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**SURVEY OF REFRACTORY URANIUM COMPOUNDS**

by

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## SURVEY OF REFRACTORY URANIUM COMPOUNDS

Luther D. Loch, Glen B. Engle,  
M. Jack Snyder, and Winston H. Duckworth

*Chemical and physical data on twenty binary uranium compounds that may prove suitable for refractory nuclear fuels were assembled. The compounds were those with aluminum, boron, carbon, iron, nickel, nitrogen, silicon, or sulfur.*

*Too little is known at this time about the compounds to evaluate any of them for fuel. The program is being extended in an effort to provide the needed data.*

### INTRODUCTION

A need exists in our nuclear-energy program for fuel compounds that are stable at high temperatures. Considerable research and development is being done on one such compound,  $UO_2$ . However, a number of other refractory uranium compounds are receiving little attention. The first phase of a research effort to supply needed data on them is summarized in this report.

As indicated, the present interest is in compounds that are resistant to melting or decomposition at high temperatures. Also, in general, a nuclear fuel should contain a high concentration of fissionable material and should have a low absorption cross section for slow neutrons. Other properties of particular interest in this program include vapor pressure, free energy of formation, thermal conductivity, thermal expansion, Young's modulus, and corrosion resistance.

The results of a literature survey are given in this report together with data obtained to date in a concurrent laboratory effort. Further reports will be issued as particular compounds are prepared and measurements of their properties are completed.

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SELECTION OF COMPOUNDS

Twenty binary uranium compounds, with aluminum, boron, carbon, iron, nickel, nitrogen, silicon, or sulfur, appeared interesting on the basis of uranium content and refractoriness. Compounds melting much below 800 C were arbitrarily excluded. Melting points and uranium contents of the twenty compounds are shown in Table 1. Two nitrides,  $U_2N_3$  and  $UN_2$ , and one sulfide,  $US_2$ , were excluded from Table 1 because of reported low stabilities at high temperatures (1, 2), although they had the desired high melting points and uranium contents.

Table 2 lists the absorption cross sections and comparative induced radioactivities for each of the eight combining elements in Table 1. The induced activities were computed for 1 g of combining element irradiated for 1 yr in a thermal-neutron flux of  $10^{14}$  neutrons/( $cm^2$ )(sec). In each case, in computing the activity, the decay chains were continued until a stable isotope was reached. In the case of boron, calculations were made for the low-absorption natural isotope, boron-11.

For comparison with Table 2, the activity of the fission products of uranium-235 was estimated to be  $1.85 \times 10^{11}$  curies per g, 1 hr after removal from a reactor operating at a thermal flux of  $10^{14}$  nv. Therefore, in each compound considered, the uranium will introduce a much larger amount of activity than is associated with the combining element.

URANIUM CARBIDES, NITRIDES, AND SULFIDES

Preparation

Uranium carbides, nitrides, or sulfides are prepared by a variety of reactions. Equations for these are given in Table 3.

The carbides usually are prepared by arc melting stoichiometric mixtures of the elements or by reaction of uranium oxides with carbon. The reaction of monatomic carbon and  $UO_2$  is carried out in a graphite crucible at about 1800 C. The reaction is essentially complete when the evolution of CO markedly decreases and should be stopped at this point to avoid further pickup of carbon from the crucible. (6, 8) UC can be prepared by passing methane over fine uranium powder (prepared from  $UH_3$ ) at 650-700 C. (7)

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(1) References at end.

TABLE 1. URANIUM CONTENTS AND MELTING POINTS OF URANIUM COMPOUNDS

Compound	Uranium Content		Melting Point, C	Reference
	w/o	G per Cm <sup>3</sup> (a)		
UC	95.19	12.97	2350-2400	(3)
U <sub>2</sub> C <sub>3</sub>	92.97	11.97	1775 (decomposition)	(3)
UC <sub>2</sub>	90.83	10.61	2450-2500	(3)
UN	94.44	13.52	2650 ± 100	(4)
US	88.12	9.58	>2000	(1)
U <sub>2</sub> S <sub>3</sub>	83.40	7.32	--	
U <sub>3</sub> Si	96.21	14.99	930 <sup>(b)</sup>	(5)
U <sub>3</sub> Si <sub>2</sub>	92.70	11.31	~1650	(5)
USi	89.44	9.30	~1600	(5)
Alpha USi <sub>2</sub>	80.91	7.27	~1600	(5)
Beta USi <sub>2</sub>	80.91	7.48	~1600	(5)
USi <sub>3</sub>	73.86	6.02	~1500	(5)
UB <sub>2</sub>	91.66	11.75	>1500	(6)
UB <sub>4</sub>	84.61	7.94	>1500	(6)
U <sub>6</sub> Ni	96.05	16.90	790 <sup>(c)</sup>	(5)
UNi <sub>2</sub>	66.98	9.02	985 <sup>(c)</sup>	(5)
UNi <sub>5</sub>	44.77	--	1300	(5)
UAl <sub>2</sub>	81.52	6.64	~1590	(5)
U <sub>6</sub> Fe	96.20	17.00	815 <sup>(c)</sup>	(5)
UFe <sub>2</sub>	68.00	8.98	1235	(5)

(a) Based on product of X-ray density of compound and w/o uranium.

(b) Peritectoid temperature.

(c) Peritectic temperature.

TABLE 2. ABSORPTION CROSS SECTIONS AND INDUCED RADIOACTIVITIES OF COMBINING ELEMENTS IN REFRACTORY URANIUM COMPOUNDS

Element	Thermal-Neutron-Absorption Cross Section, millibarns per atom	Induced Activity <sup>(a)</sup> , curies per g of element
Carbon	3.2	0.0000282
Nitrogen	1880	0.025
Sulfur	490	2.25
Silicon	130	0.2
Boron-11	50	0.738 <sup>(b)</sup>
Nickel	4600	1.16
Aluminum	230	14.0
Iron	2530	3.77

(a) Activated for 1 yr in a thermal-neutron flux of  $10^{14}$  neutrons/(cm<sup>2</sup>)(sec).

(b) Three seconds after removal from the neutron flux this activity will be attenuated by a factor of  $10^{-8}$ .



TABLE 3. PREPARATIONS OF URANIUM CARBIDES, NITRIDES, AND SULFIDES

Compound	Physical Appearance	Liquid-Solid Reactions	Solid-Solid Reactions	Gas-Solid Reactions
<u>Carbides</u>				
UC	Bright hard crystals	$U + C \rightarrow UC$ (2100 C) <sup>(7)(a)</sup> $U + C \rightarrow UC$ (1600-1700 C) <sup>(8)</sup>	$UO_2 + 3C \rightarrow UC + 2CO$ (1750-1800 C) <sup>(6)</sup>	$U + C_2H_2 \rightarrow UC + C + H_2$ <sup>(7)</sup> $U + CH_4 \rightarrow UC + 2H_2$ <sup>(7)</sup>
U <sub>2</sub> C <sub>3</sub>	Bright hard crystals	$2U + 3C \rightarrow UC + UC_2$ (2000 C) <sup>(9)</sup>	$UC + UC_2 \rightarrow U_2C_3$ (1600 C) <sup>(9)</sup>	
UC <sub>2</sub>	Gray metallic crystals	$U + 2C \rightarrow UC_2$ <sup>(10)</sup>	$UO_2 + 4C \rightarrow UC_2 + 2CO$ (1750-1800 C) <sup>(8)</sup> $U_3O_8 + 14C \rightarrow 3UC_2 + 8CO$ (2400 C) <sup>(10)</sup>	
<u>Nitrides</u>				
UN	Gray metallic crystals			$U + N_2 (< 1000 C) \rightarrow UN_x (x > 1); UN_x \rightarrow UN$ (1300-1600 C) <sup>(4)</sup> $UCl_4 + NH_3$ (red heat) $\rightarrow UN_x (x > 1); UN_x \rightarrow UN$ (1300-1600 C) <sup>(11)</sup> $U + NH_3 (< 1000 C) \rightarrow UN_x (x > 1); UN_x \rightarrow UN$ (1300-1600 C) <sup>(4)</sup>
<u>Sulfides</u>				
US	Gray metallic crystals		$UOS + C \rightarrow US + CO$ (1900 C) <sup>(3)</sup>	$UO_2 + H_2S \rightarrow UOS + H_2O$ (<1200 C in graphite crucible); $UOS + CS \rightarrow US_2 + CO$ (>1200 C); $US_2 \rightarrow US + S$ (in vacuo at 1600 C) <sup>(1)</sup> $2UH_3 + 2H_2S \rightarrow 2US + 5H_2$ (500-600 C) <sup>(12)</sup>
U <sub>2</sub> S <sub>3</sub>	Gray metallic crystals	$U + 3US_2 \rightarrow 2U_2S_3$ (1800 C) <sup>(12)</sup>		$2UH_3 + 3H_2S \rightarrow U_2S_3 + 6H_2$ (500-600 C) <sup>(10)</sup>

(a) Superscript numbers are references at the end of the report.

Uranium sesquicarbide ( $U_2C_3$ ) can be formed by heating a stoichiometric mixture (7.03 w/o carbon) at 2000 C in vacuo and then reheating at 1600 C while shaking the material about in the crucible. Samples containing up to 90 w/o  $U_2C_3$  phase have been obtained in this manner. (9)

UN is prepared by reducing higher nitrides in vacuo at 1300-1650 C. The higher nitrides can be prepared by several methods, as shown in Table 3. Chiotti<sup>(4)</sup> reported sintering UN crucibles at temperatures between 2000 and 2100 C to approximately 85 per cent of theoretical density. These crucibles contained about 0.43 w/o carbon.

Brewer<sup>(12)</sup> reported that US can be prepared by reacting  $UH_3$  with  $H_2S$  in a vacuum tube at 400-550 C. Hydrogen evolved from the reaction is removed by evacuation through a liquid-air cold trap. The reaction product is crushed and heated at 500-600 C to decompose any remaining hydride, then reheated at 1800-1900 C in a molybdenum crucible to obtain a uniform product.

Another method of making US is to form  $US_2$  by one of the methods described by Brewer<sup>(12)</sup> and to react the  $US_2$  stoichiometrically with  $UH_3$ . The mixture of  $US_2$  and  $UH_3$  is heated to 400-600 C to decompose the hydride and then to 2000-2200 C to homogenize the product.

US also can be formed by reacting  $UO_2$  and  $H_2S$  in the presence of carbon to form  $US_2$  and subsequent reduction of  $US_2$  to US in vacuo at 1600 C. (1)  $UO_2$  was heated in  $H_2S$  in a graphite crucible below 1200 C and UOS was formed; the temperature was then raised above 1200 C and CS was formed by the reaction of  $H_2S$  and the graphite crucible. CS reacted with UOS to form  $US_2$ .

### Crystallography

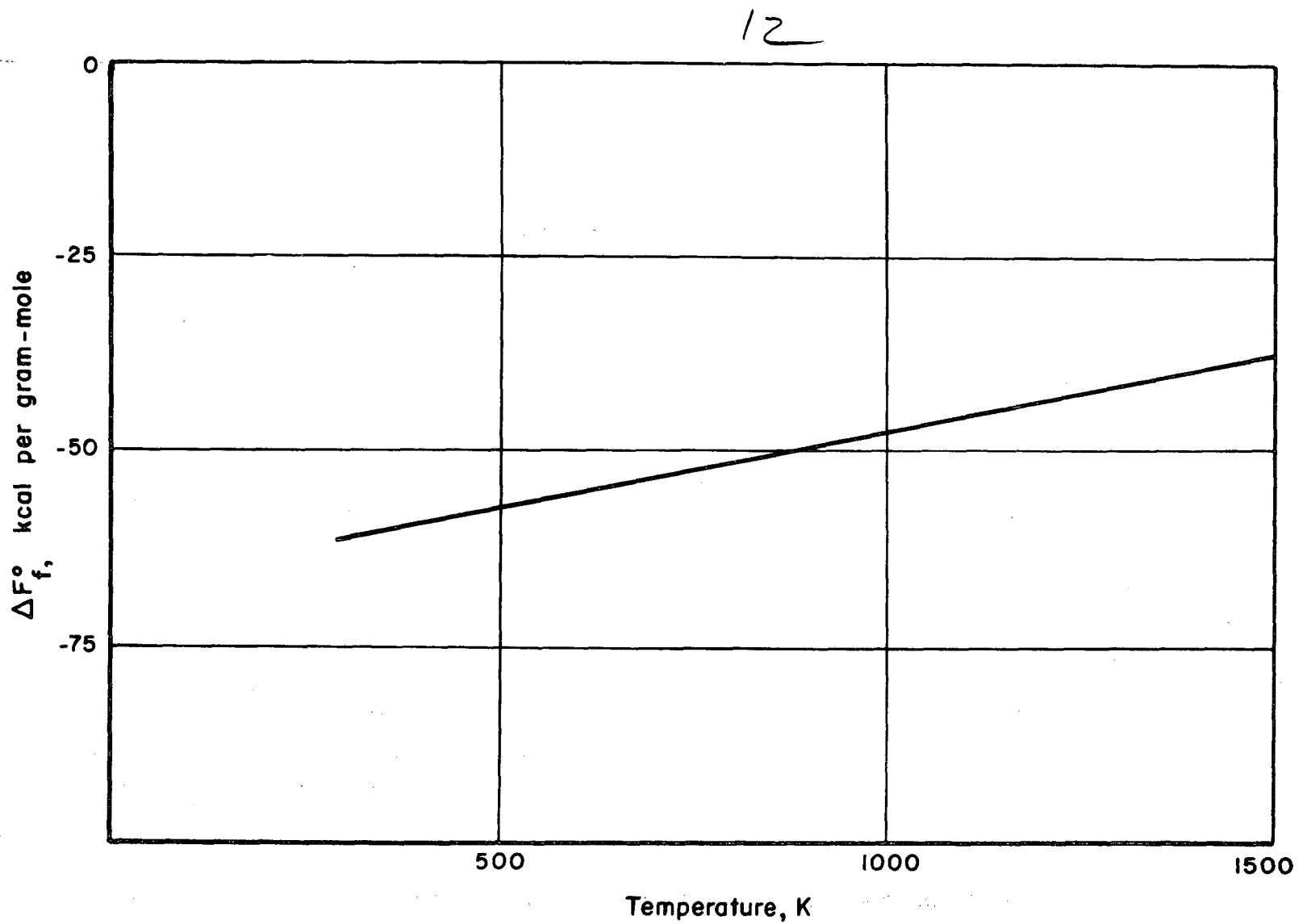
Crystallographic data for the carbides, nitrides, and sulfides are given in Table 4.

### Thermochemical Aspects

The standard free energy of formation of  $UC_2$  at 298 K was calculated to be -42,000 calories, based on Rossini's<sup>(13)</sup> values for  $\Delta H$  and  $\Delta S$  at 298 K.  $\Delta F_T$  up to 1500 K was computed from Kubaschewski's rule<sup>(14)</sup> by assuming  $\Delta C_p = 0$ .

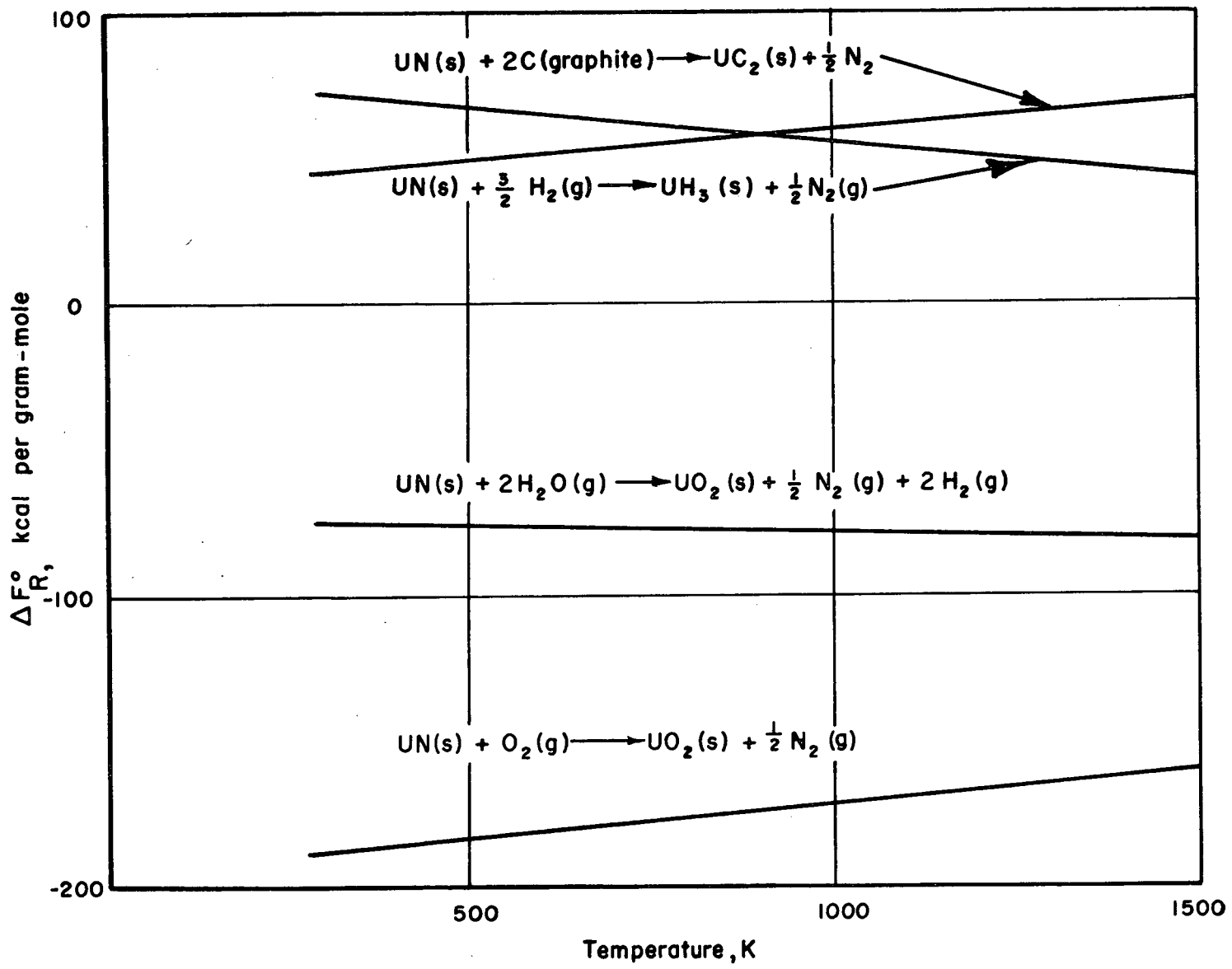
TABLE 4. CRYSTALLOGRAPHY OF URANIUM CARBIDES, NITRIDES, AND SULFIDES

Compound	Unit Cell		Molecules per Unit Cell	X-Ray Density, g per cm <sup>3</sup>	Space Group	Remarks	Reference
	Type	Dimensions, A					
UC	Fcc	a = 4.961	4	13.63	--	NaCl-type structure	(10,2)
U <sub>2</sub> C <sub>3</sub>	Bcc	a = 8.088 ± 0.001	8	12.88	143d	Isostructural with P <sub>2</sub> C <sub>3</sub>	(9)
UC <sub>2</sub>	Bc tetragonal	a = 3.524 c = 5.999	2	11.68	14/mmm	CaC <sub>2</sub> structure	(10,2)
UN	Fcc	a = 4.880 ± 0.001	4	14.32	--	NaCl-type structure, com- pletely soluble with UC	(2)
US	Bcc	a = 5.484 ± 0.002	4	10.87	--	NaCl-type structure, soluble with ThS and CeS	(1)
U <sub>2</sub> S <sub>3</sub>	Orthorhombic	a = 10.41 ± 0.02 b = 10.65 ± 0.02 c = 3.89 ± 0.01	4	8.78	Pbnm	Sb <sub>2</sub> S <sub>3</sub> -type structure, isomorphous with Np <sub>2</sub> S <sub>3</sub> and Th <sub>2</sub> S <sub>3</sub>	(1)



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FIGURE 1. FREE ENERGY OF FORMATION OF UN

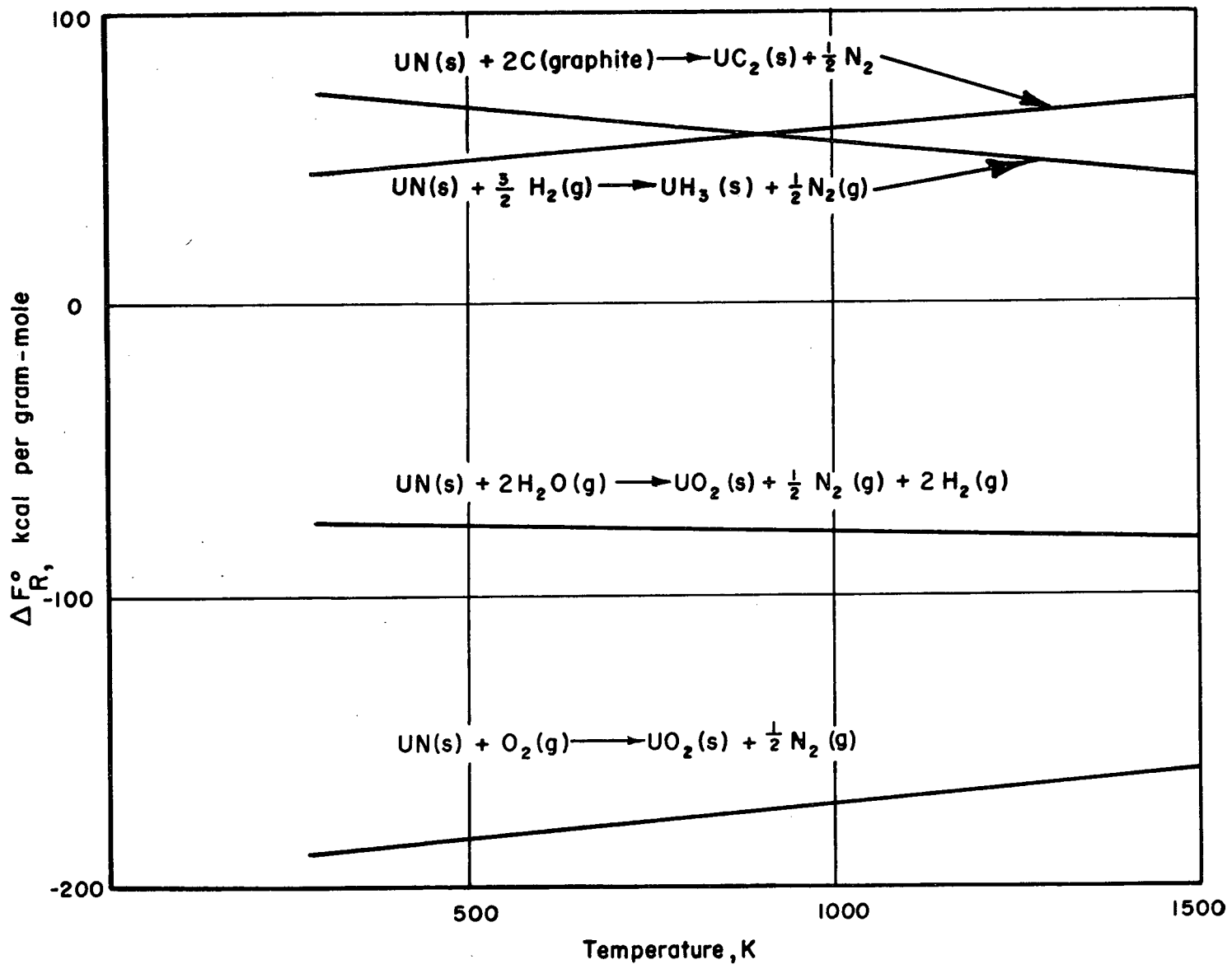


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FIGURE 2. STANDARD FREE ENERGIES FOR REACTIONS OF UN WITH COMMON REAGENTS

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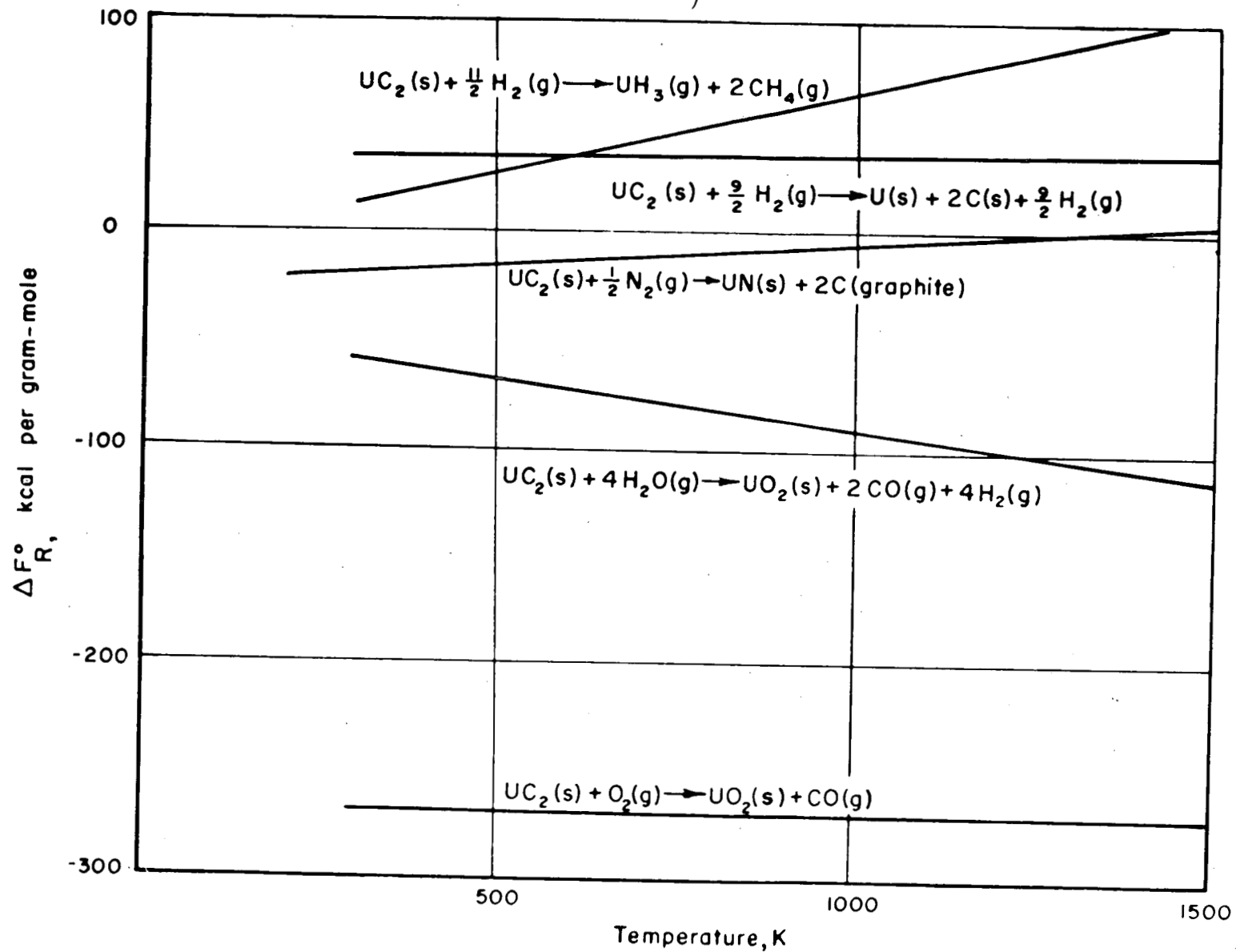
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FIGURE 2. STANDARD FREE ENERGIES FOR REACTIONS OF UN WITH COMMON REAGENTS

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FIGURE 3. STANDARD FREE ENERGIES FOR REACTIONS OF  $UC_2$  WITH COMMON GASES

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Standard free energy of formation values for UN were calculated up to 1500 K and are presented in Figure 1. These calculations were based on experimental data of Kubaschewski and Evans<sup>(14)</sup>.

Standard free-energy changes of several reactions of UN and of UC<sub>2</sub> with some common gases and with carbon are presented in Figures 2 and 3.

The large negative values of standard free-energy change indicate that UN and UC<sub>2</sub> should react readily with oxygen, water, or steam. They are shown to be thermodynamically unreactive with hydrogen.

Standard free-energy changes for the reaction of US with oxygen, based on an estimated value for the heat of formation of US, are shown in Figure 4. Because of the large negative values for the calculated  $\Delta F_R^0$ , it is highly improbable that the estimated heat of formation is sufficiently in error that the actual  $\Delta F_R^0$  would be positive. Thus, it is fairly certain that, thermodynamically, US will have poor resistance to oxidation. A similar calculation showed that US is not thermodynamically resistant to steam.

#### Chemical Properties and Corrosion Data

Reactions of UC<sub>2</sub> with some common elements or compounds are given in Table 5.

UC<sub>2</sub> reacts with water at 82 C to give hydrogen, CH<sub>4</sub>, paraffins, and traces of C<sub>2</sub>H<sub>2</sub>, CO, and CO<sub>2</sub>.<sup>(15)</sup> At 248 C, approximately 96 per cent of the gaseous reaction product is hydrogen.

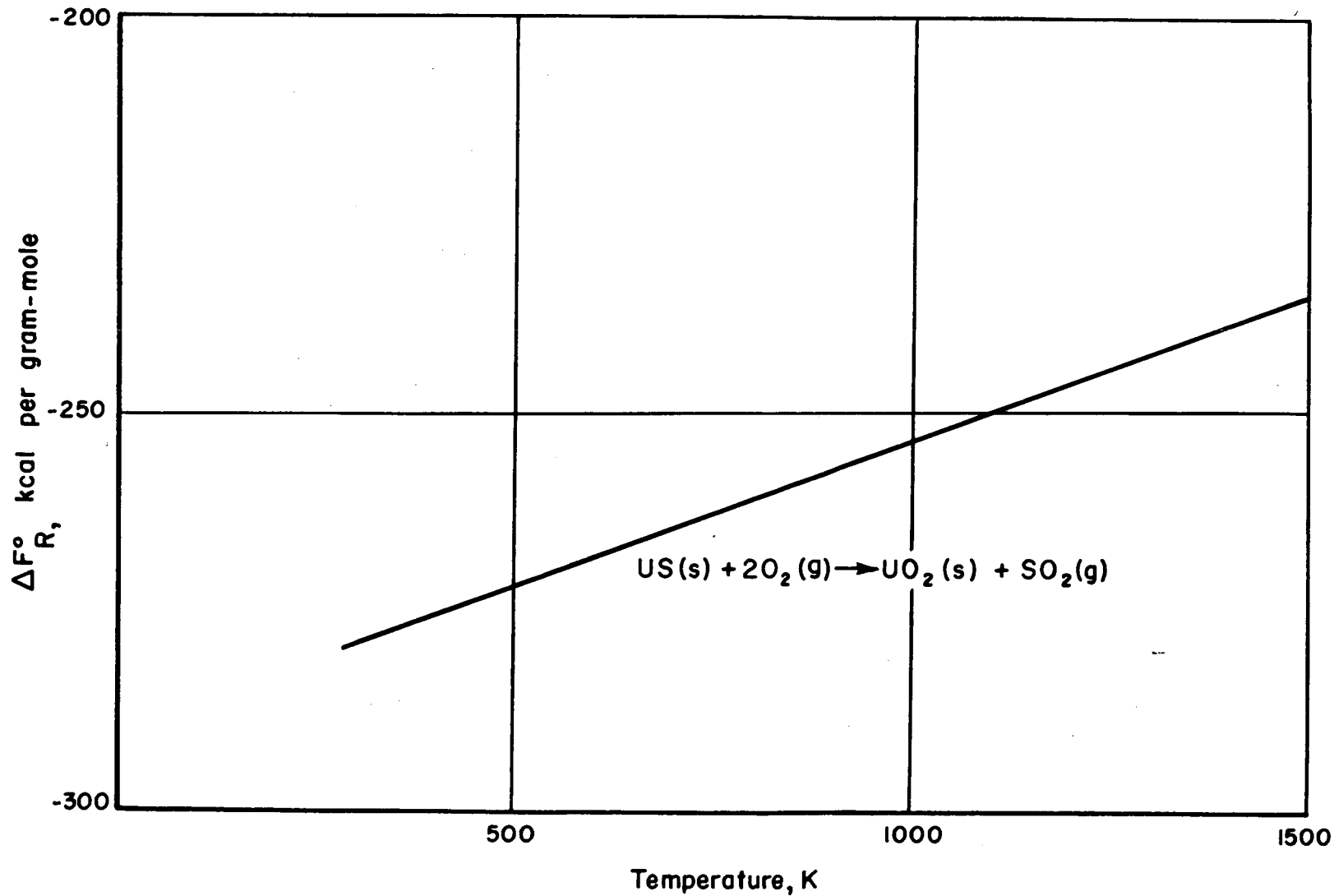
Moissan<sup>(16)</sup> reported UC<sub>2</sub> to be decomposed by dilute HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>, giving yellow uranyl salt solutions. Concentrated acids, except HNO<sub>3</sub>, react only slowly with UC<sub>2</sub> at room temperature but very rigorously when heated. Daane<sup>(17)</sup> reported a slow reaction with H<sub>3</sub>PO<sub>4</sub> at room temperature and a vigorous reaction when heated.

UC<sub>2</sub> was reported by Rideal<sup>(18)</sup> to be readily decomposed by alkalis.

UC decomposes in water at 83 C with the evolution of a gaseous mixture composed of approximately 78 per cent CH<sub>4</sub> and 12 per cent hydrogen. As the temperature is increased, the ratio of hydrogen increases until at 400 C the mixture contains 99.2 per cent hydrogen.<sup>(15)</sup>

US has been found to be stable in boiling water if it is well sintered.<sup>(1)</sup>





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FIGURE 4. STANDARD FREE ENERGIES FOR REACTION OF US WITH OXYGEN

TABLE 5. CHEMICAL REACTIVITY OF  $UC_2$ 

Reactant	Reaction Temperature, C	Products of Reaction	Remarks	Reference
$O_2$	370	$U_3O_8$ and $CO_2$	--	(16)
$O_2$	400-500	--	Oxidized completely within 4 hr in an air stream	(22)
$N_2$	1100	--	--	(16)
$N_2$	1180	Uranium nitride	After 12 hr all carbide is converted to nitride	(23)
$Cl_2$	350	Volatile chloride	--	(16)
$Cl_2$	600	$UCl_4$	--	(24)
$F_2$	30	No reaction	--	(16)
$F_2$	Slightly above 30	Explosive reaction	--	(16)
$Br_2$	390	--	Carbide ignites in bromine vapor	(16)
$Br_2$	800-900	$UBr_4$	--	(25, 26)
$I_2$	500	$UI_4$	--	(27)
$NH_3$	Red heat	--	Partial decomposition of $UC_2$	(16)
$H_2S$	600	A sulfide	$UC_2$ ignited in hydrogen sulfide	(16)
S	--	Uranium sulfide and carbon disulfide	--	(16)
HCl	600	A uranium chloride	--	(16)
$H_2O$	--	Hydrocarbons	Decomposes slowly at room temperature, decomposes rapidly when heated	(16)

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Physical Properties

The boiling point of  $UC_2$  was estimated by Mott<sup>(19)</sup> to be 4370 C under 760 mm of mercury.

Two values for the thermal conductivity of  $UC_2$  have been reported: 0.078<sup>(20)</sup> and 0.082<sup>(21)</sup> cal/(sec)(cm<sup>2</sup>)(C/cm). The former value is for a temperature of 44 C while the temperature of the latter measurement was not specified.

The average coefficient of thermal expansion of  $UC_2$  for the temperature range 20-235 C was reported to be  $12.5 \times 10^{-6}$  per deg C. (28)

URANIUM SILICIDES AND BORIDES

Preparation

Uranium silicides ( $U_3Si$ ,  $U_3Si_2$ ,  $USi$ , alpha  $USi_2$ , beta  $USi_2$ , and  $USi_3$ ) were prepared as part of the present research by heating stoichiometric mixtures of the elements in an electric arc furnace. Fabrication of shapes from the arc melts was accomplished by ceramic techniques.

Some of the as-cast uranium-silicon compounds crystallized as multiphase materials and had to be annealed to remove extraneous phases. This generally was done by extended heating of the ingot in an inert atmosphere near the melting or decomposition temperature. Annealing also was affected during sintering processes.

$U_3Si$  is more ductile than the other uranium silicides. It has been coextruded with other metals at 750-800 C. (29)

Brewer<sup>(6)</sup> and Zalkin<sup>(30)</sup> prepared gray metallic crystals of  $UB_2$  and  $UB_4$  by heating stoichiometric mixtures of uranium and boron powder in an inert atmosphere in molybdenum crucibles at 1500 C for about 1 hr.

Crystallography

Crystallographic data on the uranium silicides and borides are listed in Table 6.

TABLE 6. CRYSTALLOGRAPHY OF URANIUM SILICIDES AND URANIUM BORIDES

Compound.	Unit Cell		Molecules per Unit Cell	X-Ray Density, g per cm <sup>3</sup>	Space Group	Remarks	Reference
	Type	Dimensions, A					
U <sub>3</sub> Si	Bc tetragonal	a = 6.029 ± 0.002	4	15.58	14 mcm	--	(31)
		c = 8.697 ± 0.003					(32)
U <sub>3</sub> Si <sub>2</sub>	Tetragonal	a = 7.3298 ± 0.0004 c = 3.9003 ± 0.0005	2	12.20	P <sub>4</sub> /mbm	--	(33)
USi	Orthorhombic	a = 5.66 ± 0.01 b = 7.66 ± 0.01	4	10.40	Pbnm	Isomorphous with FeB	(31, 32)
Alpha USi <sub>2</sub>	Bc tetragonal	a = 3.98 ± 0.03 c = 13.74 ± 0.08	4	8.98	14/amd	Isomorphous with ThSi <sub>2</sub> , PuSi <sub>2</sub> , CeSi <sub>2</sub> , and NpSi <sub>2</sub>	(31, 32)
Beta USi <sub>2</sub>	Hexagonal	a = 3.86 ± 0.01 c = 4.07 ± 0.01	1	9.25	C6/mmm	Isomorphous with AlB <sub>2</sub> and TiB <sub>2</sub>	(33)
USi <sub>2</sub>	Cubic	a = 4.035	--	7.80	--	--	(34)
USi <sub>3</sub>	Cubic	a = 4.03	1	8.15	Pm3m	L12-type AuCu <sub>3</sub> ordered structure	(31, 32)
UB <sub>2</sub>	Hexagonal	a = 3.12 c = 3.96	1	12.82	--	May be isomorphous with AlB <sub>2</sub>	(29)
UB <sub>4</sub>	Tetragonal	a = 7.075 ± 0.004 c = 3.979 ± 0.002	4	9.38	P <sub>4</sub> /mbm	Isomorphous with ThB <sub>4</sub> and CeB <sub>4</sub>	(30)

The constitutional diagram of the uranium-silicon system, as determined by Kaufmann<sup>(31, 32)</sup> indicates the existence of the intermediate phases,  $U_3Si$ ,  $U_5Si_3$ ,  $USi$ ,  $U_2Si_3$ ,  $USi_2$ , and  $USi_3$ . However, there is some doubt whether this diagram is accurate in the region 5 to 30 w/o silicon. In later work, Zachariasen<sup>(33)</sup> rejected the formulas  $U_5Si_3$  and  $U_2Si_3$ . His interpretation of the X-ray diffraction data was that  $U_5Si_3$  should be replaced by  $U_3Si_2$ , and that the phase identified by Kaufmann as  $U_2Si_3$  is an allotrope of  $USi_2$  with a hexagonal structure. Zachariasen called this compound beta  $USi_2$ . It is not quite clear whether Zachariasen's samples were of the same composition as those of Kaufmann as no chemical analyses were given.

Brauer and Haig<sup>(34)</sup> identified a cubic phase with the  $USi_2$  composition. Their samples were prepared in a molten aluminum bath and analyzed 19 w/o silicon and 80.7 w/o uranium.

#### Thermochemical Aspects

No experimental thermochemical data were found on the uranium silicides or borides. Estimates of the standard free energies of reaction of  $USi_2$  and  $UB_2$  with oxygen and water are shown in Figure 5. The predictions are based on Battelle estimates of heats of formation. The large negative values of the standard free-energy changes indicate that neither  $USi_2$  nor  $UB_2$  is thermodynamically resistant to oxidation. As  $USi_2$  probably is the most stable of the uranium silicides, none of the other silicides would be expected to have thermodynamic resistance to oxygen.

The silicides and borides appear to be thermodynamically resistant to hydrogen but not to water vapor, on the basis of Battelle estimates.

#### Chemical Properties and Corrosion Data

Data obtained at Battelle on the chemical stability of  $U_3Si$  and alpha  $USi_2$  in acidic and basic solutions and in hydrogen gas are shown in Table 7. The results of corrosion tests in water of  $U_3Si$  and alpha  $USi_2$  are given in Table 8.

$U_3Si$  is reported to resist oxidation in air at 100 and 200 C, but not at 300 C.<sup>(35)</sup> It corrodes only slightly faster in steam at 125 psi than in boiling water.<sup>(35)</sup> The surface was roughened and a slight weight gain was observed after 5 hr in a lead-bismuth eutectic mixture at 425 C.<sup>(35)</sup>

Measurements made at Battelle on air oxidation of uranium silicides at 400 C are given in Table 9. In general, oxidation resistance in air

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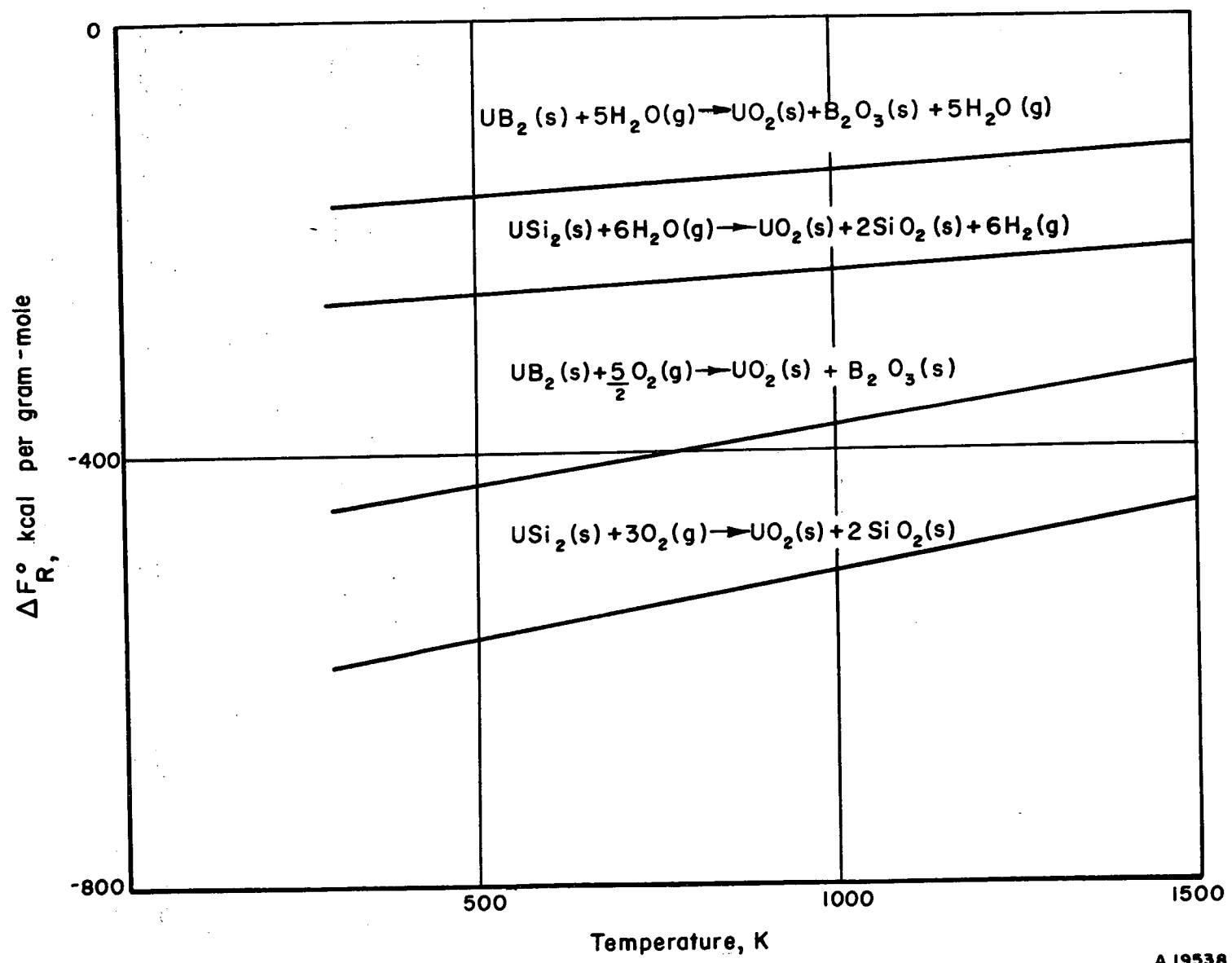


FIGURE 5. STANDARD FREE ENERGIES FOR REACTIONS OF  $USi_2$  AND  $UB_2$  WITH  $H_2O$  AND  $O_2$

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TABLE 7. CHEMICAL STABILITY OF  $U_3Si$  AND ALPHA  $USi_2$ <sup>(a)</sup>

Compound	Stability in Indicated Concentrated Acid			Stability in 1N NaOH	Weight Change After 1-Hr Exposure in 500 C Hydrogen, per cent
	HCl	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>		
$U_3Si$ <sup>(b)</sup>	Reacted	Reacted	Reacted	No reaction	+0.62
Alpha $USi_2$ <sup>(b)</sup>	Reacted	Reacted	Reacted	No reaction	+0.60
Alpha $USi_2$ <sup>(c)</sup>	Reacted	Reacted	Slow reaction	No reaction	+0.08

(a) Data obtained at Battelle.

(b) Arc melt.

(c) Compact sintered at 1400 C in argon.

TABLE 8. CORROSION RESISTANCE OF  $U_3Si$  AND ALPHA  $USi_2$  IN WATER

Compound	Weight Loss After 1 Hr in Boiling Water, per cent	Weight Change in 650 F Water, mg/(cm <sup>2</sup> )(hr)
$U_3Si$ <sup>(a)</sup>	0.00	-1.00
$U_3Si$ <sup>(b)</sup>	--	-1.00
$USi_2$ <sup>(c)</sup>	0.00	-2.00

(a) Data obtained at Battelle on epsilonized arc melt.

(b) Data obtained by WAPD<sup>(29)</sup> on extruded bar.

(c) Data obtained at Battelle on compact sintered at 1400 C in argon.

TABLE 9. OXIDATION IN AIR OF URANIUM SILICIDES

Compound	Silicon Content, w/o	Weight Gain in 7-1/2 Hr at 400 C, per cent
U <sub>3</sub> Si	3.8	19.6 (disintegrated)
U <sub>3</sub> Si <sub>2</sub>	7.25	18.5 (disintegrated 1.4 <sup>(a)</sup> )
USi	10.5	16.5 (disintegrated)
Alpha USi <sub>2</sub>	19.0	0.19 <sup>(b)</sup> 0.14 <sup>(a)</sup>
USi <sub>3</sub>	26.0	0.07 <sup>(c)</sup>

(a) Contained approximately 3 to 5 w/o iron.

(b) Contained approximately 1 w/o tungsten.

(c) Contained approximately 4 w/o tungsten.

Note: Data obtained at Battelle. Specimens weighed approximately 2.5 g, and were 1/2 in. in diameter by 1/4 in. long.



increased with increasing silicon content, although the results on  $USi_2$  and  $USi_3$  may have been influenced by impurities. The presence of 3 to 5 w/o iron in  $U_3Si_2$  greatly improved its oxidation resistance.

### Physical Properties

The thermal conductivity of  $U_3Si$  was measured by Foote<sup>(36)</sup>, with the following results:

<u>Temperature, C</u>	<u>Thermal Conductivity, cal/(sec)(cm<sup>2</sup>)(C/cm)</u>
25	0.036
50	0.041

Coefficients of linear thermal expansion for  $U_3Si$ ,  $U_3Si_2$ , and  $USi_3$  are given in Table 10.

The data of Kaufmann<sup>(32)</sup> on the strength of  $U_3Si$  in compression and tension are given in Table 11.

## COMPOUNDS WITH METALS

### Preparation

Compounds of uranium with aluminum, iron, or nickel were prepared at Battelle by melting stoichiometric mixtures of the elements in an electric arc furnace. The products were brittle, and fabrication of shapes required ceramic techniques.

### Crystallography

Crystallographic data for compounds of uranium with aluminum, iron, or nickel are given in Table 12.

The compound  $UAl_2$  was tentatively identified by Gordon and Kaufmann<sup>(37)</sup> on the basis of microscopic examination of alloys and X-ray determinations of crystal structure. Because of difficulties with chemical

TABLE 10. THERMAL EXPANSIONS OF URANIUM SILICIDES<sup>(a)</sup>

Temperature Range, C	Mean Coefficient of Linear Thermal Expansion, 10 <sup>-6</sup> per deg C		
	U <sub>3</sub> Si <sup>(b)</sup>	U <sub>3</sub> Si <sub>2</sub> <sup>(c)</sup>	USi <sub>3</sub> <sup>(d)</sup>
20-200	13.0	15.5	13.4
20-300	13.4	15.3	13.6
20-400	14.2	15.2	14.3
20-500	14.9	15.3	14.6
20-600	15.8	15.2	14.9
20-700	16.8	15.1	15.4
20-750	17.5	--	--
20-800	--	15.0	15.7
20-900	--	14.7	16.1
20-950	--	14.6	16.3

(a) Data obtained at Battelle.

(b) As-cast ingot epsilonized at 800 C for 168 hr.

(c) U<sub>3</sub>Si<sub>2</sub> powder sintered at 1400 C in argon for 15 hr.

(d) USi<sub>3</sub> powder sintered at 1250 C in argon for 15 hr. Contained approximately 4 w/o tungsten.

TABLE 11. STRENGTH OF  $U_3Si$ (a)

Temperature, C	Yield Strength, psi		Ultimate Strength, psi	
	Tension	Compression	Tension	Compression
25	37,000	115,000	37,000	280,000
600		55,000		
700		18,000		
750		10,000		
850		4,000		

(a) From Kaufmann.<sup>(32)</sup>

TABLE 12. CRYSTALLOGRAPHY OF URANIUM COMPOUNDS WITH METALS

Compound	Unit Cell		Number of Molecules	X-Ray Density, g per cm <sup>3</sup>	Space Group	Remarks	Reference
	Type	Dimensions, A					
UAl <sub>2</sub>	Fcc	a = 7.811	8	8.14	Fd 3m	C15-type Cu <sub>2</sub> Mg structure	(37)
U <sub>6</sub> Ni	Bc tetragonal	a = 10.37 ± 0.04 c = 5.31 ± 0.02	4	17.6	14/mcm, 142 or 14 c 2	Isomorphous with U <sub>6</sub> Fe, U <sub>6</sub> Co, and U <sub>6</sub> Mn	(40)
UNi <sub>2</sub>	Hexagonal	a = 4.966 c = 8.252	4	13.46	C6/mmc	C14-type MgZn <sub>2</sub> structure	(40)
UNi <sub>5</sub>	Fcc	a = 6.7830 ± 0.0005	4	--	F43m or F23	Similar to MgCu <sub>2</sub> structure, but of lower symmetry; isomorphous with UCu <sub>5</sub> , PdBe <sub>5</sub> , and AuBe <sub>5</sub>	(40)
U <sub>6</sub> Fe	Bc tetragonal	a = 10.31 ± 0.04 c = 5.24 ± 0.02	4	17.7	14/mcm, 142 or 14 c 2	Isomorphous with U <sub>6</sub> Mn, U <sub>6</sub> Co, and U <sub>6</sub> Ni	(41)
UFe <sub>2</sub>	Fcc	a = 7.042	8	13.21	Fd 3m	C15-type MgCu <sub>2</sub> structure; isomorphous with UAl <sub>2</sub>	(41)

analyses and with inhomogeneity in their alloys, the composition could not be fixed to better than  $\pm 2$  a/o. However, the measured density (8.21 g per  $\text{cm}^3$ ) of their sample corresponded closely with the calculated X-ray density (8.38 g per  $\text{cm}^3$ ).

The uranium-nickel system has been investigated by Grogan and Pleasance<sup>(38)</sup>, Foote<sup>(39)</sup>, and Baenziger<sup>(40)</sup>. The data in Table 12 are from Baenziger. He also attempted to analyze the pattern of an alloy with the composition UNi but was unable to resolve its complex structure.

### Properties

No data on the physical or chemical properties of these compounds were found. Also, there are no reliable methods of estimating their thermodynamic properties.

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