Report No. BMI-1313
UC-25 Metallurgy and Ceramics
(TID-4500, 14th Ed.)

Contract No. W-7405-eng-92

FURTHER STUDIES OF SINTERED REFRACTORY URANIUM COMPOUNDS

by

Arch B. Tripler, Jr.
M. Jack Snyder
Winston H. Duckworth

January 27, 1959

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus 1, Ohio

DISCLAIMER

TABLE OF CONTENTS

APPENDIX

FURTHER STUDIES OF SINTERED REFRACTORY URANIUM COMPOUNDS

Arch B. Tripler, Jr., M. Jack Snyder, and Winston H. Duckworth

The refractory uranium compounds UC and UC_2 *were prepared by arc-melting methods, UN by gas-solid reactions, and* UB_2 *and* UBe_{13} *by solid-solid reactions. Techniques for sintering powder compacts of these compounds to densities 90 per cent of theoretical or greater were developed.*

Mean linear thermal-expansion coefficients of 7.9×10^{-6} *per F for UC and* 9.3×10^{-6} *per F for* UBe_{13} *were obtained in the range 68 to 1800 F. The thermal conductivity of sintered* UBe_{13} *increased from 0.050 cal/(sec)(cm)(C) at 100 C to 0.064 cal/(sec)(cm)(C) at 650 C. The electrical resistivity of sintered* UBe_{13} *was 113 microhm-cm at 27.6 C. Knoop microhardness values varied from 500 for sintered* UC_2 *to 1155 for sintered* UBe_{13}*.*

Sintered UC and UC_2 *decompose rapidly in boiling (atmospheric pressure) water. A sintered* UBe_{13} *compact lost 2.2 mg per* cm^2 *(average), after 72 hr in boiling water (atmospheric pressure).*

UC_2 *reacts more rapidly with nitrogen and oxygen than does pure uranium.* UB_2 *and* UBe_{13} *were less reactive with oxygen and nitrogen than is pure uranium.*

The heat of formation of UC was -20 ± 5 *kcal per mole at 25 C. Standard free-energy-of-formation equations were estimated for UN,* USi_2*, US,* UB_2*,* UC_2*, and UC.*

INTRODUCTION

The properties of a number of refractory binary compounds of uranium that may have potential application as nuclear fuels are being investigated at Battelle. The results of a literature survey and initial experimental work were reported in BMI-1124.(1) Subsequent experimental work was reported in BMI-1223.(2)

Methods of preparation, fabrication, and some physical and chemical properties of UC, UC_2, UBe_{13}, UN, and UB_2 are given in this report.

EXPERIMENTAL RESULTS

Preparation and Fabrication of Compounds

The details of the apparatus and methods used in the preparation and fabrication of the uranium compounds discussed in this report are given in the Appendix.

---

(1) References at end of text of report.

The results of the preparations and fabrications of the compounds are given in Table 1 together with some of the properties determined and the results of metallographic, chemical, and X-ray analyses.

Uranium Monocarbide

Uranium monocarbide was prepared by arc melting stoichiometric amounts of center-cut, biscuit uranium and high-purity carbon to form 100 to 200-g buttons. In recent research(3) direct casting of similar buttons was successfully adapted as a means of producing specimens of uranium monocarbide. In this research, however, the objective was to study sintered uranium carbide. Thus, the arc-melted button was crushed in a diamond mortar under an argon atmosphere and then ball milled in a porcelain jar with high-alumina porcelain balls until the average particle size was less than 10 μ. During ball milling, the carbide was immersed in trichloroethylene to prevent oxidation. After the material was separated from the balls and removed from the jar, most of the trichloroethylene was decanted and the carbide was dried in an argon atmosphere.

The UC powder was compacted hydrostatically at 100,000 psi(4), and then sintered in a resistance-heated vacuum furnace.

Table 1 gives some typical examples of the varying conditions under which UC and other uranium compounds were prepared and sintered, and the results of the experiments. In the table, references are made to the photomicrographs which follow.

The first preparation listed (12829-74A) is an example of UC prepared by arc melting, and which is virtually single-phase material (see Figure 1). The photomicrograph is included for purposes of comparison with those of sintered compacts.

In Experiments 12829-96 and -99, the specimens were sintered from a 9-μ (average particle size) powder under varying conditions of temperature and time. A cross section of the specimen sintered at the higher temperature (1925 C) and the shorter time (1 hour) (see Figure 2) showed a core having small (2 to 6 μ) grains and an outer ring of relatively large (150 to 200 μ) grains. The largest grains are not shown in Figure 2. The grain-boundary phase appeared to be uranium rich and this is supported by the fact that the microhardness of the grain-boundary layer was much lower than that of the grains. In Experiment 12829-99, the temperature was 1800 C and the time was 4-1/2 hr. No core was observed and the grain size was comparatively uniform (Figure 3). There was considerable grain growth, however, and the uranium-rich grain boundaries were again present, this time to a larger proportion, accounting for the higher bulk-density value. It should be noted also that the uranium, as determined by chemical analysis was in excess. Neither of the above structures was considered acceptable.

Satisfactory results were achieved by sintering a 5-μ (average particle size) material at about 1800 C for 1 hr (Figure 4). Chemical analysis showed this material to be more nearly stoichiometric than that used in previous trials. It has been observed in subsequent work that a slight excess of carbon in the starting material will result in more nearly stoichiometric proportions in the sintered specimens.

TABLE 1 PREPARATION AND FABRICATION CONDITIONS AND RESULTS FOR VARIOUS URANIUM COMPOUNDS

Specimen	Starting Materials	Proportions	Reaction or Fabrication Method	Average Particle Size of Powder	Final Sintering Tempera-ture and Time	Sintered Bulk Density g per cm^3	Density, per cent of theo-retical	Knoop Micro-hardness	Photo-micro-grapn	Chemical Analysis			X-Ray Analysis	Remarks
										Element	w/o	a/o		
							Uranium Monocarbide (Reported Melting Point 2350-2400 C X-Ray Density, 13 63 G per Cm^3)							
12829-74A	U + C	Stoichiometric	Arc melted	–	–	14 20 (arc melt)	104	935 (100 g)	N43491 (Figure 1)	Combined C Free C U	4 59 0 05 Not determined	– – –	–	Mostly single phase some evidence of UC_2
12829-89	U + C	Stoichiometric	Arc melted	–	–	–	–	–	–	–	–	–	–	Ground to 9-μ average particle size used for sintering
12829-96	12829-89	–	Vacuum sintered	9 μ	1925 C, 1 hr	12 79	93 8	Matrix, 751 grain boundary, 242	N45743 (Figure 2)	U C	95 6 4 39	52 3 47 7	–	Metallographic examination UC matrix with grain-boundary phase porous core with small grains (2-6 μ in diameter), dense outer ring with large grains (150-200 μ in diameter)
12829-99	12829-89	–	Vacuum sintered	9 μ	1800 C, 4-1/2 hr	13 57	99 5	Matrix 752, grain boundary 225	N45740 (Figure 3)	U C	95 9 4 12	54 46	–	Metallographic examination generally uniform grain structure, UC matrix with grain-boundary phase, grain size, 30-150 μ
14099-26	U + C	Stoichiometric	Arc melted	–	–	–	–	–	–	U C	93 5 4 6	50 6 49 4	–	Ground to 5-μ average particle size, used for sintering
14335-10	14099-26	–	Vacuum sintered	5 μ	1815 C, 1 hr	12 87	94	700 (200 g) 738 (100 g)	N48148 (Figure 4)	–	–	–	Only UC detected	Metallographic examination UC matrix phase, Widmanstatten lines are UC_2 typical of uranium carbon alloys having about 5 w/o carbon, a very slight amount of UO_2 present in grain boundaries
							Uranium Dicarbide (Reported Melting Point 2450-2500 C X-Ray Density 11 68 G per Cm^3)							
12829-74B	U + C	Stoichiometric	Arc melted	–	–	11 28 (arc melt)	96 5	620 (100 g)	N43490 (Figure 5)	U Combined C	91 4 8 19	36 64	–	–
12829-31	U C	Stoichiometric	Arc melted	–	–	–	–	–	–	U C	90 2 8 6	34 6 65 4	Single phase only UC_2	Ground to minus 100 mesh, used for sintering
12829-50	12829-31	–	Vacuum sintered	Minus 100 mesh	1650 C 1 hr	8 807	75	–	–	–	–	–	–	Carbowax used as a binder during hydrostatic pressing, cooled rapidly, no breakage
12829-31G	12829-31	–	–	–	–	–	–	–	–	–	–	–	–	Ball milled to 5-μ average particle size
12829-56	12829-31G	–	Vacuum sintered	5 μ	1820 C 1-3/4 hr	10 67	91 4	474 (200 g) 575 (100 g)	–	–	–	–	–	Carbowax binder used, after sintering furnace cooled rapidly (5 amp per 5 min) and specimen broke into many pieces, metallographic examination no free carbon voids about 10 per cent, UC precipitated as broad bands along selected planes in UC_2 matrix, 5-10 per cent UC estimated, carbon content estimated at 8 2 per cent
12829-58	12829-31G	–	Vacuum sintered	5 μ	1820 C 1 hr	10 89	93 3	457 (200 g)	–	–	–	–	UC_2 + 15 w/o UC (estimated)	Carbowax binder used; furnace cooled slowly (2 amp per hr) and sample broke into two pieces; metallographic examination same as Specimen 12829-56 except grain size slightly larger
12829-69	12829-31G	–	Vacuum sintered	5 μ	1850 C 1-1/4 hr	10 35	88 6	–	N43906 (Figure 6)	–	–	–	–	Carbowax binder used, furnace cooled slowly (2 amp per hr) and, when cooled, pressure was increased to atmospheric with argon, specimen in one piece metallographic examination UC_2 *is major phase, a phase resembling UC is present as bands across the* UC_2 *grains* there is a third phase which resembles U_2C_3, voids 5-10 per cent, 7 5 per cent carbon (estimated), no free carbon

TABLE 1. (Continued)

Specimen	Starting Materials	Proportions	Reaction or Fabrication Method	Average Particle Size of Powder	Final Sintering Temperature and Time	Sintered Bulk Density, g per cm^3	Density, per cent of theoretical	Knoop Microhardness	Photomicrograph	Chemical Analysis Element	Chemical Analysis w/o	Chemical Analysis a/o	X-Ray Analysis	Remarks
Uranium Beryllide UBe_{13} (Reported Melting Point 2000 C X-Ray Density 4 37 G per Cm^3 Theoretical Composition, 7 14 a/o Uranium 93 3 a/o Beryllium)														
128[illegible]5-2[illegible]	UH_3 Be	Stoichiometric	Solid-solid argon atmosphere	Minus 325 mesh	1500 C 3 4 hr 1750 C for about 5 min	Top unmelted 3 69 Bottom melted 4 66	89 3 10[illegible]	1092 (200 g) 962 (200 g)	N4117b (Figure 9) N4117c (Figure 10)	– –	– –	– –	UBe_{13} + U (C O) UBe_{13}	At 1750 C material was observed to be vaporizing metallographic examination unmelted portion – matrix phase is UBe_{13} spherical dark-gray patches may be evidence of UC or of the grain-boundary phase found in melted portion grain size 20-50 μ melted portion – matrix phase is UBe_{13} grain boundary is probably uranium rich grain size 50-150 μ
12[illegible]29-4[illegible]	UH_3 Be	[illegible] w/o excess beryllium	Solid-solid argon atmosphere	Minus 325 mesh	1500 C 1 2 hr heated to 2000 C in 6 min at 2000 C 4 min	4 46[illegible]	10[illegible]	1111 (100 g)	–	–	–	–	–	Metallographic examination matrix phase is UBe_{13} voids observed many of which appear to be lined with UO_2 grain-boundary material believed to be uranium rich
12[illegible]-56	UH_3 Be	UBe_1	Solid-solid argon atmosphere 1500 C 20 min attempt to flash off volatile [illegible]	Minus [illegible] mesh	See under Reaction or Fabrication Method	3 78 (average)	[illegible] 5	1160 (100 g)	–	U Be	64 [illegible] 33 5	6 7 93 3	–	Metallographic examination matrix phase is UBe_{13} dark gray to black areas are voids unidentified phase in grain boundaries grain size 32-600 μ specimen ground to minus 100 mesh
[illegible]-7	12[illegible]	–	–	Minus 10[illegible] mesh	1500 C 1-1 3 hr	4 6[illegible]	1[illegible]	–	–	–	–	–	–	High bulk-density figure indicates loss of beryllium by volatilization
14[illegible]-67	UH_3 Be	UBe_{14}	Solid-solid argon atmosphere 1550 2 hr	Minus 325 mesh	–	2 67	[illegible]	1237 (100 g)	N4673A (Figure 7)	U Be	67 1 32 6	7 2 92 [illegible]	–	Metallographic examination black areas consist of voids filled with mounting material light areas are UBe_{13}, specimen ball milled to minus 325 mesh
[illegible]	14[illegible]-67	–	–	Minus 325 mesh	1550 C 1 hr	4 2[illegible]	97 [illegible]	1143 (100 g)	N4753A (Figure 6)	U Be Al	65 6 32 5 0.15 (spectrographic)	7.10 92 6	Cross examination shows single phase UBe_{13} (see Remarks)	Metallographic examination more dense than 6A major phase is UBe_{13} some of the extraneous phase was probed out and UC and BeO were identified by X-ray specimen machined for use in physical testing
Uranium Mononitride (Reported Melting Point, 2630 ± 50 C, X-Ray Density, 14.32 G per Cm^3)														
13900-22	U N	$2U + 3/2\ N_2 \xrightarrow{850\ C} U_2N_3$ $U_2N_3 \xrightarrow[Vac]{1300\ C} 2UN + 1/2\ N_2$	Gas-solid	66 μ	–	–	–	–	–	–	–	–	Single-phase UN	
12829-80	13909-22	–	Vacuum sintered	66 μ	1850 C, 1 hr	11 83	82 7	–	–	–	–	–	Single-phase UN	Low density
12829-85	12829-80	–	Vacuum sintered	66 μ	1850 C, additional 3 hr	12 03	83 9	–	–	–	–	–	–	Low density

TABLE 1. (Continued)

Specimen	Starting Materials	Proportions	Reaction or Fabrication Method	Average Particle Size of Powder	Final Sintering Temperature and Time	Sintered Bulk Density, g per cm^3	Density, per cent of theoretical	Knoop Microhardness	Photomicrograph	Chemical Analysis			X-Ray Analysis	Remarks
										Element	w/o	a/o		
Uranium Mononitride (Reported Melting Point, 2630 ± 50 C, X-Ray Density, 14.32 G per Cm^3) (Continued)														
13909-22B	13909-22	–	–	–	–	–	–	–	–	–	–	–	–	Ball milled to 7-μ average particle size
12829-94	13909-22B	–	Vacuum sintered	7μ	1850 C, 1-1/2 hr	12.65	88.3	410 (200 g), 463 (100 g)	N45515 (Figure 11)	–	–	–	–	Metallographic examination: black areas are voids, matrix phase appearing as light and dark gray grains is UN, the white patches are a phase resembling UO$_2$, grain size 3.5 to 18 μ
12829-98	12829-94	–	Vacuum sintered	7μ	1820 C, 2-3/4 hr additional	12.93	90.2	542 (100 g)	N45738 (Figure 12)	–	–	-	–	Metallographic examination: UN phase ranges from dark gray to white, only small amounts of an impurity phase, probably UO$_2$, present; latter can be seen as small white patches in grain boundaries and also within the grains, grain size 5-15 μ
Uranium Diboride (Reported Melting Point, 2440 C: X-Ray Density, 12.82 G per Cm^3)														
12829-17	UH$_3$ + B	Stoichiometric	Solid-solid, 1400 C, 1/2 hr, *in vacuo*	Minus 325 mesh	–	–	–	–	–	–	–	–	–	Specimen ground and sintered (see 12829-18 below)
12829-18	12829-17	–	Vacuum sintered	–	1670 C 1 hr	7.676	60	–	–	U B	89.3 9.5	30 70	–	Low density experiment repeated, see below
12829-71	UH$_3$ + B	Stoichiometric	Solid-solid, 1320 C, 1 hr, *in vacuo*	Minus 325 mesh	–	–	–	–	–	–	–	–	–	Specimen ground and sintered, see 12829-73 below
12829-73	12829-71	–	Vacuum sintered	–	1690 C, 1 hr	7.60	59.2	–	–	–	–	–	–	Apparently maximum density obtainable by this method is 60 per cent of theoretical sintered specimen will be arc melted to obtain specimen of higher density
12829-73A	12829-73	–	Arc melted	–	–	12.78	99.6	1508 (200 g), white phase; 870 (200 g), light-gray phase 679 (200 g), dark phase	N44645 (Figure 13)	–	–	–	–	Metallographic examination: three phases, white, light gray, and dark grain-boundary phase, the latter is probably a eutectic of a uranium-rich solid solution and UB$_2$
12829-82	UH$_3$ + B	2 w/o excess boron	Solid-solid, 1320 C, 1 hr, *in vacuo*	Minus 325 mesh	–	–	–	–	–	–	–	–	–	Specimen ground and sintered, see 12829-84 below
12829-84	12829-82	–	–	–	1690 C, 1 hr	–	–	–	–	–	–	–	–	
12829-84A	12829-84	–	Arc melted	–	–	12.38	96.5	1077 (200 g)	N47841 (Figure 14)	–	–	–	–	Metallographic examination: white, light-gray phases; considerably less of grain boundary phase than in 73A

250X N43491

Etchant: HNO_3-Acetic Acid-H_2O (Equal Volumes)

FIGURE 1. MICROSTRUCTURE OF ARC-MELTED UC

The material is mostly single phase. The white dots may be UC_2. Specimen 12829-74A.

500X N45743

Etchant: HNO_3-Acetic Acid-H_2O (Equal Volumes)

FIGURE 2. MICROSTRUCTURE OF UC SINTERED 1 HR AT 1925 C

Outer ring shows UC matrix with grain-boundary phase. Core is porous. Specimen 12829-96.

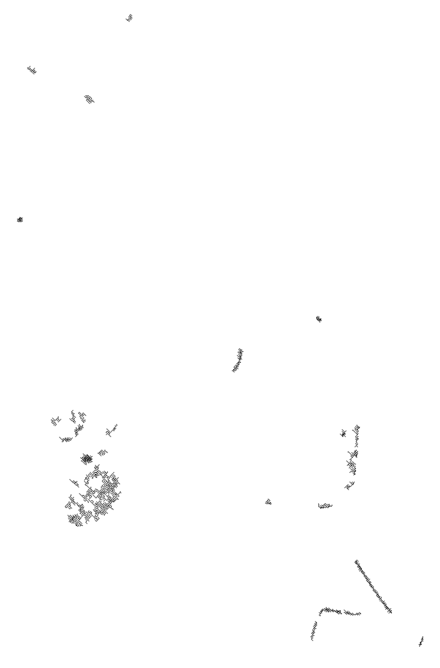


FIGURE 3. MICROSTRUCTURE OF UC SINTERED 4-1/2 HR AT 1800 C

Generally uniform grain structure. UC matrix with grain-boundary phase. Specimen 12829-99.

250X N45740

Etchant: HNO_3-Acetic Acid-H_2O (Equal Volumes)

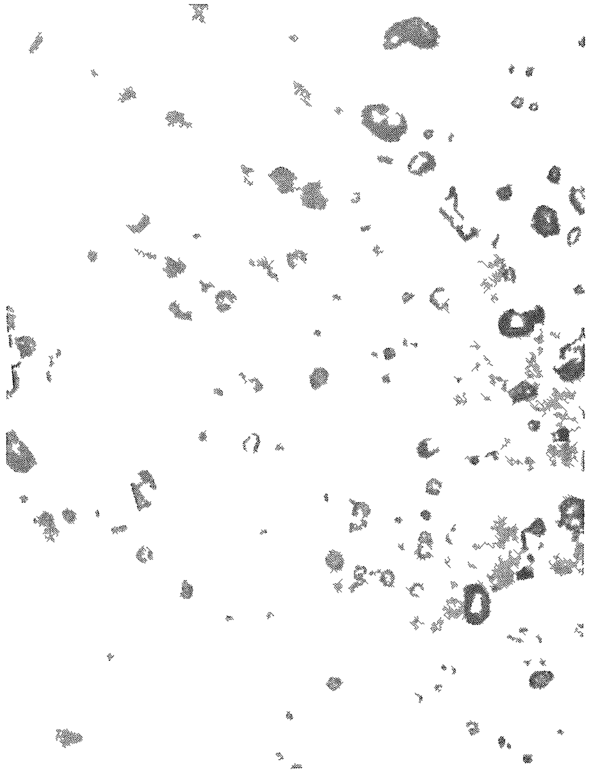


FIGURE 4. MICROSTRUCTURE OF UC SINTERED 1 HR AT 1800 C

UC matrix phase. A very slight amount of UO_2 is present in grain boundaries. The Widmanstätten lines are UC_2, typical of uranium-carbon alloy having about 5 w/o carbon. Specimen 14335-10.

500X N48148

Etchant: HNO_3-Acetic Acid-H_2O (Equal Volumes)

The thermal expansion and some chemical properties of sintered UC are reported in later sections of this report. The heat of combustion was also measured.

Uranium Dicarbide

Uranium dicarbide was prepared and fabricated in the same way as the monocarbide except that a small amount of Carbowax 4000* (about 5 ml of a 1 to 2 w/o solution in CCl_4 for 15 to 20 g of UC_2) was used as a binder in forming the hydrostatically pressed compact.

As with UC, a photomicrograph of arc-melted UC_2 (Figure 5) is included for comparison with sintered UC_2.

The first sintered specimens were fabricated from minus 100-mesh powder, but had densities of only 75 per cent of theoretical. With powder of 5-μ average particle size, bulk densities of approximately 90 per cent of theoretical were achieved.

After sintering, rapid cooling caused UC_2 specimens to break into many pieces. Slow cooling minimized the breaking (Specimen 12829-58). No breakage occurred when slow cooling was followed by the introduction of argon into the vacuum furnace instead of air, which had been used previously. It is not certain that the use of argon is a factor in preventing breakage. Figure 6 shows a typical structure for sintered UC_2.

Microhardness and some chemical properties of UC_2 were measured and are reported later.

Uranium Beryllide

In general, uranium beryllide (UBe_{13}) was prepared by the solid-solid reaction of a hydrostatically compacted mixture of UH_3 and beryllium powders in an induction furnace at about 1550 C. The reaction was carried out under a pressure of argon slightly above atmospheric in order to minimize volatilization of beryllium. Details of typical experiments are given in Table 1.

The experiments demonstrated that an excess of beryllium was necessary in the starting materials in order to finish with a stoichiometric or near-stoichiometric composition in the sintered specimens.

A two-step procedure was adopted after the initial experiments because the single-step preparation did not produce sufficiently dense specimens. The UBe_{13} was formed by heating the compacted mixture of UH_3 and beryllium. The relatively porous compact which resulted was ground to powder and then repressed and sintered. Experiments 12829-66, 12829-78, and 14099-6A and 14099-6A-2 are examples of the two-step procedure. The difference in porosity between Step 1 and Step 2 of the procedure can be seen in Figures 7 and 8.

---

*Carbide and Carbon Chemicals Company, New York, New York.

FIGURE 5. MICROSTRUCTURE OF ARC-MELTED UC_2

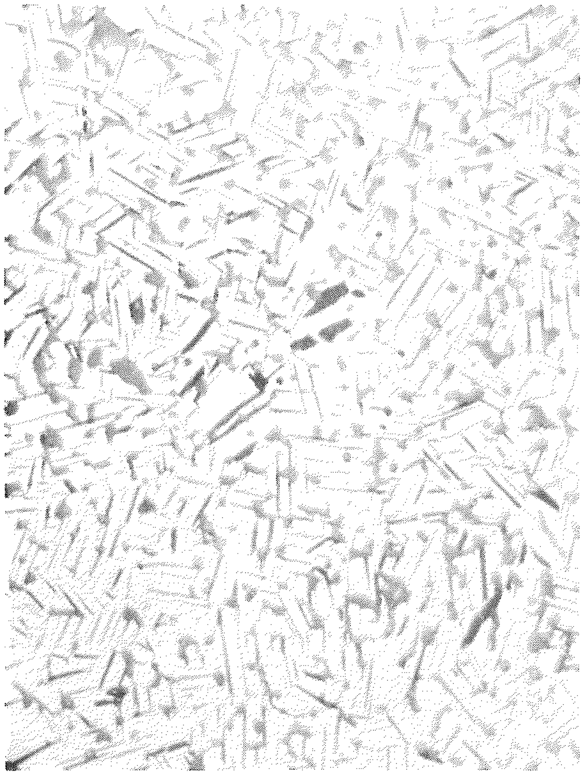
Major phase is UC_2. The light lines running across the grains are evidence of precipitated UC. Specimen 12829-74B.

250X N43490

Etchant: HNO_3-Acetic Acid-H_2O (Equal Volumes)

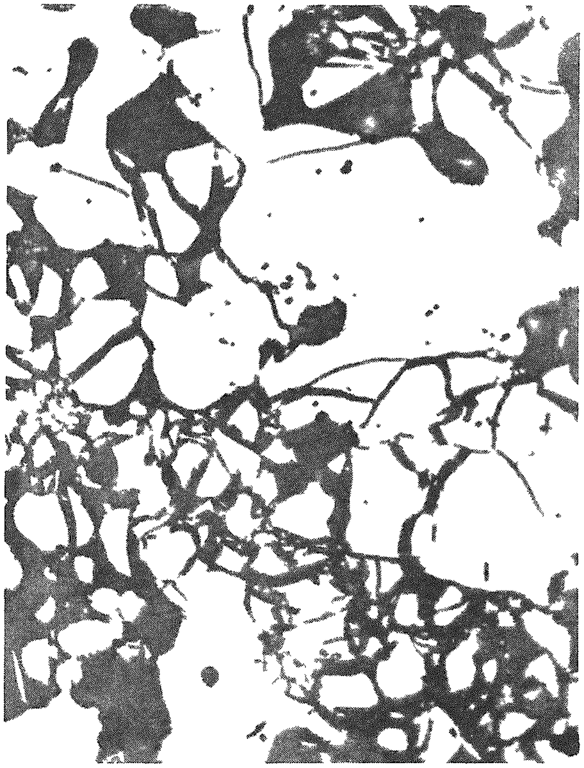
FIGURE 6. MICROSTRUCTURE OF UC_2 SINTERED 1-1/2 HR AT 1850 C

UC_2 is the major phase here. A phase resembling UC is present as bands across the UC_2 grains. There is a third phase resembling U_2C_3. Specimen 12829-69.



500X N43906

Etchant: HNO_3-Acetic Acid-H_2O (Equal Volumes)

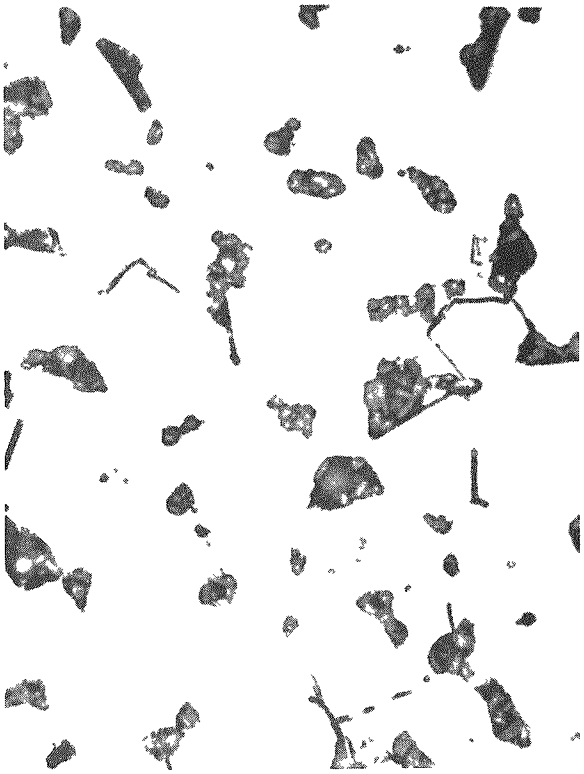


500X N46738

Etchant: 1 HF-10 HNO_3-30 Lactic Acid (Parts by Volume)

FIGURE 7. MICROSTRUCTURE OF UBe_{13} AFTER FIRST HEATING

The compound is formed using approximately 7 w/o excess beryllium. Black areas are voids filled with mounting material. Light areas are UBe_{13}. Specimen 14099-6A.



500X N47534

Etchant: H_2O-0.25 Volume Per Cent HF, on Wheel

FIGURE 8. MICROSTRUCTURE OF UBe_{13} SAMPLE SINTERED FROM GROUND MATERIAL SHOWN IN FIGURE 7

Major phase is UBe_{13}. Some of the extraneous phase was probed out, and UC and BeO were identified by X-ray. Specimen 14099-6A-2.

In the initial single-step experiments (12829-28 and 12829-47) high-bulk density was achieved by flash melting of the specimens. Figures 9 and 10 are metallographic sections of the unmelted and melted portions of a specimen which was partly flash melted. At the temperature necessary for melting, there is the danger of losing beryllium with a resultant uranium-rich phase such as is shown in Figure 10.

The coefficient of expansion, the thermal and electrical conductivities, and some chemical properties of UBe_{13} are given in a later section of this report.

Uranium Nitride

Uranium sesquinitride was prepared by reacting high-purity nitrogen with uranium metal at 850 C. The resulting sesquinitride was then heated at 1300 C to a final pressure of 18 μ of mercury, which converted the sesquinitride to UN. The material as prepared had an average particle size of 66 μ. This material compacted satisfactorily in the hydrostatic press, but the sintered bulk density was only about 84 per cent of theoretical. By reducing the particle size to an average of 7 μ and sintering for a total of 4-1/4 hr in the range 1820 to 1850 C, a specimen having a bulk density of 90 per cent of theoretical was obtained. Figures 11 and 12 show the metallographic structures of specimens having bulk densities of about 88 and 90 per cent, respectively.

The microhardness of UN was determined and is given in Table 1.

Uranium Diboride

Uranium diboride was prepared by the solid-solid reaction in a hydrostatically pressed compact of mixed UH_3 and boron powder at 1300 to 1400 C in a vacuum furnace. The resulting very porous compact was ground, and the powder was hydrostatically pressed. The compact was sintered at about 1680 C in a vacuum furnace. Two attempts (12829-17 and 12829-71) resulted in sintered compacts having bulk densities of about 60 per cent of theoretical. These results are detailed in Table 1.

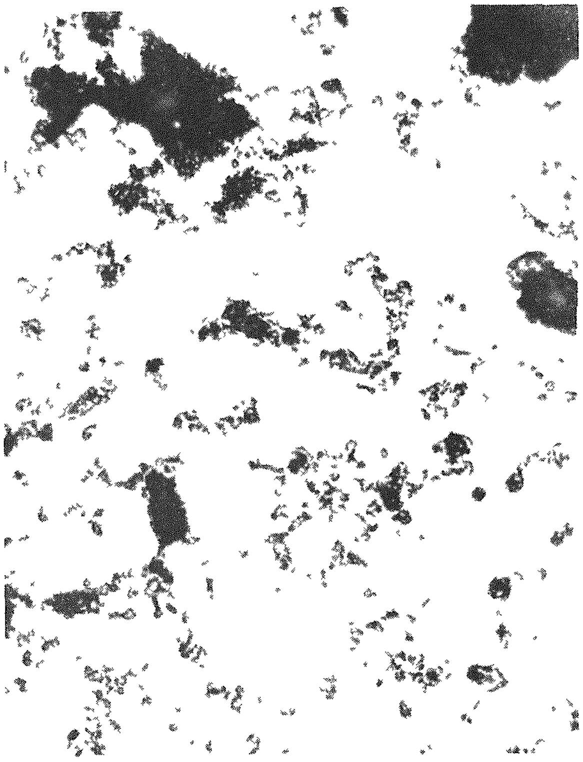
It was believed that, while higher temperature and longer time might have resulted in increased density, the final bulk density would not have reached 90 per cent or higher. In order to attain a higher density quickly, one of the porous sintered compacts was arc melted. This made possible a study of some of the properties of dense UB_2. The arc-melted material had a bulk density of 12.78 g per cm^3, which is 99.6 per cent of theoretical. Metallographic examination showed a uranium-rich phase at the grain boundaries (see Figure 13).

The experiment was repeated using 2 w/o excess boron over the stoichiometric amount (12829-82, -84, and -84A). This resulted in a material which had considerably less of the uranium-rich grain-boundary phase than previously (see Figure 14).

It should be noted that one phase of Specimen 12829-73A showed the highest microhardness (1508) value measured in this work.

FIGURE 9. MICROSTRUCTURE OF UNMELTED PORTION OF UBe_{13} SAMPLE FORMED FROM STOICHIOMETRIC AMOUNTS OF UH_3 AND BERYLLIUM

Matrix phase is UBe_{13}. Gray patches may be evidence of UO_2 or of grain-boundary phase found in melted portion (see Figure 8). Specimen 12829-28.



250X N41175

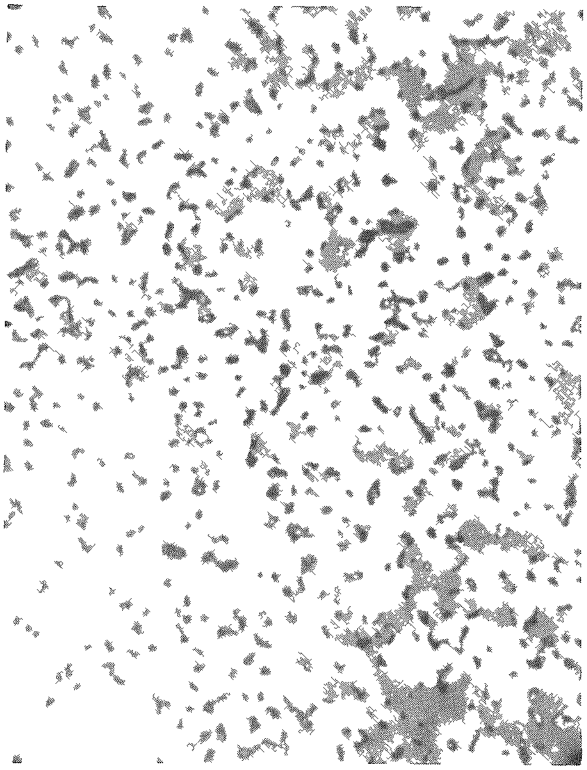
Etchant: H_2O-1 Volume Per Cent HF, on Wheel

FIGURE 10. MICROSTRUCTURE OF MELTED PORTION OF UBe_{13} SPECIMEN SHOWN IN FIGURE 9

Matrix phase is UBe_{13}. Grain boundary is probably uranium-rich. Specimen 12829-28.

250X N41173

Etchant: H_2O-1 Volume Per Cent HF, on Wheel

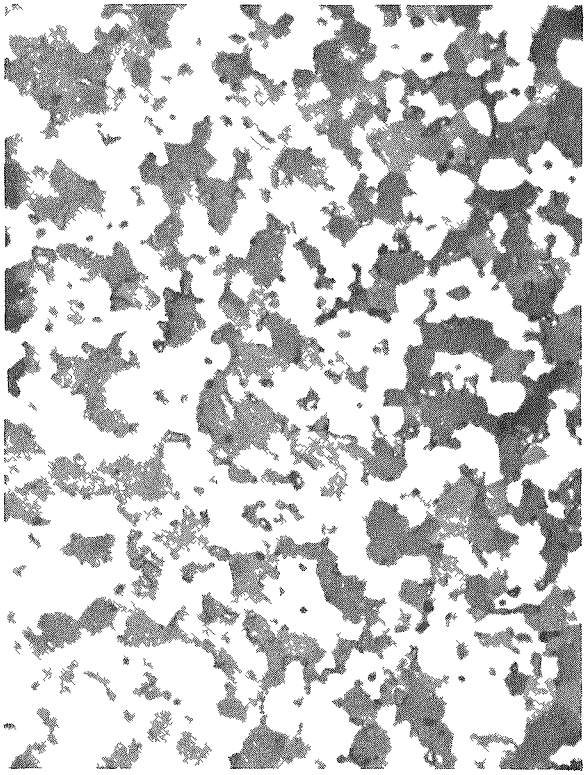


500X N45515

Etchant. 1 HF-10 HNO_3-30 Lactic Acid (Parts by Volume)

FIGURE 11. MICROSTRUCTURE OF UN FABRICATED FROM 7-μ POWDER AND HEATED FOR 1-1/2 HR

Black areas are voids. Major phase is UN. White patches are a phase resembling UO_2. Density is 88.3 per cent of theoretical. Specimen 12829-94.



500X N45738

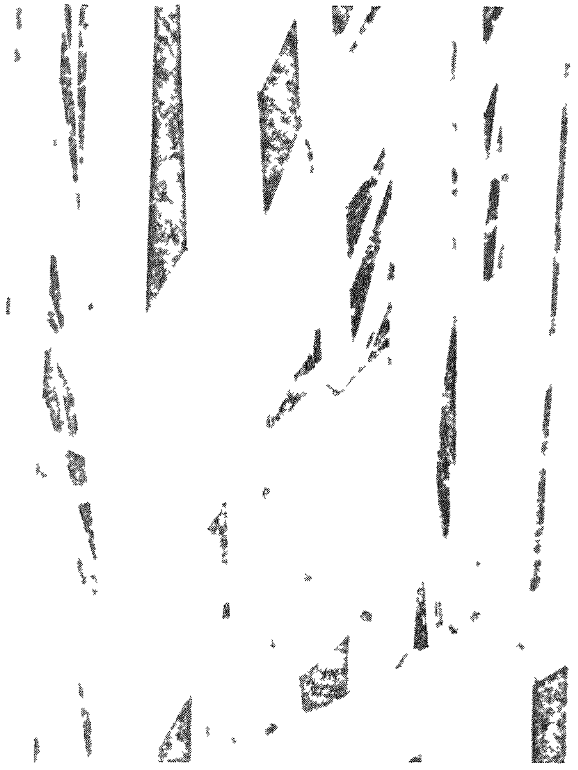
Etchant: 1 HF-10 HNO_3-30 Lactic Acid (Parts by Volume)

FIGURE 12. SAME SPECIMEN AS SHOWN IN FIGURE 11, HEATED 2-3/4 ADDITIONAL HR TO INCREASE DENSITY

UN phase ranges from dark gray to white. Only small amounts of an impurity phase, probably UO_2. Latter can be seen as small white patches in grain boundaries. Density is 90.2 per cent of theoretical. Specimen 12829-98.

FIGURE 13. MICROSTRUCTURE OF UB_2 MADE WITH STOICHIOMETRIC QUANTITIES OF UH_3 AND BORON

Three phases are present, white, light gray, and a dark grain-boundary phase. The latter is probably a eutectic of a uranium-rich solid solution and UB_2. Specimen 12829-73A.



250X N44645

Etchant: H_2O-1 Volume Per Cent HF, on Wheel

FIGURE 14. MICROSTRUCTURE OF UB_2 MADE WITH SLIGHT EXCESS OF BORON

The white and light-gray phases are present, but there is much less of the grain-boundary phase. Specimen 12829-84A.

250X N47841

Etchant: H_2O-1 Volume Per Cent HF, on Wheel

Some chemical properties of UB_2 were measured and are given in a subsequent section of this report.

Physical Properties

(Work done by A. R. Noe, E. A. Eldridge,
H. W. Deem, and A. F. Gerds)

Data were obtained on the thermal expansion of sintered UC and UBe_{13} specimens, on the thermal conductivity and electrical resistivity of UBe_{13}, and on the microhardness of UC, UC_2, UBe_{13}, UN, and UB_2. Observations on the machinability of UC and UBe_{13} and on the melting points of the uranium silicides were also made.

Microhardness

The microhardness values given in Table 1 are consolidated in Table 2 to enable the values for different materials to be compared more conveniently.

Thermal-Expansion Measurements of Sintered UC and UBe_{13}

Thermal-expansion measurements were made in a recording vertical quartz-tube dilatometer having a vacuum of approximately 5 x 10^{-5} mm of mercury. A heating and cooling rate of approximately 5 F per min was maintained throughout the measurements.

Table 3 contains the mean linear-thermal-expansion coefficients for sintered UC and UBe_{13} over temperature ranges from room to 1800 F. The thermal-expansion data(3) recently obtained on arc-cast UC of about 5.0 to 5.2 w/o carbon were about 1 μin. per in. per F lower than the values in Table 3. This difference may be due to the higher carbon content of the cast material. Figures 15 and 16 show the linear expansion as a function of temperature for UC and UBe_{13}, respectively. The error of measurement is estimated not to exceed ±2 per cent.

The mean linear-thermal-expansion coefficients of sintered UBe_{13} and UC for the temperature range 68 to 1800 F are compared with coefficients of other uranium materials in Table 4. The data for the silicides and the aluminide are taken from BMI-1223.(2) The values for the beryllide, silicides, and the aluminide are about the same. The monocarbide is appreciably lower.

Electrical Resistivity of Sintered UBe_{13}

The electrical resistivity of UBe_{13} was determined at room temperature using the voltage-drop method. The resistivity of a sintered specimen was 113 microhm-cm at 27.6 C. The error of the measurement was estimated not to exceed ±1 per cent.

TABLE 2. KNOOP MICROHARDNESS VALUES FOR VARIOUS SINTERED URANIUM COMPOUNDS

Compound	Method of Preparation	Load Used in Measurement, g	Knoop Microhardness	Remarks
UC	Arc melted	100	935	--
UC	Sintered	100	750	--
UC_2	Arc melted	100	620	--
UC_2	Sintered	--	500	Average of values using 100-g and 200-g loads
UBe_{13}	Melted during sintering	200	962	--
UBe_{13}	Sintered	--	1155	Average of values using 100-g and 200-g loads
UN	Sintered	--	455	Ditto
UB_2	Arc melted	200	1508 Max, 1077 Min	--

TABLE 3. MEAN LINEAR-THERMAL-EXPANSION COEFFICIENTS FOR UC AND UBe_{13}

Temperature Range, F	Mean Coefficient Over the Temperature Ranges Shown, 10^{-6} per F			
	First Cycle Heating	First Cycle Cooling	Second Cycle Heating	Second Cycle Cooling
		Uranium Monocarbide		
68-200	6.9	6.7	7.1	7.0
68-400	7.0	7.0	7.1	7.1
68-600	7.2	7.2	7.3	7.2
68-800	7.3	7.3	7.6	7.5
68-1000	7.6	7.5	7.7	7.7
68-1200	7.6	7.6	7.9	7.8
68-1400	7.6	7.7	7.9	7.9
68-1600	7.6	7.9	8.0	8.0
68-1800	7.4	8.1	8.0	8.1
		Uranium Beryllide		
68-200	7.2	7.3	7.1	7.7
68-400	7.6	7.6	7.4	8.0
68-600	8.0	7.9	7.8	8.3
68-800	8.4	8.2	8.3	8.5
68-1000	8.7	8.4	8.6	8.7
68-1200	8.9	8.7	8.9	8.9
68-1400	9.1	8.9	9.0	9.1
68-1600	9.1	9.1	9.2	9.2
68-1800	9.1	9.4	9.3	9.5

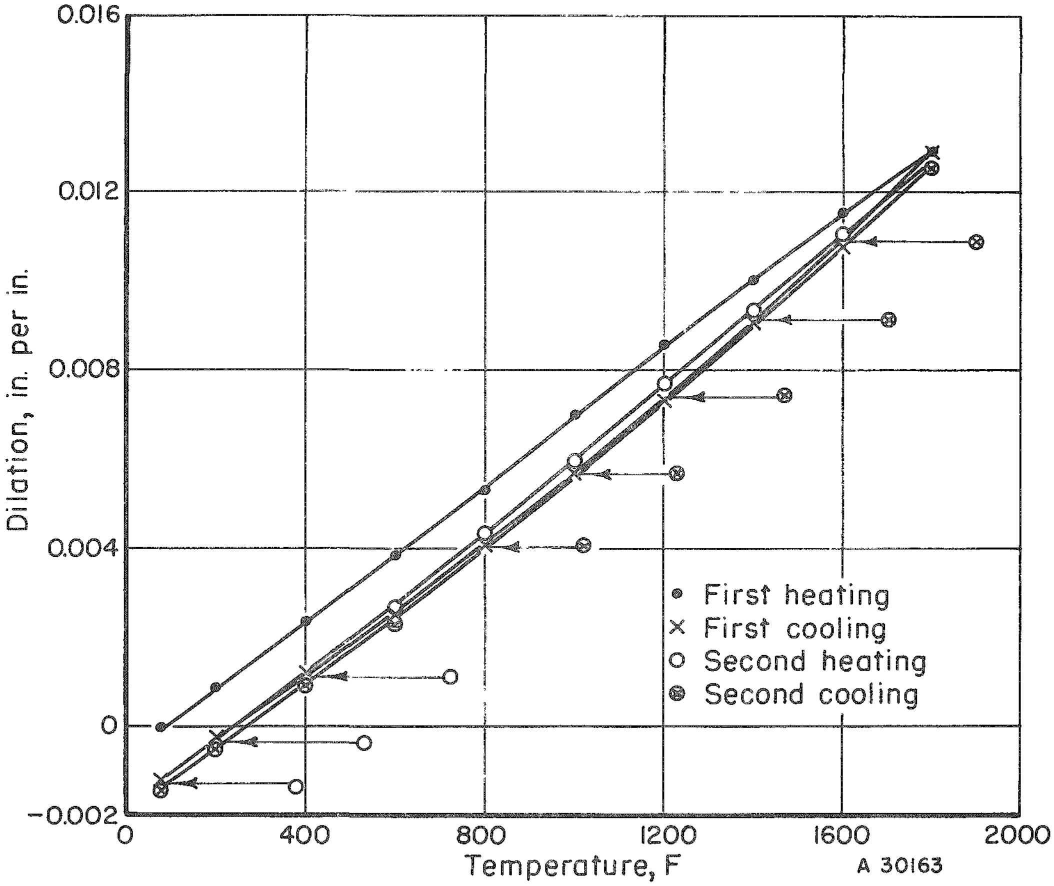


FIGURE 15. LINEAR EXPANSION VERSUS TEMPERATURE FOR UC

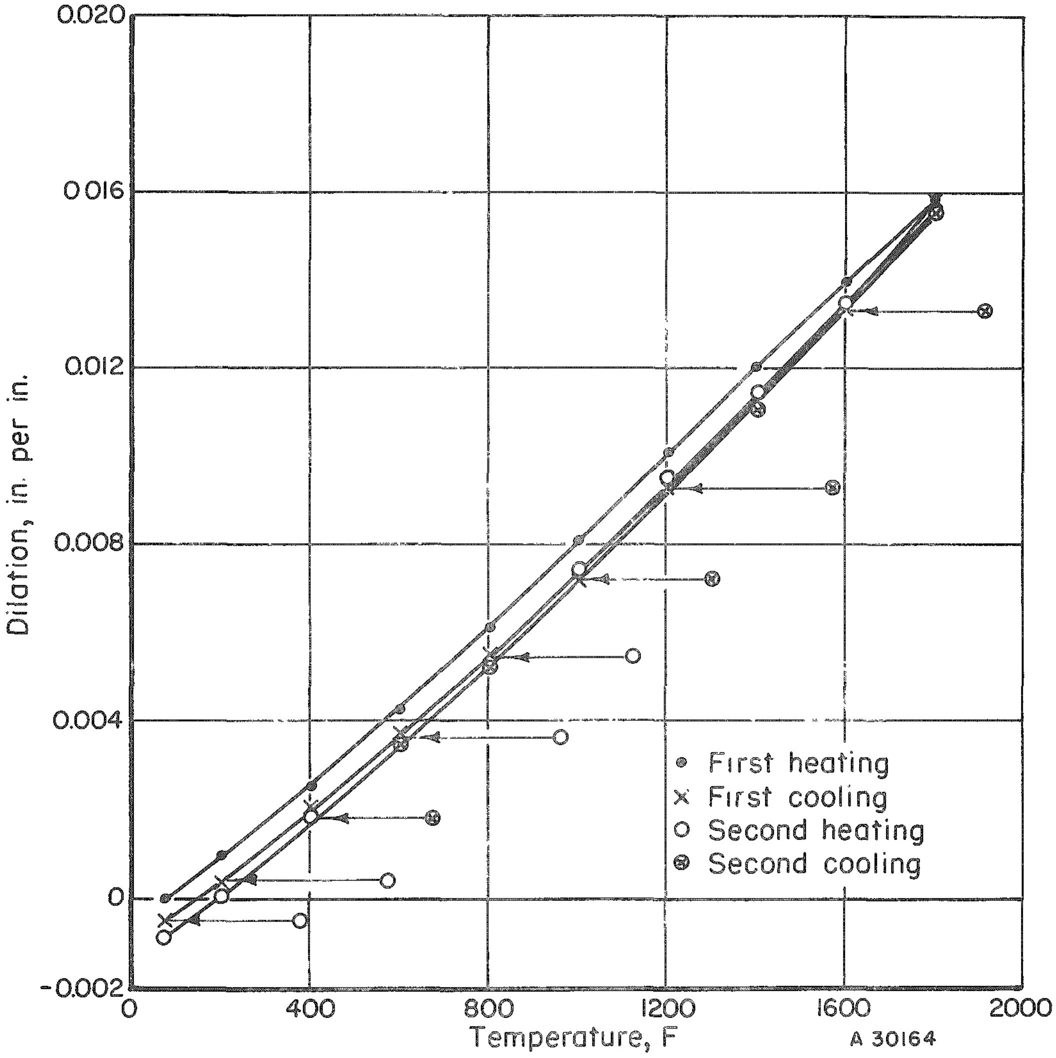


FIGURE 16. LINEAR EXPANSION VERSUS TEMPERATURE FOR UBe_{13}

Thermal Conductivity of Sintered UBe_{13}

The thermal conductivity of sintered UBe_{13} was measured in the range 100 to 650 C. The results are shown in Table 5 and in Figure 17. The method used is described in the Appendix. Errors of the interpolated thermal-conductivity values are estimated not to exceed ±8 per cent. It should be remembered that because of size limitations in the vacuum sintering furnace, the specimen was smaller than usually used for thermal conductivity measurement. This undoubtedly accounts for the spread in values.

The Wiedemann-Franz-Lorenz relation between the thermal and electrical conductivities was calculated for UBe_{13}. This relationship is expressed by

$$\frac{k}{\sigma T} ,$$

where

k = thermal conductivity, cal/(sec)(cm)(C)

σ = electrical conductivity, $ohm^{-1} cm^{-1}$

T = temperature, K.

The Wiedemann-Franz-Lorenz coefficient for sintered UBe_{13} (Specimen 14099-6A-2) was calculated to be 1.7×10^{-8} cal-ohm/(sec)(K^2),

where

$k = 0.0045$ cal/(sec)(cm)(C)*

$\sigma = 8.85 \times 10^3 \ ohm^{-1} cm^{-1}$

$T = 301$ K.

No thermal-conductivity data were obtained for sintered UC because no satisfactory way of tinning the specimens was found. With UBe_{13}, the end surfaces were easily nickel plated and then tinned. Because of the reactivity of UC, pretreatment and plating did not prove feasible. Attempts to flow indium metal on the ends by means of a "cold" soldering iron resulted in adherence of the indium to the UC for a short time only.

Machinability

Sintered specimens of UC and UBe_{13} could be ground to within ±0.001 in. of desired dimensions by use of standard grinding techniques. No difficulty was encountered in grinding the UBe_{13}. Examination of the ground surface of the UC specimens at a magnification of about 4 or 5X showed that tiny particles had been pulled out during the grinding. Other than this, the operation was satisfactory. Recent experiments with arc-melted UC bodies indicate that proper dressing of the grinding wheel or use of carbide wheels may eliminate the pulling out of particles.

---

*Extrapolated from Figure 17.

TABLE 4. COMPARISON OF MEAN LINEAR-THERMAL-EXPANSION COEFFICIENTS FOR VARIOUS SINTERED URANIUM COMPOUNDS

Uranium Material	Mean Coefficients From 68 to 1800 F, 10^{-6} per F
UC	7.9
UBe_{13}	9.3
USi	9.2
USi_2	9.3
USi_3	9.5
UAl_2	9.3
UO_2	5.6
U (metal)	8.3

TABLE 5. THERMAL CONDUCTIVITY OF UBe_{13}

Temperature, C	Thermal Conductivity, cal/(sec)(cm)(C)
100	0.050
200	0.055
300	0.058
400	0.061
500	0.062
600	0.064
650	0.064

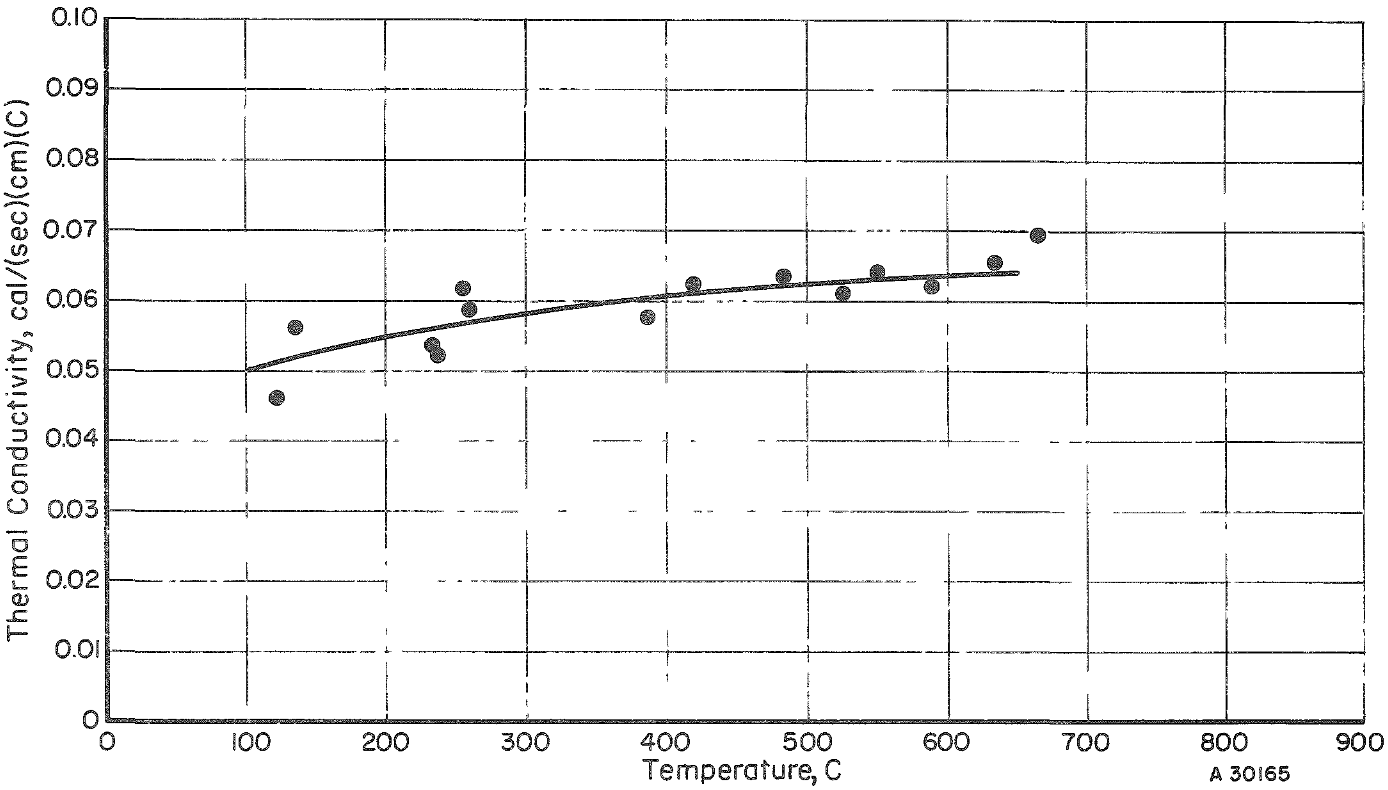


FIGURE 17. THERMAL-CONDUCTIVITY VALUES VERSUS TEMPERATURE FOR UBe_{13}

Specimens of UC, UC_2, UBe_{13}, UN, and UB_2 as well as the silicides were cut without difficulty using a diamond cutoff wheel with a stream of trichloroethylene as a coolant.

Observations on Melting Points of Silicides

During the sintering of several uranium-silicon compounds, temperature readings were carefully made and the specimens were observed for incipient melting. In some cases, incipient melting was observed. This gives a close approximation to the melting point. The observations are listed below.

Compound	Reported Approximate Melting Point	Observation
U_3Si_2	1665 C	Incipient melting at 1560 C
USi	1570 C	Melted at 1621 C No melt at 1520 C
USi_2	1700 C	No melt at 1554 C
USi_3	1510 C	Incipient melting at 1493 C

Chemical Properties

The corrosion of UC, UC_2, and UBe_{13} was studied in boiling water at atmospheric pressure. Quantitative studies were made at various temperatures of the reactions of UC_2, UBe_{13}, and UB_2 with oxygen, nitrogen, and $H_2O(g)$. Qualitative observations were made of the reactions between oxygen and arc-melted UC and UC_2.

Corrosion of Sintered UC, UC_2, and UBe_{13} in Boiling Water

Sintered compacts of UC and UC_2 disintegrated in boiling water (1 atm pressure) within 1 hr. Both carbide compacts disintegrated so rapidly that it was not possible to estimate which was the more stable. The disintegration was accompanied by rapid oxidation of the carbides.

Based on the original area of the specimens, sintered compacts of UBe_{13} showed an average weight loss of 2.2 mg per cm^2 after 72 hr in boiling water (1 atm pressure). Under the same conditions, uranium is reported(5) to lose 180 mg per cm^2. No disintegration of the sintered UBe_{13} compacts was observed during the first 30 hr. After 72 hr, approximately 70 per cent of the original compacts were in massive form. The remainder of the material was in the form of coarse grains.

At various times during the 72-hr boiling-water test, weight measurements were made on the UBe_{13}. The rate was very erratic, there being weight gains as well as weight losses. The value given above is the average for the entire test. Consideration must be given to the fact that the actual area was much larger than the apparent area used to calculate the corrosion rate.

Reactions of Uranium Compounds With Oxygen, Nitrogen, and Water Vapor

(Work done by W. M. Albrecht and B. G. Koehl)

The reaction of the uranium compounds with the various gases followed the general equation

$$w = kt^n ,$$

where

w = weight gain, mg per cm^2

k = rate constant

t = time, sec.

The value of n depends upon the rate law followed; that is, $n = 1$ for the linear law, $n = 0.5$ for the parabolic law. Values of n are obtained from plots of logarithms of w against logarithms of t. Values of the rate constant, k, are obtained from the slope of the linear or parabolic plot of w against t.

The variations of rate constants with temperature are shown by the familiar plots in which the logarithms of the rate constants are plotted against the reciprocals of the absolute temperatures. These data are expressed by equations of the Arrhenius type,

$$k = A \exp(-E/RT) ,$$

obtained from least-square calculations for each of the reactions. Values of A, the frequency factor, and E, the activation energy, are thus determined.

Reactivity of UC_2. A sintered compact of UC_2 (Specimen 12829-69) having a density about 89 per cent of theoretical was investigated. Data of representative rate experiments obtained with nitrogen, oxygen, and water vapor are shown in Figure 18.

The reaction of UC_2 with nitrogen and oxygen at about a 1-atm pressure followed a parabolic rate law in the ranges 400 to 700 C, and 150 to 250 C, respectively. The reaction with water vapor at 29 ± 3 mm of mercury followed the linear rate law from 50 to 200 C. Slopes of the log-log plots and the rate constants of the reactions are given in Table 6. It can be seen that at 300 C the oxidation of UC_2 proceeded anisothermally, that is, the temperature of the specimen increased and caused the rate of reaction to increase rapidly with time. It was estimated that the temperature of the specimen rose to above 1000 C in less than 1 min.

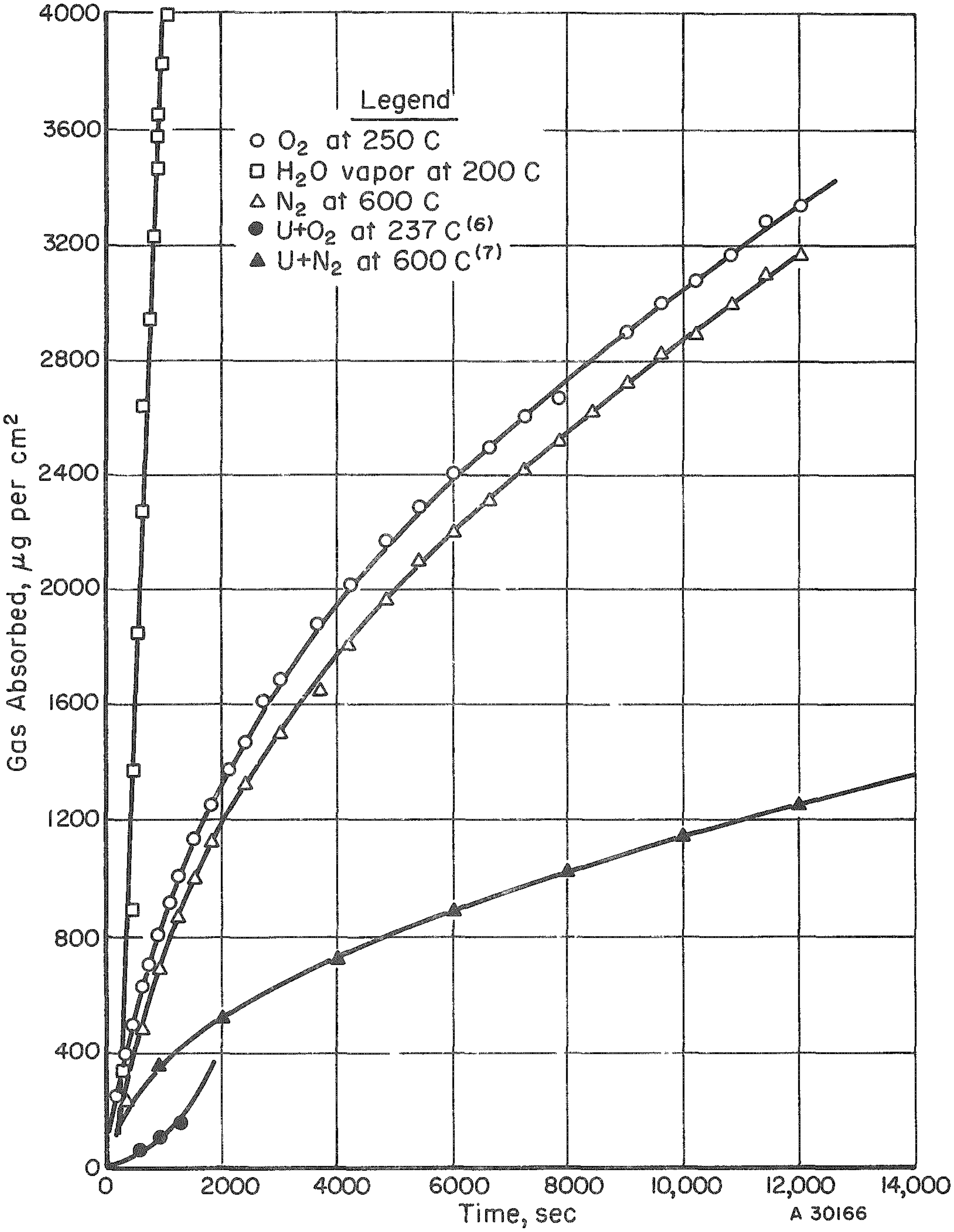


FIGURE 18. REACTION OF UC_2 WITH NITROGEN, OXYGEN, AND WATER VAPOR

TABLE 6. REACTIONS OF UC_2 WITH NITROGEN, OXYGEN, AND WATER VAPOR

Gas Reacted	Temperature, C	Slope of Log-Log Plot	Rate Constant, k		Constants for $k = A \exp(-E/RT)$	
			Linear, $\mu g/(cm^2)(sec)$	Parabolic, $(\mu g/cm^2)^2/sec$	A	E, cal per mole
Nitrogen	400	0.46	--	16	4.40×10^8	22,600 ± 1,200
	500	0.49	--	260		
	600	0.55	--	860		
	700	0.51	--	3300		
Oxygen	150	0.61	--	6.1	5.6×10^{11}	21,200 ± 1,100
	200	0.53	--	75		
	250	0.52	--	900		
	300(a)	--	--	--		
Water vapor	50	1.0	0.044	--	1.88×10^4	8,350 ± 710
	150	0.95	0.66	--		
	200	0.99	3.2	--		

(a) Reacted anisothermally.

TABLE 7. SUMMARY OF X-RAY ANALYSES OF REACTION PRODUCTS

Compound	Reacting Gas	Reaction Products
UC_2	Nitrogen	UN_x(a)
	Oxygen	UC, UO_2
	Water vapor	UC, UO_2
UBe_{13}	Nitrogen	UN_2, UN
	Oxygen	U_3O_8
	Water vapor	UO_2
UB_2	Nitrogen	UN_x(a)
	Oxygen	U_3O_8
	Water vapor	UO_2

(a) x is between about 1.5 and 2.

The variations of the rate constants with temperature are shown in Figures 19 and 20. The values of the frequency factor, A, and the energy of activation, E, obtained from these plots are also given in Table 6.

Comparison of all the data in Figures 18, 19, and 20 shows that the reactivity of UC_2 with the gases increases in the order, nitrogen, oxygen, and water vapor. Also, the reactivity of UC_2 is greater than that of pure uranium with either oxygen or nitrogen. This is in contrast with the results of Cubicciotti(6), who found that the reaction of oxygen with uranium proceeded initially according to a linear law but after a short period the rate increased with time.

X-ray analyses were obtained on several reacted specimens. A summary of the identifiable reaction products is given in Table 7. The product UN_x where x is between 1.5 and 2 was formed during the nitrogen reaction. UO_2 and some UC were produced in both the oxygen and water vapor reactions.

Reactivity of UBe_{13}. An induction-melted compact of UBe_{13} (Specimen 12829-28) was investigated. This compound had a density 107 per cent of theoretical, which indicates that there was an excess of uranium in the compact.

Representative rate curves obtained for the reaction of the UBe_{13} with nitrogen, oxygen, and water vapor are shown in Figure 21. The reaction with nitrogen followed a parabolic rate law from 500 to 800 C. The initial reactions with oxygen and water vapor followed a linear rate in the ranges 350 to 600 C and 600 to 975 C, respectively. In both cases, the rates decreased with time after the initial linear rate. This decrease was quite rapid in the oxygen reaction, as exemplified in Figure 21. At all temperatures the reaction became extremely slow after about 15 per cent of the total oxygen required to completely oxidize the UBe_{13} to U_3O_8 had reacted.

Slopes of the log-log plots, rate constants, and Arrhenius constants for the initial reactions are given in Table 8. The temperature variations of the rate constants are shown in Figures 22 and 23.

The initial reactivity of the UBe_{13} with the gases increases in the order water vapor, nitrogen, and oxygen as shown in Figures 21, 22, and 23. Also, the reactivity of the UBe_{13} with nitrogen is about the same as that of pure uranium with nitrogen. However, the reaction of UBe_{13} with oxygen and water vapor is slower than that of uranium with oxygen.

The reaction products that could be detected by X-ray analysis as seen in Table 7 were: UN and UN_2 for the nitrogen reactions, U_3O_8 for the oxygen reaction, and UO_2 for the water-vapor reaction.

Reactivity of UB_2. A sintered compact of UB_2 (Specimen 12829-84), arc melted to a density 96.5 per cent of theoretical, was investigated. Representative experimental curves for the reaction with nitrogen, oxygen, and water vapor are shown in Figure 24.

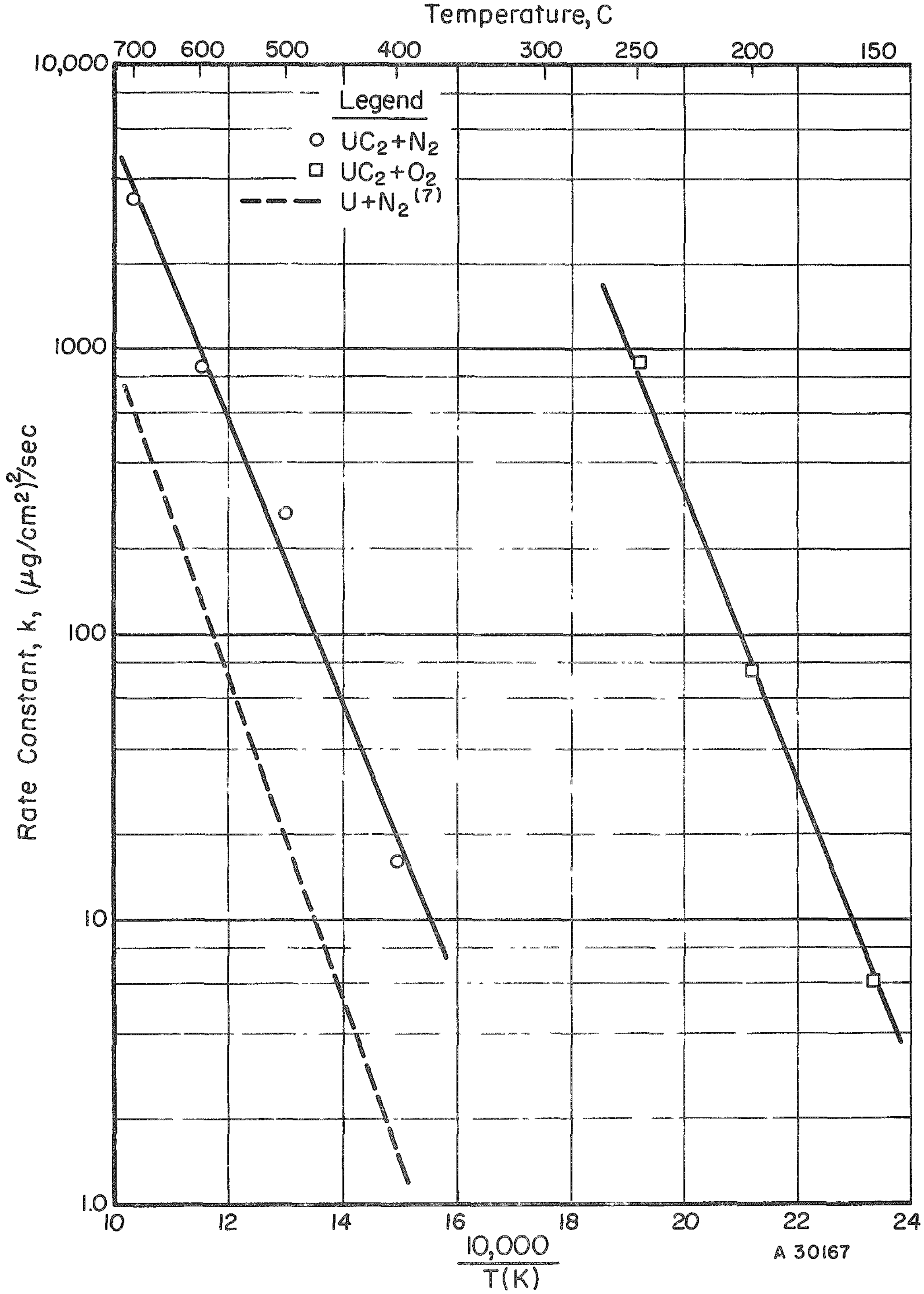


FIGURE 19. TEMPERATURE VARIATION OF THE PARABOLIC RATE CONSTANT FOR THE REACTIONS OF UC_2 WITH NITROGEN AND OXYGEN

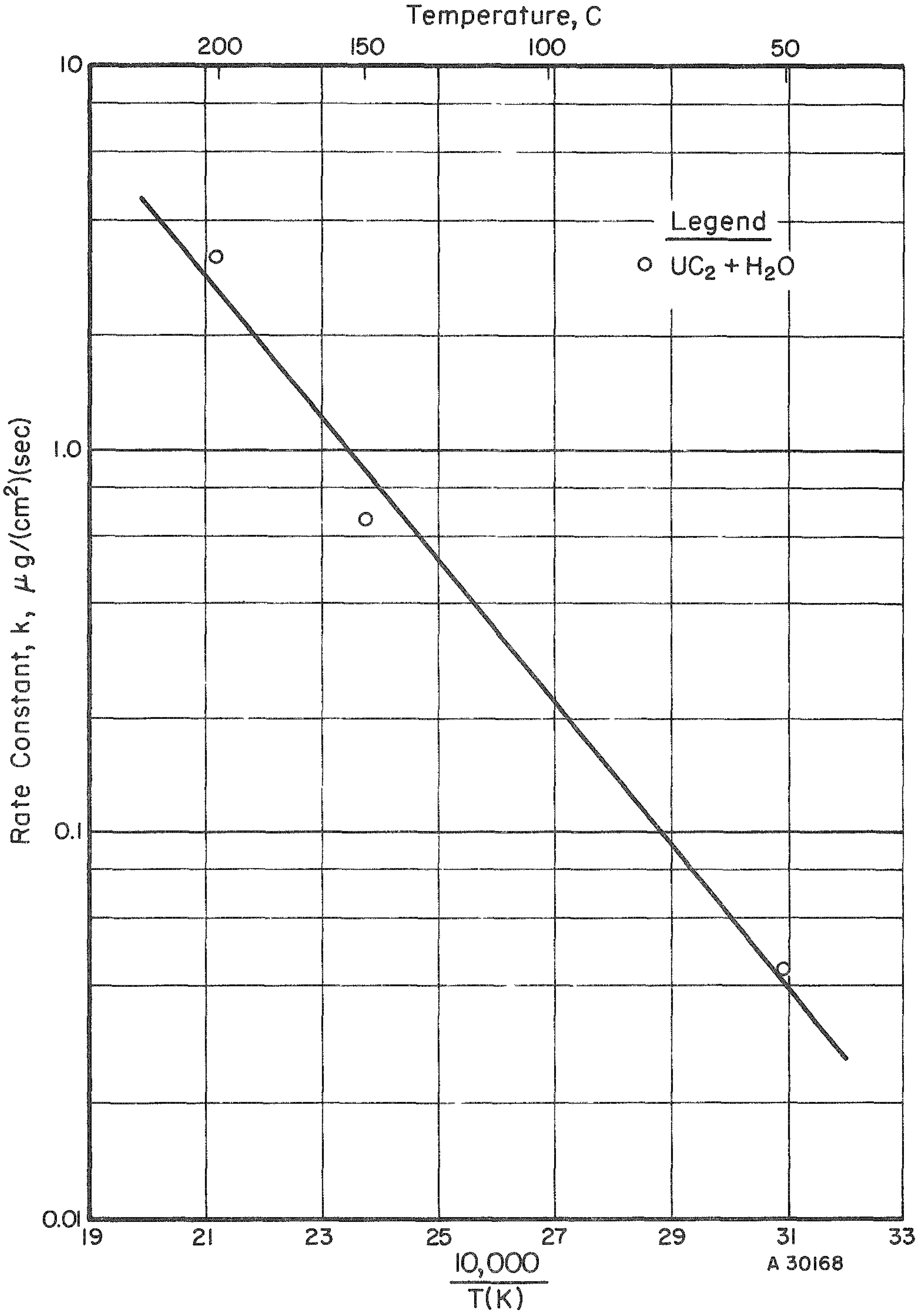


FIGURE 20. TEMPERATURE VARIATION OF THE LINEAR RATE CONSTANT FOR THE REACTION OF UC_2 WITH WATER VAPOR

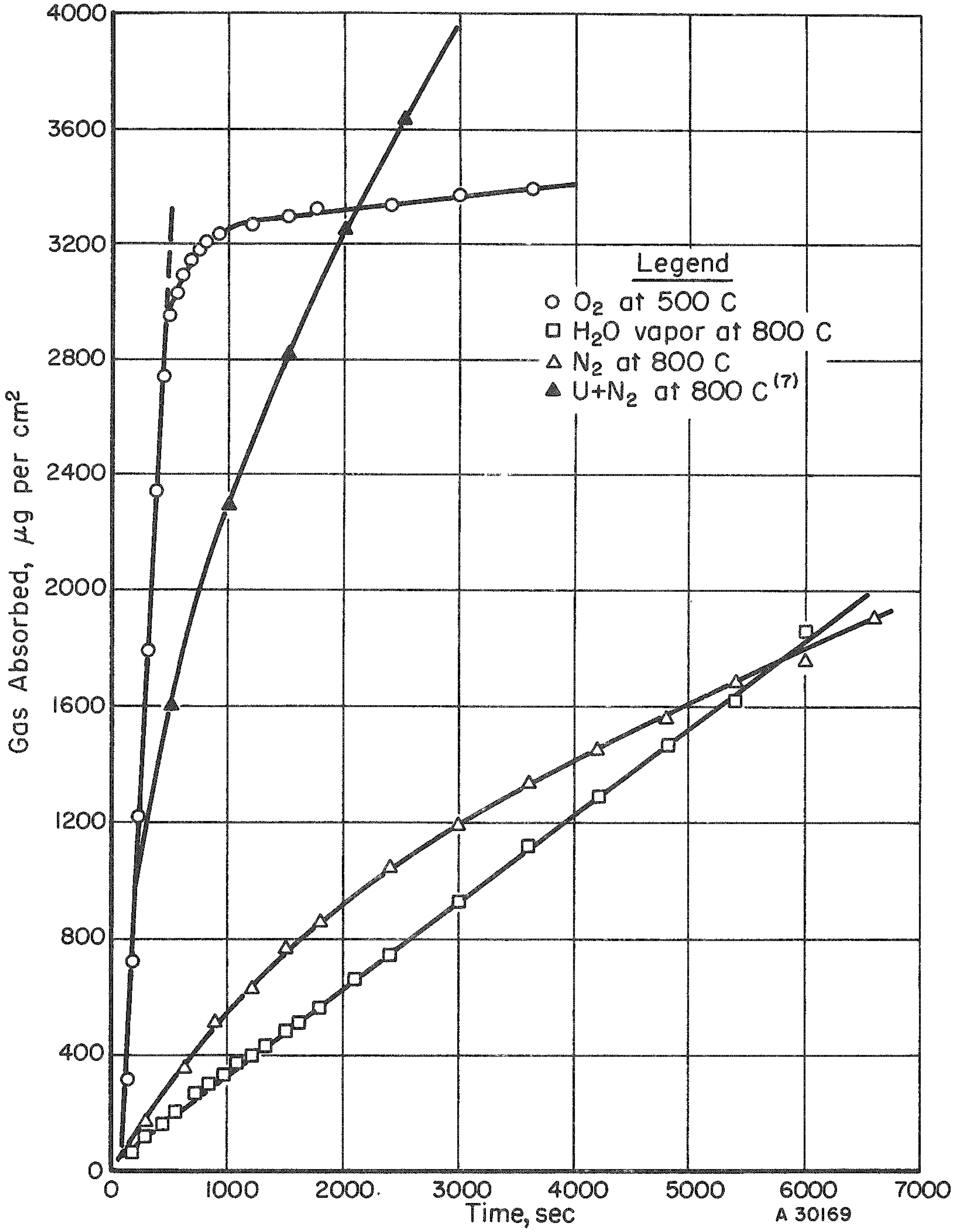


FIGURE 21. REACTIONS OF UBe_{13} WITH NITROGEN, OXYGEN, AND WATER VAPOR

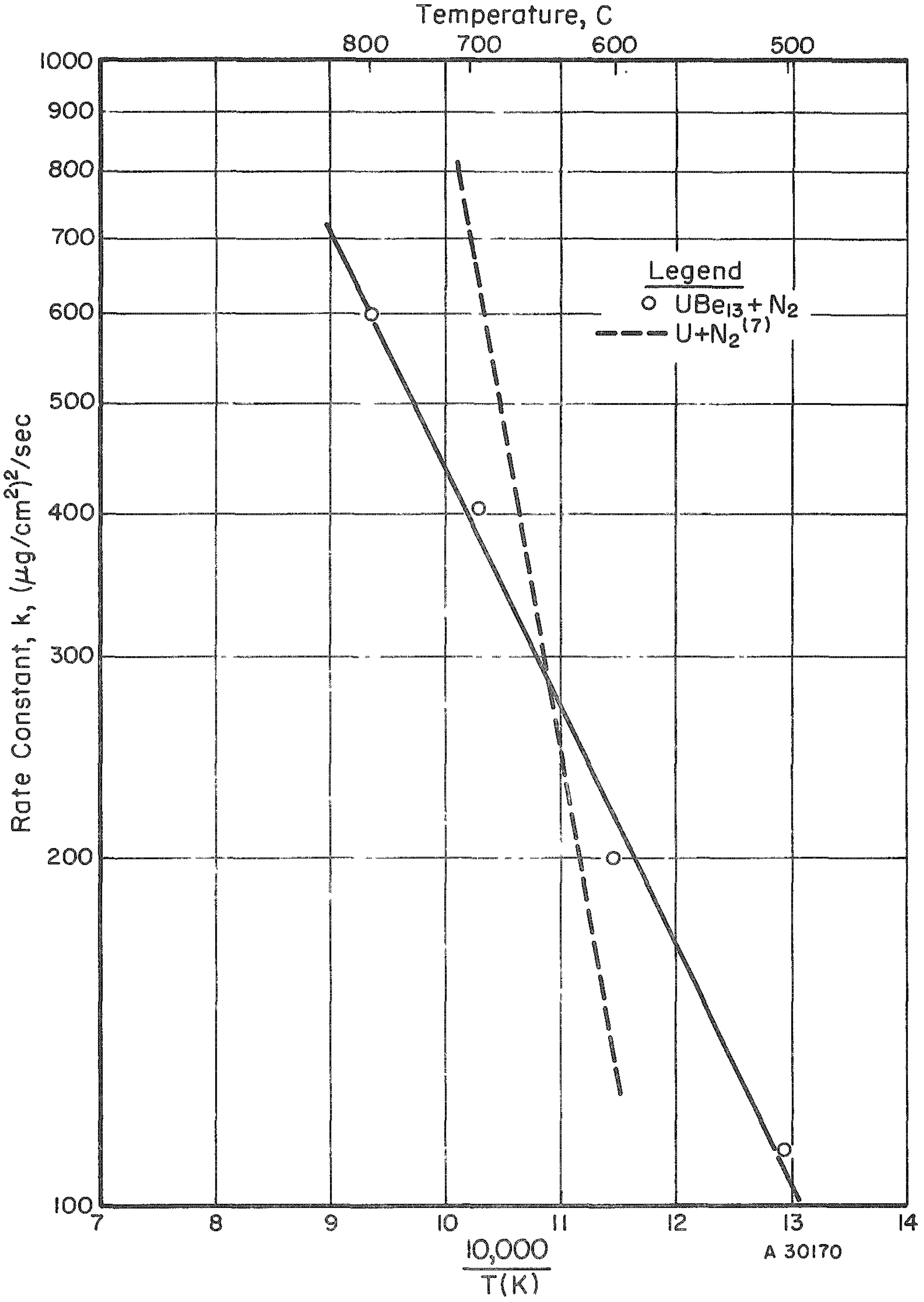


FIGURE 22. TEMPERATURE VARIATION OF THE PARABOLIC RATE CONSTANT FOR THE REACTION OF UBe_{13} WITH NITROGEN

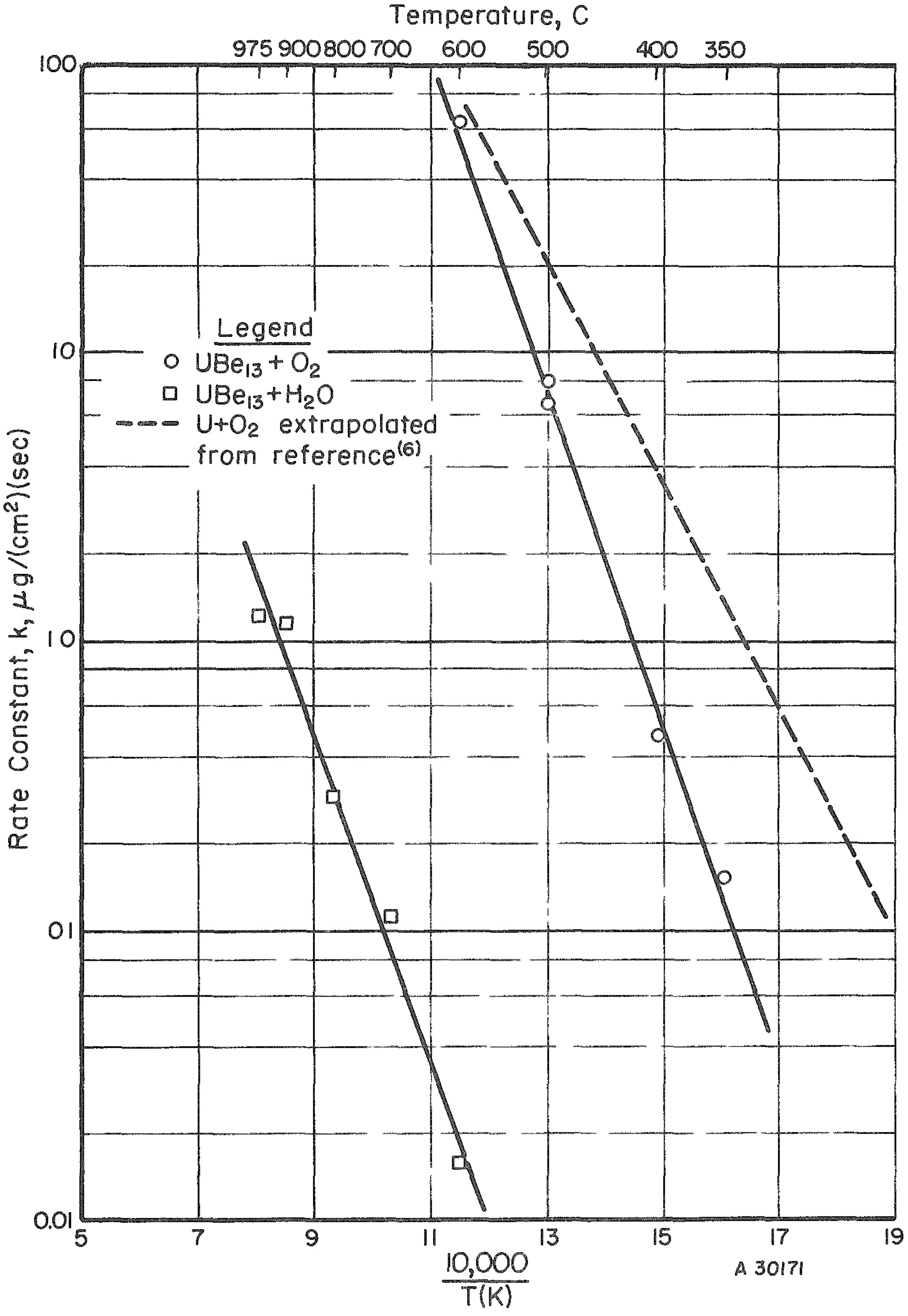


FIGURE 23. TEMPERATURE VARIATION OF THE LINEAR RATE CONSTANT FOR THE REACTIONS OF UBe_{13} WITH OXYGEN AND WATER VAPOR

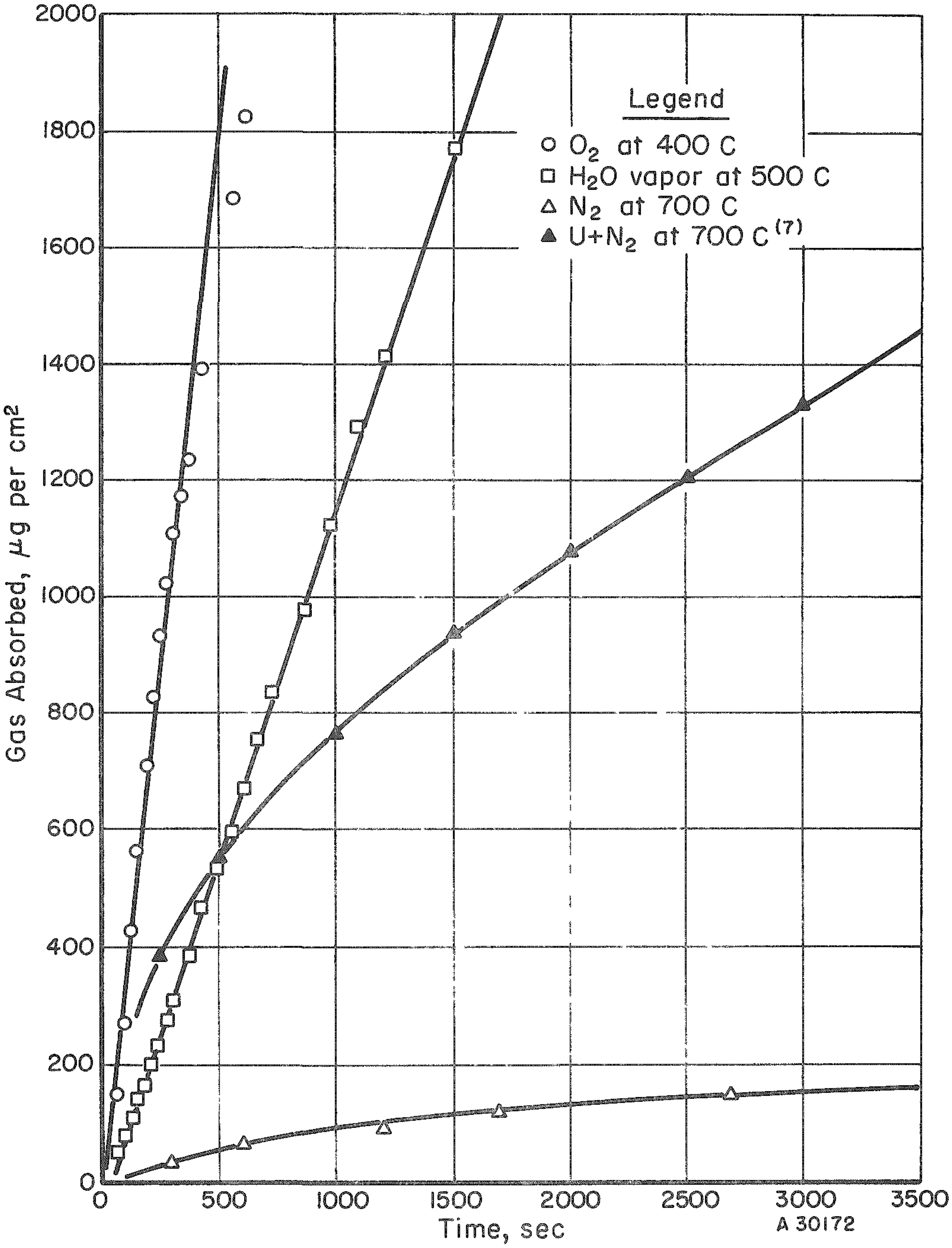


FIGURE 24. REACTIONS OF UB_2 WITH NITROGEN, OXYGEN, AND WATER VAPOR

The reaction of UB_2 with nitrogen determined from 700 to 800 C followed parabolic behavior. Both the oxygen and the water vapor reacted linearly initially in the ranges 200 to 400 C and 500 to 600 C, respectively. In all cases, the reaction started to decrease slowly with time after the initial linear reaction. Slopes of the log-log plots, rate constants, and Arrhenius constants are given in Table 9. It can be seen that the oxygen reaction proceeded anisothermally at 500 C. The variations of the rate constants with temperature are plotted in Figures 25 and 26.

Comparison of the data in Figures 24, 25, and 26 shows that the reactivity of UB_2 with the gases increases in the order nitrogen, water vapor, and oxygen. Also, the reaction of UB_2 with nitrogen is considerably slower than that of uranium with nitrogen. There appears to be very little difference in the reactivities of either UB_2 or uranium with oxygen.

The reaction products, given in Table 7, that were detected by X-ray analysis were: UN_x where x is between 1.5 and 2 for the nitrogen reaction, U_3O_8 for the oxygen reaction, and UO_2 for the water-vapor reaction.

Comparison of Reactivities. The data described above supplement those for the study of the reactions of UAl_2, USi, USi_2, USi_3, and U_3Si_2 with nitrogen and oxygen reported in BMI-1223.(2) A comparison of all the data is presented below.

The rates of reaction of oxygen with UBe_{13}, UB_2, and USi increase in that order, and initially follow a linear rate law up to 400 C. Above about 400 C, both the UB_2 and USi reacted anisothermally, that is, the temperature of the specimens increased and caused the rate of reaction to increase rapidly with time. This resulted in complete combustion within a short time. In contrast, the UBe_{13} reaction was isothermal up to 600 C and stopped almost entirely, long before complete oxidation occurred. The reactions of oxygen with the compounds, listed in order of increasing rates, USi_3, U_3Si_2, USi_2, and UC_2 follow a parabolic rate law up to about 400 C, while the oxidation of UAl_2 follows a cubic law. In contrast, pure uranium oxidizes linearly at these temperatures. In nearly all cases, U_3O_8 was the only product which was detected by X-ray analysis.

The reaction of nitrogen with all the compounds follows a parabolic law at temperatures up to 600 to 800 C. UB_2 was the only material that reacted more slowly with nitrogen than did uranium under similar conditions. However, in all cases the reactions of the compounds with nitrogen were slower than the reactions with oxygen at the same temperatures. The nitrogen reaction product in each case was principally UN_x, where x is between about 1.5 and 2.

The reactions of water vapor at 29 mm of mercury with UBe_{13}, UB_2, and UC_2 follow a linear rate law with the exception of UC_2. These reactions are slower than the reaction of oxygen with the compounds. UO_2 was the only product of reaction with water vapor which was detected by X-ray analysis.

Reactivity of Arc-Melted UC and UC_2. Some qualitative data were obtained at 200 C for the reaction of oxygen with arc-melted UC and UC_2. The reactions appeared to follow a parabolic rate law, and the UC_2 reacted a little more slowly with oxygen than did the UC. Also, both the arc-melted UC and UC_2 reacted slightly more slowly with oxygen than did the sintered UC_2.

TABLE 8. REACTION OF UBe$_{13}$ WITH NITROGEN, OXYGEN, AND WATER VAPOR

Gas Reacted	Temperature, C	Slope of Log-Log Plot	Rate Constant, k Linear, $\mu g/(cm^2)(sec)$	Rate Constant, k Parabolic, $(\mu g/cm^2)^2/sec$	Constants for k = A exp (-E/RT) A	Constants for k = A exp (-E/RT) E, cal per mole
Nitrogen	500	0.46	--	112	5.10×10^4	9,450 ± 520
	600	0.56	--	200		
	700	0.53	--	408		
	800	0.53	--	599		
Oxygen	350	1.0	0.15	--	1.98×10^8	26,200 ± 750
	400	0.98	0.44	--		
	500	1.0	8.0	--		
	500	1.0	6.6	--		
	600	0.92	6.2	--		
Water vapor	600	0.75	0.016	--	5.46×10^4	25,800 ± 1,500
	700	0.98	0.11	--		
	800	0.91	0.29	--		
	900	0.98	1.16	--		
	975	1.0	1.23	--		

TABLE 9. REACTION OF UB$_2$ WITH NITROGEN, OXYGEN, AND WATER VAPOR

Gas Reacted	Temperature, C	Slope of Log-Log Plot	Rate Constant, k Linear, $\mu g/(cm^2)(sec)$	Rate Constant, k Parabolic, $(\mu g/cm^2)^2/sec$	Constants for k = A exp (-E/RT) A	Constants for k = A exp (-E/RT) E, cal per mole
Nitrogen	700	0.59	--	12.6	1.42×10^5	18,000 ± 480
	750	0.62	--	20.5		
	800	0.52	--	30.0		
Oxygen	200	0.96	0.016	--	4.18×10^5	16,100 ± 1,900
	300	0.99	0.18	--		
	400	1.0	3.3	--		
	500$^{(a)}$	--	--	--		
Water vapor	500	1.1	1.2	--	2.01×10^6	22,000 ± 800
	550	0.96	3.1	--		
	600	0.91	6.1	--		

(a) Reacted anisothermally.

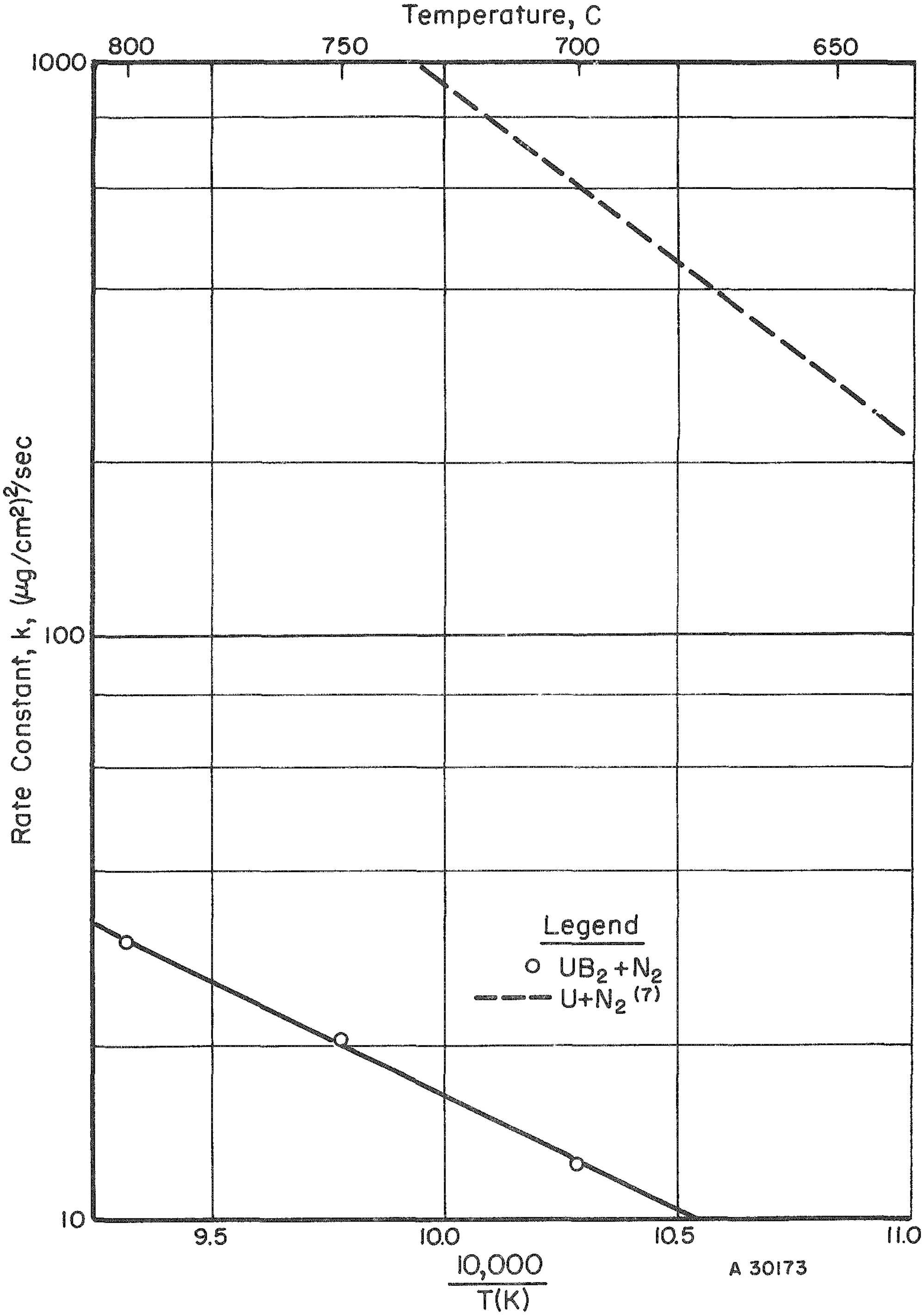


FIGURE 25. TEMPERATURE VARIATION OF THE PARABOLIC RATE CONSTANT FOR THE REACTION OF UB_2 WITH NITROGEN

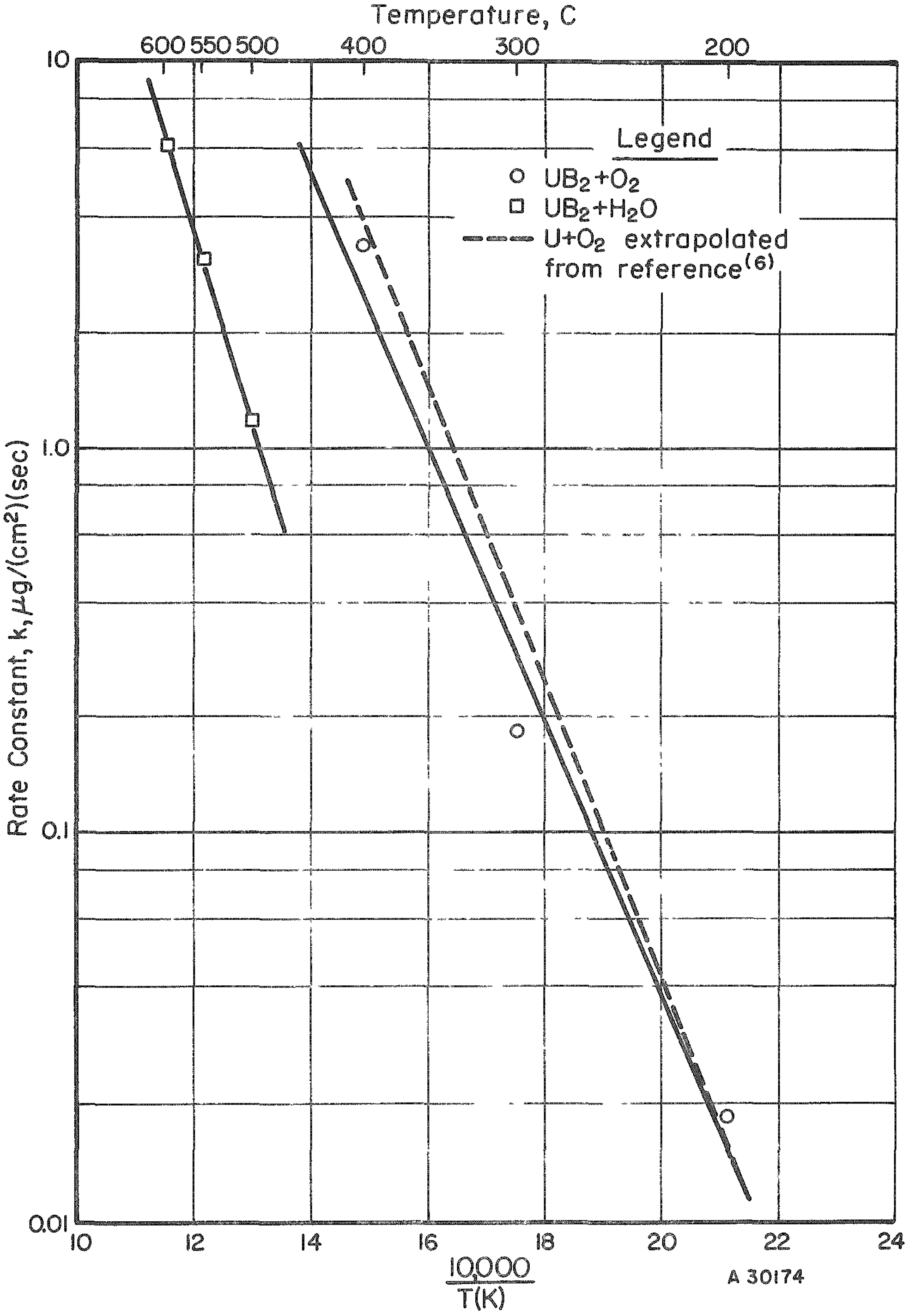


FIGURE 26. TEMPERATURE VARIATION OF THE LINEAR RATE CONSTANTS FOR THE REACTIONS OF UB_2 WITH OXYGEN AND WATER VAPOR

Thermodynamic Measurements and Estimates

Heat-of-Formation Measurements for UC

(Work done by J. W. Droege, A. W. Lemmon, Jr.,
and R. B. Filbert, Jr.)

The heat of formation of UC was determined. An oxygen-bomb calorimeter was used to determine the heat of combustion. This result was combined with the known heats of formation of U_3O_8 and CO_2 to give a value of -20.0 ± 5.0 kcal per mole of UC for the heat of formation at 25 C from the elements in their standard states. In connection with this work, the heat of combustion of UO_2 also was investigated.

The experimental details of the heat-of-formation measurements are given in the Appendix.

Estimated Thermodynamic Values

(Work done by J. J. Ward)

Estimated Heat-Capacity Equations. Heat-capacity equations were estimated for a number of binary uranium compounds using the methods given by Kubaschewski and Evans(8). The C_p values estimated from these equations may be used in the thermal-diffusivity equation, or in calculating the change with temperature of the standard free energy of formation of the compounds. The estimated heat-capacity equations are given in Table 10.

Specific heats of three of the silicides given in Table 10 were determined by enthalpy measurements. The experimental results were given in Table 6 on page 22 of BMI-1223.(2) Estimated specific-heat values calculated from the equations for USi_3 and U_3Si are compared with the experimental measurements for 200 C in Table 11.

It can be seen that there is good agreement between the estimated and measured values.

Estimated Free Energies of Formation. In BMI-1124(1), free energies of formation for several binary uranium compounds were estimated, and these estimated values were then used to calculate free energies of reactions with common reagents. In estimating the free energies of formation it was assumed that $\Delta C_p = 0$. This was in accord with the method used by Brewer.(10) Later in the program, the heat-capacity equations given in the previous section were estimated and these were then used to re-estimate the free energies of formation of the same five binary uranium compounds. In addition, the equation for the free energy of formation of UC was estimated using the experimentally determined heat of combustion which was reported at the beginning of this section.

TABLE 10. ESTIMATED HEAT-CAPACITY EQUATIONS FOR SEVERAL BINARY URANIUM COMPOUNDS

Compound	Equation [C_p = Heat Capacity in Cal/(Gram Mole) (K)]	Temperature Range, K
$UC(s)$	$C_p = 7.6 + 2.85 \times 10^{-3}T$	298 - 2400
$UC_2(s)$	$C_p = 8.92 + 3.95 \times 10^{-3}T$	No range given[a]
$UN(s)$	$C_p = 10.6 + 7.0 \times 10^{-3}T$	298 - 3000
$UAl_2(s)$	$C_p = 16.0 + 6.4 \times 10^{-3}T$	298 - 1863
$US(s)$	$C_p = 13.0 + 1.5 \times 10^{-3}T$	298 - 2000
$UB_2(s)$	$C_p = 10.9 + 3.6 \times 10^{-3}T$	298 - 2000
$UB_4(s)$	$C_p = 15.3 + 7.0 \times 10^{-3}T$	298 - 2000
$USi_2(s)$	$C_p = 17.24 + 2.04 \times 10^{-3}T - 2.12 \times 10^{+5}T^{-2}$	1100 - 1873
$USi_3(s)$	$C_p = 26.84 + 3.06 \times 10^{-3}T - 3.18 \times 10^{+5}T^{-2}$	298 - 1500
$U_3Si(s)$	$C_p = 33.06 + 1.02 \times 10^{-3}T - 1.06 \times 10^{+5}T^{-2}$	298 - 900

(a) From Reference (9).

TABLE 11. COMPARISON OF SPECIFIC HEATS OF USi_3 AND U_3Si AS ESTIMATED AND AS MEASURED AT 200 C

Compound	Specific Heat, cal/(g)(C) Estimated	Measured
USi_3	0.084	0.081
U_3Si	0.045	0.042

TABLE 12. ESTIMATED STANDARD FREE-ENERGY EQUATIONS AS A FUNCTION OF TEMPERATURE FOR SOME BINARY URANIUM COMPOUNDS

Reaction	Temperature Range, K	Standard Free Energy Equation: Free Energy, ΔF_T°, at Temperature, T, K
$U(\alpha) + 1/2\ N_2(g) \rightarrow UN(s)$	298.16 - 935	$\Delta F_T^\circ = -81{,}320 - 8.94T\log_{10}T - 0.77 \times 10^{-3}T^2 + 0.35 \times 10^5T^{-1} + 43.16T$
$U(\beta) + 1/2\ N_2(g) \rightarrow UN(s)$	935-1045	$\Delta F_T^\circ = -79{,}100 + 6.70T\log_{10}T - 4.78 \times 10^{-3}T^2 + 1.89T$
$U(\gamma) + 1/2\ N_2(g) \rightarrow UN(s)$	1045 - 1405	$\Delta F_T^\circ = -81{,}270 + 4.44T\log_{10}T - 4.78 \times 10^{-3}T^2 + 7.01T$
$U(\ell) + 1/2\ N_2(g) \rightarrow UN(s)$	1405 - above	$\Delta F_T^\circ = -84{,}470 + 4.44T\log_{10}T - 4.78 \times 10^{-3}T^2 + 9.29T$
$U(\alpha) + 2\ Si(s) \rightarrow USi_2(s)$	298.16 - 935	$\Delta F_T^\circ = -35{,}577 - 5.23T\log_{10}T + 3.55 \times 10^{-3}T^2 - 0.32 \times 10^5T^{-1} + 14.18T$
$U(\beta) + 2\ Si(s) \rightarrow USi_2(s)$	935 - 1045	$\Delta F_T^\circ = -33{,}360 + 10.41T\log_{10}T - 0.46 \times 10^{-3}T^2 - 0.67 \times 10^5T^{-1} - 30.87T$
$U(\gamma) + 2\ Si(s) \rightarrow USi_2(s)$	1045 - 1405	$\Delta F_T^\circ = -35{,}530 + 8.15T\log_{10}T - 0.46 \times 10^{-3}T^2 - 0.67 \times 10^5T^{-1} - 21.96T$
$U(\ell) + 2\ Si(s) \rightarrow USi_2(s)$	1405 - above	$\Delta F_T^\circ = -38{,}730 + 8.15T\log_{10}T - 0.46 \times 10^{-3}T^2 - 0.67 \times 10^5T^{-1} - 19.68T$
$U(\alpha) + 1/2\ S_2(g) \rightarrow US(s)$	298.16 - 935	$\Delta F_T^\circ = -56{,}900 - 12.30T\log_{10}T + 3.33 \times 10^{-3}T^2 + 0.15 \times 10^5T^{-1} + 55.67T$
$U(\beta) + 1/2\ S_2(g) \rightarrow US(s)$	935 - 1045	$\Delta F_T^\circ = -54{,}680 + 5.34T\log_{10}T - 0.68 \times 10^{-3}T^2 - 0.20 \times 10^5T^{-1} + 10.62T$
$U(\gamma) + 1/2\ S_2(g) \rightarrow US(s)$	1045 - 1405	$\Delta F_F^\circ = -56{,}850 + 1.08T\log_{10}T - 0.68 \times 10^{-3}T^2 - 0.20 \times 10^5T^{-1} + 19.52T$
$U(\ell) + 1/2\ S_2(g) \rightarrow US(s)$	1405 - above	$\Delta F_T^\circ = -60{,}050 + 1.08T\log_{10}T - 0.68 \times 10^{-3}T^2 - 0.20 \times 10^5T^{-1} + 21.80T$
$U(\alpha) + 2\ B(s) \rightarrow UB_2(s)$	298.16 - 935	$\Delta F_T^\circ = -90{,}470 + 10.20T\log_{10}T - 6.61 \times 10^{-3}T^2 - 0.35 \times 10^5T^{-1} - 19.63T$
$U(\beta) + 2\ B(s) \rightarrow UB_2(s)$	935 - 1045	$\Delta F_T^\circ = -88{,}750 + 25.84T\log_{10}T - 10.62 \times 10^{-3}T^2 - 0.70 \times 10^5T^{-1} - 64.68T$
$U(\gamma) + 2\ B(s) \rightarrow UB_2(s)$	1045 - 1405	$\Delta F_T^\circ = -90{,}920 + 23.58T\log_{10}T - 10.62 \times 10^{-3}T^2 - 0.70 \times 10^5T^{-1} - 55.78T$
$U(\ell) + 2\ B(s) \rightarrow UB_2(s)$	1405 - above	$\Delta F_T^\circ = -94{,}120 + 23.58T\log_{10}T - 10.62 \times 10^{-3}T^2 - 0.70 \times 10^5T^{-1} - 53.50T$

TABLE 12. (Continued)

Reaction	Temperature Range, K	Standard Free Energy Equation: Free Energy, ΔF°_T, at Temperature, T, K
$U(\alpha) + 2\,C(graph) \rightarrow UC_2(s)$	298.16 - 935	$\Delta F^\circ_T = -39{,}760 + 6.15 T\log_{10}T + 3.05 \times 10^{-3}T^2 - 1.75 \times 10^5 T^{-1} - 21.67T$
$U(\beta) + 2\,C(graph) \rightarrow UC_2(s)$	935 - 1045	$\Delta F^\circ_T = -37{,}540 + 21.79 T\log_{10}T - 0.96 \times 10^{-3}T^2 - 2.10 \times 10^5 T^{-1} - 66.72T$
$U(\gamma) + 2\,C(graph) \rightarrow UC_2(s)$	1045- 1405	$\Delta F^\circ_T = -39{,}710 + 19.53 T\log_{10}T - 0.96 \times 10^{-3}T^2 - 2.10 \times 10^5 T^{-1} - 57.82T$
$U(\delta) + 2\,C(graph) \rightarrow UC_2(s)$	1405 - above	$\Delta F^\circ_T = -42{,}910 + 19.53 T\log_{10}T - 0.96 \times 10^{-3}T^2 - 2.10 \times 10^5 T^{-1} - 55.54T$
$U(\alpha) + C(graph) \rightarrow UC(s)$	298.16 - 935	$\Delta F^\circ_T = -19{,}290 - 0.25 T\log_{10}T + 1.55 \times 10^{-3}T^2 + 0.70 \times 10^5 T^{-1} + 0.37T$
$U(\beta) + C(graph) \rightarrow UC(s)$	935 - 1045	$\Delta F^\circ_T = -17{,}070 + 15.39 T\log_{10}T - 2.46 \times 10^{-3}T^2 + 0.35 \times 10^5 T^{-1} - 44.68T$
$U(\gamma) + C(graph) \rightarrow UC(s)$	1045 - 1405	$\Delta F^\circ_T = -19{,}240 + 13.13 T\log_{10}T - 2.46 \times 10^{-3}T^2 + 0.35 \times 10^5 T^{-1} - 35.78T$
$U(\delta) + C(graph) \rightarrow UC(s)$	1405 - above	$\Delta F^\circ_T = -22{,}440 + 13.13 T\log_{10}T - 2.46 \times 10^{-3}T^2 + 0.35 \times 10^5 T^{-1} - 33.50T$

TABLE 13. COMPUTED STANDARD FREE-ENERGY VALUES

Reaction	ΔF_f°, cal per mole, At Temperature Shown					
	1000 K	1100 K	1200 K	1300 K	1400 K	1500 K
$U(\beta, \gamma, \ell) + 1/2N_2(g) \rightarrow UN(s)$	-61,890	-64,490	-63,340	-62,260	-61,270	-60,140
$U(\beta, \gamma, \ell) + 2Si(s) \rightarrow USi_2(s)$	-33,530	-33,040	-32,490	-31,920	-31,330	-30,500
$U(\beta, \gamma, \ell) + 1/2S_2(g) \rightarrow US(s)$	-34,740	-32,610	-30,430	-28,270	-26,110	-23,750
$U(\beta, \gamma, \ell) + 2B(s) \rightarrow UB_2(s)$	-86,600	-86,310	-86,080	-85,980	-86,020	-85,970
$U(\beta, \gamma, \ell) + 2C(graph) \rightarrow UC_2(s)$	-40,060	-39,330	-38,490	-37,600	-36,670	-35,480
$U(\beta, \gamma, \ell) + C(graph) \rightarrow UC(s)$	-18,010	-17,620	-17,170	-16,730	-16,300	-15,610

TABLE 14. SOURCES OF DATA USED IN ESTIMATING THERMODYNAMIC EQUATIONS

Compound or Element	Sources of Indicated Thermodynamic Functions(a)			
	ΔF°_{f298}	ΔH°_{f298}	ΔS°_{f298}	C_p(b)
U(α)	--	--	--	1
U(β)	7	3	7	1
U(γ)	7	3	7	1
U(ℓ)	7	3	7	3
S_2(g)	--	--	--	1
Si(s)	--	--	--	1
B(s)	--	--	--	1
N_2(g)	--	--	--	1
UN(s)	6	6	6	2
USi_2(s)	7	2	2	2
UB_2(s)	7	2	2	2
UC_2(s)	6	6	6	2
US(s)	7	2	2	2
UC(s)	7	4	5	2

(a) Sources:

1. Kelley, K. K., Bulletin 476, U. S. Bureau of Mines (1949).
2. Estimated.
3. Coughlin, J. P., Bulletin 542, U. S. Bureau of Mines (1952).
4. This report.
5. Campbell, I. E., High Temperature Technology, John Wiley and Sons, Inc., New York (1956).
6. Rossini, F. D., Circular 500, National Bureau of Standards (1952).
7. Computed by derived functions.

(b) ΔC_p values calculated from these C_p values.

The method used in estimating the free energy of formation as a function of temperature is essentially the one described on pp 173 and 174 of Lewis and Randall(11).

The estimated free-energy-of-formation equations are given in Table 12. There are four equations for each compound, corresponding to the four states of uranium. This makes possible the computation of free energies over a complete range of temperatures. Table 13 contains numerical values for the free energies of formation over a range of temperatures. Table 14 gives the sources for the data used in these computations.

REFERENCES

(1) Loch, L. D., Engle, G. B., Snyder, M. J., and Duckworth, W. H., "Survey of Refractory Uranium Compounds", BMI-1124 (August 7, 1956).

(2) Snyder, M. J., and Duckworth, W. H., "Properties of Some Refractory Uranium Compounds", BMI-1223 (September 9, 1957).

(3) Secrest, A. C., Foster, E. L., Jr., and Dickerson, R. F., "Preparation and Properties of Uranium Monocarbide Castings", BMI-1309 (January 2, 1959).

(4) Wagner, H. E., and Harman, C. G., "Hydrostatic Pressing as a Fabrication Technique", Amer. Ceram. Soc. Bull., 30, 341 (1951).

(5) The Reactor Handbook, Vol. 3, Section 1, "General Properties of Materials", AECD-3647 (March, 1955) p 407.

(6) Cubicciotti, Daniel, "The Reaction Between Uranium and Oxygen", J. Am. Chem. Soc., 74, 1079 (1952).

(7) Mallett, M. W., and Gerds, A. F., "Reaction of Nitrogen With Uranium", J. Electrochem. Soc., 102, 292 (1955).

(8) Kubaschewski, O., and Evans, E. L., Metallurgical Thermochemistry, Academic Press Inc., New York (1951), pp 167-174.

(9) Katz, J. J., and Rabinowitch, E., The Chemistry of Uranium, McGraw-Hill Book Co., Inc., New York (1951), p 219.

(10) Brewer, Leo, Bromley, L. A., Gilles, P. W., and Lofgren, N. L., Paper No. 4, "Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics", L. L. Quill, ed., National Nuclear Energy Series, McGraw-Hill Book Co., Inc., New York (1950).

(11) Lewis, G. N., and Randall, M., Thermodynamics and the Free Energy of Chemical Substances, McGraw-Hill Book Co., Inc., New York (1923).

(12) Van Dusen, M. S., and Shelton, S. M., "Apparatus for Measuring Thermal Conductivity of Metals up to 600 C", J. Research, National Bureau of Standards, 12, 429 (1934).

(13) Hoge, H. J., "Vapor Pressure and Fixed Points of Oxygen and Heat Capacity in the Critical Region", J. Research, National Bureau of Standards, 44, 321 (1950).

(14) Coops, J., Van Nes, K., Kentie, A., and Diensk, J. W., Rec. Trav. Chim. des Pays-Bas, 66, 113 (1947).

(15) Hubbard, W., Scott, D. W., and Waddington, G., Chapter 5, Experimental Thermochemistry, F. D. Rossini, ed., Interscience Publishers, Inc., New York (1956).

(16) Huber, E. J., Holley, C. E., Jr., and Meierkord, B. H., J. Am. Chem. Soc., 74, 3406 (1952).

ABT:MJS:WHD/bjw

APPENDIX

EXPERIMENTAL APPARATUS AND METHODS

APPENDIX

EXPERIMENTAL APPARATUS AND METHODS

Preparation and Fabrication of Uranium Compounds

Arc Melting

A description of the arc-melting furnace and technique of operation was given on pages 2 and 3 of BMI-1223.(2)

Solid-Solid Reactions

In addition to the vacuum-furnace technique described on pages 2 through 5 of BMI-1223, a second technique was employed in the preparation and fabrication of UBe_{13}. Beryllium is volatile at relatively low temperatures and, accordingly, UBe_{13} cannot be prepared in a vacuum furnace. Uranium hydride and beryllium powder were intimately mixed in an argon atmosphere, hydrostatically compacted, and heated in an induction furnace under argon at a 1-atm pressure. The temperature was raised slowly until all the hydrogen had evolved. The temperature was then raised quickly to the point at which rapid formation of UBe_{13} took place.

In some cases, the resultant, porous compact of UBe_{13} was ground, compacted, and sintered again under the same conditions to provide a more dense specimen.

Gas-Solid Reactions

Uranium nitride was prepared by direct reaction between metallic uranium and purified nitrogen.

Uranium metal in the form of 1/8-in.-thick sheet was cut into pieces approximately 1/4 in. square and then pickled in 1:1 HNO_3 solution. After rinsing in distilled water and drying with cp acetone, about 200 g of the metal was placed in a Vycor reaction tube which was then sealed to the vacuum apparatus. The apparatus was evacuated, the uranium was heated to 850 C, and Matheson prepurified nitrogen (>99.99 per cent pure) was introduced into the apparatus, where it reacted to form U_2N_3. Upon completion of nitriding, the U_2N_3 was heated for about 1 hr at 1300 C to a final pressure of 18 μ of mercury. The heating dissociated the U_2N_3 to UN.

Crushing and Grinding

Arc-melted material was first crushed in a diamond mortar to minus 20 mesh in an argon atmosphere after which it was ball milled in 1/2-pt porcelain jars with high-alumina porcelain balls. During ball milling, the material was covered with an inert

---

(2) References at end of text of report.

organic material such as petroleum ether or trichloroethylene to minimize oxidation. Late in the program, ball milling was done in a pint-size rubber-lined mill with uranium slugs.

After ball milling, the average particle sizes were determined by standard petrographic techniques.

Thermal-Conductivity Measurements

Apparatus and Method

The apparatus and method used in making the thermal-conductivity measurements was similar to those described by Van Dusen and Shelton.(12) The method in brief consisted of heating one end of a cylindrical specimen, measuring the temperature gradients along the specimen, and determining the rate of heat flow through the specimen by means of a metal standard of known thermal conductivity attached to the cold end of the specimen. Radial heat flow into or away from the specimen was minimized by radiation shielding and an encircling guard tube in which temperatures were adjusted to match those in the specimen and standard at corresponding levels. The radiation shielding was provided by filling the annular space between the specimen assembly and the guard cylinder with small pellets rolled from fractional-mil-thick tantalum foil. Three 36-gage Chromel-Alumel thermocouples were placed in the Armco iron standard. This permitted the calculation of two thermal-conductivity values, each at a different mean temperature, for each thermal equilibrium. The specimens were protected from oxidation by a vacuum of 2×10^{-5} mm of mercury.

Gas-Reaction Studies

Apparatus

A Sartorius Electrona microbalance was used to measure the rate of weight gain of a sample. This balance is essentially an electronically controlled null-type instrument. The amount of current necessary to maintain balance is measured on a microammeter which is calibrated directly in micrograms.

The balance was evacuated by a three-stage mercury-diffusion pump backed by a mechanical vacuum pump. A liquid-nitrogen cold trap was placed between the pumping system and the microbalance to prevent back diffusion of mercury into the balance section. System pressures were measured by an ionization gage connected in the system between the cold trap and balance.

Pressure changes during the reactions were minimized by the large volume of the system.

The specimen was placed in a 1/4-in.-square platinum boat to prevent loss of material should flaking of the specimen occur during the reaction. The boat was suspended from the beam of the balance inside the reaction tube by a platinum wire 0.005 in. in diameter and 24 in. long. Boat and specimen were heated by a resistance-wound furnace. Temperatures were controlled to ±5 C.

Method

Rates of reaction of the uranium compounds with nitrogen, oxygen, and water vapor were determined from weight-gain measurements.

Irregular polyhedral specimens about 3/16 in. across and roughly equiaxed were cut from sample material. Specimen weights ranged from 0.05 to 0.35 g. The specimens were dry abraded with 240-, 400-, and 600-grit silicon carbide paper and suspended in the Vycor reaction tube of the microbalance. After heating to the desired temperature in a vacuum at a pressure of $<0.05\ \mu$ of mercury, the reaction was initiated by the addition of gas to the reaction tube. Reactions with either nitrogen or oxygen were made at 740 ± 5 mm of mercury. For reactions with water vapor the pressure was maintained at 29 ± 3 mm of mercury. Rate data were not taken until about 1 min after the reaction was started to allow for adsorption of the vapor by the platinum suspension wire, the platinum boat, and the balance beam. Preliminary experiments showed this time to be sufficient to establish equilibrium within the apparatus. Weight-gain measurements were made for 3 hr at 1/2 to 20-min intervals, depending on the rate of reaction.

The density of the uranium compounds for this study ranged from essentially 100 to about 89 per cent of theoretical for the most porous materials. Porosity plays a large role in determining the actual surface area of a specimen. However, in order to evaluate kinetic results, it is necessary to have a common basis of comparison. Therefore, the geometrical surface area was used in calculating the reaction rates in terms of weight gain per unit surface area.

The oxygen used in the oxidation reactions was obtained from the thermal decomposition of degassed potassium permanganate as described by Hoge.(13) The nitrogen was the Matheson prepurified grade which was dried by passing through a dry ice-acetone cold trap. Water vapor was obtained from deaerated distilled water prepared by boiling for 5 min at atmospheric pressure and then by holding for 1/2 hr in a vacuum at about 10 mm of mercury pressure to remove dissolved gases.

Electroplating Nickel on Uranium Silicide (USi) and Uranium Beryllide (UBe_{13})

Solutions Used

A. Alkaline cleaner

KOH	75 g per liter
Current density	50 amp per ft^2 cathodic
Temperature	25 C

B. Acid dip

HNO_3 (sp gr 1.42)	100 ml
H_2O	100 ml
Temperature	25-35 C

C. Anodic treatment

H_3PO_4 (85 per cent)	300 ml
H_2O	500 ml
HCl (concentrated)	16 ml
Current density	See below
Temperature	35-45 C
Cathodes	Carbon

D. Nickel-plating solution

$NiSO_4 \cdot 7H_2O$	145 g per liter
$MgSO_4$	75 g per liter
NH_4Cl	15 g per liter
H_3BO_3	15 g per liter
XXX-D*	20 ml per liter
pH	5.5 ± 0.1
Temperature	38 C
Current density	
Strike	30 amp per ft^2 1/2 min
Plate	15 amp per ft^2

Procedure for Plating on USi

(1) Clean cathodically in Solution A for 5 min

(2) Rinse in distilled water

(3) Dip in Solution B for 4 min

(4) Rinse with distilled water

(5) Treat anodically in Solution C at 25 amp per ft^2 for 10 min

(6) Rinse with distilled water

(7) Remove by lightly abrading with a 240-grit paper the loose powdery material that forms on the surface of the USi in Step (5)

(8) Rinse in distilled water

(9) Repeat Step (1)

(10) Rinse with distilled water

(11) Dip in Solution B for 4 min

(12) Rinse with distilled water

(13) Plate for 20 to 40 min.

---

*Harshaw Chemical Company, Cleveland, Ohio.

Procedure for Plating Nickel on UBe_{13}

(1) Clean cathodically in Solution A for 5 min

(2) Rinse with distilled water

(3) Dip in Solution B for 4 min

(4) Rinse with distilled water

(5) Treat anodically in Solution C at 50 amp per ft^2 for 5 min

(6) Rinse with distilled water

(7) Dip in Solution B for 4 min

(8) Rinse with distilled water

(9) Plate 20 to 40 min.

Experimental Details of Heat-of-Formation Measurements

Materials Used

The UC used in this work was prepared by repeated melting of a sample of uranium and carbon in a vacuum arc furnace. The product was ground in a dry box to pass through a 200-mesh sieve. The sample was normally kept in a dry box, but it evidently changed very little on exposure to air.

The purity of the sample was a source of major concern. It was, therefore, subjected to analysis by several techniques. As spectroscopic analysis showed no impurities greater than 0.02 w/o, it was assumed that the sample contained only uranium, carbon, and oxygen. Upon ignition at 800 C to U_3O_8, the sample gained weight by the factor 1.1224. Since U_3O_8 contains 84.804 w/o uranium, the sample consisted of 95.18 w/o uranium. Vacuum-fusion analysis showed 1410 ppm oxygen. After exposure to air, analysis showed 1400 and 1600 ppm oxygen. If a value of 1450 ppm oxygen is chosen, and if the further assumption is made that this is present as UO_2, then the complete analysis is 95.18 w/o uranium, 0.145 w/o oxygen, and 4.68 w/o carbon (by difference), which is equivalent to 97.24 w/o UC, 1.22 w/o UO_2, and 1.54 w/o uranium. This analysis was assumed to be correct for the sample used. It may be compared with the chemical analysis, which showed 95.4 w/o uranium and 4.73 w/o carbon. A powder sample submitted to X-ray diffraction showed only a clear UC pattern. Petrographic examination in reflected light showed cubic crystals of UC. No other phase could be detected. It was assumed that no free carbon was present. Since the heat of combustion of UC is not greatly different from that of U + C, no appreciable error is involved in this assumption.

Experimental Techniques

The calorimeter used was a modified Parr adiabatic instrument. The modification consisted in the addition of a heater and mercury thermostat to maintain a constant temperature in the jacket. Thus, the calorimeter was used as an isothermal instrument. The temperature of the jacket was maintained at 30 ± 0.01 C. A Parr double-valve self-sealing bomb was used. A copper heating wire was wound around the bomb to aid in adjusting the starting temperature such that the final temperature would be very close to the temperature of the jacket. The electrodes were replaced with platinum rods, to one of which was welded a platinum pan. An 8-cm length of 36-gage platinum-20 w/o iridium wire was gold-soldered between the electrodes. A small current was passed through this wire to ignite the sample. A correction, usually amounting to about 5 cal, was applied for the heat produced in the wire. A Leeds and Northrup resistance thermometer was used in conjunction with a Gl Mueller bridge and sensitive galvanometer for measuring the temperature of the water in which the bomb was immersed.

The method of calculation was that outlined by J. Coops and co-workers.(14) The energy equivalent was determined with Standard Sample 39g of benzoic acid, provided by the National Bureau of Standards. The standard deviation of eight determinations from the mean of 2470.9 cal per deg was 1.8 cal per deg.

Samples were weighed on an analytical balance. All weighings were reduced to vacuum. Results in absolute joules were converted to calories by dividing by 4.1840. Washburn corrections were made where applicable following the outline given by Hubbard.(15)

Preliminary determinations were made of the heat of combustion of UO_2, cotton thread, and Du Pont Mylar film, which were used as combustion aids. The UO_2 was used as received from Mallinckrodt. Its composition was determined by ignition at 800 C to U_3O_8 to be $UO_{2.033}$.

Three methods were used in the combustion of UC. In three experiments, by the first method, a powdered UC sample was placed in a U_3O_8-lined platinum crucible. An oxygen pressure of 30 atm was used. The UC burned to a black fused pellet, in one case melting through the crucible. Some of the product was vaporized and deposited on the walls of the bomb.

In another series of experiments, the UC was mixed with from 3 to 10 times its own weight of UO_2 and sealed inside an envelope of 0.5-mil Mylar film. The sample was placed in a platinum crucible and burned with 10 atm of oxygen. The dilution of the sample with UO_2 served to keep the temperature of the combustion low, so that only a few small beads of fused oxide resulted. The original purpose of the Mylar bag was to protect the sample from oxidation until the moment of ignition. This protection was probably not necessary, but the Mylar also served to insure the ignition of all the particles of sample. There was no assurance, however, that the Mylar was completely burned.

A third series of experiments was conducted in such a way as to exclude water from the bomb. It was hoped in this way to be able to determine the exact amount of unreacted sample at the conclusion of the combustion and so to make suitable corrections for incomplete combustion. Dried UO_2 was mixed with UC in a platinum crucible and burned in 10 to 20 atm of oxygen. No cotton fuse or other combustion aid was used. The precautions against water were apparently insufficient, however, as an uncertainty in the final weight of about 0.03 per cent persisted. This was enough to vitiate the results from the entire series, especially since the combustions were somewhat less complete than in the first two series.

Runs of the first two series were calculated on the basis of the assumption that combustion was complete except in those cases where ignition of the residue at 800 C resulted in a further gain of weight, in which cases the runs were discarded.

Calculations

Heat of Formation of UC. From the data, the heat of combustion at constant volume was calculated. These results were converted to heat of combustion at constant pressure and corrected to 25 C. A correction was added for the UO_2 and uranium impurities. The results for the three runs in which UC was burned alone were -358.6, -357.8, -356.3 kcal per mole with a mean of -357.6 kcal per mole. The mean for ten runs with UO_2 and Mylar was -358.8 kcal per mole with a standard deviation of 1.0 kcal per mole. The excessive scatter in the results is believed to be due to incomplete combustion, for which it was not possible to apply suitable corrections. Weighing all runs equally, the final result for the reaction

$$UC + 2\ 1/3\ O_2 \longrightarrow 1/3\ U_3O_8 + CO_2$$

was ΔH_c^o at 25 C = -358.5 kcal per mole. Huber, Holley, and Meierkord(16) have reported for the heat of formation of U_3O_8 a value of -853.5 ± 1.6 kcal per mole. Using this value, and -94.0 kcal per mole for CO_2, the heat of formation of UC is found to be -20.0 ± 5.0 kcal per mole.

The error was estimated as follows. The uncertainty in the calorimetric work was estimated to be 2.0 kcal (twice the standard deviation). The uncertainty in the heat of formation of U_3O_8 contributes 0.5 kcal. The correction for UO_2 in the sample was 4.0 kcal. To this value was assigned an uncertainty of 2.0 kcal. The correction for excess uranium in the sample was 1.0 kcal, with an assumed uncertainty of 0.5 kcal. The total uncertainty is, therefore, assumed to be 5.0 kcal, the sum of these.

The value usually given for the heat of formation of UC, -40 kcal, is based on Brewer's estimate, as reported by Quill.(10) This estimate was based on a rather uncertain value for UC_2 which, in turn, was based on a high value for UO_2. Although the value obtained in the present work certainly does not represent a complete solution to the problem, it would seem to be more suitable for thermodynamic calculations than the older value.

The following improvements in procedure would probably be required for a more reliable determination: A sample should be prepared which contains much less oxygen, to reduce the rather large uncertainty associated with the unknown form of the oxygen in the sample. The carbon content should be more carefully determined. Further work is required to determine whether the combustion product is actually U_3O_8, or whether, perhaps, it contains more oxygen. A very careful analysis of the combustion product for water, oxygen, and carbon would be required in order to make corrections for incomplete combustion.

Heat of Combustion of UO_2. Since most of the determinations involved the use of UO_2 as a combustion aid, it was necessary to determine the heat produced in its combustion. Samples weighing about 30 g were burned in 10 to 30 atm of oxvgen. For the reaction $UO_{2.033} + 0.3168\ O_2 \longrightarrow 1/3\ U_3O_8$, the average of five experiments showed

$$\Delta H_c^o \text{ at } 25\text{ C} = -24.55 \text{ kcal per mole.}$$

The standard deviation was 0.11 kcal. This seems to be in satisfactory agreement with the results of Huber, Holley, and Meierkord(16) for a sample of similar composition. If a correction of 48 kcal per g atom of oxygen is applied for the oxygen in excess of UO_2, then for

$$3\ UO_2 + O_2 \longrightarrow U_3O_8$$

we find ΔH_c^o at 25 C = -78.4 kcal. This is not in good agreement with the value of -76.01 kcal reported by these authors. The discrepancy is not such as to increase the uncertainty in the UC results, however.