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EQUILIBRIA OF URANIUM CARBIDES IN THE MOLTEN FLUORIDE SOLUTIONS OF UF_3 AND UF_4 CONTAINED IN GRAPHITE AT 850°K*

L. M. TOTH and L. O. GILPATRICK
Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenessee 37830

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Abstract—The equilibration of dilute molten fluoride solutions of UF_4 with UC, U_2C_3 and UC_2 at 850°K has been investigated to establish that a UC_2 phase, possibly oxygen stabilized, is the stable carbide phase in contact with dilute UF_3-UF_4 solutions contained in graphite. The carbides were identified by X-ray powder patterns. Lattice parameters for these carbides are included. UF_3 and UF_4 concentrations in solution were measured by near i.r.-visible adsorption spectrophotometry. Equilibrium quotients, $Q = (UF_3)^4/(UF_4)^3$ were calculated for each of the carbides in contact with the molten fluoride solution based on the reaction:

$$UC_x + 3UF_4 \rightleftarrows 4UF_3 + xC.$$

INTRODUCTION

THE REDOX equilibrium of dilute molten fluoride solutions of UF_3 in contact with graphite:

$$4UF_3 + xC \rightleftarrows 3UF_4 + UC_x \qquad (1)$$

to form soluble UF_4 and an unidentified solid phase carbide denoted as UC_x is a subject of interest in the development of molten salt breeder reactors. These reactors are designed to operate on liquid fuel systems which include these components. The above equilibrium determines the maximum concentration of UF_3 that can be maintained in the fuel solution before the undesirable loss of uranium to the moderator graphite occurs. In the laboratory, LiF–BeF_2 (66–34 mol %) at 500–700°C has been used as the solvent mixture for this 3-phase equilibrium study while in the reactor a slightly more complex molten fluoride mixture is used.

In an effort to unambiguously identify the carbide phase, UC_x, as well as to further demonstrate the validity of the above equilibrium as written in Eqn (1), the back reaction at 850°K has also been investigated by separately reducing dilute solutions, typically less than 0·1 mole %, of UF_4 with the three known carbides of uranium:

$$2UC + 3UF_4 \rightleftarrows 4UF_3 + UC_2{}^\dagger \qquad (2)$$

$$1/2U_2C_3 + 3UF_4 \rightleftarrows 4UF_3 + 3/2C \qquad (3)$$

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†The inclusion of UC_2 as a reaction product in Eqn (2) will be explained in the discussion.

$$UC_2+3UF_4 \rightleftarrows 4UF_3+2C \tag{4}$$

and measuring UF_3 and UF_4 concentrations in situ during and after equilibration.

From previously published thermodynamic data for the carbides of uranium[1, 2], the free energies of formation at 850°K given in Table 1 were calculated. From these free energies of formation the order of the equilibrium quotients, $Q = (UF_3)^4/(UF_4)^3$, for reactions (2), (3) and (4) can be predicted since the solutions are identical and therefore have the same activity coefficients for UF_3 and UF_4. It is expected then that $Q_2 \leqslant Q_3 < Q_4$. The work reported here describes the actual measurement of the equilibria written in Eqns (2), (3) and (4).

Table 1. Currently accepted free energies of formation for uranium carbides at 850°K in kcal/mole. Taken from thermodynamic data of Storms[1] and Behl and Egan[2]

	UC	$1/2U_2C_3$	UC_2
$\Delta G^\circ_{850°K}$	−24·9[1]	−24·9[2]	−22·8[1] −22·8[2]

EXPERIMENTAL

Approximately 0·5 cm^3 of salt solution plus the reagent carbide were contained in a diamond-windowed spectrophotometric cell fabricated from graphite and fitted with Type II-a diamond windows[3]. The entire cell assembly was placed in an optical furnace surrounded by an atmosphere of purified helium. Equilibrium concentrations of UF_3 and UF_4 were quantitatively determined by measuring their absorption spectra in the 2500–300 μm region on a Cary 14-H recording spectrophotometer. Intensities of the respective absorption peaks were converted to concentrations using Beer's law, $A = \epsilon c l$, where A is the measured absorbance due to the soluble species, ϵ is the absorption coefficient determined from previously measured calibration spectra [4, 5], c is the concentration of the light absorbing species in mole/l. and l is the path length of the solution. The major sources of error in the experiment were due to the uncertainty in the spectral baseline determination and to the calibration of the absolute absorption coefficients for UF_3 and UF_4 at selected wavelength regions. Although these errors affect the numerical value of the equilibrium quotients which are calculated from the data, they do not alter the relative reactivities which have been determined. The solid phases were analyzed before and after the equilibration process. The carbides used in this work were prepared at the Los Alamos Scientific Laboratory and shipped in sealed glass ampules. An X-ray analysis of each reagent carbide showed no detectable contaminants or other carbides. Reactor-grade ATJ graphite spectrophotometric cells were H_2-fired at 1000°C for 4 hr before usage. Handling of the carbides and fluoride salt components throughout this work was performed in an inert atmosphere glove box of less than 1 ppm H_2O and O_2 content. Equilibria were achieved by heating the samples at temperatures for 2–3 days with periodic stirring in the presence of excess carbide. When the concentration of UF_3 and UF_4 ceased to change, the temperature was dropped and the equilibrium allowed to shift back. Equilibria were approached both from high and low temperatures by this procedure and all values measured until no change was noted. In addition to the equilibration experiments conducted in the diamond-windowed spectrophotometric cell, the same reactions were carried out in sealed nickel capsules that were held for 10 days at 850°K under constant agitation in an atmosphere 4% H_2 and 96% argon. These nickel

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1. E. K. Storms, *The Refractory Carbides*, Vol. 2, pp. 171–213. Academic Press, New York (1967).
2. W. K. Behl and J. J. Egan, *J. elec. Soc.* **113**, 376 (1966).
3. L. M. Toth, J. P. Young and G. P. Smith, *Analyt. Chem.* **41**, 683 (1969).
4. J. P. Young, *Inorg. Chem.* **6**, 1486 (1967).
5. L. M. Toth, *J. phys. Chem.* **75**, 631 (1971).

capsule experiments were performed to demonstrate that trace impurities in the graphite spectrophotometric cells were not altering the course of the equilibration between uranium carbide and molten fluoride solution of UF_3 and UF_4. The residual carbides from this series of tests were analyzed by the Debye–Sherrer X-ray technique and the results were identical to those found using the graphite cells.

RESULTS AND DISCUSSION

The mole fractions of UF_3 and UF_4 determined from their absorption spectra in solution at equilibrium and the computed equilibrium quotients are listed in Table 2 along with the experimental uncertainty in the q values. The two reagents, UC_2 and U_2C_3 were found to be very similar in their reducing power while UC was found to be much stronger. The order of the Q values within the experimental error is then given as $Q_{\text{Eqn }(2)} > Q_{\text{Eqn }(3)} \geqslant Q_{\text{Eqn }(4)}$ which is opposite that predicted from the $\Delta G°$ values listed in Table 1.

Table 2. Measured concentrations of UF_3 and UF_4 (mole fraction) and equilibrium quotients, $Q = (UF_3)^4/(UF_4)^3$ for dilute $UF_4 + UF_3$ in LiF–BeF_2 (66–34 mole %) at 850°K

	Eqn (2)	Eqn (3)	Eqn (4)
Reagent carbide	UC	U_2C_3	UC_2
$[UF_3] \times 10^4$	6·72	2·5	2·0
$[UF_4] \times 10^4$	4·95	5·7	6·7
$Q \times 10^3$	$1{\cdot}7\binom{+3{\cdot}5}{-1{\cdot}3}$	$0{\cdot}02\binom{+0{\cdot}020}{-0{\cdot}012}$	$0{\cdot}006\binom{+0{\cdot}0045}{-0{\cdot}0040}$

Errors in the equilibrium quotients are given in parentheses.

Uranium dicarbide was positively identified by X-ray analysis as a product of the UC reaction with UF_4 in both the graphite spectrophotometric cell and the sealed nickel capsule experiments. It is therefore included as a product in Eqn (2). No other carbides were produced in the reactions using either U_2C_3 or UC_2. Consequently Eqns (3) and (4) are written with only graphite as the solid phase produce of the reaction.

It has been generally regarded from phase diagram studies that UC_2 is metastable below 1500°C [1] forming U_2C_3 and C. Furthermore the reaction

$$UC + C \rightarrow UC_2 \tag{5}$$

has been established as having a negative free energy of reaction only above 1500°C [6]. Previous instances of UC_2 formation below 1500°C such as the pyrolysis of methane with uranium metal at 700°C have been reported [7] but a mechanism involving reaction with an active form of carbon has been used to explain its formation as a metastable phase [6]. The formation of a UC_2 phase via the equilibrium mechanism, Eqn (2), using UC as the reagent is an example that does not involve an activated carbon. The uranium dicarbide phase is formed as a product even when UC is equilibrated with the molten fluoride solution of UF_3 and UF_4 in a nickel capsule in the absence of carbon. These results suggest that the UC_2

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6. J. M. Leitnaker and T. G. Godfrey, *J. nucl. Mat.* **21**, 175 (1967).
7. H. S. Kalish, Second Uranium Carbide Meeting, Battelle Memorial Inst., Columbus, Ohio. TID-7589, p. 59 (1960).

phase is a stable phase with respect to decomposition into other carbides and graphite at 850°K.

Contamination of the reagent carbides during an experiment by atmospheric impurities such as oxygen and nitrogen are most often cited as causes for discrepancies in the carbide behavior[1]. However, no uranium oxides were identified in the X-ray analyses of the reaction products indicating that oxygen had not obviously interferred with the equilibria. The solubility of oxygen in UC to form UC_xO_{1-x} can account for a decrease in the UC activity which would result in a subsequent decrease in the value of Q_{UC}. To examine this possibility, the lattice parameters of the carbides were measured before and after equilibration. They are given in Table 3 along with the currently accepted values. Lattice parameters have been shown to be a useful means to monitor the amount of dissolved oxygen especially in the case of UC where quantitative data are available[8]. Little change in the lattice parameters for UC is noted in Table 3 as a result of the equilibration, and it is concluded that oxygen had not altered the stability of the monocarbide phase.

The effect of oxygen on the lattice constants of U_2C_3 and UC_2 is less clearly defined. Henry *et al.*[9, 10] observe that U_2C_3 is unique with regard to the constancy of its lattice parameter and suggest that the oxygen content of U_2C_3 never does become significant. In the case of UC_2 an increase in the oxygen content has generally been regarded as causing a decrease in the lattice parameters[11]. In Table 3 the experimental parameters show a slight increase as a result of the equilibration reaction. Since it is not consistent with previous observations, it was not possible to determine the significance of this change.

As a further test, some melt equilibrations were interrupted by freezing the reaction mixture directly in the graphite spectrophotometric cells after the concentrations of UF_3 and UF_4 in solution had ceased to change. The cell was transferred to the helium dry box without exposure to the air and additional reagent carbides added. The cell was then returned to the furnace and reheated to the same temperature as before to demonstrate that the reagent carbides (1) had not been

Table 3. Lattice parameters for reagent uranium carbides before and after equilibration reactions in Å. (Errors in Å × 10^4 in parentheses)

	Accepted value*	Before	After
UC	$a = 4·9605\,(2)$	4·9617 (7)	4·9607 (3)
U_2C_3	$a = 8·0889\,(9)$	8·0881 (4)	8·0917 (42)
UC_2	$a = 3·5251\,(5)$	3·5198 (14)	3·5317 (11)
	$c = 5·9962\,(8)$	5·9900 (14)	5·9900 (11)

*Taken from Ref. [1].

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8. (a) F. Anselin, G. Dean, R. Lorenzelli and R. Pascard, *Carbides in Nuclear Energy*, (Edited by L. E. Russell), Vol. 1, pp. 113–161. Macmillian, London (1964).
   (b) N. H. Brett, E. A. Harper, H. J. Hedger and J. S. Pottinger, *ibid.* pp. 162–183 (1964).
9. J. Henney, N. A. Hill and D. T. Livey, AERE-R4175 (1962).
10. J. Henney, D. T. Livey and N. A. Hill, AERE-R4176 (1963).
11. P. E. Potter, AERE-R6438 (1970).

totally consumed and (2) had not reacted with trace impurities during the experiment. The equilibrium quotients before and after the addition were found to be the same. It is recognized, however, that this test does not eliminate the possibility that UC_2 had been affected by impurities before usage.

Using the Q values of Table 3 at 850°K and the previously established $\Delta G^\circ_{850^\circ K} = -49{\cdot}8$ kcal/mole* for U_2C_3 an estimate of $\Delta G^\circ_{850^\circ K}$ for UC and UC_2 can be made assuming that the activities of the pure phase carbides are unity and that the activity coefficients for UF_3 and UF_4 do not change from Eqns (2–4). These values are found to be $-27{\cdot}0 \pm 2{\cdot}5$ and $-22{\cdot}3 \pm 2{\cdot}5$ kcal mole for UC_2 and UC, respectively. The value for UC agrees within the experimental error with the previously reported free energy of formation given in Table 1 but suggests here that UC is less stable than U_2C_3 at 850°K. This observation cannot be made from the previously reported data. The value for UC_2 is however unusually low.

It is impossible to ignore the extensive work summarized by Storms[1] which has led to establish that UC_2 decomposes with the formation of U_2C_3 and C at approximately 1500°C and is therefore metastable at lower temperatures. The failure of UC_2 to decompose has been explained as an "oxygen stabilization" of the dicarbide phase. Such a mechanism could be used to explain the results which are given in Table 2 but there is no evidence from the X-ray analyses to support this conclusion. It must also be noted that UC should also be affected by oxygen in a similar manner, realizing that it can accommodate oxygen up to $U(C_{0\cdot65}, O_{0\cdot35})$[11]. Yet no change in the lattice parameter nor increased stability was observed for UC. If UC_2 is oxygen stabilized, then it is unique in this behavior with respect to both UC and U_2C_3.

The usage of a molten fluoride medium such as UF_3 and UF_4 in a LiF–BeF_2 solvent enables a much more rapid and complete equilibrium of solid carbides with graphite than would otherwise be possible at temperatures below 1000°C. This is achieved by the redox mechanism of Eqn (1) which permits equilibria to be achieved within a day. The observation that a UC_2 *phase* is the most stable component in equilibrium with uranium fluoride solutions contained in graphite is of prime interest because it determines the maximum UF_3/UF_4 ratio which may be safely held in a reactor system without decomposition of UF_3.

In conclusion, the results of this work have shown that UC_2 is the stable uranium carbide phase in equilibrium with a LiF–BeF_2 (66–34 mole %) solution of UF_3 and UF_4 contained in a graphite cell. The formation of UC_2 at 850°K via Eqn (2) suggests that it may not be metastable at this temperature. "Oxygen-stabilization" of UC_2 which could cause its formation and increased stability cannot be dismissed because an examination of this possibility has not been conclusive. Additional data describing the mechanism of "oxygen-stabilization" and the extent to which it quantitatively affects the UC_2 stability at these temperatures are necessary in order to resolve this question.

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*The value of $\Delta G^\circ_{850^\circ K}$ for U_2C_3 was chosen as fixed because previous data existed at this temperature region and the influence of atmospheric contaminants was expected to be minimal.