11. HIGH-TEMPERATURE RESEARCH ON CARBIDES FOR FUEL AND STRUCTURAL APPLICATIONS

(7073)

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The objective of this program was to determine the high-temperature physico-chemical properties of refractory carbides for fuel and structural applications.

This program terminated at the end of Fiscal Year 1967; significant results are presented below.

11.1 PREPARATION AND FABRICATION OF REFRACTORY CARBIDES

The results of reaction studies for the preparation of well-characterized carbides of Ta, Zr, and Hf from their respective oxides are shown in Table 11.1. Spectrographic-grade graphite – oxide reactions require higher temperatures, in the range of 2200° to 2300°C, to form well-crystallized single-phase material. While zirconium oxide reacts with C to form ZrC in about 1 to 2 hours at temperatures between 1850° and 2000°C, com-

TABLE 11.1

X-RAY DIFFRACTION AND CHEMICAL ANALYSES OF CARBIDES PRODUCED FROM THE METAL OXIDES IN VACUUM

Material	Reaction Temperature, °C	Time at Temperature, hr	Lattice Parameter, Å	Combined Carbon, wt % (± 0.05) ^a	Uncombined Carbon, wt %	Oxygen, ppm	Nitrogen, ppm	Combined Carbon-to-Metal Ratio
TaC ^c	1800	1	Two phases TaC + Ta ₂ C	4.91	1.48 $\pm$ 0.05	700 $\pm$ 100	23 $\pm$ 20	0.79 $\pm$ 0.01
TaC ^c	1800	5	TaC + Ta ₂ C	—	—	—	—	—
TaC ^c	2000	1	4.455	5.74	0.37 $\pm$ 0.05	700 $\pm$ 100	< 5 $\pm$ 5	0.93 $\pm$ 0.01
TaC ^c	2000	5	4.456	5.86	0.28 $\pm$ 0.02	600 $\pm$ 100	< 5 $\pm$ 5	0.94 $\pm$ 0.01
TaC ^c	2200	1	4.455	6.07	0.12 $\pm$ 0.02	350 $\pm$ 30	< 5 $\pm$ 5	0.98 $\pm$ 0.01
TaC ^c	2200	5	4.456	6.23	0.10 $\pm$ 0.02	1640 $\pm$ 100	< 5 $\pm$ 5	1.00 $\pm$ 0.01
ZrC ^b	1850	2	4.698	11.47	0.529 $\pm$ 0.05	—	330 $\pm$ 30	0.99 $\pm$ 0.01
ZrC ^b	2000	1%	4.649	12.39	0.18 $\pm$ 0.02	450 $\pm$ 30	77 $\pm$ 30	1.08 $\pm$ 0.01
ZrC ^b	2150	%	4.699	11.74	0.18 $\pm$ 0.02	1140 $\pm$ 100	398 $\pm$ 30	1.01 $\pm$ 0.01
ZrC ^c	2000	5	4.698	10.07	1.31 $\pm$ 0.05	430 $\pm$ 30	580 $\pm$ 100	0.86 $\pm$ 0.01
ZrC ^c	2200	1	4.699	11.31	0.62 $\pm$ 0.05	1340 $\pm$ 100	252 $\pm$ 30	0.97 $\pm$ 0.01
ZrC ^c	2200	5	4.698	11.59	0.56 $\pm$ 0.05	1300 $\pm$ 100	5 $\pm$ 5	1.00 $\pm$ 0.01
HfC ^c	2200	2	4.638	5.84	0.36 $\pm$ 0.05	920 $\pm$ 100	350 $\pm$ 30	0.92 $\pm$ 0.02
HfC ^c	2300	2	4.638	6.35	0.36 $\pm$ 0.05	720 $\pm$ 100	280 $\pm$ 30	1.01 $\pm$ 0.01
HfC ^c	2300	5	4.638	5.94	0.62 $\pm$ 0.05	470 $\pm$ 30	350 $\pm$ 30	0.95 $\pm$ 0.01

^aPercent carbon for stoichiometric carbides (1:1 C/M) are as follows:

TaC 6.22

ZrC 11.63

HfC 6.30

^bPrepared from oxide and carbon.

^cPrepared from oxide and spectrographic graphite.

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plete reaction between this oxide and spectrographic-grade graphite requires 5 hours at 2200 °C to produce single-phase ZrC. Hafnium oxide – graphite reactions to form HfC require temperatures of at least 2300 °C to obtain a well-crystallized, homogeneous, single-phase product.

Typical analyses of scaled-up lots (2 kg) of TaC, ZrC, and HfC (preparation based on the conditions determined in the above experiments) are shown in Table 11.2.

Analyses of Ta and Zr carbides prepared from the hydrides appear in Table 11.3. These data indicate that a 2200 °C treatment was required to form single-phase TaC, whereas single-phase ZrC was formed at 1800 °C. Reacting the Zr hydride with C at 2000 °C and above, however, produced a higher carbon-to-metal ratio. In general, the oxygen content of the product is lower than in the graphite – oxide reactions; the nitrogen content is about the same.

Vacuum hot pressing was used to form dense cylindrical specimens of various carbides. Table 11.4 summarizes the results. TiC and ZrC were fabricated at nearly theoretical density by hot pressing in graphite dies at 2125 °C for 5 to 30 minutes. TaC and HfC required temperatures of 2200° to 2300 °C for 15 to 30 minutes to achieve densities from 94 to 97 percent of theoretical.

TABLE 11.2
CHEMICAL AND X-RAY ANALYSES OF TYPICAL BATCHES OF TaC, ZrC,
AND HfC PREPARED BY OXIDE-GRAPHITE REACTION IN VACUUM

Material	Reaction Conditions	Free Carbon, %	Oxygen, ppm	Nitrogen, ppm	X-Ray Analysis
TaC	5 hr at 2200°C	0.16	950	8	Single-phase fcc
ZrC	5 hr at 2200°C	0.56	1300	<5	Single-phase fcc
HfC	2 hr at 2400°C	0.28	91	52	Single-phase fcc

TABLE 11.3
X-RAY DIFFRACTION AND CHEMICAL ANALYSES OF ZrC AND TaC PRODUCED FROM
METAL HYDRIDE – GRAPHITE REACTIONS IN VACUUM

Material	Reaction Temperature, °C	Phases	Combined Carbon, wt % (± 0.05)	Uncombined Carbon, wt %	Oxygen, ppm	Nitrogen, ppm	Combined Carbon-to-Metal Ratio (± 0.01)
TaC ^a	1800	Inhomogeneous TaC plus graphite	5.67	0.39 $\pm$ 0.05	320 $\pm$ 30	13 $\pm$ 5	—
TaC ^b	1800	Inhomogeneous TaC plus graphite	5.50	0.56 $\pm$ 0.05	280 $\pm$ 30	34 $\pm$ 10	—
TaC ^a	2000	Inhomogeneous TaC	5.73	0.29 $\pm$ 0.05	330 $\pm$ 30	<5 $\pm$ 5	—
TaC ^b	2000	Inhomogeneous TaC	5.89	0.27 $\pm$ 0.05	2.90 $\pm$ 30	18 $\pm$ 5	—
TaC ^a	2200	TaC, $a_0 = 4.453_7$	6.07	0.050 $\pm$ 0.007	260 $\pm$ 30	29 $\pm$ 10	0.97
TaC ^b	2200	TaC, $a_0 = 4.454_1$	6.07	0.032 $\pm$ 0.005	180 $\pm$ 30	<5 $\pm$ 5	0.97
ZrC ^a	1800	ZrC, $a_0 = 4.698_5$	10.83	0.40 $\pm$ 0.05	650 $\pm$ 50	345 $\pm$ 30	0.93
ZrC ^b	1800	ZrC, $a_0 = 4.698_1$	10.94	0.38 $\pm$ 0.05	590 $\pm$ 50	369 $\pm$ 30	0.94
ZrC ^a	2000	—	11.55	0.18 $\pm$ 0.02	310 $\pm$ 30	299 $\pm$ 30	0.99
ZrC ^b	2000	—	11.16	0.33 $\pm$ 0.05	350 $\pm$ 30	351 $\pm$ 30	0.96
ZrC ^a	2200	ZrC, $a_0 = 4.697_9$	11.33	0.075 $\pm$ 0.005	1570 $\pm$ 100	96 $\pm$ 20	0.97
ZrC ^b	2200	ZrC, $a_0 = 4.697_7$	11.36	0.19 $\pm$ 0.02	2910 $\pm$ 100	133 $\pm$ 20	0.98

^aMaterial prepared by reaction of stoichiometric 1:1 graphite-to-metal ratio.

^bMaterial prepared with 0.5 percent excess graphite.

TABLE 11.4
DENSITY OF VARIOUS CARBIDE COMPACTS PREPARED
BY VACUUM HOT-PRESSING

Material ^a	Vacuum Hot-Pressing Conditions				Density, percent of theoretical
	Temperature, °C	Time, min	Pressure, kg/cm ²	Vacuum, 10 ⁻² Torr	
TiC	1750	5	105.4	5.0	97.4
TiC	2030	5	105.4	2.0	100.0
TiC	2135	15	140.6	1.5	100.0
ZrC	2000	45	126.5	2.5	99.9
ZrC	2125	30	140.6	1.5	99.76
ZrC	2125	30	140.6	1.5	99.2
HfC	2175	30	105.4	3.5	90.1
HfC	2225	30	140.6	2.5	94.5
TaC ^b	2150	30	105.4	8.0	89.6
TaC ^c	2225	30	140.6	2.5	~85
TaC ^d	2250	20	140.6	0.8	95.3
TaC ^d	2235	15	140.6	2.5	96.8

^aCylindrical samples about 2.54 cm diameter x 3.18 cm high.

^bPressed from commercial powder.

^cPressed from powder prepared by vacuum reaction of Ta and carbon.

^dPressed from powder prepared by vacuum reaction of Ta₂O₅ and carbon.

This work was discussed in detail in a previous report.¹

11.2 Ta CARBIDE

THERMAL STABILITY

The kinetics of the evaporation of TaC were studied in Ar + 3H₂ (vol %) and in hydrogen atmospheres, at temperatures between 2000° and 3000°C. Weight loss from TaC in its homogeneity range followed a parabolic rate law indicating a diffusion-controlled mechanism. Rates of C loss at the surface, determined by following surface compositional changes by X-ray analysis, were atmosphere dependent. In each atmosphere the surface lattice parameter (and, therefore, the composition) decreased more rapidly at higher temperatures.

Color changes were observed on the surface of the sample during vaporization tests. Surface depletion of C results in a change from the characteristic golden color of TaC to a silver-gray color. The interior of the samples, however, retained the golden color, as, for example, did samples heated for 100 hours in hydrogen at 2000°C and 55 hours at 2930°C in Ar + 3H₂. X-ray analysis showed that the center was nearly stoichiometric TaC in both cases. These observations indicate a severe compositional gradient near the surface of the test samples and are consistent with a diffusion-controlled mechanism for loss of C from TaC in this temperature range.

Diffusion coefficients were calculated from the weight changes for the loss of C from TaC through a C deficient (TaC_{1-x}) layer. The results are shown in Table 11.5.

The loss of carbon from TaC is a reversible process. Carbon evaporates preferentially from TaC in an atmosphere of C activity lower than that of the solid throughout its homogeneity range. Substoichiometric TaC will absorb C from atmospheres of higher C activities. Thus, by controlling the C activity of the atmosphere, preferential evaporation of

¹"Fourth Annual Report — High-Temperature Materials and Reactor Component Development Programs, Volume II — Materials," GE-NMPO, GEMP-334B, February 26, 1965, pp. 107–112.

TABLE 11.5
DIFFUSION COEFFICIENTS FOR CARBON IN TaC_{1-x}

Specimen	Atmosphere	Temperature, °C	Diffusion Constant, cm^2/sec
22A	Ar + 3H_2	2000	1.45×10^{-10}
22B	Ar + 3H_2	2300	$\begin{cases} 3.22 \times 10^{-10} \\ 9.42 \times 10^{-10} \end{cases}$
16	Ar + 3H_2	2930	1.37×10^{-8}
18B	H_2	2300	$\begin{cases} 9.32 \times 10^{-10} \\ 1.99 \times 10^{-9} \end{cases}$
20	H_2	2650	2.74×10^{-9}

C from a TaC_{1-x} sample of any composition in the single-phase region can be suppressed. When this is accomplished, the C activity of the solid in equilibrium with an atmosphere of known activity is also known.

The stability studies have been reported in detail previously.^{2,3}

EFFECT OF STRAIN ON LATTICE PARAMETERS

As noted above, severe compositional gradients occur due to preferential C evaporation from heat-treated TaC. X-ray lattice parameter measurements indicate that carbide surfaces are often strained due to this C depletion. These strains, in turn, cause the calculated lattice parameters to be biased, and significant errors are introduced into compositions estimated from lattice parameter. X-ray data from the present studies on TaC, as well as from similar data on NbC reported in the literature,⁴ were analyzed to develop a means for determining when strain exists and to develop an analytical technique for taking strain into account when estimating composition from lattice parameter measurements.

The relative magnitude and direction of the strain may be calculated from lattice parameters measurements on carbides with the cubic NaCl structure. The parameters of TaC_{1-x} in this study were calculated from both the $\text{Cu K}\alpha_1$ and $\text{Cu K}\alpha_2$ peaks of the (331), (420), (422), and (333) (511) planes. These parameters were analyzed statistically by multiple regression against the variables $\cos\theta \cot\theta$ for the instrumental error, and a strain parameter Γ^* for the error due to strain.

These studies have shown that strain effects are present in lattice parameter measurements whenever Ta or Nb carbides are heated under non-equilibrium conditions. The degree and sense of the strain is dependent upon the thermal history of the specimen.

On the basis of these analyses, an analytic expression was derived which permits determination of the lattice parameter (a_0) from the measured parameter (a) corrected for instrumental error ($\cos\theta \cot\theta$ term) and the strain parameter (Γ term) by the following equation:

$$a = a_0 + b \cos\theta \cot\theta + c (\Gamma - \Gamma_0).$$

A positive strain coefficient (c) indicates that the strain is due to C depletion from the surface, whereas a negative coefficient indicates a higher C concentration at the surface.

* Γ is a parameter which varies roughly in proportion to Poisson's ratio, and which for planes in cubic lattices equals $(h^2k^2 + k^2l^2 + l^2h^2)/(h^2 + k^2 + l^2)^2$.

²GEMP-334B, pp. 114-120.

³"Fifth Annual Report - High-Temperature Materials Program, Part B," GE-NMPO, GEMP-400B, February 28, 1966, pp. 140-143.

⁴E. K. Storms, N. H. Kirkorian, and C. D. Kempter, "Crystallographic Data: Niobium Carbide," Analytical Chemistry, Vol. 32, No. 12, 1960, p. 1722.

The coefficient is zero for a constant composition within the layer penetrated by the X-ray beam, as, for example, when the carbide has been equilibrated with an atmosphere of fixed C activity.

The analysis of compositional gradients in carbides and strain analyses based on these measurements were discussed more fully in a previous report.⁵

11.3 NON-STOICHIOMETRY IN Ta AND U MONOCARBIDES

Refractory carbides, such as TaC_x and UC_x , are of interest for high-temperature applications principally because of their high melting points. These materials, however, characteristically undergo compositional variations and deviations from stoichiometry at high temperatures; hence, the reactivity of C must be examined from the standpoint of C activity as a function of composition. The object of this work was, therefore, to establish the C activity of Ta and U monocarbides as a function of composition and temperature. Related thermodynamic properties were deduced from an analysis of the data making use of the model proposed by Hoch⁶ for nonsubstitutional solid solutions.

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of equilibrating the monocarbide powder with an atmosphere of controlled C activity. The desired C activities were obtained by introducing hydrogen-methane gas mixtures at a pressure of 1.2 atmosphere into a Re muffle, as shown in Figure 11.1. The exterior portions of the furnace were maintained in hydrogen at 1.1 atmosphere. Carbon content of the controlled atmosphere was checked by chemical analysis of the exit gas, and oxygen content, as water, by a Beckman Electrolytic Hygrometer. Unit C activity was achieved in some runs by heating the powders in hydrogen in a closed graphite crucible in the presence of graphite powder. The principal gas species in the atmosphere in each run were determined by use of the thermodynamic functions of McBride, et al.⁷ The measured amount of CH_4 at room temperature was taken to be the total C in all species at the temperature of the experiment, except where unit C activity was assumed to calculate the concentration of the gaseous species in hydrogen in equilibrium with graphite. The methane content of the gas was varied between 1 and 100 ppm, and the oxygen content was found to vary between 1 and 15 ppm.

Tantalum monocarbide samples consisted of powder of average particle size < 44 microns whose X-ray and chemical analyses are given in Table 11.6. These powders, in Re crucibles, were equilibrated with the gas mixtures at temperatures between 1800° and 2350°C. X-ray diffraction analysis of equilibrated powders showed no evidence of strain due to compositional gradients.

Samples were heated in increments of 1 to 12 hours depending upon temperature. After each interval, the samples were weighed and lattice parameters were measured to establish when equilibrium was being approached; i. e., powders were heated until the strain effect due to compositional gradients was insignificant and lattice parameters varied by less than 0.0010 Å between successive readings. Compositions were calculated from the lattice parameter a_0 , corrected for strain effects and instrumental error, using the equation determined by Bowman⁸ for the variation of lattice parameter with C-to-Ta ratio.

⁵GEMP-400B, pp. 143-146.

⁶M. Hoch, "Statistical Model for Nonsubstitutional Solutions," Trans. Met. Soc. of AIME, Volume 230, 1964, p. 138.

⁷B. J. McBride, S. Heimel, J. C. Ehler, and S. Gordon, "Thermodynamic Properties to 6000°K for 210 Substances Involving the First 18 Elements," NASA SP-3001, 1963.

⁸A. L. Bowman, "The Variation of Lattice Parameter with Carbon Content of Tantalum Carbide," J. Phys. Chem., Vol. 65, 1961, p. 1596.

Fig. 11.1 — Schematic diagram of experimental set-up for equilibrium studies

TABLE 11.6

CHEMICAL AND X-RAY ANALYSES OF TANTALUM CARBIDE,
COMPOSITIONS USED IN EQUILIBRATION EXPERIMENTS

Nominal Composition	TaC _{0.8}	TaC _{0.90}	TaC _{0.99}
Carbon, %	4.94	5.76	6.32
Uncombined carbon, ppm	134	<100	2700
Oxygen, ppm	167	177	163
Nitrogen, ppm	105	40	21
X-ray lattice parameter (a_0), Å	4.42577	4.44303	4.45585
C/Ta (chemical analysis)	0.784	0.921	0.973
C/Ta (X-ray analysis) ^a	0.800	0.910	0.992

^aBased on: A. L. Bowman, "The Variation of Lattice Parameter with Carbon Content of Tantalum Carbide," Journal of Physical Chemistry, Vol. 65, 1961, pp. 1596–1598.

To ensure equilibrium, $\text{TaC}_{0.80}$ and $\text{TaC}_{0.99}$ powders were heated side-by-side in a divided crucible in some tests. The change in composition of each powder was determined periodically by lattice parameter measurements. An exponential curve of the form $A = A_{\infty} + Be^{-Ct}$ fitted to the data yielded the asymptotic lattice parameter from which equilibrium compositions were calculated by Bowman's⁸ equation. Results of a typical run are shown in Figure 11.2. The calculated compositions for samples approaching equilibrium from both sides in this manner agree to within 1.0 percent.

Fig. 11.2 — Extrapolated lattice parameter versus time at 1800°C for $\text{TaC}_{0.800}$ and $\text{TaC}_{0.994}$ in $\text{H}_2 + 14 \text{ ppm CH}_4$

Uranium monocarbide samples consisted of powders (< 44 microns particle size) encapsulated in 0.05-cm-thick Re capsules formed from Re sheet and sealed in vacuum by electron-beam welding. Since Re does not form a stable carbide but dissolves up to 11.7 atomic percent C,⁹ it serves as a membrane permeable to C through which the carbide may be equilibrated with the C activity of the outside gas atmosphere. In this way, evaporation of U is suppressed.

The composition of the commercially processed starting material is given in Table 11.7.

The samples were heated at 1500°C and 1700°C in the hydrogen – methane mixtures. They were weighed at regular intervals and assumed to have achieved equilibrium when a weight change less than 0.01 percent of the sample weight was observed in a 6-hour period. The total weight loss in a 2.5-g sample was about 0.030 g. Samples for X-ray diffraction analysis of the starting powder and of equilibrated powders after each series of runs were sealed in glass capillary sample holders under argon to avoid exposure of the sample to air.

⁹J. E. Hughes, "A Survey of the Rhenium-Carbon System," J. Less Common Metals, Vol. 1, 1959, p. 377.

Results

The C activity versus composition data measured for TaC_x and UC_x at various temperatures are summarized in Tables 11.8 and 11.9, respectively, along with a calculated activity coefficient for each data point, using a method described below.

In the TaC studies, chemical analyses showed the oxygen content to be less than 600 ppm in all the samples analyzed. This concentration is low enough to be ignored in subsequent discussions. In the case of UC_x , however, the oxygen content is high enough that the system under study must be considered as a portion of the U-C-O ternary system, as discussed below.

DISCUSSION

The variation of the C activity with composition and temperature was analyzed in terms of the statistical model of Hoch⁸ to (1) study the implications of deviations from stoichiometry in TaC and UC, (2) establish the defect interaction energies, and (3) to determine the Frenkel

TABLE 11.7
CHEMICAL AND X-RAY ANALYSES
OF URANIUM CARBIDE USED IN
EQUILIBRIUM EXPERIMENTS

Carbon, %	4.77
Uncombined carbon, ppm	2300
Oxygen, ppm	6300
Nitrogen, ppm	140
X-ray lattice parameter (a_0), Å	4.960 ^a
C/U (chemical analysis)	0.951

^aVery diffuse lines.

TABLE 11.8
CARBON ACTIVITY AS A FUNCTION OF TEMPERATURE AND COMPOSITION IN TaC_x

Temperature, °C	x in TaC_x		Oxygen, ppm	Carbon Activity (a_c)	$A = RT \ln \left(\frac{1-x}{a_c} \right)$
	X-Ray Analysis	Chemistry			
1800	0.805			0.0014	-32.8
1800	0.926			0.0247	-25.7
1800	0.931			0.0283	-25.4
1800	0.925			0.0147	-25.6
1800	0.936			0.0283	-25.7
1830	0.927	0.864	390	0.0418	-23.9
2035	0.928	0.959	561	0.0287	-28.0
2035	0.933	0.955	369	0.0450	-26.3
2150	0.845			0.0085	-31.0
2150	0.823			0.0073	-31.0
2220	0.914	0.869	547	0.0342	-28.4
2220	0.924			0.0449	-27.5
2250	0.995			1.0000	-26.5
2260	0.897			0.0401	-27.1
2300	0.872			0.0185	-30.2
2300	0.875			0.0225	-29.3
2300	0.869			0.0225	-29.1
2300	0.866			0.0185	-30.0
2300	0.994			1.0000	-26.3
2345	0.900			0.0292	-29.8
2345	0.994			1.0000	-26.6
					avg. -27.9 ± 1.9

TABLE 11.9
CARBON ACTIVITY AS A FUNCTION OF TEMPERATURE
AND COMPOSITION IN $UC_xO_{0.999}$

Temperature, °C	Composition, x + y	Carbon Activity a_c	$RT \ln \left(a_c \frac{1-x-y}{x} \right)$ kcal/mole
1500	0.992	0.010	-32.8
1500	0.994	0.044	-29.4
1500	0.991	0.039	-28.4
1700	0.990	0.061	-29.5
1700	0.971	0.010	-32.5
1700	0.993	0.033	-32.4
1700	0.952	0.012	-29.9
			avg. -30.7 ± 1.6

energy associated with a transfer of a C atom from a singly occupied site to a site already occupied by another C atom in the U monocarbide phase region.

Activity coefficients for TaC derived in this analysis are included in Table 11.8. The activity coefficient, to a first approximation, is independent of composition for $0.805 < x < 0.995$ and may be only slightly dependent on temperature for $1800^\circ < T < 2350^\circ\text{C}$. The average value for the activity coefficient, $RT \ln \left(a_c \frac{1-x}{x} \right)$, is -27.9 ± 1.9 kcal/mole. This agrees with the value of approximately -27 kcal/mole obtained by Hoch¹⁰ in an analysis of the evaporation rate data of Fries¹¹ for NbC, and of Coffman, et al.,¹² for TaC.

The experimental results for U carbide ($UC_xO_{0.999}$) are given in Table 11.9. The data show that the activity coefficient is fairly constant as a function of temperature and composition, with an average value of -30.7 ± 1.6 kcal/mole. If the carbon-oxygen interaction energy is assumed to be equal to the value deduced by Hoch⁶ for the carbon-oxygen interaction in the iron-carbon-oxygen system (-26.4 kcal/mole), the activity coefficient for C in UC_x ($x < 1$) to a first approximation is

$$RT \ln \left(a_c \frac{1-x}{x} \right) = -28.1 \pm 1.6 \text{ kcal/mole.}$$

This value was deduced from data on compositions close to stoichiometry (average $x = 0.983$), ignoring double occupancy of some C lattice sites. When double occupancy is taken into account, the activity coefficient becomes:

$$RT \ln \left(a_c \frac{1-x}{x} \right) = -26.9 \pm 1.6 \text{ kcal/mole.}$$

Calculations of the C activity coefficient using the data of Storms¹³ for $UC_{0.995}$ gives

$$\begin{aligned} RT \ln \left(a_c \frac{1-x}{x} \right) &= -25.9 \text{ kcal/mole (T = 2100}^\circ\text{K)} \\ &= -25.3 \text{ kcal/mole (T = 2300}^\circ\text{K)} \end{aligned}$$

This agrees with the above value.

¹⁰M. Hoch, private communication.

¹¹R. J. Fries, "Vaporization Behavior of Niobium Carbide," Journal of Chemical Physics, Vol. 37, No. 2, July 1962, pp. 320-327.

¹²J. A. Coffman, G. M. Kibler, T. R. Riethoff, and A. A. Watts, "Carbonization of Plastics and Refractory Materials Research, Part I," WADD-TR-60-646, Part I, February 1961.

¹³E. K. Storms, "A Mass Spectrographic Study of the Vapor Pressure of U(g) and UC_2 (g) Over Various Compositions in the Uranium-Carbon System," Thermodynamics, Vol. 1, IAEA, Vienna, 1966.

The activity coefficient for the second C atom on a C site in U monocarbide is 6.8 ± 0.5 kcal/mole. Therefore, the Frenkel energy for UC_x , i.e., the energy required to move a C atom from a C site to a second site already occupied by a C atom, is 33.7 ± 1.7 kcal/mole.

Based on this analysis, the disorder in stoichiometric uranium carbide ($UC_{1.0}$) was estimated. The results indicated that at 2000°K the fraction of available C sites occupied is 0.986; at 2500°K, it is 0.967. In other words, in $UC_{1.0}$ at 2000°K, 1.4 percent of the C sites are doubly occupied; at 2500°K, 3.3 percent are doubly occupied.

The experimental procedure and results for the equilibration studies have been discussed extensively in previous reports.^{14, 15} A detailed discussion of the data analysis in terms of the statistical model has been published.¹⁶

11.4 PLANS AND RECOMMENDATIONS

This task terminated June 30, 1967. A topical report will be issued covering the work accomplished in this program.

¹⁴GEMP-400B, p. 146-155.

¹⁵"Sixth Annual Report - High-Temperature Materials Program, Part A," GE-NMPO, GEMP-475A, March 31, 1967.

¹⁶M. Hoch, E. F. Juenke, and L. H. Sjodahl, "Non-Stoichiometry of Tantalum Carbide and Uranium Monocarbide," GE-NMPO, GEMP-540, prepared for presentation at IAEA Symposium on Thermodynamics of Nuclear Materials, Vienna, Austria, September 4-8, 1967.