_T - H_{298.16} = 31.92T + 2.91 \times 10^6 T^{-1} - 10493 (298-550^\circ\text{K.}, 0.3\%)$$

The corresponding heat-capacity equations are

(9) Shomate, *THIS JOURNAL*, **66**, 928 (1944).

$$\begin{aligned} \text{Zr}(\alpha): C_p &= 6.83 + 1.12 \times 10^{-3}T - 0.87 \times 10^6 T^{-2} \\ \text{Zr}(\beta): C_p &= 7.27 \\ \text{ZrO}_2(\alpha): C_p &= 16.64 + 1.80 \times 10^{-3}T - 3.36 \times 10^6 T^{-2} \\ \text{ZrO}_2(\beta): C_p &= 17.80 \\ \text{ZrN}(\text{c}): C_p &= 11.10 + 1.68 \times 10^{-3}T - 1.72 \times 10^6 T^{-2} \\ \text{ZrSiO}_4(\text{c}): C_p &= 31.48 + 3.92 \times 10^{-3}T - 8.08 \times 10^6 T^{-2} \\ \text{ZrCl}_4(\text{c}): C_p &= 31.92 - 2.91 \times 10^6 T^{-2} \end{aligned}$$

Summary

Heat contents above 298.16°K. were measured for zirconium, zirconium oxide, zirconium nitride, zirconium silicate, and zirconium tetrachloride to the respective temperatures, 1370, 1841, 1672, 1823 and 567°K.

The heat of transition of zirconium metal is 920 cal. per mole. The temperature and heat of transition of zirconium oxide were found to be 1478°K. and 1420 cal. per mole, respectively.

A table of smooth values of heat-content and entropy increments above 298.16°K. was constructed, and representative heat-content and heat-capacity equations were derived.

BERKELEY, CALIFORNIA RECEIVED NOVEMBER 9, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Diffusion Coefficient of Potassium Chloride in Water at 4°

BY HERBERT S. HARNED AND CHARLES A. BLAKE

Accurate values of the diffusion coefficient of potassium chloride in dilute solutions at 20 and 30° and at concentrations between 0.001 and 0.55 molar at 25° have been the subject of recent communications from this Laboratory.^{1,2,3,4} Owing to the interest of biological chemists in diffusion coefficients in the neighborhood of the freezing point of water, we have determined this quantity for potassium chloride at 4° over the concentration range between 0.01 and 0.6 molar.

Experimental Results

The technique and operation of the conductance method has been described in detail in the above communications. At 4° difficulty was encountered with the cells with larger electrodes due to the difference in the coefficients of expansion of the lucite and metal electrodes. As a result, our experiments were restricted to the cell with electrodes of 1 mm. diameter. These electrodes, which consisted of tapered rods of platinum screwed into the lucite, proved to be sufficiently tight and yielded satisfactory results. However, this type of cell cannot be relied upon to yield as accurate values in dilute solution as the cells with larger electrode surfaces. The accuracy of our mean values appears to be of the order of $\approx 0.5\%$.

(1) Harned and French, *Ann. N. Y. Acad. Sci.*, **46**, 267 (1945).

(2) Harned and Nuttall, *ibid.*, **61**, 781 (1949).

(3) Harned and Nuttall, *THIS JOURNAL*, **69**, 736 (1947).

(4) Harned and Nuttall, *ibid.*, **71**, 1460 (1949).

Table I contains the results. As before, five readings at two-hour intervals were made each day and this procedure was continued for five or six days. The values recorded in the table under column heading (1-2) are each the mean of five determinations according to the equation

$$D = \frac{a^2}{\pi^2} \left[\frac{\Delta \ln (K_B - K_T)}{\Delta t} \right] \Delta t = 86,400 \text{ sec.} \quad (1)$$

where $\Delta \ln (K_B - K_T)$ is the difference in the natural logarithm of the difference in the conductances at the bottom and top of the cell taken on the first and second days, Δt is the number of seconds in a day, and a is the depth of the cell. The results in the columns (2-3), (3-4), etc., refer to similar results taken from the second to the third days,

TABLE I

OBSERVED AND THEORETICAL DIFFUSION COEFFICIENTS OF POTASSIUM CHLORIDE IN WATER AT 4°

(1-2) (2-3) etc. are the values of $D \times 10^5$ (cm.² sec.⁻¹) obtained from readings taken on first to second, second to third, etc., days.

c_1	(1-2)	(2-3)	(3-4)	(4-5)	(5-6)	D × 10 ⁵ (mean)	D × 10 ⁵ (theory)
0.0166	1.084	1.083	1.070	1.082	1.084	1.080	1.082
.168	...	1.034	1.045	1.035	...	1.038	1.039
.307	...	1.034	1.034	1.040	...	1.036	1.036
.379	1.030	1.040	1.037	1.041	...	1.037	1.036
.558	1.041	1.050	1.039	1.041	...	1.042	1.040

$T = 277.16^\circ \text{C.}$; $D = 86.43$; $\eta_0 = 15.676 \times 10^{-8}$; $\lambda^\circ_{\text{K}} = 45.50$; $\lambda^\circ_{\text{Cl}} = 46.17$; $A' = 1.170$; $\delta = 3.6$; $B = 0.014$; $S_{(1)} = 0.4913$; $d(4^\circ) = 1.0000 + 0.05099c - 0.0031c^{3/2}$.