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A FUSED KCl-LiCl/ZINC SYSTEM.

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REACTIONS OF URANIUM CARBIDE IN A FUSED KCl-LiCl/ZINC SYSTEM

by

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1964

## TABLE OF CONTENTS

	Page
INTRODUCTION	1
PREPARATION OF MATERIALS	10
Carbide Preparation	10
Salt Purification	14
EXPERIMENTAL APPARATUS AND PROCEDURES	18
Rocking Furnace Equilibrations	18
Large Scale Equilibrations	19
Fused Salt Cell EMF Measurements	24
Separation Methods	30
Analytical Procedure	31
EXPERIMENTAL RESULTS	32
UC-Zn Equilibrations	32
Large Scale $\text{ZnCl}_2$ -UC Equilibrations	57
UC- $\text{ZnCl}_2$ Equilibrations--Rocking Furnace	69
Electromotive Force Measurements	91
CONCLUSIONS	111
SUMMARY	119
LITERATURE CITED	121
ACKNOWLEDGEMENTS	126
APPENDIX	127

## INTRODUCTION

Uranium carbide fuels have become increasingly important in high temperature reactor technology during recent years. Consequently, several international symposia on carbide fuels have been held throughout the world, (1,2,3,4,5,6) and intensive investigations of the carbides have been carried out at many laboratories. This increased interest has developed because uranium carbide possesses many of the advantages of the oxide as a nuclear fuel and in addition has better thermal conductivity and a higher uranium density (7). The advantages seem to indicate that uranium carbide may soon be in extensive use as a reactor fuel. Therefore, it has become desirable to study the behavior of the carbides in the various pyrometallurgical recovery methods developed at Ames Laboratory (8,9, 10,11) and elsewhere (12,13,14).

An investigation of the separation of various components from uranium by oxidation-reduction reactions in a liquid KCl-LiCl/zinc system was reported by Chiotti and Parry (8). They determined the order in which the metals iron, molybdenum, niobium, chromium, yttrium, zirconium, thorium, uranium, protactinium and cerium were oxidized into the salt by zinc chloride and the order in which they were reduced from the

the salt by the addition of magnesium. Their data indicated that a good separation of uranium from iron, molybdenum, niobium, zirconium, and chromium could be achieved in a single equilibration. Yttrium was oxidized simultaneously with uranium, and portions of the thorium, cerium and protactinium were oxidized before all of the uranium was oxidized. The possibility of obtaining a high degree of separation of uranium from these remaining contaminants by multiple extraction techniques has been considered (15). The separation of cerium, yttrium and neodymium from thorium has been investigated by J. Klepfer (16). With the addition of preliminary reactions, a KCl-LiCl/zinc system can be used for reprocessing any type of fuel element. In the case of the oxide or carbide fuels a preliminary step in which the reactor fuels are converted to the chloride would be necessary. The carbide might be converted to the chloride in a KCl-LiCl/zinc system by the addition of zinc chloride or by passing controlled amounts of chlorine or hydrogen chloride gas into the system with the uranium carbide.

The purpose of this investigation was to determine the behavior of uranium monocarbide in a fused salt-liquid zinc system. Available thermodynamic data, summarized in Table 1,

indicated a number of possible reactions. Two systems or types of reactions were investigated. The reaction of uranium carbide with liquid zinc was considered first. Secondly, the oxidation of uranium carbide by the addition of  $\text{ZnCl}_2$  to the  $\text{LiCl-KCl/zinc-UC}$  system was considered.

Table 1. Pertinent thermodynamic data for a  $\text{KCl-LiCl-ZnCl}_2/\text{Zn}(\ell)\text{UC}_x(\text{s})$  system\*

Compound	- $\Delta F^\circ$ Standard free energy of formation Kcal/mole				Ref.
	500°C	600°C	700°C	800°C	
$\text{UC}_2$	39.4	39.0	38.6	38.2	18
	41.7	41.0	40.3	39.6	17
	28.9	28.8	28.7	28.4	19
	20.3	20.6	20.9	21.2	20
	24.1	24.2	24.3	24.4	21
$\text{U}_2\text{C}_3$	46.7	46.3	46.0	45.7	20
	49.1	49.2	49.3	49.3	21
$\text{UC}$	18.7	18.4	18.0	17.5	17
	20.7	20.7	20.7	20.5	19
	19.8	19.7	19.5	19.4	20
	23.0	23.2	23.42	23.6	21
$\text{UCl}_3$	172.0	168.0	163.0	158.0	22
$\text{U}_2\text{Zn}_{17}$	54.0	46.0	38.0	30.0	22
$\text{ZnCl}_2$	74.0	72.0	70.0	68.0	22

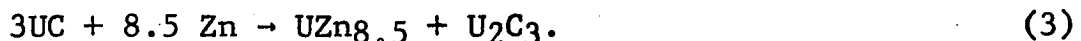
\*The activity coefficient for  $\text{ZnCl}_2$  in  $\text{KCl-LiCl}$  eutectic is given by the equation

$\log_{10}(\gamma_{\text{ZnCl}_2}) = (-1909/T - 0.393)(1 - N_{\text{ZnCl}_2})^2$  (23).  
The activity coefficient of  $\text{UCl}_3$  in the same salt is approximately unity (24,25,26).

The most probable reactions between uranium monocarbide and liquid zinc were considered to be the following:



or possibly



The free energies of reaction as calculated from the data of Table 1 for the Reactions 1-3 are shown in Table 2. It is evident from these data that there is considerable uncertainty in the thermodynamic data and that there is still some question as to which, if any, of the higher carbides are stable at temperatures below 1000°C. As early as 1950, Snow (27) had reported the existence of the sesquicarbide,  $\text{U}_2\text{C}_3$ , but had concluded that it was stable only above 1800°C. In 1960, researchers at Battelle (17) proposed a phase diagram of the uranium-carbon system which indicated that uranium sesquicarbide was stable only below 1700°C. In 1963, a panel of experts at the Symposium on Carbide Fuels in Vienna (21) concluded that uranium dicarbide was not stable below 1750°C, and that uranium sesquicarbide was the only higher carbide phase at lower temperatures. Experimental evidence that uranium dicarbide was not stable at lower temperatures had been

Table 2. Standard free energy change for some reactions involving uranium compounds

Reaction	$\Delta F^0$ for reaction Kcal				Ref*
	500°C	600°C	700°C	800°C	
1. UC + 8.5 Zn	-8.3	-4.6	-1.0	+2.5	17
UZn <sub>8.5</sub> + C	-6.3	-2.3	+1.7	+5.5	19
	-7.2	-3.3	+0.5	+4.4	20
	-4.0	+0.2	+4.4	+8.6	21
2. 2UC + 8.5 Zn	-31.3	-27.2	-23.2	-19.6	17
UZn <sub>8.5</sub> + UC <sub>2</sub>	-14.5	-10.4	-6.3	-2.4	19
	-7.7	-4.2	-0.9	+2.6	20
	-5.1	-0.8	+3.5	+7.8	21
3. 3UC + 8.5 Zn	-14.3	-10.2	-6.5	-2.5	20
UZn <sub>8.5</sub> + UC <sub>2</sub>	-7.1	-2.6	+1.9	+6.5	21
4. UZn <sub>8.5</sub> + 3/2 ZnCl <sub>2</sub>	-34.0	-37.0	-39.0	-41.0	22
UCl <sub>3</sub> + 10 Zn					
5. 2UC + 3/2 ZnCl <sub>2</sub>	-65.3	-64.2	-62.3	-60.6	17
UCl <sub>3</sub> + UC <sub>2</sub>	-48.5	-47.4	-45.3	-43.4	19
	-41.7	-41.4	-39.9	-38.4	20
	-39.1	-37.8	-35.5	-31.6	21
6. UC <sub>2</sub> + 3/2 ZnCl <sub>2</sub>	-19.3	-19.0	-18.4	-16.4	17
UCl <sub>3</sub> + 3/2 Zn + 2C	-32.1	-31.2	-29.6	-27.6	19
	-40.7	-39.4	-36.8	-34.8	20
	-36.9	-35.8	-33.6	-31.6	21
	-21.6	-21.0	-19.4	-17.8	18
7. 3UC + 3/2 ZnCl <sub>2</sub>	-48.3	-47.2	-45.5	-43.5	20
U <sub>2</sub> C <sub>3</sub> + UCl <sub>3</sub> + 3/2 Zn	-41.1	-39.8	-37.1	-34.5	21
8. U <sub>2</sub> C <sub>3</sub> + 3/2 ZnCl <sub>2</sub>	-75.3	-73.7	-70.0	-66.3	20
2UCl <sub>3</sub> + 3C + 3Zn	-72.9	-71.8	-66.8	-62.7	21
9. UC + 3/2 ZnCl <sub>2</sub>	-42.3	-41.6	-40.0	-38.5	17
UCl <sub>3</sub> + 3/2 Zn + C	-40.3	-39.3	-37.3	-35.5	19
	-41.2	-40.3	-38.5	-36.6	20
	-38.0	-36.8	-34.6	-32.4	21

\*The references give the sources from which the free energy of formation of the uranium carbides were obtained.

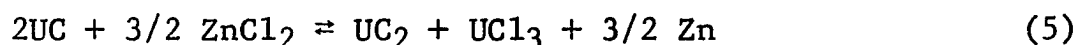
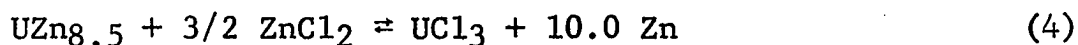


observed (28) much earlier but had been disregarded.

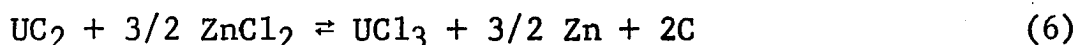
In a carbide/zinc system the activities of the various components of Reactions 1, 2 and 3 may be assumed to be unity. This assumption of unit activity is based on the observation that there is little or no mutual solubility between the liquid zinc and the compounds indicated. Consequently, if  $\Delta F^0$  for the most favorable reaction is negative, the reaction will go to completion. If  $\Delta F^0$  is positive, the reaction will not begin. The standard free energy of formation for  $\text{UZn}_{8.5}$  shows a strong temperature dependence (29) whereas the uranium carbides do not. It should, therefore, be possible to find a temperature at which the reaction will reverse. Determination of the actual temperature of reversal, for which the free energy of the reaction is zero, and identification of the equilibrium phases will yield information concerning the free energy of formation of the uranium carbides. Metallographic and x-ray diffraction data of the quenched or separated phases were obtained for the purpose of determining the nature of the equilibrium phases or compounds. At the reversal temperature the free energy change for the reaction is zero and the free energy of formation of uranium monocarbide can be calculated since the thermodynamic values of all the other constituents

are known. If, however, Reaction 2 or 3 takes place, only the ratio between the free energy of uranium monocarbide and the higher order uranium carbide product can be calculated.

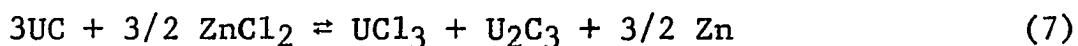
For the KCl-LiCl/zinc-UC system to which stepwise additions of  $\text{ZnCl}_2$  were made, the following additional reactions were considered:



followed by



or



followed by



The standard free energy changes for the Reactions 4, 5, 6, 7, and 8, as calculated from the data of Table 1, are also shown in Table 2.

The thermodynamic data reported prior to 1960 indicated that Reaction 6 would result in a measurable equilibrium quantity of zinc chloride and uranium trichloride in the salt phase, and therefore, with the data for the activity coefficients, Table 1, and the salt analysis, the equilibrium

constant could be determined. Knowledge of the equilibrium constant permits calculation of the free energy of formation of the dicarbides. The more recent data on uranium dicarbide and the data on uranium sesquicarbide indicate that no measurable amount of zinc chloride should be present at equilibrium in the salt phase for either Reactions 6 or 8.

If Equation 6 represents the equilibrium reaction, the standard free energy of formation of  $UC_2$  may be calculated by the relations given below. The standard free energy change for the forward reaction may be written as

$$\begin{aligned}\Delta F^0 &= -RT \ln K_a = -RT \ln \frac{(a_{UCl_3})_s}{(a_{ZnCl_2})_s^{3/2}} \\ &= -RT \ln \frac{(N_{UCl_3})_s (\gamma_{UCl_3})_s}{(N_{ZnCl_2})_s^{3/2} (\gamma_{ZnCl_2})_s^{3/2}} \\ &= \Delta F_{UCl_3}^0 - 3/2 \Delta F_{ZnCl_2}^0 - \Delta F_{UC_2}^0\end{aligned}$$

therefore

$$\Delta F_{UC_2}^0 = \Delta F_{UCl_3}^0 - 3/2 \Delta F_{ZnCl_2}^0 + RT \ln \frac{(N_{UCl_3})_s (\gamma_{UCl_3})_s}{(N_{ZnCl_2})_s^{3/2} (\gamma_{ZnCl_2})_s^{3/2}} \quad (10)$$

where  $(a_{UCl_3})_s$  and  $(a_{ZnCl_2})_s$  represent the activity of  $UCl_3$  and  $ZnCl_2$  in the salt phase, respectively;  $N$  and  $\gamma$  represent mole fraction and activity coefficient respectively. If the equilibrium carbide is  $U_2C_3$  (Reaction 7) an analogous treat-

ment gives

$$\Delta F_{U_2C_3}^O = 2\Delta F_{UCl_3}^O - 3\Delta F_{ZnCl_2}^O + RT \ln \frac{(N_{UCl_3})_s^2 (\gamma_{UCl_3})_s^2}{(N_{ZnCl_2})_s^3 (\gamma_{ZnCl_2})_s^3} \quad (11)$$

which is twice the value that would be calculated for  $UC_2$  since the right-hand side of Equation 11 is equal to the right-hand side of Equation 10 multiplied by two.

The electromotive force of the cell  $UC_x/KCl-LiCl-UCl_3/Zn$ ,  $U_2Zn_{17}$  was measured in order to study the effect of oxygen contamination on the stability of the monocarbide. Various compositions  $UO_xC_{1-x}$  were considered.

## PREPARATION OF MATERIALS

The zinc used in this study was Bunker Hill zinc which is 99.99% pure. The uranium was Ames Laboratory production uranium with typical purity given in Table 3.

Table 3. Average impurity concentrations of uranium metal utilized in investigation

Impurity	Conc. (ppm)	Method of analysis
Iron	200	Chemical
Silicon	100	"
Carbon	30	"
Nitrogen	75	"
Hydrogen	5	"
Oxygen	50	"
Nickel	50	Spectrographic
Chromium	100	"
Magnesium	100	"
Calcium	5	"

## Carbide Preparation

Arc melting

Initially the uranium carbide billets were obtained by arc melting of uranium with an appropriate amount of spectrographic grade graphite. These samples were melted several times in order to achieve homogeneity. There was a considerable loss of graphite during melting and the billet often cracked on cooling. Three 150 gram billets were prepared by this method. Analysis of these samples indicated a carbon

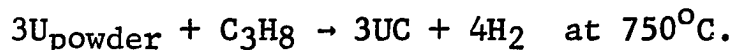
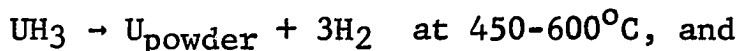
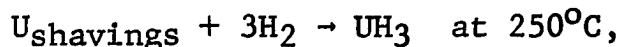
content of slightly less than the stoichiometric amount for uranium monocarbide, (4.5-4.6 wt pct).

#### UO<sub>2</sub> reduction

A sample of uranium dicarbide was prepared by reduction of UO<sub>2</sub> with powdered graphite. Compacted mixtures of UO<sub>2</sub> and graphite were heated to 1500°C in an induction furnace and held at this temperature until the vacuum was lowered to one micron. The temperature was then raised to 2000°C and held for one hour with the vacuum being maintained at one micron. The resulting alloy analyzed 7.7 wt pct carbon which is considerably under stoichiometric UC<sub>2</sub> (9.16%). An x-ray powder pattern indicated pure uranium dicarbide.

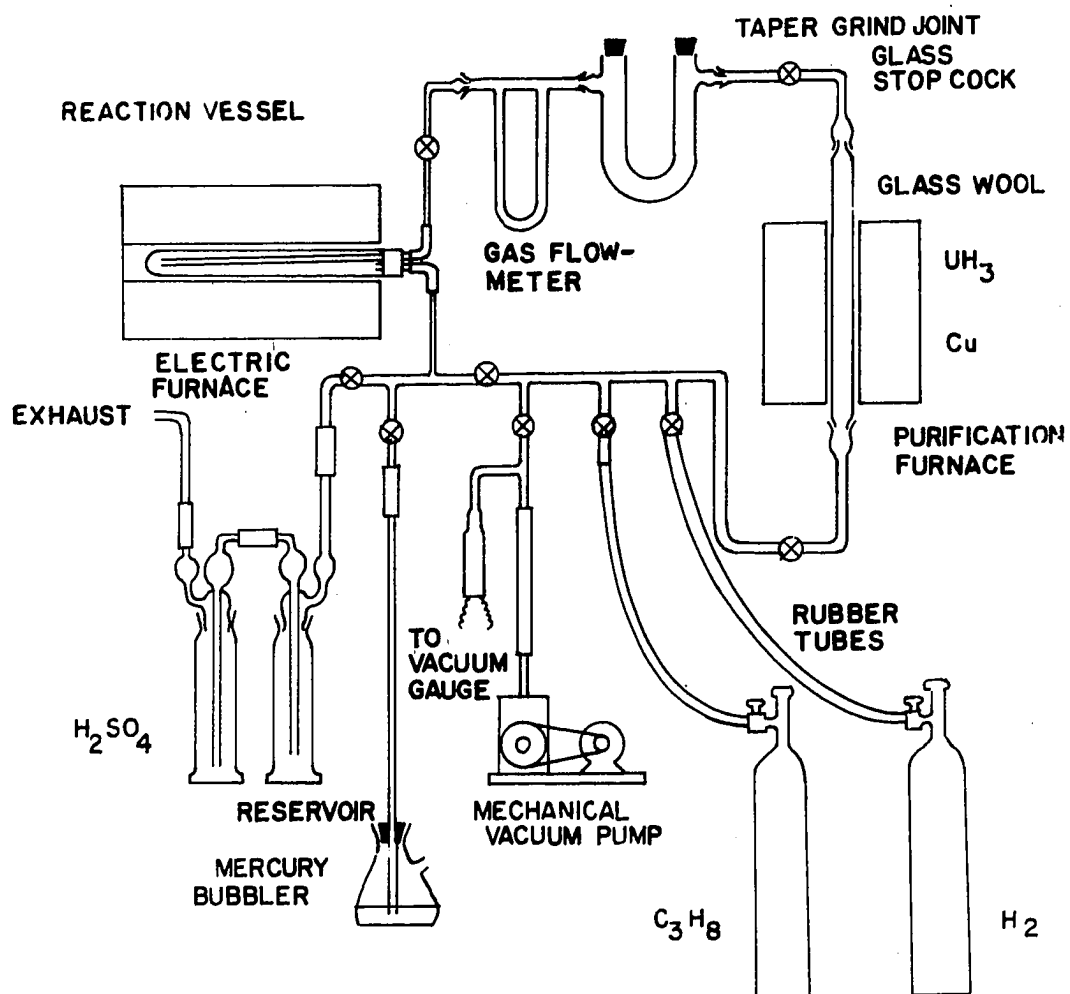
#### Propane reduction

A glass apparatus (Figure 1) was designed and constructed by Dr. Masayoshi Kanno according to the procedure indicated by Sato (30). In this procedure the monocarbide is prepared by several reaction steps as follows:



Several of the samples of uranium monocarbide utilized in this investigation were prepared by this method on this

Figure 1. Diagram of apparatus for production of uranium monocarbide by propane reduction





apparatus. Powder diffraction patterns of some of the first uranium monocarbide alloys prepared in this apparatus showed the presence of considerable amounts of UN. The formation of this impurity was corrected by putting uranium shavings in the gas purification train. Diffraction patterns on subsequent carbides had no lines that indicated UN or any other impurity. However, oxygen analysis at a later date indicated that these carbides contained from 3000-9000 ppm of oxygen. This may have been due to oxygen pickup during transfer of the freshly prepared carbide to the desiccator for storage or during subsequent handling of the carbide.

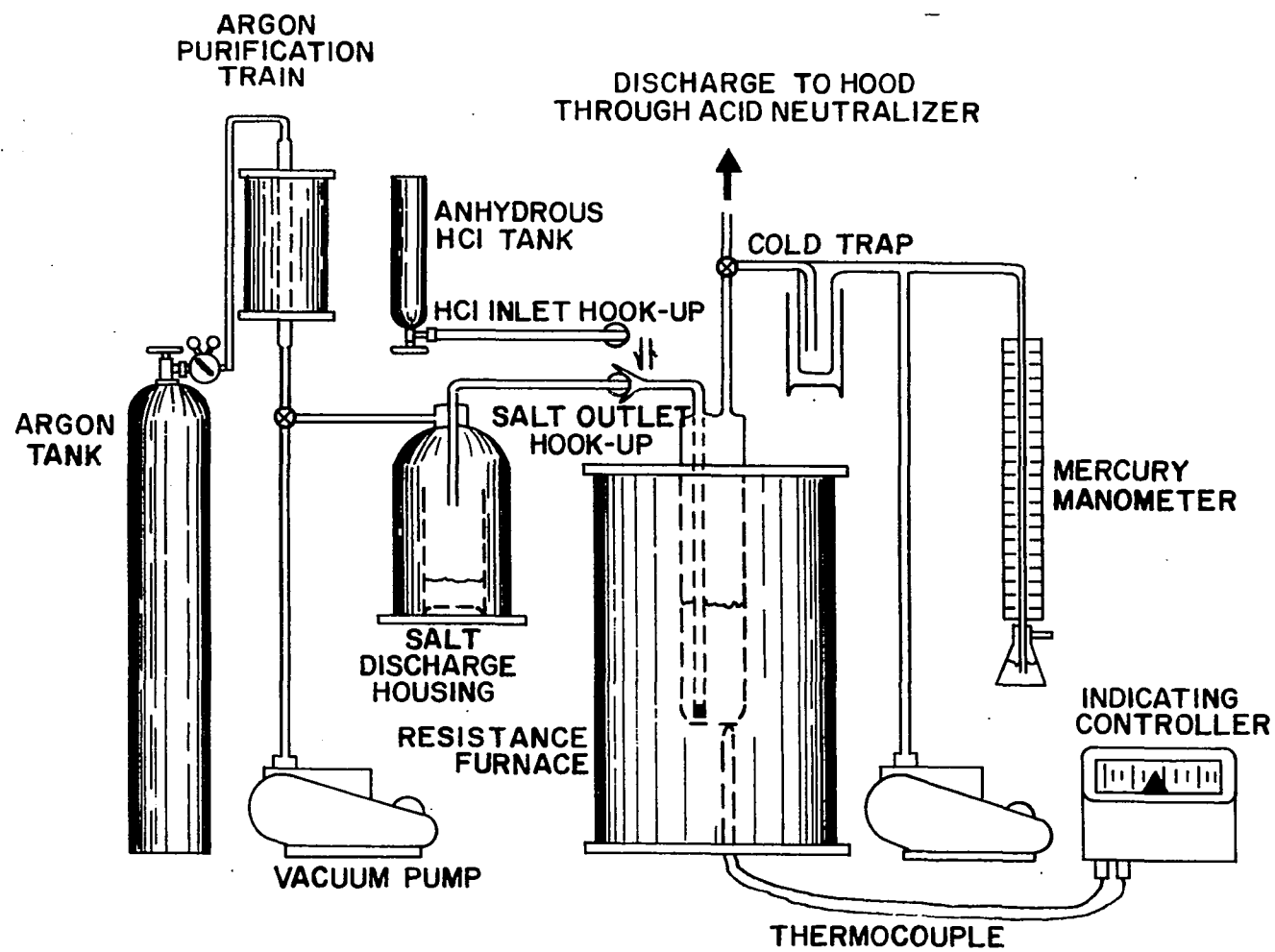
#### Salt Purification

Reagent grade potassium chloride, lithium chloride and zinc chloride salts were employed as starting materials. The LiCl 55.5 wt pct KCl and  $\text{ZnCl}_2$  35.0 wt pct KCl eutectic mixtures were purified by a method similar to the one described by other investigators (31,32).

The procedure can be summarized as follows: 1. heat below the melting point under vacuum to remove water; 2. melt with anhydrous HCl bubbling through the liquid; 3. flush system by bubbling argon gas through the melt; 4. remove residual HCl by vacuum; and 5. directly discharge the liquid

through a porous glass filter into the tantalum crucible used in the equilibrations. Quantities of purified salt were also stored in sealed jars in the dry box for use in small scale experiments. This salt was crushed as needed in the dry box in an argon atmosphere. A diagram of the salt purification apparatus is shown in Figure 2.

Figure 2. Diagram of salt flux preparation equipment



## EXPERIMENTAL APPARATUS AND PROCEDURES

## Rocking Furnace Equilibrations

The dried salts and metallic components were sealed in tantalum or graphite containers for rocking furnace experiments. All of the containers were one inch in diameter and about four inches long. In many runs, graphite containers were enclosed in a tantalum container. The ends of the tantalum containers were fitted with drawn caps and sealed by heli-arc welding. The graphite containers were fitted with threaded caps. All charging and welding operations were performed under an argon atmosphere. The dried salts and uranium carbide were crushed under argon, sealed in small glass bottles and transported in a desiccator to the welding dry box. The total initial charge usually weighed from 30 to 50 grams and was sealed in a tantalum or graphite container which in turn was contained in a welded 304 stainless steel casing. This assembly was heated in an oscillating furnace to 750 or 800°C and agitated for a period of time before being cooled to the temperature of interest for the final equilibration. Equilibration times ranged from three hours to one week. The charges were allowed to settle for one-half hour or more and were water quenched. The containers were then removed, and

the salt and metal phases separated. The salt phase was analyzed for uranium and zinc, and the metal phase was subjected to metallographic examination. The carbide was separated from the zinc by various techniques and subjected to X-ray diffraction analysis.

### Large Scale Equilibrations

The uranium monocarbide was expected to react at temperatures below  $590^{\circ}\text{C}$  with liquid zinc according to Reactions 2 or 3. The postulated products are the uranium-zinc compound and a higher order uranium carbide. A LiCl-KCl eutectic salt was added to a liquid zinc phase which had been equilibrated with uranium monocarbide. Stepwise additions of  $\text{ZnCl}_2$  were added to this LiCl-KCl phase. The first additions of  $\text{ZnCl}_2$  were expected to react with the uranium-zinc compound according to Reaction 4. When the uranium-zinc compound was exhausted, the  $\text{ZnCl}_2$  should react with the higher order uranium carbide according to Reactions 6 or 8.

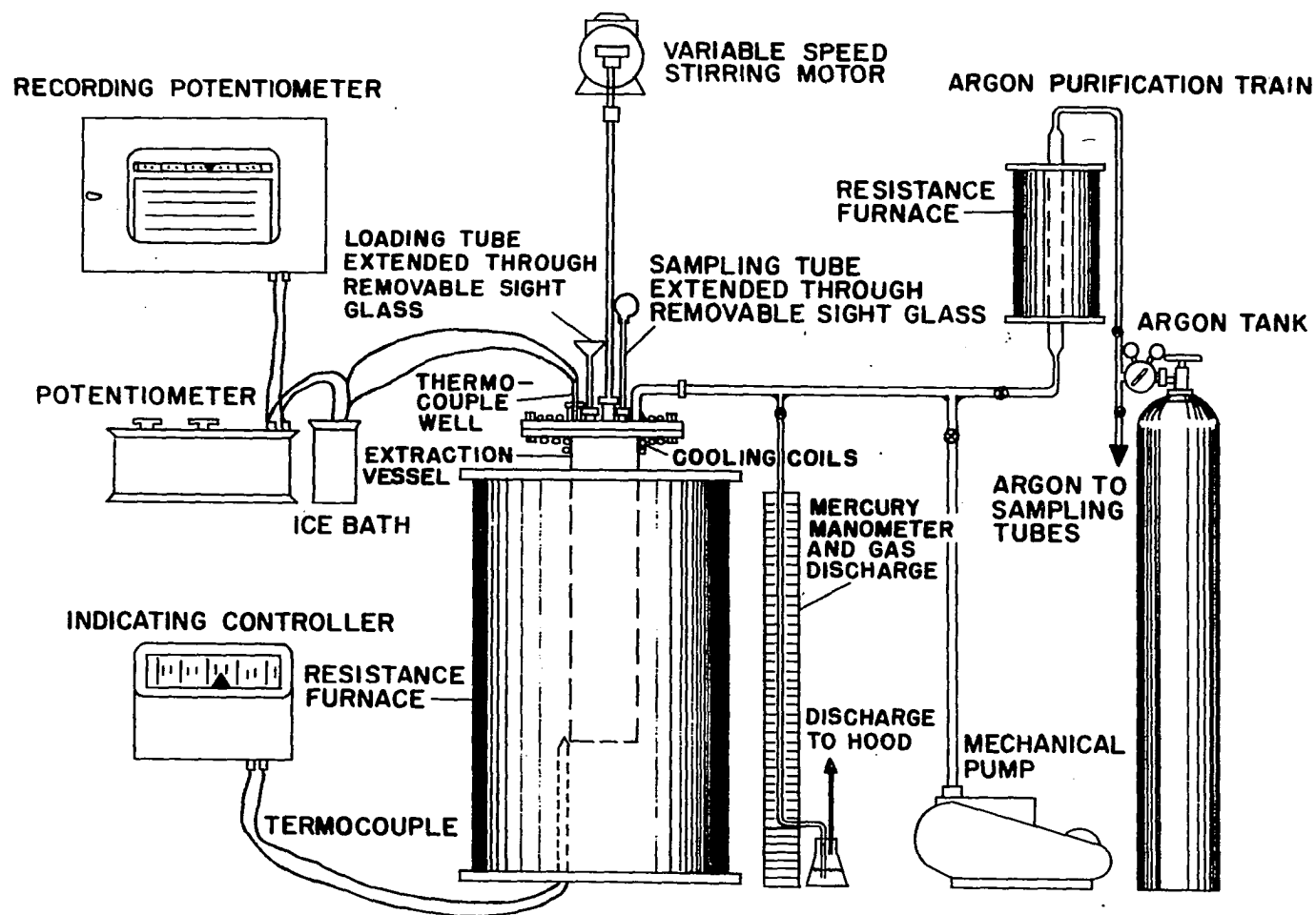
An apparatus which could accommodate a much larger charge was constructed to permit periodic additions of  $\text{ZnCl}_2$  and sampling of the charge. It was considered more suitable for these experiments than the small batch type equilibration apparatus described in the preceding section. The apparatus employed

has been described by Paul Woerner (33) and is shown schematically in Figure 3. The reaction vessel contained a  $3\frac{1}{2}$  inch diameter by 8 inch high crucible constructed from either 30 mil tantalum or graphite. The stirrer was made from  $\frac{1}{4}$  inch tantalum rod with paddles made from 30 mil tantalum welded to one end of the rod. The stirrer could be raised or lowered manually. An MgO block  $3\frac{1}{2}$  inches in diameter and 2 inches high supported the equilibration container, and a MgO sleeve  $3\frac{3}{4}$  inches in diameter and 12 inches high separated the equilibration container from the walls of the steel reaction vessel. A typical charge consisted of 1000 grams of LiCl-KCl eutectic salt, 400 grams of zinc and 50 grams of uranium carbide.

The LiCl-KCl eutectic salt was discharged directly into the equilibration container from the salt purification apparatus. The zinc and uranium carbide were placed on the top of the salt and the container lowered into the reaction vessel in air. The head was immediately placed on the reaction vessel, and the system evacuated. The system was heated to the melting point ( $356^{\circ}\text{C}$ ) of the LiCl-KCl eutectic under vacuum in order to remove moisture which may have been acquired during loading. The zinc and uranium carbide charges sank to the

Figure 3. Diagram of apparatus for continuous equilibrations  
of UC-ZnCl<sub>2</sub>





bottom of the melt when the LiCl-KCl salt melted. The system was then filled with argon, raised to the desired equilibration temperature and stirred for at least two hours which allowed the uranium monocarbide to react with the liquid zinc. The first portion of anhydrous 65.0 wt pct  $\text{ZnCl}_2$ -KCl eutectic was then added through a long stemmed tantalum funnel inserted into a sight glass port. After this addition, the salt-metal bath was stirred for two hours and allowed to settle for  $\frac{1}{2}$  hour. The salt was sampled and then restirred for one hour, settled for  $\frac{1}{2}$  hour and sampled again. This procedure was repeated for each subsequent addition of  $\text{ZnCl}_2$ . Samples were taken of the salt phase by siphoning salt into a four millimeter quartz tube using a rubber hand bulb. The samples were allowed to freeze in the colder upper region of the reaction chamber before they were exposed to the atmosphere. The solidified salt did not adhere to the quartz tube and was easily forced from the tube by means of a  $\frac{1}{8}$  inch brass rod. The samples, average weight about three grams, were immediately placed in glass vials and deposited in a desiccator. A much smaller number of samples of the zinc phase were taken for uranium analysis; the concentration of uranium in the zinc phase was usually determined from a material balance. A con-

stant flow of purified argon was maintained through the system during the  $\text{ZnCl}_2$ -KCl additions and while taking samples in an attempt to limit or prevent influx of air into the reaction chamber.

#### Fused Salt Cell EMF Measurements

The EMF between a uranium carbide electrode and a  $\text{UZn}_{8.5}$ -zinc or pure uranium electrode was studied as a function of temperature. At a particular temperature the EMF between two of the electrodes was observed as a function of time. When the EMF, as measured by a Rubicon B potentiometer, remained constant for at least three hours, the reading was recorded and the temperature changed. Some of the initial experiments involving EMF measurement were performed in a glass apparatus, Figure 4, designed by Kanno.

For later experiments it became desirable to accomodate a larger charge, add an additional electrode, and stir the melt between readings. The apparatus shown in Figure 5 was utilized for these experiments. A typical initial charge to this apparatus was 600 grams LiCl-KCl and 250 grams of zinc-10 wt pct uranium alloy. A 11.0 gram portion of KCl-65 wt pct  $\text{ZnCl}_2$  was added after the LiCl-KCl was molten. The uranium-zinc compound reacted with the  $\text{ZnCl}_2$  according to Reaction 4 and

Figure 4. Diagram of glass apparatus for measurement of EMF in LiCl-KCl/zinc system

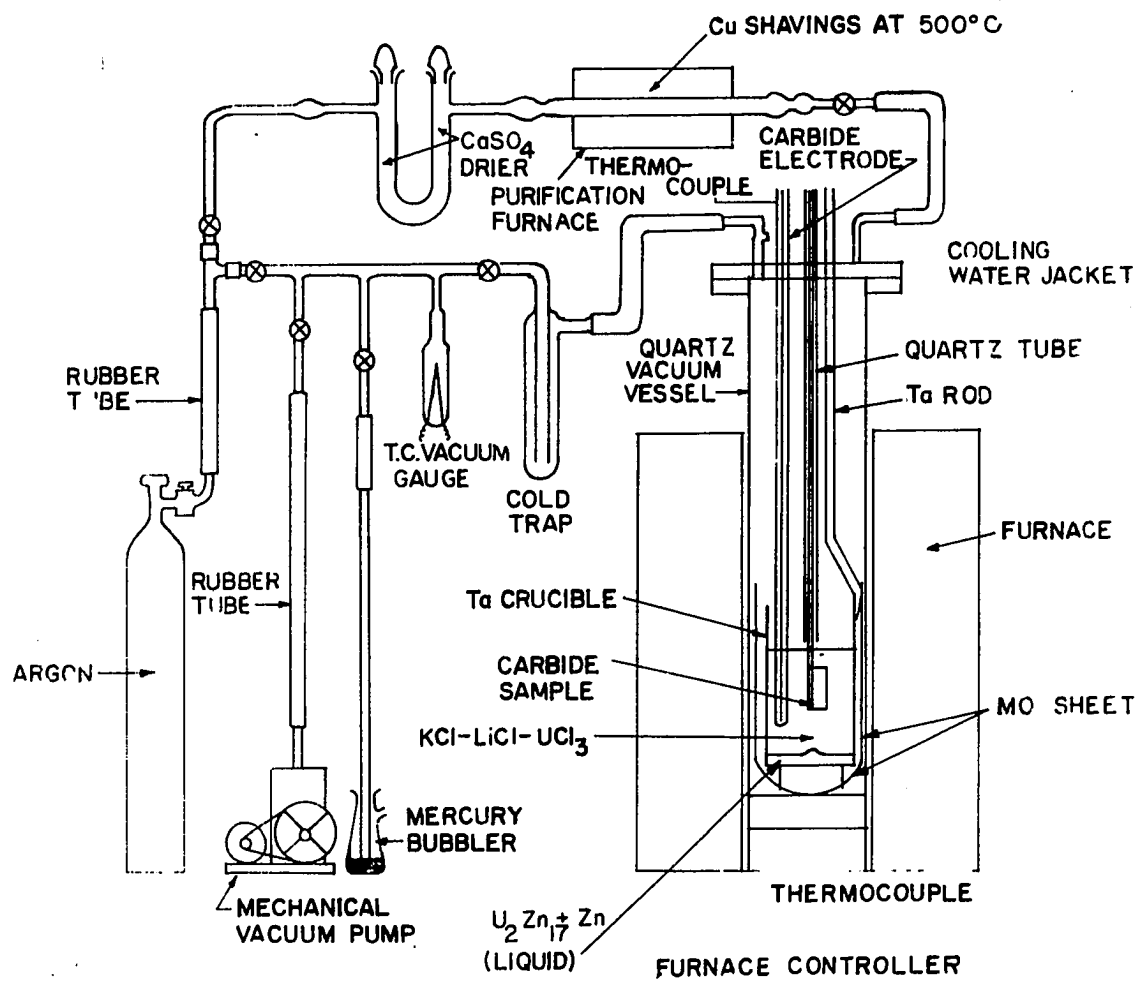
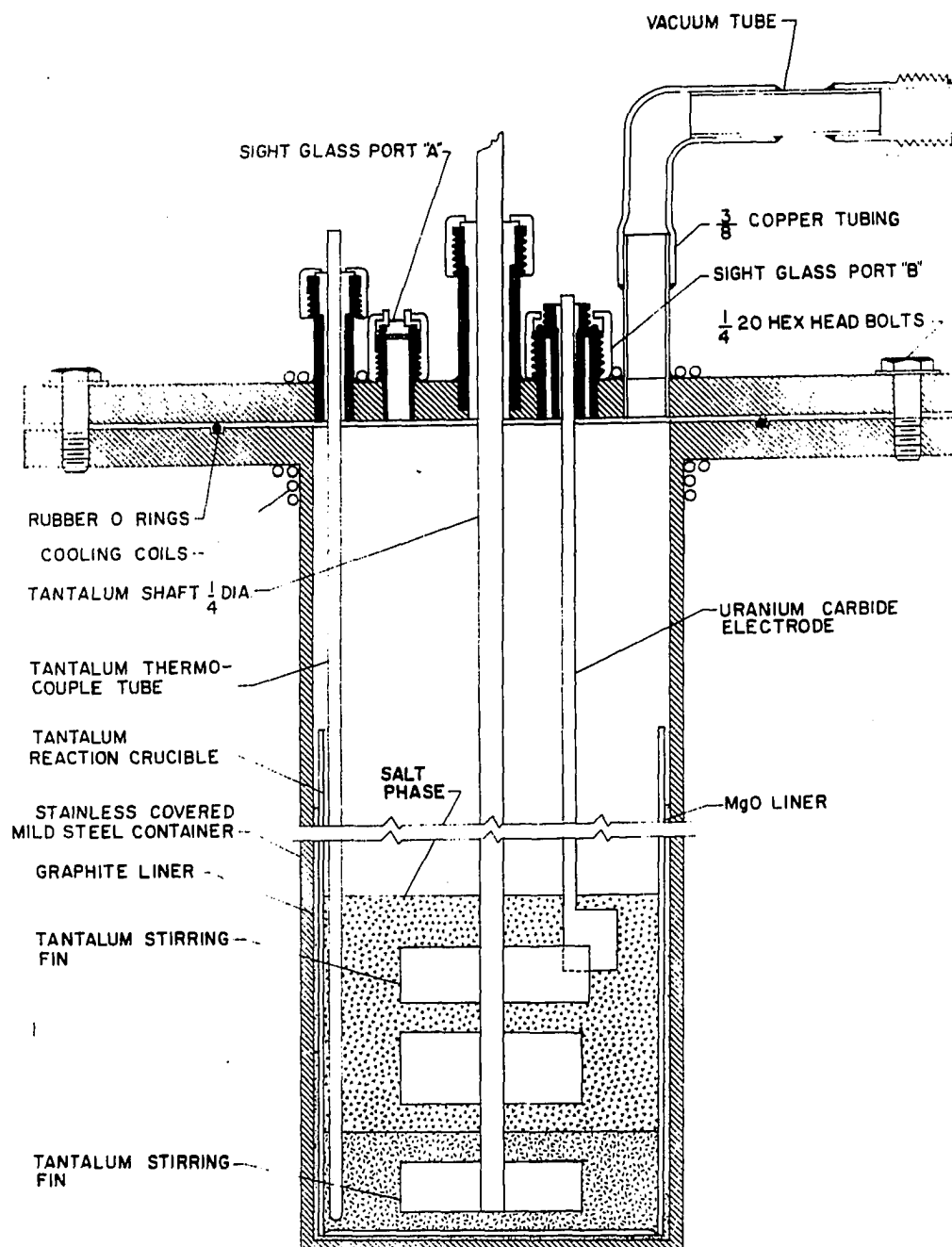


Figure 5. Diagram of metal apparatus for measurement of EMF in LiCl-KCl/zinc system



produced a LiCl-KCl-2.0 wt pct  $\text{UCl}_3$  salt. This concentration of  $\text{UCl}_3$  remained constant for the total equilibration. A constant flow of purified argon was maintained through the system.

Two types of container material, graphite and copper, were used for the uranium monocarbide electrode. These electrodes were designed in the following manner. The graphite electrode had a threaded cap with four  $1/16$  inch holes drilled in the side of the  $\frac{1}{2}$  inch electrode and was attached to a tantalum rod by means of a stainless steel coupling. The copper electrode was an open cup with a  $\frac{1}{2}$  inch outside diameter and a  $3/8$  inch inside diameter. The rods attached to both electrodes were covered by a 6 millimeter quartz umbrella which extended from about three inches from the top of the electrode to  $3/4$  inch from the end of the rod.

The uranium electrode consisted of a solid uranium rod  $1/8$  inch diameter by three inches long fastened to the end of a  $1/8$  inch diameter by 18 inches long tantalum rod. The two rods were held together by means of a tantalum sleeve,  $1/32$  inch wall thickness, which was fitted over the adjacent ends of the rods and swaged to produce a firm bond. The tantalum rod extended through a rubber stopper fitted into one of the



sight-glass ports.

Both the stirrer and the tantalum thermocouple well extended into the metal phase and both were used as leads for the uranium-zinc electrode. The melt was stirred as the temperature was being changed, this change requiring approximately  $\frac{1}{2}$ -hour. It was impossible to obtain a constant EMF with the stirrer operating so all EMF readings were taken with the stirrer turned off and the temperature held constant to  $\pm 1.5^{\circ}\text{C}$ . It was often necessary to wait as long as 24 hours for the EMF between the uranium-zinc and uranium monocarbide electrode to become constant.

#### Separation Methods

It was possible to recover the original carbide which remained in the zinc matrix by twisting or striking the zinc, thereby causing the brittle carbide to crumble away from the matrix. This procedure was used, however, only when the carbide remained in large enough deposits to make the procedure applicable. In many of the experiments the uranium carbide particles in the initial charge would pass a 300 mesh screen. These particles could not be separated from the zinc following equilibration by the previously discussed method. The separation methods used were dissolution of the zinc in nitric acid

and distillation of the zinc. There was a possibility of oxygen contamination of the remaining carbide in both cases. However, blanks were run in which uranium monocarbide was placed in  $\text{HNO}_3$  of the concentration used in the dissolution process for the time necessary to dissolve the zinc, and very little contamination was observed. In the distillation process, the sample was kept under constant vacuum, and in cases where  $\text{U}_2\text{Zn}_{17}$  was present in the equilibration zinc phase, the pure uranium was left behind after the zinc was distilled and could be found on the powder patterns with little or no trace of  $\text{UO}_2$  contamination.

#### Analytical Procedure

The analyses for uranium and zinc in the  $\text{LiCl-KCl}$  eutectic salt were carried out by the analytical group. The uranium was determined by passing a chloride solution of the sample through a lead reductor, collecting the effluent in iron(III) chloride and titrating the iron(II) formed with standard cerium(IV) sulphate. The zinc was determined polarographically. The supporting electrolyte was a mixture of acetic acid and sodium acetate and the maximum suppressor was methyl red. The uranium had to be oxidized to uranium(VI) before the polarogram was run, but no separation was necessary.

## EXPERIMENTAL RESULTS

## UC-Zn Equilibrations

Uranium monocarbide was equilibrated with liquid zinc at temperatures ranging from 540 to 800°C in both tantalum and graphite containers. The experimental data for these equilibrations are summarized in Table 4-5. Experiments involving the equilibration of uranium, graphite and zinc or uranium-zinc compound and graphite are also summarized in Table 4-5.

In all of the equilibrations involving uranium monocarbide and zinc at 725°C and below there was a partial reaction of the carbide with zinc to form a carbide phase and a uranium-zinc compound. Figure 6 shows photomicrographs which depict sections of the longitudinally cut zinc billet of the uranium monocarbide-zinc equilibration, WCR-1-111, which was carried out in a tantalum container. The grey irregularly shaped clusters in Figure 6A are the uranium-zinc compound, the small black particles constitute the carbide phase and the light phase is the nearly pure zinc matrix. Segregation of the carbide phase toward the bottom of the zinc billet is apparent. Figure 6A shows the relative amounts of these phases near the center of the billet and Figure 6B shows the top portion of the billet with only the uranium-zinc compound suspended in

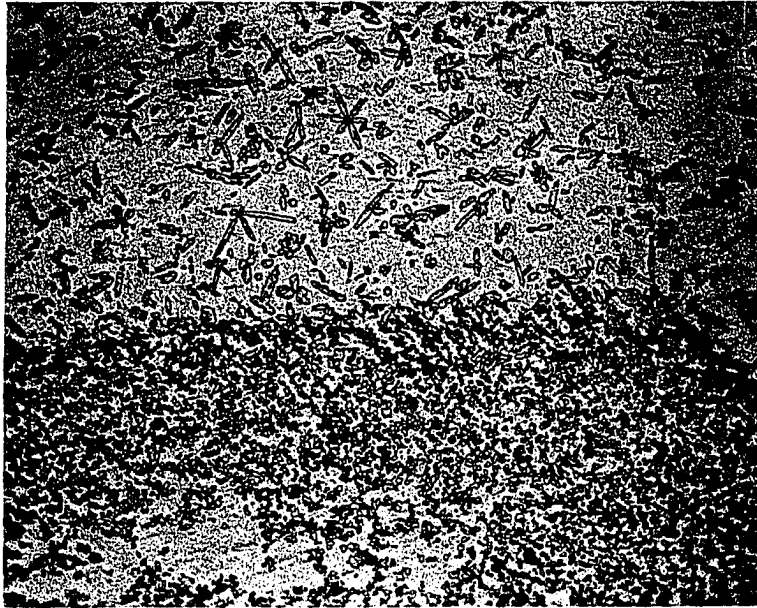
Table 4-5. Experimental data for uranium monocarbide-zinc equilibrations

Equilibration	Initial composition (gms)		Temp history			Container	Phases observed*
			°C	Hr rock	Hr settle		
WCR-1-69	UC <sub>2</sub> -5.8	Zn-43.5	500	70	4	Ta	UC <sub>2</sub>
WCR-1-61	UC-8.6	Zn-35.6	540	46	13	Ta	A,B,B'',C
WCR-1-25	U-7.9 C-0.6	Zn-85.7	550	14	$\frac{1}{2}$	Ta	A,B'',C
WCR-2-11A	UC-1.0	Zn-21.6	595	26	1	C	A,B
WCR-2-18A	UC-1.3	Zn-18.6	600	48	$1\frac{1}{2}$	C	A,B
WCR-1-5	UC-9.5	Zn-21.0	635	7	$\frac{1}{2}$	Ta	A,B
WCR-2-20A	UC-1.0	Zn-18.4	650	38	1	C	A,B
WCR-1-118	UC-4.0	Zn-98.5	700	48	3	Ta	A,B,A',B',B''
WCR-1-133	UC-5.0	Zn-31.2	700	170	6	C	A,B,B''
WCR-2-11B	UC-1.0	Zn-18.0	700	36	$\frac{1}{2}$	C	A,B
WCR-2-18B	UC-1.5	Zn-19.2	700	21	3	C	A,B
WCR-2-21	U-10.0 C-1.0	Zn-103.9	700	158	1	C	A,B
WCR-1-97	U-11.5	Zn-165	708	24	6	C	A
WCR-1-111	UC-6.0	Zn-130.0	715	7	$\frac{1}{2}$	Ta	A,B,A',B',B''
WCR-2-11C	UC-1.0	Zn-19.0	725	25	4	C	A,B
WCR-2-20B	UC-1.1	Zn-15.3	725	13	1	C	A,B
WCR-2-11D	UC-1.0	Zn-23.9	800	29	1	C	B
WCR-1-91	U-38.3 C-20	Zn-320.0	800	47	1	Ta	A,A',B,B',B'',C
WCR-1-109	U-18.6 C-2.0	Zn-203	800	169	1	C	A,B,B''
WCR-2-24	UZn <sub>8.5</sub> -50.0 C-2.0		800	0	48	C	B''
WCR-2-22	U-8.0	Zn-80.1	800	159	1	C	A

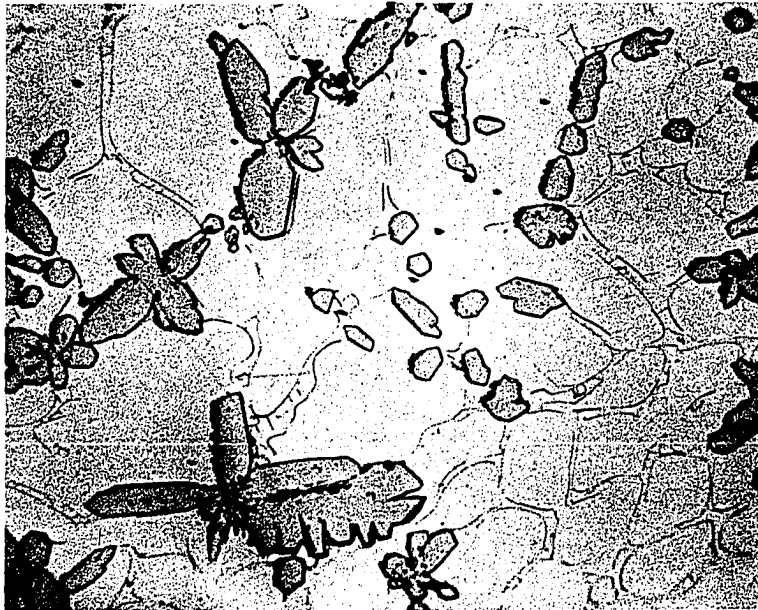
\*A-Intermetallic compound UZn<sub>8.5</sub> observed in microstructure; B-Uranium monocarbide inferred from microstructure; A',B'-Intermetallic compound UZn<sub>8.5</sub> and uranium monocarbides respectively, identified from x-ray diffraction patterns; B'',C-Uranium monocarbide and tantalum carbide (Ta<sub>2</sub>C or TaC), respectively, identified from x-ray powder patterns of residue obtained by dissolution or distillation of zinc matrix.

Figure 6. Photomicrographs of various regions of a zinc-rich billet from the equilibration of uranium monocarbide with liquid zinc, equilibration WCR-1-111

- A.  $\text{UZn}_{8.5}$  suspended above UC particles in Zn matrix. 50X. Shows division of phases. Small black particles are UC, grey particles are  $\text{UZn}_{8.5}$
- B.  $\text{UZn}_{8.5}$  in Zn matrix. Top portion of zinc billet. 250X



A

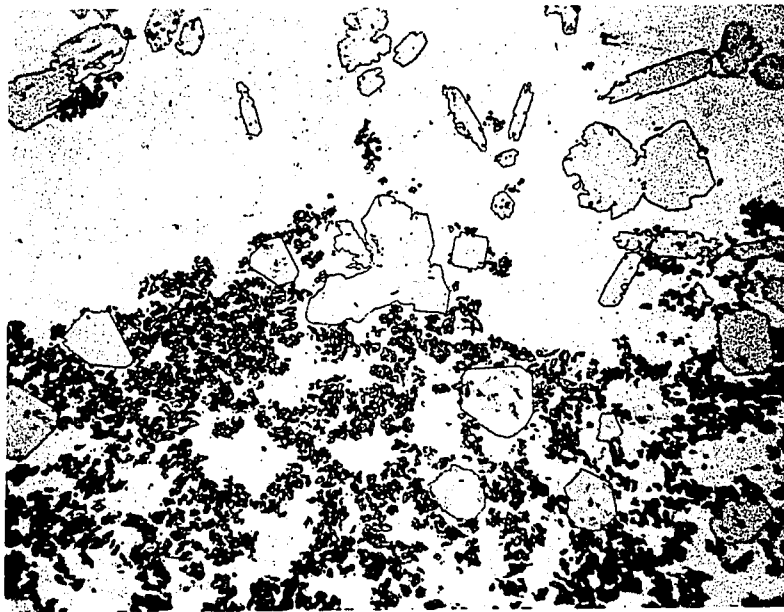


B

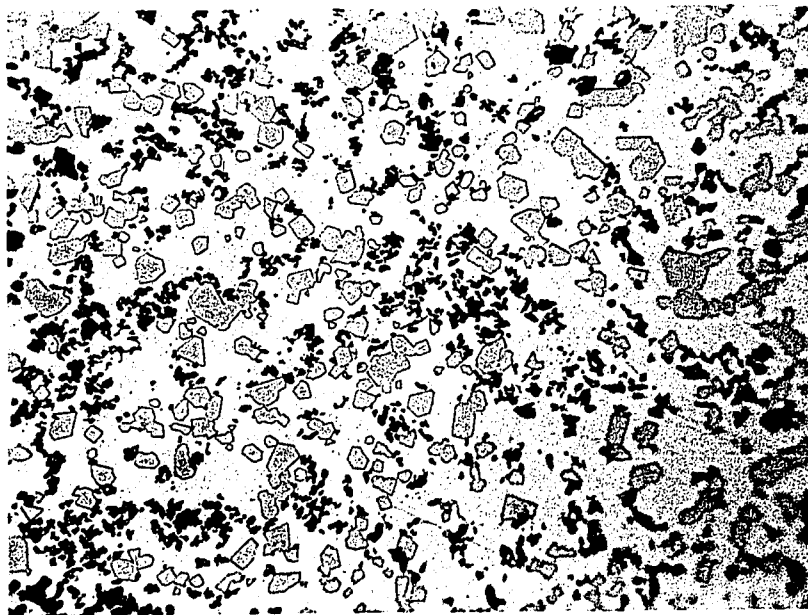
Figure 6

Figure 6. (Continued)

- C.  $\text{UZn}_{8.5}$  above top portion of uranium carbide particles. Middle portion of zinc billet. 250X
- D. Uranium carbide particles (black) with small uranium-zinc particles (grey) in bottom portion of zinc billet. 250X



C



D

Figure 6, (continued)

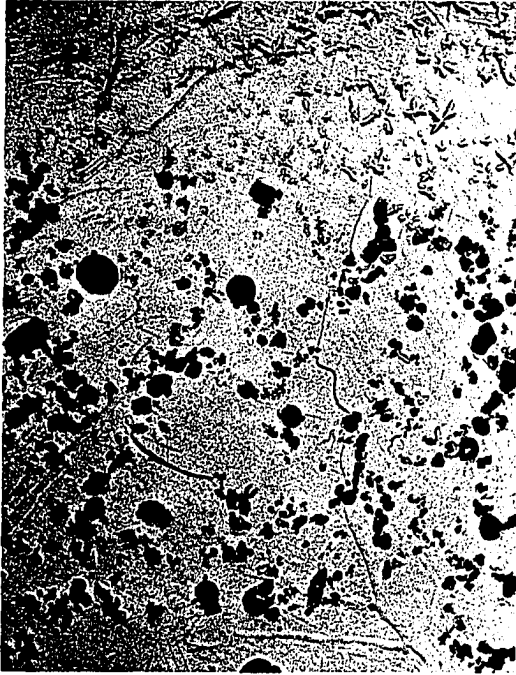


the zinc matrix. Figure 6C is a 250X magnification of the region near the top of the segregated layer of the carbide phase, and Figure 6D is a 250X magnification of the bottom portion of the billet showing the fine black uranium carbide particles and small grey uranium-zinc compound particles dispersed in zinc. It is evident from these microstructures that the reaction of the monocarbide with zinc did not go to completion. As will be shown later in this section, the residual carbide phase was not a higher carbide but still exhibited a face centered cubic lattice characteristic of the monocarbide. The microstructures showed that the amount of the intermetallic compound formed from the uranium monocarbide-liquid zinc reaction could not be increased by longer equilibration times. For instance, equilibration WCR-1-118 was equilibrated for 51 hours and the amount of unreacted uranium monocarbide was the same as that found in the above sample, WCR-1-111, which was equilibrated for only  $7\frac{1}{2}$  hours.

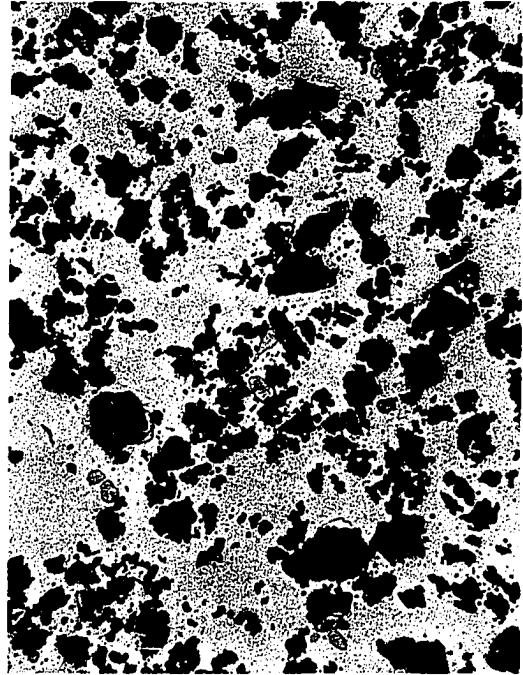
When a graphite container was used for the equilibration, the amount of unreacted monocarbide at any given temperature below  $725^{\circ}\text{C}$  was somewhat greater than the amount present for similar equilibrations in tantalum. Figure 7 depicts the center and bottom portions of the longitudinally cut zinc

Figure 7. Photomicrographs of two regions of a zinc-rich billet from the equilibration of uranium monocarbide with liquid zinc, equilibration WCR-2-11B

- A.  $\text{UZn}_{8.5}$  suspended above uranium carbide particles in zinc matrix. 50X. Shows division of phases. Black particles are uranium carbide. Star-shaped grey clusters are  $\text{UZn}_{8.5}$ . White matrix is zinc
- B. Uranium carbide particles (black) with small uranium-zinc particles in bottom portion of white zinc billet. 250X



A



B

Figure 7

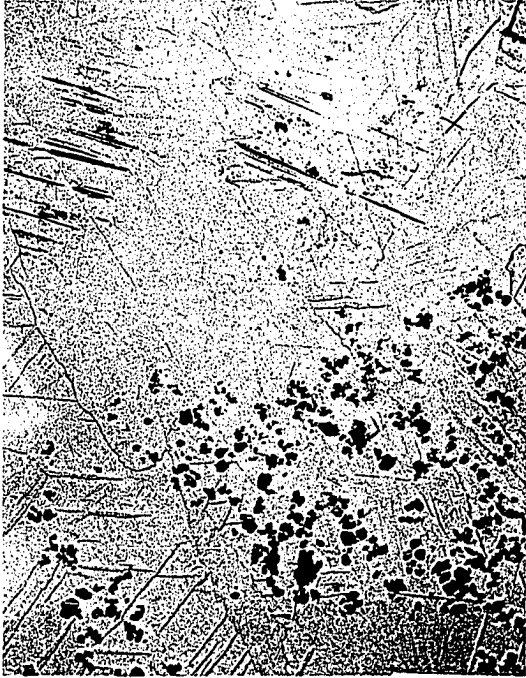
billet of run WCR-2-11B which was contained in graphite. It can be seen from this photomicrograph that the relative amount of uranium carbide phase to uranium-zinc phase is larger in this equilibration than in WCR-1-111 which was contained in tantalum.

At 800°C, there was no evidence of reaction between the uranium monocarbide and liquid zinc. Figure 8 shows the center and bottom portions of the longitudinally cut zinc billet, equilibration WCR-2-11D, which was obtained by equilibrating uranium monocarbide with zinc at 800°C for thirty hours. Only the carbide phase is present in the zinc matrix.

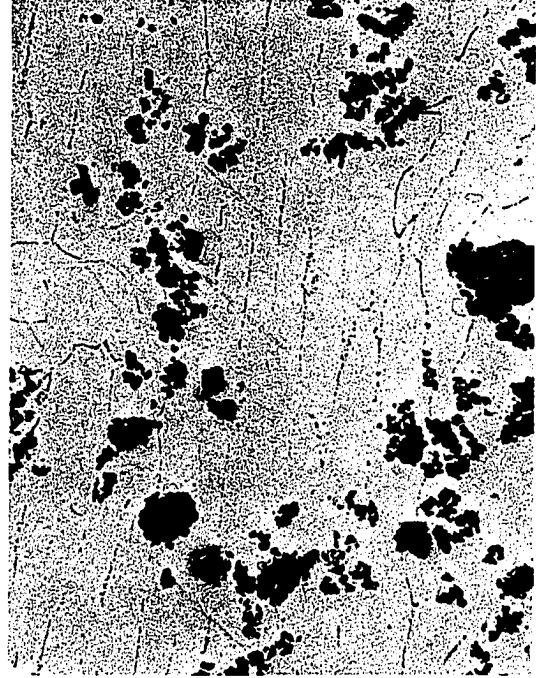
A series of equilibrations, WCR-1-25,91,97,109 and WCR-2-21,22, was performed in which the charge consisted of either uranium, powdered graphite and zinc or uranium and zinc in a graphite crucible instead of the uranium monocarbide and zinc. At equilibrium the same phases should exist in either case. In the reactions in which uranium and zinc were equilibrated in a graphite crucible with no powdered graphite present, there seemed to be very little tendency of the uranium-zinc compound to react with the graphite to form a uranium carbide product. Figure 9 is a photomicrograph of the bottom portion of the zinc billet of equilibration WCR-1-97. It shows only

Figure 8. Same as Figure 7. WCR-2-11D

- A. Black carbide particles in zinc phase.  
No  $\text{UZn}_{8.5}$  present. Shows the tendency  
of carbide particles to sink in liquid  
zinc. 50X
- B. Uranium carbide particles (black) in  
zinc matrix 250X



A



B

Figure 8

Figure 9. Photomicrographs of bottom portion of zinc-rich billet from the equilibration of uranium and zinc in a graphite crucible, WCR-1-97. 250X. Shows large  $\text{UZn}_{8.5}$  particles in zinc matrix

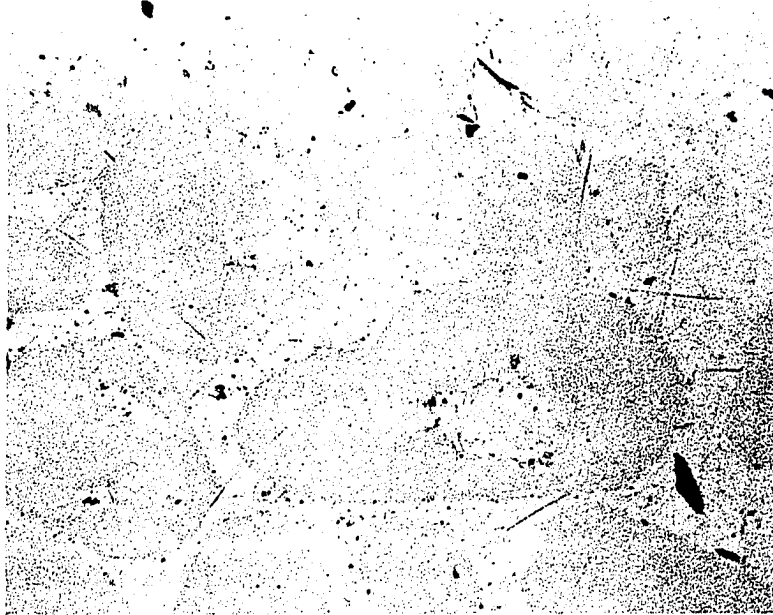


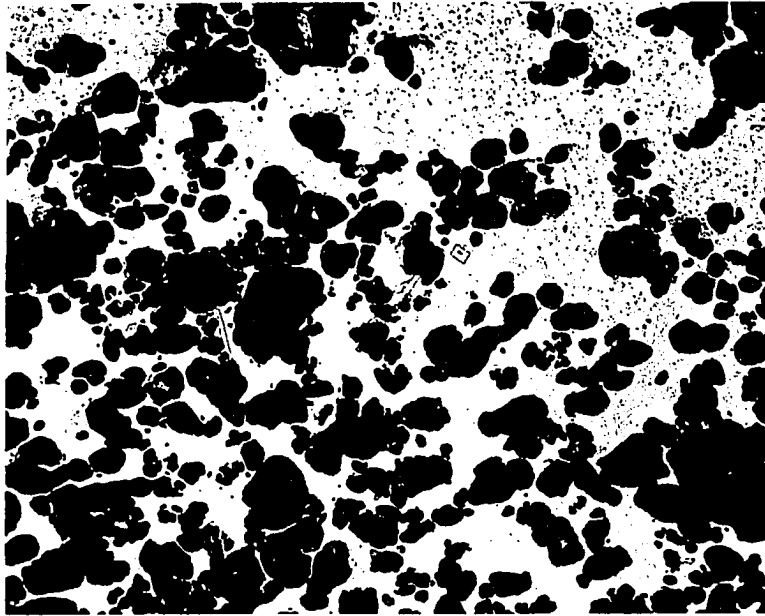
Figure 9



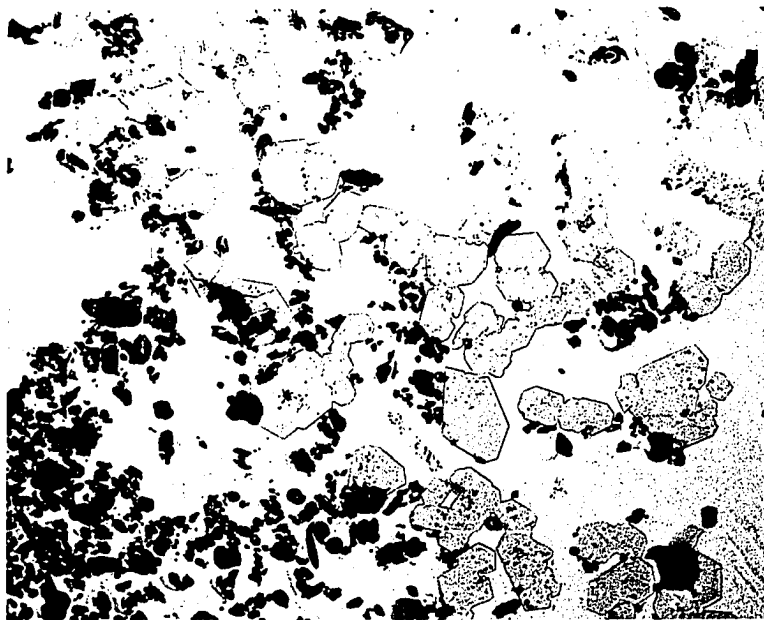
large uranium-zinc compound crystallites in the zinc matrix. There was no evidence of uranium carbide in this or other regions of the zinc-rich billet. Equilibration WCR-2-22 which also involved uranium and zinc in a graphite crucible was equilibrated for 160 hours at  $800^{\circ}\text{C}$  and there was no indication of formation of a carbide phase. However, when powdered graphite was added along with the uranium and zinc, a uranium carbide product was formed. Figure 10A shows the bottom portion of the longitudinally cut zinc billet of equilibration WCR-1-109 which was equilibrated at  $800^{\circ}\text{C}$  for 170 hours. A very large amount of uranium carbide is apparent with a very few small crystallites of uranium-zinc compound appearing. Figure 10B shows the bottom portion of the longitudinally cut zinc billet of equilibrations WCR-2-21 which was equilibrated at  $700^{\circ}\text{C}$  for 159 hours. A much larger amount of uranium-zinc compound and a correspondingly smaller amount of uranium carbide is present. In equilibration WCR-1-91 the uranium, zinc and powdered graphite charge was equilibrated in tantalum for 48 hours at  $800^{\circ}\text{C}$ . Figure 11 shows a photomicrograph of the bottom portion of the longitudinally cut zinc billet obtained from this reaction. The black particles are interpreted as being graphite which is reacting at the surface with uranium-

Figure 10. Photomicrographs of the bottom portions of the zinc-rich billets from the equilibrations of uranium zinc and powdered graphite in graphite crucible equilibrations WCR-1-109, WCR-2-21

- A. WCR-1-109. Black uranium carbide particles in white zinc matrix with a very few small particles of grey  $\text{UZn}_{8.5}$  phase. 50X.  $800^{\circ}\text{C}$
- B. WCR-2-21. Black uranium carbide particles and grey  $\text{UZn}_{8.5}$  particles in white zinc matrix. 50X.  $700^{\circ}\text{C}$



A



B

Figure 10

Figure 11. Photomicrograph of bottom portion of zinc-rich billet from the equilibration of uranium, zinc and powdered graphite in tantalum crucible, equilibration WCR-1-91. 250X. Depicts partial reaction of graphite particles to form uranium carbide. 800°C

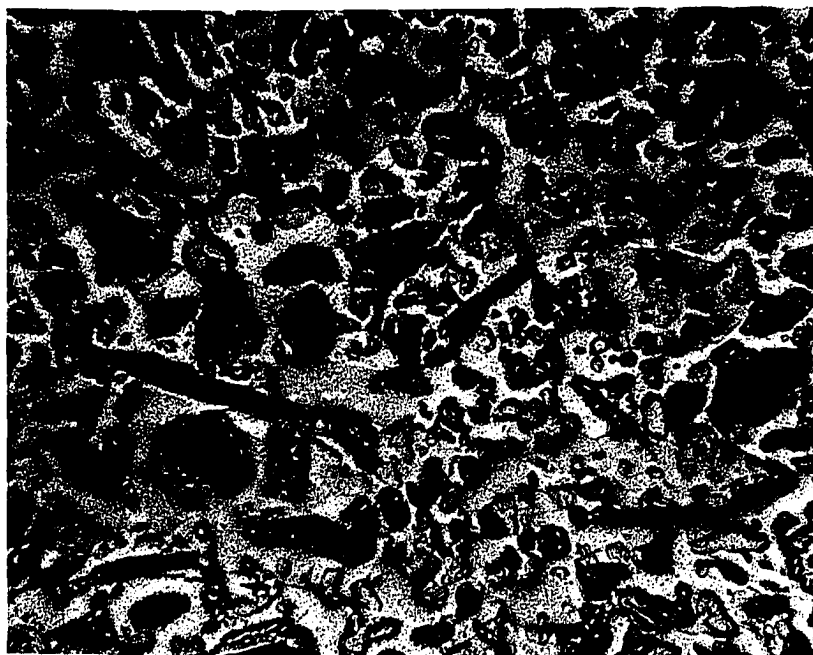


Figure 11

zinc compound. It is impossible to tell what phase each particle is from the photomicrograph.

An equilibration, WCR-2-24, between the uranium-zinc compound and graphite was performed in a differential thermal analysis apparatus. Fifty grams of stoichiometrically prepared  $U_2Zn_{17}$  alloy was crushed to a particle size of less than 100 mesh and thoroughly mixed with two grams of powdered graphite. A portion of the resulting mixture was pressed into a small cylinder 1/2 inch in diameter and 1/2 inch high and placed into a graphite crucible. The graphite crucible was inserted into a sealed tantalum crucible and heated in a helium atmosphere at  $700^{\circ}C$  for 36 hours in a differential thermal analysis apparatus. When the charge was cooled through  $419^{\circ}C$ , the melting point of zinc, there was no thermal arrest indicating no free zinc in the alloy. The charge was then heated to  $800^{\circ}C$  and held for 48 hours. When the charge was cooled through  $419^{\circ}C$ , there was a thermal arrest which indicated the presence of pure zinc in the alloy. This zinc could have been formed only by the reaction of the uranium-zinc compound and the graphite to produce a uranium carbide product and free zinc. This reaction had proceeded at  $800^{\circ}C$  but had not proceeded to a measurable extent at  $700^{\circ}C$ .

The equilibrium phases formed from the equilibrations listed in Table 5 were identified by x-ray diffraction techniques. The results of this investigation are summarized in Table 5. As indicated in the footnotes, three methods were employed; the phases present were observed in x-ray spectrometer patterns taken from the polished longitudinal alloy sections, and by powder patterns of residues obtained by vaporization of the zinc matrix and also by dissolving the zinc matrix with  $\text{HNO}_3$  solution or sodium hydroxide.

X-ray examination of the uranium carbide reaction product at no time indicated the presence of  $\text{UC}_2$  or  $\text{U}_2\text{C}_3$ . This absence of higher order carbides eliminates Reactions 2 and 3 as possible equilibrium reactions. The uranium dicarbide has been accepted to be unstable at temperatures below  $1750^\circ\text{C}$  although it is possible for oxygen to stabilize the uranium dicarbide phase at lower temperatures (21). Uranium sesquicarbide is very difficult to form, particularly at temperatures below  $1200^\circ\text{C}$  (34). Its formation is reported to be prohibited by impurities (21,35). In view of these considerations it is not surprising that no indication of either uranium dicarbide or uranium sesquicarbide was found as an equilibrium product in these experiments.

The only other possibility postulated in the Introduction for the equilibrium reaction between uranium monocarbide and zinc was Reaction 1. It was shown in the Introduction that Reaction 1 would either go to completion or not begin at all. However, uranium monocarbide was observed to undergo partial reaction with liquid zinc in every uranium monocarbide-zinc reaction listed in Table 5 that was equilibrated at 725°C or below. This necessitates the postulation of a mechanism which allows one of the components of Reaction 1 to have a variable activity. The mechanism was suspected to be due to an increase in oxygen content causing stabilization of the uranium monocarbide lattice.

The concentrations of oxygen in the last uranium monocarbide samples prepared were measured and are listed in Table 6. Unfortunately, the measurements were made a considerable length of time after the carbides were prepared so there may have been additional oxygen pickup during storage. All of the monocarbide samples in Table 6 were prepared by the propane reduction method and the resulting monocarbide formed had a particle size of less than 300 mesh. This material was examined by x-ray powder pattern techniques and the patterns obtained indexed as uranium monocarbide with no extraneous lines



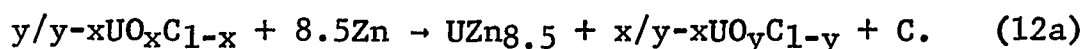
present. However it was shown by Sano (36) that the uranium monocarbide could contain a large amount of oxygen and still exhibit the same pattern with a very small change in lattice constant. The oxygen is present as a substituted atom in the uranium monocarbide lattice. This may be regarded as a solid solution of uranium monoxide and uranium monocarbide. The uranium monoxide phase has been reported previously (37) and the total solubility of uranium monoxide in the uranium monocarbide lattice has been reported by various authors (36,38, 39). The reported solubilities vary from 25 to 79 mole per cent UO.

Table 6. Oxygen concentrations of uranium monocarbide samples prepared by propane reduction

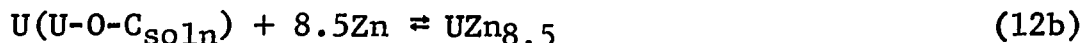
Sample	Oxygen (ppm)	Mole % UO (to nearest whole %)
K-3	9600	14
K-5	5170	8
K-6	4150	7
K-8	3540	5

A portion of the oxygen found by analysis of the samples listed in Table 6 will be present as a substituted atom in the uranium monocarbide lattice. Comparison of the free energy of

formation of  $\text{UO}_2$ ,  $-223 \text{ kcal/mole U}$  at  $600^\circ\text{C}$  (40), with those of the carbides, Table I, indicates the uranium-oxygen bond is much stronger than the uranium-carbon bond. Therefore, the uranium atoms surrounded by carbon would be expected to react more readily than those partially surrounded by oxygen. The resulting reaction of such a uranium-oxycarbide phase with zinc can be expressed as follows:



This reaction will continue until the oxygen content of the oxycarbide phase becomes high enough to prohibit further reaction. The equilibrium reaction may be written:



which indicates that the activity of the uranium in the oxycarbide phase is equal to the activity of uranium in the uranium-zinc phase.

The oxycarbide product  $\text{UO}_y\text{C}_{1-y}$  of Reaction 12a will have a higher oxygen concentration than the carbide charged, since all of the oxygen is assumed to remain with the oxycarbide product and the uranium content is being depleted. The uranium carbide product of equilibrations WCR-1-111, 118, and 133 was separated from the zinc matrix by distillation. Oxygen analyses on the resulting residues indicated an average oxygen

concentration of about 1.5 wt pct oxygen which is two to three times higher than the oxygen concentration of the oxycarbides utilized in the charge.

The stability of this oxygen-stabilized uranium monocarbide phase should be dependent on the oxygen concentration of the phase. It should be possible to remove more of the uranium from the uranium oxycarbide phase thereby producing a still higher oxygen concentration in the phase by using  $\text{ZnCl}_2$  to oxidize the uranium since the  $\text{ZnCl}_2$  reaction with uranium monocarbide (Reaction 9) has a much larger negative  $\Delta F^0$  than Reaction 1. Therefore to further study the stabilization of the monocarbide by oxygen it became desirable to equilibrate the alloy formed from the uranium monocarbide-liquid zinc reaction with a liquid salt phase containing  $\text{ZnCl}_2$ .

The complete conversion of the uranium in the uranium oxycarbide phase to  $\text{UCl}_3$  by oxidation with  $\text{ZnCl}_2$  would be advantageous in some of the proposed pyrometallurgical re-processing methods.

#### Large Scale $\text{ZnCl}_2$ -UC Equilibrations

Continuous equilibrations were performed between a liquid zinc phase containing uranium monocarbide and a liquid salt phase containing  $\text{ZnCl}_2$ . Samples of the salt phase were

taken after each increment of zinc chloride was added to the melt as indicated in the section on experimental procedure. The transfer of the uranium from the zinc phase to the salt was followed during the stepwise additions of zinc chloride to the system. The initial charges and results of experiments WCR-1-82, 113, 121, and 127 are presented in Tables 7, 8, 9 and 10. The results are shown graphically in Figure 12 which is a plot of the moles of  $UCl_3$  in the salt as a function of the total moles of  $ZnCl_2$  added to the equilibrated mixture. The analysis of the last sample taken after a particular addition of zinc chloride was used for the calculation of the plotted curves of Figure 12. Consideration of Table 7 indicates that equilibrium was not being achieved in the first two hours of stirring for WCR-1-82 because the second sample taken after an addition of  $ZnCl_2$  indicated further oxidation of uranium into the salt during the period between sampling. This was not observed in the latter portion of WCR-1-82 or in subsequent runs. All of the analyses indicated that a maximum concentration of  $UCl_3$  was attained with only a small concentration of  $ZnCl_2$  being present in the salt. The  $ZnCl_2$  content then began to increase at a constant uranium concentration and continued to increase until the end of the equilibration.

Table 7. Oxidation of uranium carbide in run WCR-1-82\*

Sample	Total grams ZnCl <sub>2</sub> added	Chemical analysis		Sample wt gms	K <sub>N</sub> **
		% Zn	% U		
WCR-82-1	0	0.03	0.07	2.94	
WCR-82-2	5.17	0.005	0.295	2.81	
WCR-82-3	5.17	0.063	0.355	3.42	
WCR-82-4	10.43	0.157	0.570	3.12	
WCR-82-5	10.43	0.121	0.767	2.71	
WCR-82-6	16.11	0.245	0.932	2.92	
WCR-82-7	16.11	0.200	1.03	3.41	61
WCR-82-8	21.41	0.287	1.27	3.06	
WCR-82-9	21.41	0.240	1.61	2.91	
WCR-82-10	26.88	0.342	1.72	2.84	
WCR-82-11	26.88	0.292	1.96	3.49	
WCR-82-12	32.02	0.359	2.15	3.61	
WCR-82-13	32.02	0.324	2.36	2.21	
WCR-82-14	37.33	0.423	2.28	2.28	
WCR-82-15	37.33	0.440	2.45	3.07	
WCR-82-16	42.40	0.580	2.32	2.52	30
WCR-82-17	42.40	0.580	2.45	2.71	
WCR-82-18	47.90	0.830	2.51	2.84	
WCR-82-19	47.90	0.820	2.49	3.47	
WCR-82-20	53.58	1.06	2.45	2.86	
WCR-82-21	53.58	1.06	2.45	3.12	
WCR-82-22	59.17	1.30	2.45	3.56	
WCR-82-23	59.17	1.29	2.45	3.31	
WCR-82-24	64.85	1.50	2.42	2.17	
WCR-82-25	64.85	1.51	2.39	2.84	
WCR-82-26	70.15	1.73	2.35	2.11	
WCR-82-27	70.15	1.73	2.36	3.15	5.5
WCR-82-28	76.06	1.94	2.33	3.26	
WCR-82-29	76.06	1.94	2.33	8.51	4.6

\*Initial charge consisted of 57.72 gms UC, 495 gms Zn and 1035 gms LiCl-KCl. After each ZnCl<sub>2</sub> addition the charge was stirred 2 hrs and settled  $\frac{1}{2}$  hr before the first sample was taken and stirred an additional hr and settled  $\frac{1}{2}$  hr before the second sample was taken.

\*\*K<sub>N</sub> =  $N_{UCl_3} / (N_{ZnCl_2})^{3/2}$  where  $N_{UCl_3}$  and  $N_{ZnCl_2}$  are mole fraction UCl<sub>2</sub> and mole fraction ZnCl<sub>2</sub>, respectively, in the salt phase.

Table 8. Oxidation of uranium carbide in run WCR-1-113\*

Sample	Total grams ZnCl <sub>2</sub> added	Chemical analysis		Sample wt gms	K <sub>N</sub> **
		% Zn	% U		
WCR-113-1	2.85	<100 ppm	0.28	3.13	
WCR-113-2	2.85	<100 ppm	0.28	1.76	
WCR-113-3	5.54	<100 ppm	0.57	2.42	
WCR-113-4	5.54	<100 ppm	0.58	3.17	
WCR-113-5	8.30	0.22	0.77	4.22	
WCR-113-6	10.90	0.07	0.88	3.16	
WCR-113-7	10.90	0.08	0.93	2.25	
WCR-113-8	13.68	0.13	0.94	4.03	
WCR-113-9	13.68	0.11	0.97	1.79	145
WCR-113-10	16.76	0.02	1.00	3.61	
WCR-113-11	16.76	0.16	1.01	2.81	
WCR-113-12	19.42	0.27	1.08	3.14	
WCR-113-13	19.42	0.35	1.08	2.92	
WCR-113-14	22.42	0.39	1.05	2.74	
WCR-113-15	22.42	0.35	1.14	1.96	29
WCR-113-16	25.21	0.44	1.15	2.22	
WCR-113-17	25.21	0.54	1.16	2.81	
WCR-113-18	25.21	0.63	1.15	3.16	
WCR-113-19	25.21	0.46	1.15	2.83	
WCR-113-20	32.03	1.82	1.20	2.51	
WCR-113-21	32.03	1.24	1.20	2.71	
WCR-113-22	38.96	0.84	1.17	2.68	8.1
WCR-113-23	38.96	0.76	1.25	1.94	

\*Initial charge consisted of 40.09 gm UC, 1035 gm LiCl-KCl and 1285 gm Zn. Sampling procedure is described in Table 7.

\*\*Same quantity is defined in Table 7.

Table 9. Oxidation of uranium carbide in run WCR-1-121\*

Sample	Total grams ZnCl <sub>2</sub> added	Chemical analysis		Sample wt gms	KN**
		% Zn	% U		
WCR-121-1	0	0.01	0.01	2.68	
WCR-121-2	2.83	0.02	0.12	2.45	
WCR-121-3	2.83	0.02	0.25	3.0	
WCR-121-4	5.82	0.05	0.45	2.89	
WCR-121-5	5.82	0.02	0.47	2.70	
WCR-121-6	8.49	0.08	0.425	3.15	
WCR-121-7	8.49	0.12	0.55	3.06	
WCR-121-8	8.49	0.13	0.60	2.72	70.0
WCR-121-9	8.49	0.12	0.62	3.02	
WCR-121-10	11.25	0.24	0.64	2.26	
WCR-121-11	11.25	0.24	0.64	2.56	
WCR-121-12	14.23	0.28	0.64	3.12	
WCR-121-13	14.23	0.27	0.68	3.24	
WCR-121-14	16.85	0.32	0.73	2.32	
WCR-121-15	19.83	0.48	0.735	2.40	
WCR-121-16	22.77	0.59	0.76	3.06	
WCR-121-17	22.77	0.57	0.76	2.89	9.5
WCR-121-18	25.53	0.65	0.77	2.92	
WCR-121-19	25.53	0.565	0.79	3.09	
WCR-121-20	32.38	0.78	0.79	3.18	
WCR-121-21	32.38	0.94	0.78	2.74	
WCR-121-22	39.95	0.96	0.73	2.68	
WCR-121-23	39.95	0.94	0.77	2.56	4.5
WCR-121-24	46.50	1.195	0.80	2.78	
WCR-121-25	46.50	1.23	0.79	3.12	

\*Initial charge consisted of 27.51 gm UC, 1065 gm LiCl-KCl and 985 gm Zn. Sampling procedure described in Table 7.

\*\*Same quantity is defined in Table 7.

Table 10. Oxidation of uranium carbide in run WCR-1-127\*

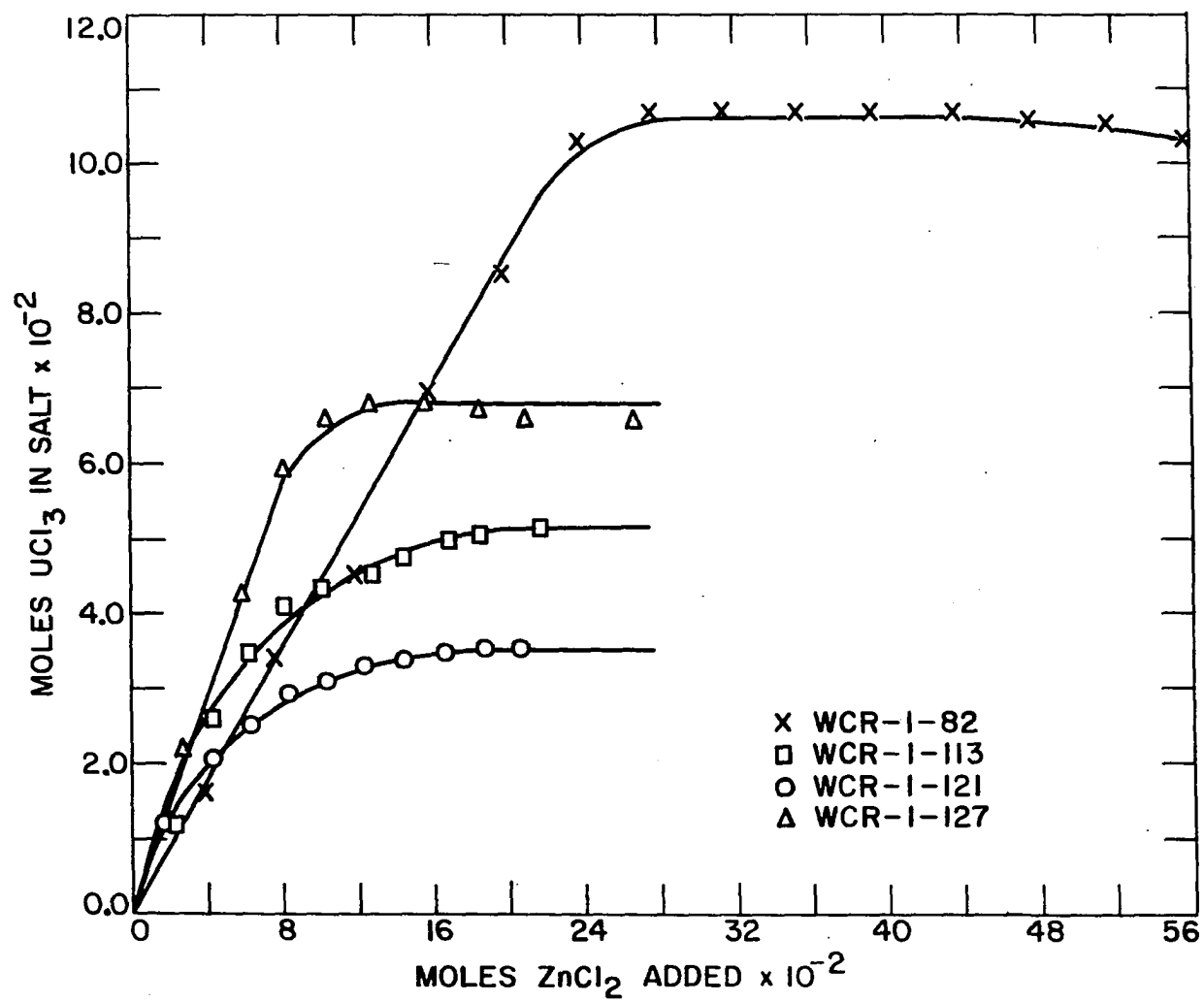
Sample	Total grams ZnCl <sub>2</sub> added	Chemical analysis		Sample wt gms	K <sub>N</sub> **
		% Zn	% U		
WCR-127-1	0	0.01	0.04	2.64	
WCR-127-2	3.90	0.08	0.46	2.79	
WCR-127-3	3.90	0.03	0.49	3.02	
WCR-127-4	7.89	<100 ppm	0.91	2.28	
WCR-127-5	7.89	<100 ppm	0.92	3.16	
WCR-127-6	11.23	0.01	1.27	3.32	
WCR-127-7	14.28	0.05	1.375	3.10	
WCR-127-8	14.28	0.05	1.43	2.82	
WCR-127-9	17.34	0.12	1.44	2.16	
WCR-127-10	17.34	0.12	1.44	2.72	190
WCR-127-11	21.47	0.25	1.46	2.56	
WCR-127-12	21.47	0.23	1.445	3.08	
WCR-127-13	25.20	0.39	1.39	3.12	
WCR-127-14	25.20	0.46	1.365	3.34	
WCR-127-15	29.22	0.46	1.36	2.16	23.4
WCR-127-16	29.22	0.59	1.365	2.50	
WCR-127-17	36.87	0.39	1.36	2.44	
WCR-127-18	36.87	0.86	1.37	2.08	9.2
WCR-127-19	44.27	0.63	1.32	2.78	
WCR-127-20	44.27	1.12	1.33	3.04	6.0

\*Initial charge consisted of 35.41 gm UC, 115 gm LiCl-KCl and 1200 gm Zn. Sampling procedure is described in Table 7.

\*\*Same quantity is defined in Table 7.



Figure 12. Moles  $\text{UCl}_3$  in salt phase versus total moles  $\text{ZnCl}_2$  added to equilibration in continuous UC- $\text{ZnCl}_2$  equilibrations



This maximum  $\text{UCl}_3$  concentration of the salt was not enough to account for all of the uranium monocarbide added to the initial charge. The unreacted uranium carbide was found at the bottom of the zinc phase. A photomicrograph of the bottom portion of the zinc billet of Equilibration WCR-1-113 is shown in Figure 13. The photomicrograph shows a black uranium carbide phase in a zinc matrix with no uranium-zinc compound phase present. The zinc matrix in Run WCR-1-113 was vaporized at  $500^\circ\text{C}$  and the X-ray powder pattern taken of the carbide residue indexed as uranium monocarbide. Chemical analysis indicated that it contained 1.5 wt pct oxygen which is about the same as is usually observed for uranium carbide residues after equilibration with liquid zinc. This indicates that the initial uranium monocarbide reacted with the liquid zinc to the extent observed previously in the uranium monocarbide-zinc reactions. The products of this reaction are uranium oxycarbide and uranium-zinc compound. The first additions of  $\text{ZnCl}_2$  reacted with the uranium-zinc compound according to Reaction 4. This reaction has been shown both theoretically and experimentally to result in quantitative reduction of the  $\text{ZnCl}_2$ . The remaining uranium oxycarbide phase sank to the bottom of the zinc phase where it was

Figure 13. Photomicrograph of bottom portion of zinc-rich billet from the equilibration of a liquid zinc phase containing uranium monocarbide with a liquid salt phase containing  $\text{ZnCl}_2$ . Shows uranium carbide particles in zinc matrix. No  $\text{UZn}_{8.5}$  present. 250X

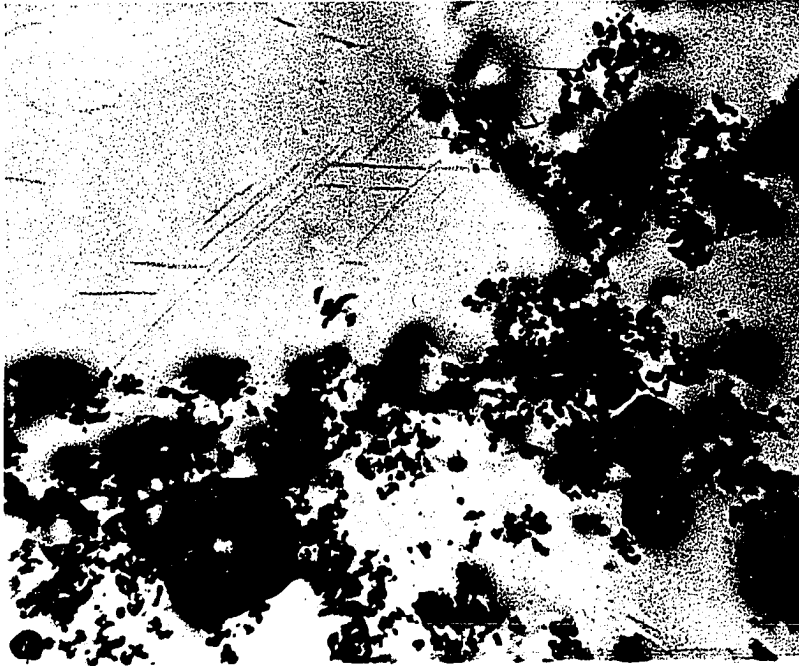


Figure 13

discovered at the end of the equilibration.

The composition of this oxycarbide indicated that it had not reacted to any extent with  $\text{ZnCl}_2$ . Therefore it was considered possible that a true equilibrium was not being attained in these reactions. The mole fraction ratio  $K_N$  was calculated for various portions of the runs and this number became quite small during the latter portion of all four equilibrations. It will be shown in the next section that a much larger fraction of the uranium should be removed from the oxycarbide lattice when  $K_N$  is less than five than the fraction removed in these equilibrations. Therefore the initial additions of  $\text{ZnCl}_2$  reacted quantitatively with the uranium-zinc compound and when the uranium-zinc compound was exhausted, the additional portions accumulated in the salt phase without coming to complete equilibrium with the uranium oxycarbide.

These experiments verified that the uranium monocarbide undergoes a partial reaction with liquid zinc. They also indicated that it was very difficult to obtain sufficient mixing of the phases by stirring to obtain equilibrium. It was decided to obtain the mixing by use of an oscillating furnace.

# UC-ZnCl<sub>2</sub> Equilibrations--Rocking Furnace

Forty-two equilibrations were made in an oscillating furnace between a liquid zinc phase containing uranium monocarbide and LiCl-KCl eutectic salt phase containing ZnCl<sub>2</sub>. The experimental data for these equilibrations are shown in Table 11. The method of preparation for the uranium monocarbide and its particle size are also given in Table 11.

Each equilibrated sample was water quenched from temperature and the salt phase was analyzed for uranium and zinc. The results of the analytical analyses of the salt phase are given in Table 12. The zinc phase was examined metallographically.

It was shown in the introduction that the thermodynamic properties of the equilibrium uranium carbide product could be calculated by measurement of the concentration of UCl<sub>3</sub> and ZnCl<sub>2</sub> in the LiCl-KCl salt if Reactions 6, 8 or 9 represented the equilibrium reaction. The reaction constant  $K_a$ , which was defined in the introduction for Reaction 6, must be calculated in order to determine these thermodynamic properties. In the introduction it was stated that

$$K_a = \frac{(N_{UCl_3})_s (\gamma_{UCl_3})_s}{(N_{ZnCl_2})_s^{3/2} (\gamma_{ZnCl_2})_s^{3/2}} = K_N K_Y \quad (13)$$

Table 11. Experimental data for oscillating furnace equilibrations of UC-ZnCl<sub>2</sub> in LiCl-KCl/zinc system

Run	Initial charge (gms)				UC part. size (mesh)	Temp (°C)	Time rock. (hrs)	Time set- tled (hrs)	Con- tainer	UC preparation method
	UC	ZnCl <sub>2</sub>	LiCl- KCl	Zn						
WCR-2-9C	0.93	1.90	15.35	9.7	<300	580	22	1	Ta	Propane reduc.
WCR-1-28A	3.7	3.0	13.20	15.8	coarse	585	10	1	Ta	Arc melt
WCR-2-9B	1.32	1.37	15.06	15.3	<300	585	23	6	Ta	Prop. red.
WCR-1-47A	6.8	3.3	13.50	12.6	<100	590	10	8	Ta	Arc melt
WCR-1-27B	8.6	4.4	17.80	20.0	coarse	598	8	1	Ta	Arc melt
WCR-1-59	6.1	3.0	16.20	19.6	<20	600	38	4	Ta	Arc melt
WCR-2-9A	1.34	1.03	14.62	10.0	<300	600	23	1	Ta	Prop. red.
WCR-2-9E	0.91	2.64	14.77	9.9	<300	600	25	7	Ta	Prop. red.
WCR-2-9D	1.29	2.49	15.51	7.5	<300	600	23	6	Ta	Prop. red.
WCR-1-30B	3.9	3.0	14.5	30.0	coarse	600	44	11	Ta	Arc melt
WCR-1-8A	10.7	7.0	28.0	30.0	coarse	602	3	½	Ta	Arc melt
WCR-1-8B	8.7	7.0	28.0	24.3	coarse	209	3	½	Ta	Arc melt
WCR-1-27A	8.5	4.8	19.2	20.0	coarse	612	21	1	Ta	Arc melt
WCR-1-15A	9.9	7.0	28.0	30.0	coarse	615	24	½	Ta	Arc melt
WCR-1-30A	4.1	3.0	14.3	30.0	coarse	615	42	1	Ta	Arc melt
WCR-1-15B	10.9	7.0	28.0	30.0	coarse	619	25	½	Ta	Arc melt
WCR-1-47B	7.4	3.3	15.0	15.2	<100	620	22	6	Ta	Arc melt
WCR-1-2A	7.0	5.0	20.0	3.0	coarse	635	4	½	Ta	Arc melt
WCR-1-2B	4.3	5.0	20.0	3.0	coarse	635	4	½	Ta	Arc melt
WCR-1-58	6.5	2.9	18.3	22.6	<40	662	18	4	Ta	Arc melt



Table 11. (Continued)

Run	Initial charge (gms)				UC part. size (mesh)	Temp (°C)	Time rock. (hrs)	Time set- tled (hrs)	Con- tainer	UC preparation method
	UC	ZnCl <sub>2</sub>	LiCl- KCl	Zn						
WCR-2-14	0.99	0.84	14.9	12.1	<300	680	23	2	C	Prop. red.
WCR-1-28B	4.3	3.0	13.0	18.5	coarse	685	20	1	Ta	Arc melt
WCR-1-27C	4.1	10.2	13.0	15.0	coarse	690	8	1	Ta	Arc melt
WCR-1-9A	7.7	7.2	28.8	27.5	coarse	692	3	½	Ta	Arc melt
WCR-1-4D	3.9	3.3	16.6	14.4	<100	700	20	23	Ta	Arc melt
WCR-1-42A	4.0	3.1	13.0	30.0	<100	700	27	1	Ta	Arc melt
WCR-1-65A	5.6	2.9	16.6	26.2	<40	700	62	4	Ta	Arc melt
WCR-1-65B	6.5	3.3	19.9	26.9	<40	700	50	4	Ta	Arc melt
WCR-2-17A	1.10	1.41	15.9	9.9	<300	700	24	3	C	Prop. red.
WCR-2-17B	1.15	1.70	15.4	10.7	<300	700	24	3	C	Prop. red.
WCR-2-17C	1.10	2.13	15.0	9.9	<300	700	21	3	C	Prop. red.
WCR-2-17D	1.15	2.82	14.1	11.3	<300	700	6	2	C	Prop. red.
WCR-1-90A	1.05	1.41	19.9	18.8	<150	700	65	5	Ta	Arc melt
WCR-1-90B	1.18	2.09	19.1	19.1	<100	700	41	11	Ta	Arc melt
WCR-1-32	5.0	3.2	13.0	22.0	<100	710	29	3	Ta	Arc melt
WCR-1-2C	9.8	8.0	32.0	20.4	coarse	718	7	1	Ta	Arc melt
WCR-1-29	7.0	3.2	14.2	26.0	coarse	735	19	1	Ta	Arc melt
WCR-1-41	3.8	2.8	13.6	25.5	<100	750	17	3	Ta	Arc melt
WCR-1-86	7.0	7.0	28.0	23.7	coarse	785	3	½	Ta	Arc melt
WCR-1-8C	10.4	7.3	29.2	55.0	coarse	790	3	½	Ta	Arc melt
WCR-1-33	5.3	3.0	13.2	28.4	<100	800	16	1	Ta	Arc melt
WCR-1-42B	4.1	3.5	13.1	16.4	<100	802	36	1	Ta	Arc melt

Table 12. Analytical data and calculated results of oscillating furnace equilibrations of UC with  $\text{ZnCl}_2$  in a  $\text{KCl-LiCl/zinc}$  system

Run	Salt analysis		Gm U in salt	Gm U charged	% U oxidized	Gm ZnCl <sub>2</sub> unaccounted for	K <sub>N</sub>	Moles ZnCl <sub>2</sub>
	% U	% Zn						mole UC
UC charged in particles of less than 100 mesh								
WCR-1-47B	17.43	0.75	3.58	7.0	51.1	-0.10	146	0.87
WCR-1-47A	19.95	0.50	3.85	6.5	59.3	-0.09	313	0.93
WCR-1-33	18.70	0.60	3.44	5.0	68.8	-0.20	110	1.10
WCR-1-32	15.80	1.30	2.72	4.8	56.7	0.40	29	1.22
WCR-1-41	16.90	0.45	3.08	3.6	85.5	0.02	145	1.25
WCR-2-9A	6.43	0.22	1.04	1.28	81.2	0.06	184	1.41
WCR-1-42A	18.70	0.76	3.34	3.8	87.9	-0.06	76	1.49
WCR-2-14	3.86	0.82	0.62	0.95	65.6	0.03	15.4	1.54
WCR-1-40	13.1	1.95	2.83	3.7	76.5	-0.02	13.5	1.63
WCR-1-42B	18.70	1.78	3.54	3.9	90.6	-0.27	21.2	1.64
WCR-2-9B	6.67	1.38	1.10	1.26	87.3	-0.12	11.5	1.89
WCR-2-17A	4.64	1.57	0.82	1.05	77.6	0.12	7.10	2.34
WCR-1-90A	3.94	1.37	0.872	1.00	87.2	-0.20	4.55	2.45
WCR-2-17B	5.38	2.18	0.95	1.09	86.8	0.09	5.09	2.73
WCR-1-90B	3.88	3.11	0.84	1.125	75.0	-0.04	2.10	3.24
WCR-2-17C	5.13	3.33	0.90	1.05	85.7	0.14	2.56	3.54
WCR-2-9C	3.95	3.24	0.69	0.88	78.0	0.13	1.90	3.74
WCR-2-9E	5.49	4.42	1.03	1.23	83.6	0.03	1.64	3.76
WCR-2-17D	5.21	6.50	0.93	1.09	85.7	-0.41	0.97	4.49
WCR-2-90	4.11	4.85	0.72	0.87	84.3	0.09	1.09	5.00

Table 12. (Continued)

Run	Salt analysis		Gm U in salt	Gm U charged	% U oxidized	Gm ZnCl <sub>2</sub> unaccounted for	K <sub>N</sub>	Moles ZnCl <sub>2</sub> mole UC
	% U	% Zn						
UC charged in particles of greater than 100 mesh								
WCR-1-29	13.69	2.36	2.58	6.7	38.5	0.02	9.2	0.88
WCR-1-58	14.45	1.20	3.45	6.2	55.6	-0.68	29	0.87
WCR-1-59	16.41	1.03	3.60	5.8	62.1	-0.58	42	0.95
WCR-1-65A	13.20	0.92	2.79	5.3	52.5	0.09	41	0.95
WCR-1-17B	6.56	2.43	1.52	8.2	18.5	-0.40	5.0	0.97
WCR-1-27A	18.46	1.70	5.08	8.1	62.7	-0.55	24	1.08*
WCR-1-15B	20.42	0.10	8.10	10.4	77.8	-0.06	2100	1.23*
WCR-1-8A	14.39	2.84	5.50	10.2	53.9	0.00	8.0	1.25
WCR-1-2A	9.28	4.95	2.42	6.7	36.1	0.17	2.4	1.30
WCR-1-28B	11.78	4.19	2.06	4.1	50.2	-0.60	5.0	1.34
WCR-1-8C	8.10	5.54	3.08	9.9	31.1	0.24	1.8	1.35
WCR-1-15A	16.55	2.38	6.50	9.4	69.1	-0.56	10.5	1.37*
WCR-1-30A	10.00	3.17	1.81	3.9	46.6	0.29	5.0	1.41
WCR-1-30B	7.10	4.87	1.29	3.7	34.8	0.20	1.8	1.48
WCR-1-8B	8.36	5.83	3.10	8.3	37.3	-0.18	1.8	1.55
WCR-1-2C	8.99	4.89	3.75	9.3	40.4	+0.48	2.2	1.57
WCR-1-9A	13.70	6.55	5.91	7.3	80.6	-2.93	2.1	1.80
WCR-1-8G	10.1	5.42	8.82	6.7	57.0	-1.00	2.3	1.91
WCR-1-2B	8.51	2.24	2.24	4.1	54.6	0.28	2.3	2.13
WCR-1-27C	13.12	13.59	3.22	3.9	82.1	0.45	0.21	4.80

\*Equilibrations WCR-1-27A, 1-15B, and 1-15A were equilibrated with last particles of first arc melted UC sample. Particles were too malleable to crush-- they were thought to be very rich in free uranium metal.

where  $N$  and  $\gamma$  represent the mole fraction and activity coefficient respectively of  $UCl_3$  and  $ZnCl_2$  in the  $LiCl-KCl$  eutectic salt. The activity coefficients are functions of both temperature and concentration. However, the maximum concentration of  $UCl_3$  and  $ZnCl_2$  obtained in these experiments represent a mole fraction  $N$  of less than 0.07. In this range the concentration dependence of  $\gamma$  is small and  $K_\gamma$  should approximate a constant at constant temperatures. Since  $\Delta F^\circ_{UC_2}$ ,  $\Delta F^\circ_{UCl_3}$ , and  $\Delta F^\circ_{ZnCl_2}$  are constant at a given temperature, consideration of Equation 10 shows that  $K_a$  must be constant at a particular temperature. Therefore, from Equation 13,  $K_N$  should be almost constant for the  $UC-ZnCl_2$  reaction at a particular temperature if the equilibrium reaction is represented by Reactions 6, 8 or 9. The reaction constant  $K_N$  has been calculated from the analytical data and is shown in Table 9. It was not constant at a constant temperature.

It was also mentioned in the introduction that if one takes the more recent values of the free energy of formation of  $UC$ ,  $U_2C_3$  or  $UC_2$  as being correct, the  $ZnCl_2$  added to the salt should be almost quantitatively reduced from the salt until the carbide is completely oxidized. The maximum

fraction of the uranium in the uranium carbide charged to ever be oxidized was 0.91. A high concentration of  $\text{ZnCl}_2$  in the salt was necessary to accomplish this 91% oxidation. Since Reactions 6, 8 and 9 would dictate that  $K_N$  be constant at constant temperature and that all of the uranium be easily oxidized into the salt, none of these reactions represent the equilibrium reaction.

Examination of the calculated  $K_N$ 's indicated that they were affected by the particle size of the uranium monocarbide utilized in the charge and by the  $\text{ZnCl}_2/\text{UC}$  ratio in the charge. There was no obvious temperature dependence. When the uranium monocarbide charged had a particle size of less than 100 mesh, there was no time dependence in  $K_N$ . When the particle size of the uranium monocarbide charged was larger than 100 mesh, longer equilibration times produced higher  $K_N$ 's. The variation of  $K_N$  with the  $\text{ZnCl}_2/\text{UC}$  ratio in the charge is shown by Figures 14 and 15 which plot  $K_N$  versus the  $\text{ZnCl}_2/\text{UC}$  ratio on semi-log paper. Figure 14 is a plot of this type for equilibrations which utilized uranium carbide in the charge which had a particle size greater than 100 mesh. Figure 15 is an identical plot for equilibrations which utilized uranium carbide particles of less than 100 mesh in the

Figure 14. Mole fraction ratio  $K_N$  versus initial moles  $ZnCl_2$ /moles UC for oscillating furnace equilibrations in which the uranium monocarbide was coarse particles ( $>100$  mesh)

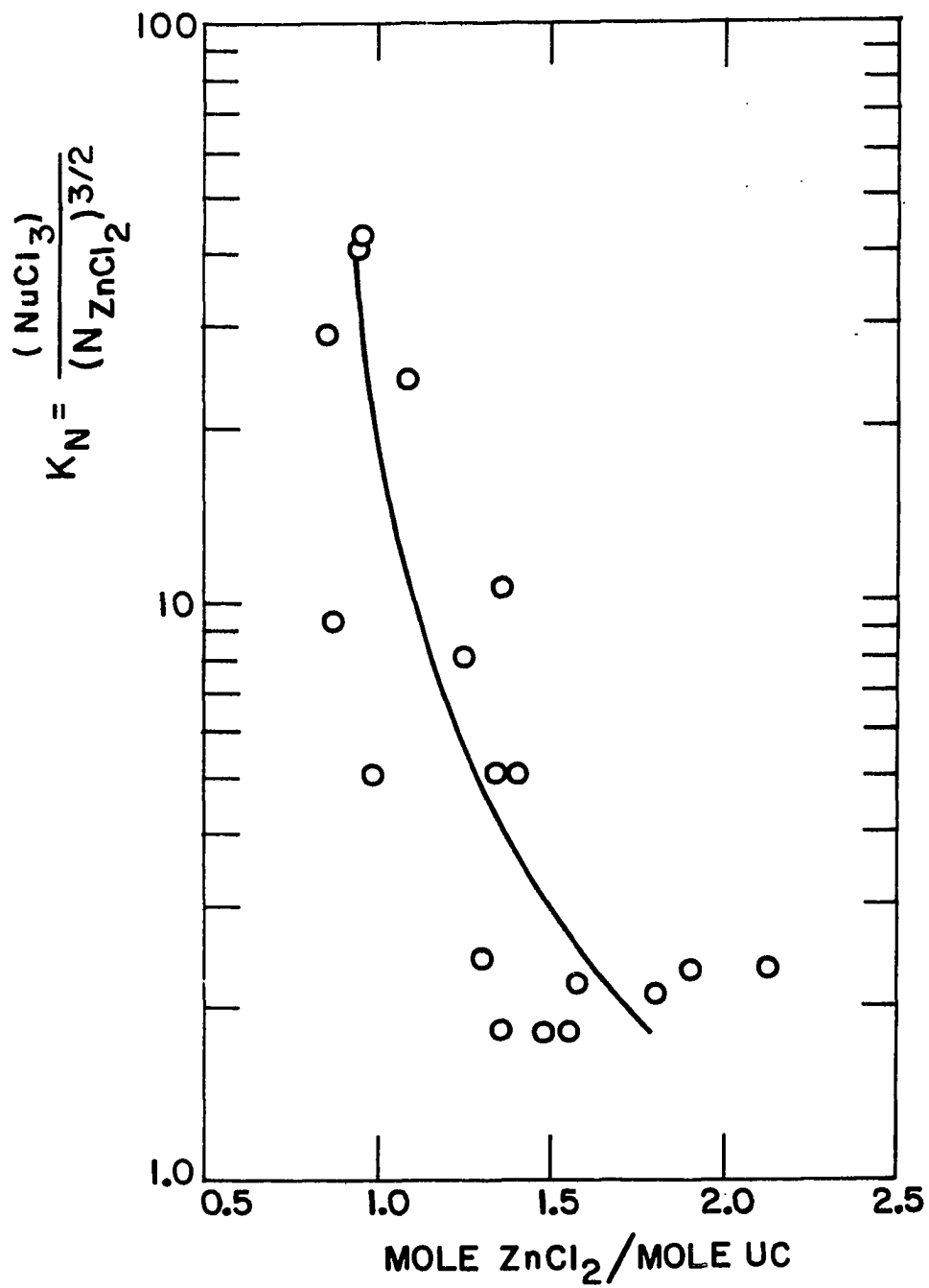
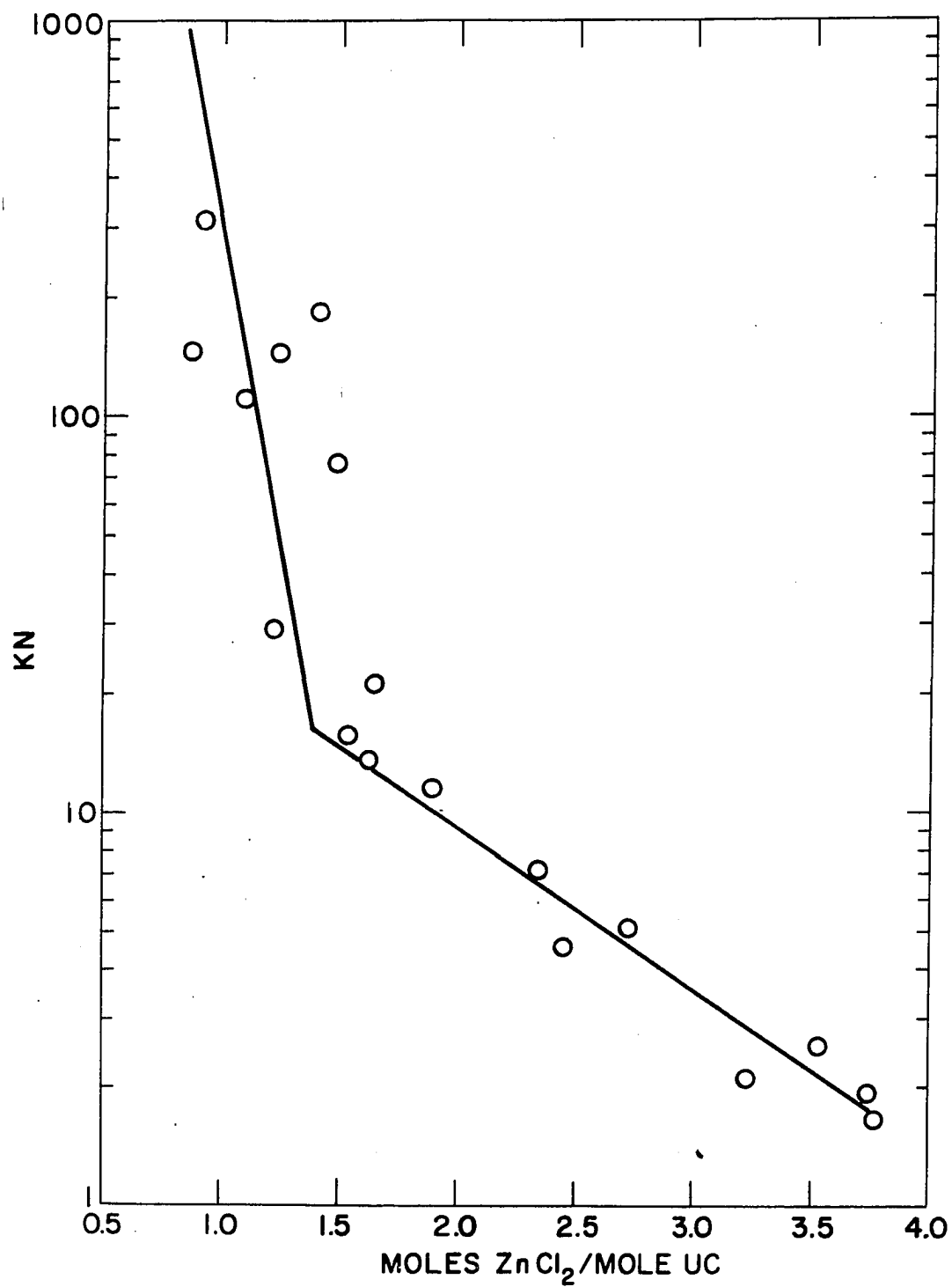


Figure 15. Mole fraction  $K_N$  versus initial moles  $ZnCl_2$ /moles UC for oscillating furnace equilibrations in which the uranium monocarbide was fine particles (<100 mesh)





charge. It is apparent from comparison of the two figures that a smaller particle size for the uranium carbide charged produced a higher  $K_N$ .

The zinc phase of these equilibrations was examined. As in previous reactions the unreacted uranium carbide phase was found near the bottom of the zinc phase. The longitudinally cut zinc billets were polished and examined metallographically and with an X-ray diffractometer. The zinc matrix in some of the samples was removed by acid dissolution, vaporization, or physical techniques, and X-ray powder patterns and qualitative spectrographic analyses were taken of the residue. The physical technique, described in the experimental procedure section, was applicable only when the uranium carbide charged was in large particles. The results of the X-ray examinations are given in Table 13. It is shown in Table 10 that X-ray powder patterns of all residues obtained after physical removal of the zinc matrix indexed as uranium monocarbide with no extraneous lines present. The powder patterns of residues obtained after the zinc matrix was vaporized or dissolved were fuzzy and more difficult to read. The principle constituent of the pattern was usually  $Ta_2C$ . Uranium dioxide was sometimes indicated, particularly in equilibrations in which  $K_N$  was less

Table 13. X-ray examination of zinc phase and residue after removal of zinc for UC-ZnCl<sub>2</sub> oscillating furnace equilibrations

Run	Temp (°C)	Total equil. time (hrs)	Method of zinc removal	Method of exam.	Strongest line d <sub>0</sub> spacing (Å)	Phases identified				Container
						UC	TaC	Ta <sub>2</sub> C	UO <sub>2</sub>	
WCR-1-25	550	14	HNO <sub>3</sub>	Powder	2.35	+	+	++	-	Ta
WCR-1-47A	590	18	HNO <sub>3</sub>	Powder	2.55, 2.35	-	++	+	-	Ta
WCR-1-59	600	42	Physical	Powder	2.84	++	-	-	-	Ta
WCR-1-30A	615	42	HNO <sub>3</sub>	Powder	2.36	+	+	++	-	Ta
WCR-1-30A	615	42	-	Diff.	2.09	+	I	+	-	Ta
WCR-2-9D	600	29	Distill	Powder	2.36	-	+	++	I	Ta
WCR-1-29	735	20	Physical	Powder	2.83	++	-	-	-	Ta
WCR-1-65A	700	66	Physical	Powder	2.86	++	I	+	-	Ta
WCR-1-65A	700	66	-	Diff.	2.09	+	-	+	-	Ta
WCR-1-90A	700	65	Distill	Powder	2.36	-	I	+	I	Ta
WCR-2-14	700	24	Distill	Powder	2.87	++	-	-	+	C

++ - dominant compound

+ - compound present

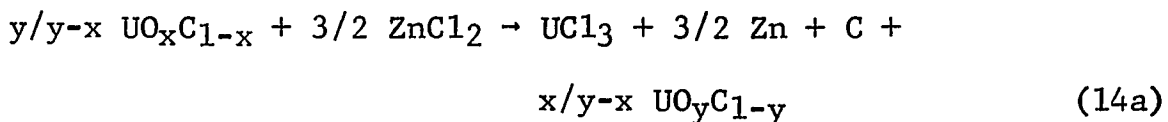
I - indicated by a few weak lines

- - compound absent

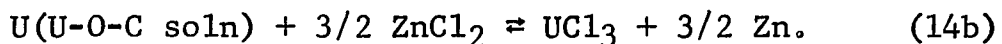
No powder patterns or diffractometer patterns indicated U<sub>2</sub>C<sub>3</sub> or UC<sub>2</sub>.

than five. However, the qualitative spectrographic analyses on all residues examined indicated the presence of uranium.

The only uranium carbide compound observed in any of the equilibrations of Table 13 was uranium monocarbide. The results of the uranium monocarbide-liquid zinc reaction also indicated that only a face centered cubic uranium monocarbide type phase was present. This uranium monocarbide phase is apparently an oxygen stabilized phase. Since some oxygen is present in the system initially and particularly in the monocarbide as prepared, the increase in oxygen content of the carbide and hence its stabilization during the equilibration process may be represented by the following reaction,



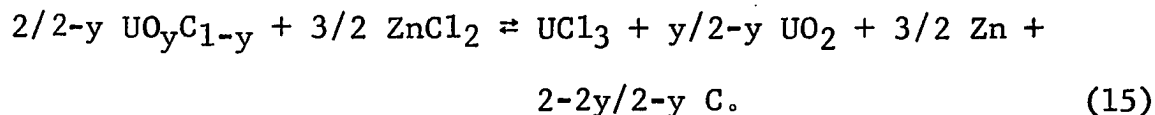
with  $y > x$ . The reaction will reach an equilibrium represented by



The stability of the uranium oxycarbide phase will be dependent on the amount of oxygen in the phase. Equation 14a is analagous to Equation 12a or similarly, Reactions 14b and 12b. In Reaction 12b the oxygen in the monocarbide phase increased until the chemical potential of the uranium in this phase is

equal to the chemical potential of uranium in the zinc solution or in  $U_2Zn_{17}$ . The chemical potential of uranium in this case is a fixed quantity at each temperature. However, in the case of the UC- $ZnCl_2$  reaction as in 14a, an increase in  $ZnCl_2$  content of the salt will further oxidize some uranium and increase the oxygen content of the residual phase. Therefore the stability of the equilibrium oxycarbide phase will be directly dependent on the fraction of the uranium that has been oxidized and will be directly proportional to the mole  $ZnCl_2$ /mole UC charged. The observed  $K_N$  will be inversely proportional to the stability of the oxycarbide phase present at equilibrium. The  $K_N$  must therefore be inversely proportional to the mole  $ZnCl_2$ /mole UC in the charge. This is exactly the result observed.

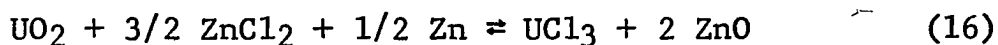
In equilibrations in which the equilibrium  $K_N$  was low,  $UO_2$  lines were observed in the X-ray powder patterns of the residues obtained after the removal of zinc. This indicates the possibility of the following reaction at high concentrations of  $ZnCl_2$ .



The  $y$  in Reaction 15 represents the maximum concentration

of oxygen in the oxycarbide phase. The equilibrium  $K_N$  established by Reaction 15 should be a constant as long as all of the indicated phases are present. If the solubility limit of oxygen in the oxycarbide phase were known, and the concentrations of  $UCl_3$  and  $ZnCl_2$  in the salt phase were measured when both  $UO_2$  and the saturated oxycarbide phase existed at equilibrium, the free energy of formation of the oxygen saturated uranium oxycarbide phase could be calculated. Unfortunately the  $Ta_2C$  and  $TaC$  lines in the powder patterns of the residues obtained by removal of the zinc from equilibrations performed in tantalum tended to obscure the other phases. However, both a uranium oxycarbide phase and the  $UO_2$  phase were observed in the X-ray powder pattern of the distillation residue from the zinc phase of Run WCR-2-14, Tables 11 and 12. In this experiment the charge was contained in graphite and the observed  $K_N$  was 15.4.

As will be shown in the next section, the continued increase of  $ZnCl_2$  content in the salt phase will result in the complete conversion of the uranium oxycarbide phase to  $UO_2$ . At that point there will be no further oxidation of uranium since the reaction



is thermodynamically unfavorable and will not proceed. The  $\Delta F^\circ$  of this reaction is +38 Kcal at 600°C. The high stability of  $UO_2$  makes it certain that any oxygen present in the system considered here will be retained or acquired by the uranium. For this reason, Reactions 12, 14 and 15 are much more thermodynamically favorable than any reaction involving the evolution of CO,  $CO_2$  or the formation of ZnO.

The theoretical behavior of a particular uranium oxycarbide in a LiCl-KCl/zinc system may be calculated if one assumes values for the initial oxygen composition, the solubility limit of oxygen in the oxycarbide and the oxygen composition of the oxycarbide that is in equilibrium with the liquid zinc. The selected values were 0.08 mole fraction UO in the initial oxycarbide, 0.75 mole fraction UO as the solubility limit of UO in UC and 0.20 mole fraction UO as the composition of the carbide in equilibrium with liquid zinc. The values of 0.08 mole fraction UO in the initial oxycarbide and 0.20 mole fraction UO as the composition of oxycarbide in equilibrium with liquid zinc were actually observed by vacuum fusion oxygen analysis. The value of 0.75 mole fraction UO for the solubility limit of UO in the oxycarbide phase was indicated by EMF measurements which will be discussed later. A value of

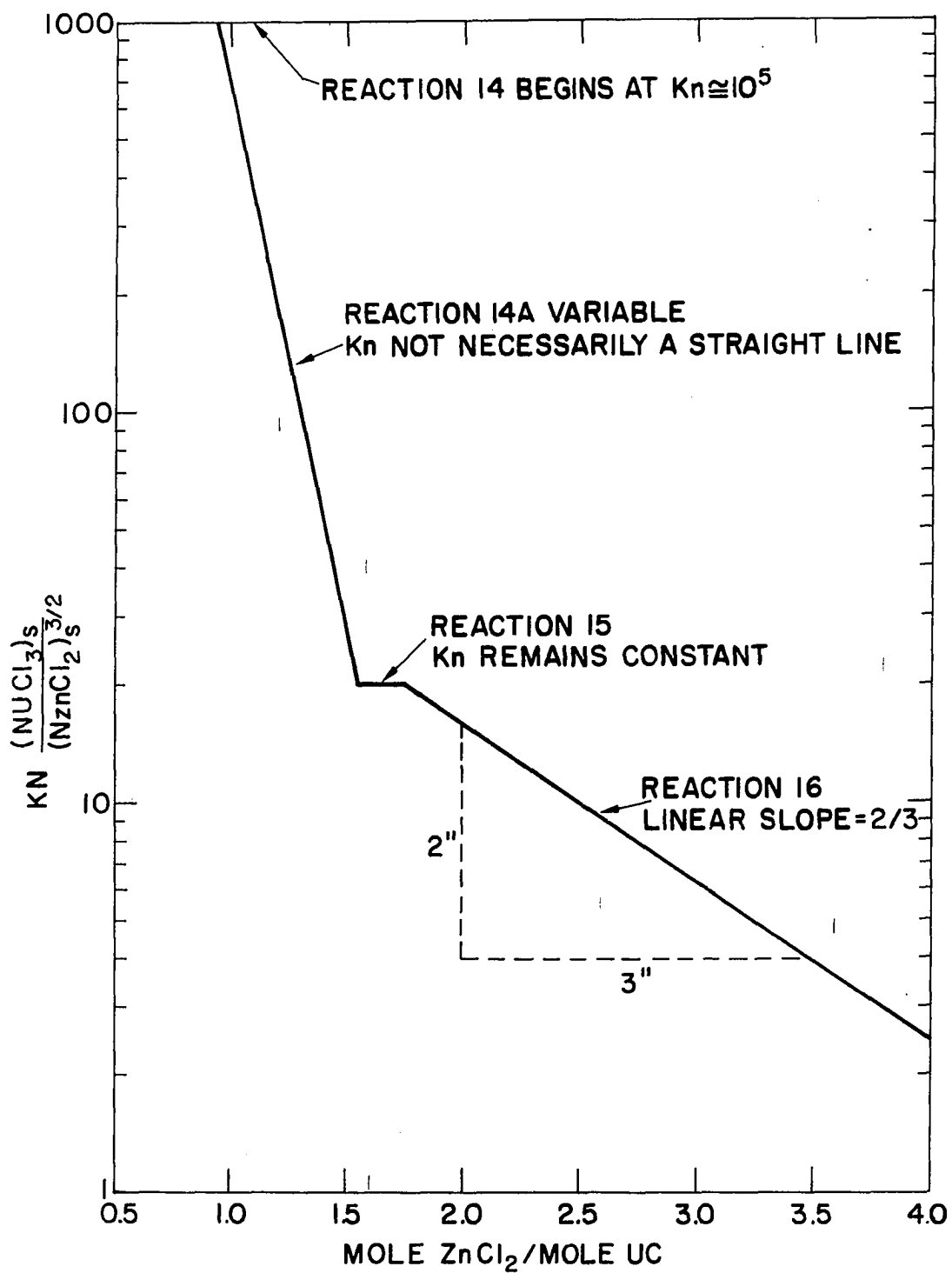
20 was selected for the  $K_N$  that would be attained by Equation 15. The data in Table 12 and Figure 15 indicate that this  $K_N$  has a value between 16 and 20. The calculated plot is shown in Figure 16. The calculations necessary to give this plot are shown in the appendix.

The curve obtained from the theoretical calculation exhibits the same general shape as the one observed experimentally for equilibrations involving UC particles of less than 100 mesh (Figure 15). There are, however, several differences. The theoretical calculation indicates that 96% of the uranium oxycarbide charged should be oxidized to  $UCl_3$ , assuming 0.08 mole fraction UO in the initial oxycarbide. The maximum removal observed was 91%, and several of the initial carbides had lower initial concentrations of oxygen than 0.08 mole fraction UO. Therefore, one must suspect that some oxygen contamination was acquired from the system. When graphite was used for the container the graphite would be one major source of oxygen contamination. The calculated  $K_N$  values in Figure XVI are somewhat higher for a given  $ZnCl_2/UC$  ratio than the experimental values in Figure 15, but the general agreement is good.

The experimentally obtained values of  $K_N$  for equilibra-



Figure 16. Calculated equilibrium  $K_N$  versus initial  $ZnCl_2/UC$  ratio at  $700^\circ C$  for equilibrations in a  $LiCl-KCl$ /zinc system based on the assumption of mole fractions of  $UO$  in the carbide of 0.08 initially, 0.20 in equilibrium with zinc and 0.75 maximum



tions in which the particle size of the uranium monocarbide charged was greater than 100 mesh are much lower than the values obtained when the particle size was less than 100 mesh. This is most probably due to surface depletion of the uranium from a coarse particle producing a high oxygen concentration at the surface, thus limiting the reaction of  $\text{ZnCl}_2$  with the carbide. When longer times of equilibrations are allowed, the oxygen at the surface of the particle gradually diffuses into the particle and further reaction with the  $\text{ZnCl}_2$  takes place. This accounts for the time dependence of  $K_N$  observed in these equilibrations. When longer times of equilibration were allowed, larger  $K_N$  values were observed for identical charges.

The straight line portion of the theoretical curve which extends from a  $\text{ZnCl}_2/\text{UC}$  ratio of 1.64 to 1.75 is that portion which represents the reaction of  $\text{ZnCl}_2$  with the oxycarbide phase to give  $\text{UCl}_3$  and  $\text{UO}_2$ . At higher  $\text{ZnCl}_2/\text{UC}$  values the  $\text{ZnCl}_2$  simply accumulates in the salt phase and the curve attains a theoretical slope of  $2/3$  as shown in Figure 16. The analogous section of the curve on Figure 15 begins at a  $\text{ZnCl}_2/\text{UC}$  ratio of about 1.50. In this figure the plateau region is not evident.

A plateau also exists at very low ratios of  $\text{ZnCl}_2/\text{UC}$ ,

which is not evident in Figure 15 and is not shown in Figure 16.

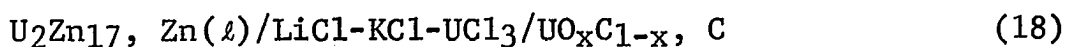
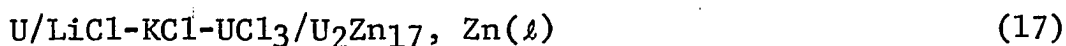
The first portions of  $\text{ZnCl}_2$  which are added to a  $\text{LiCl-KCl}$  salt in contact with a liquid zinc phase which has been reacted with uranium monocarbide will react with the uranium-zinc compound formed. This was demonstrated in the previous section. The  $K_N$  for the  $\text{UZn}_{8.5}\text{-ZnCl}_2$  reaction (Reaction 9) is very high and would result in  $\text{ZnCl}_2$  concentration in the salt too low to detect analytically. When the compound has been depleted additional  $\text{ZnCl}_2$  will react with the uranium carbide phase according to Reaction 14. The first portion of this reaction will also produce very high  $K_N$  values. The first analytically observable  $K_N$  will be produced by a reaction as represented by Equation 14a and will occur only after a considerable fraction of the uranium carbide phase has been oxidized and a sufficiently stable oxycarbide has been formed to give an observable amount of  $\text{ZnCl}_2$  in the salt phase. Therefore, Figure 14 and 15 represent only the last portions of the variable  $K_N$  of Equation 14a, the constant  $K_N$  of Equation 15 and the lower values of  $K_N$  which indicate only that excess  $\text{ZnCl}_2$  has been added to a salt in equilibrium with  $\text{UO}_2$ .

The  $\text{ZnCl}_2\text{-UC}$  equilibrations were performed over a consid-

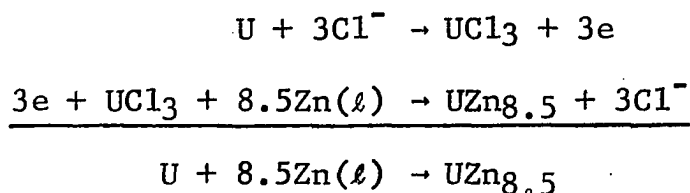
erable period of time. The uranium carbides utilized were prepared by different methods, stored for different times and crushed to different particle sizes. In view of the stabilizing effects of oxygen it is not surprising that they behaved differently in the reactions studied.

### Electromotive Force Measurements

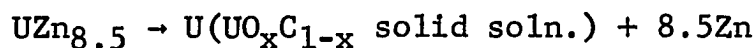
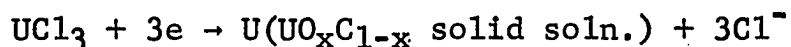
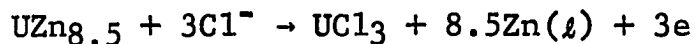
In view of the foregoing data on the stabilization of the uranium monocarbide phase by oxygen, it was decided to attempt to measure quantitatively the increase in chemical potential of uranium in the uranium oxycarbide phase as a function of oxygen composition and temperature. This was accomplished by electromotive force measurements on cells of the type



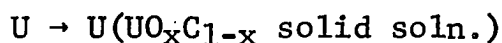
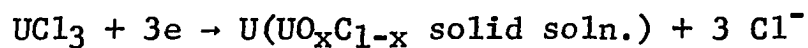
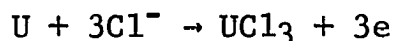
The electrode reactions and overall reaction for cell 17 may be written as



The corresponding reactions for cell 18 are



and for cell 19



The liquid zinc phase involved in Reactions 17 and 18 is nearly pure zinc in the temperature range investigated, 475-750°C. At 700°C, the solubility of uranium in zinc is 0.41 atom per cent (10). Therefore the activity of zinc in the zinc rich uranium-zinc liquid solution may be taken to be unity.

The charges for all equilibrations in which the EMF of cells 17, 18 or 19 were measured are given in Table 14. Uranium oxycarbides of various oxygen content, expressed as mole fraction UO in UC, were prepared by heating pressed compacts of UC and UO<sub>2</sub> to temperatures of 1575°C under vacuum and holding at temperature until the pressure dropped to 0.3 microns of mercury. The total time at temperature was 4½ hours. The pressure over the system was 0.3 microns of mercury before

Table 14. Experimental data for equilibrations involving measurement of electromotive force

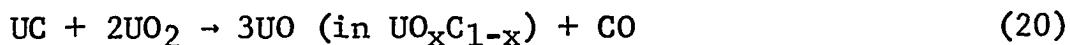
Run	Charge to Ta crucible, gm				Type uranium carbide in electrode	Container material for carbide electrode
	U	ZnCl <sub>2</sub>	LiCl- KCl	Zn		
E-14	6.25	2.80	180.2	55.1	UC <sup>1</sup>	C
E-15	7.23	3.05	178.5	64.1	UC <sub>2</sub> <sup>2</sup>	Cu
E-16	7.35	2.76	177.4	66.2	UC <sub>2</sub> <sup>2</sup>	C
E-17	15.0	5.46	610	135	UC <sub>2</sub> <sup>2</sup>	C
E-18	25.8	6.95	620	232	UC <sub>2</sub> <sup>2</sup>	C
E-19	24.5	9.10	570	220	UC <sub>2</sub> <sup>2</sup>	C
E-20	22.0	7.80	820	178	UC <sub>2</sub> <sup>2</sup>	C
E-21	35.0	9.10	790	315	UC <sup>1</sup>	Cu
E-22	28.0	8.20	810	252	UO <sub>x</sub> C <sub>1-x</sub> <sup>3</sup>	Cu
E-23	26.0	7.80	790	234	UO <sub>x</sub> C <sub>1-x</sub> <sup>3</sup>	C

<sup>1</sup>Uranium monocarbide as prepared by reaction of UH<sub>3</sub> with propane (contained 5170 ppm oxygen).

<sup>2</sup>Uranium dicarbide prepared by reduction of UO<sub>2</sub> with carbon

<sup>3</sup>Prepared by reaction of UO<sub>2</sub> with uranium monocarbide in (1).

heating and then rose to 25 microns of mercury when the temperature reached 1500°C. The temperature was finally increased to 1575°C and about two hours after the pressure had gone back down to 0.3 microns of mercury it was assumed that the reaction



had proceeded to completion. The uranium monocarbide powder employed in preparing the pressed compacts was a portion of sample K-5 of Table 6. This powder was prepared by the reaction of uranium hydride with propane and was found to contain 5170 ppm of oxygen. This oxygen and the oxygen introduced into the carbide by Reaction 20 were employed in calculating the final oxygen content of the oxycarbide. These data are summarized in Table 15. The resulting compacts for samples L-5b, L-6, L-7 and L-8 were placed in a graphite crucible under argon and sealed in a stainless steel casing. This assembly was held at 800°C for 60 hours. All compacts were analyzed for oxygen by vacuum fusion techniques. These analyses are also given in Table 15.

The results of all EMF measurements on the cells of the type represented by Equation 17 are given in Table 16. The results of EMF measurements taken in investigations in which



Table 15. Composition of oxycarbide,  $\text{UO}_x\text{C}_{1-x}$  samples

Sample	Initial components (gms)		Stoichiometry of oxycarbide based on	
	UC	UO <sub>2</sub>	nominal composition	oxygen analysis*
L-1**	5.0	--	--	UO <sub>0.08</sub> C <sub>0.92</sub>
L-2	6.6037	0.7277	UO <sub>0.21</sub> C <sub>0.79</sub>	UO <sub>0.33</sub> C <sub>0.67</sub>
L-3	3.8778	0.9267	UO <sub>0.34</sub> C <sub>0.66</sub>	UO <sub>0.55</sub> C <sub>0.45</sub>
L-4	3.3375	1.7470	UO <sub>0.54</sub> C <sub>0.46</sub>	UO <sub>0.32</sub> C <sub>0.18</sub> ***
L-5a	2.7980	3.0030	UO <sub>0.78</sub> C <sub>0.22</sub>	melted(not analyzed)
L-5b	4.1300	0.5930	UO <sub>0.25</sub> C <sub>0.75</sub>	UO <sub>0.35</sub> C <sub>0.65</sub>
L-6	3.9067	0.9703	UO <sub>0.34</sub> C <sub>0.66</sub>	UO <sub>0.50</sub> C <sub>0.50</sub>
L-7	3.0848	1.2915	UO <sub>0.48</sub> C <sub>0.52</sub>	UO <sub>0.70</sub> C <sub>0.30</sub>
L-8	2.5831	1.9970	UO <sub>0.67</sub> C <sub>0.33</sub>	UO <sub>1.0</sub> ***

\*The oxygen analysis was made after the samples had been heated to 1575°C for roughly 4.5 hours in a graphite crucible under vacuum and after samples L-5b, 7 and 8 were annealed in graphite crucibles at 800°C for 60 hours under argon.

\*\*Carbide as prepared by the reaction of  $\text{UH}_3$  with propane.

\*\*\*X-ray diffraction patterns showed UO<sub>2</sub> in addition to face centered cubic oxycarbide.

one of the electrodes was a  $\text{UO}_x\text{Cl}_{1-x}$  electrode are given in Table 17. In Run WCR-3-38 measurements between three electrodes were made at each equilibrium temperature and the additivity of the EMF's was demonstrated, that is, the algebraic sum of the EMF's of the cells represented by Equations 17 and 18 is equal to the EMF of the cell represented by Equation 19. In Run WCR-3-41 only the EMF between the uranium-zinc and the uranium oxycarbide electrodes was measured, the EMF between the pure uranium and uranium oxycarbide electrodes was computed by adding to this measured potential appropriate values from the cell 17. EMF values for the latter cell were taken from the curve in Figure 17.

Table 16. Electromotive force as measured on cell of type  $\text{U/LiCl-KCl-UCl}_3/\text{UZn}_{8.5}, \text{Zn}$

Cell WCR-3-30		Cell WCR-3-33		Cell WCR-3-38	
Temp °C	EMF (mv)	Temp °C	EMF (mv)	Temp °C	EMF (mv)
544	339	592	325	530	351
545	341	660	293	605	321
614	307	531	371	678	277
706	255	584	338	485	375
760	224			486	382
629	297			579	336
532	354			523	363
478	383			647	296
593	320			722	253
649	286			504	369
699	252			532	357
				598	324
				661	291
				732	250
				616	318

Table 17. Electromotive force of cells with oxycarbide,  $\text{UO}_x\text{C}_{k-x}$  electrodes

Run	Oxycar- bide sample	Nominal mole % UO	Temp °C	(17) mv	(18) mv	(19) mv	Analytical mole % UO
WCR-3-38 (22)	L-4	54	532	357	271	628	82
			598	324	317	641	
			661	291	332	643	
			732	250	412	662	
			616	318	330	648	
WCR-3-41 (23)	L-5	25	725		196	444	35
			679		144	418	
			532		73	431	
			480		21	404	
			566		87	423	
			600		94	410	
			690		177	445	
			494		47	424	
	L-6	34	531		125	481	50
			636		194	487	
			700		243	507	
			636		184	496	
			519		96	547	
	L-7	48	460		152	549	70
			576		243	586	
			520		200	562	
			706		355	616	
			577		254	574	
	L-8	68	466		247	639	100
			554		283	628	
			638		341	648	

(17) -  $\text{U}/\text{LiCl-KCl-UCl}_3/\text{UZn}_{8.5}(\text{s}), \text{Zn}(\ell)$ .

(18) -  $\text{UZn}_{8.5}(\text{s}), \text{Zn}(\ell)/\text{KCl-LiCl-UCl}_3/\text{UO}_x\text{C}_{1-x}, \text{C}$ .

(19) -  $\text{U}/\text{KCl-LiCl-UCl}_3/\text{UO}_x\text{C}_{1-x}, \text{C}$ ; for Runs WCR-3-41 and WCR-3-3 values were calculated from data on cells 18 and 19.

When the  $\text{UO}_x\text{C}_{1-x}$  sample utilized had a low composition of oxygen, samples L-1, 2, 3, 5b and 6 of Table 15, the initial EMF readings between the U- $\text{UO}_x\text{C}_{1-x},\text{C}$  electrodes were very close to zero. The readings between the  $\text{UZn}_{8.5},\text{Zn}(\ell)$ - $\text{UO}_x\text{C}_{1-x},\text{C}$  electrodes were negative, that is the  $\text{UO}_x\text{C}_{1-x},\text{C}$  electrode was the negative electrode. This indicates that free uranium metal was present in the original uranium monocarbide samples prepared by reaction of uranium hydride with propane and in the  $\text{UO}_x\text{C}_{1-x}$  samples prepared from  $\text{UO}_2$  and UC. With an increase in time, the EMF between the U- $\text{UO}_x\text{C}_{1-x},\text{C}$  electrodes increased with the  $\text{UO}_x\text{C}_{1-x},\text{C}$  being positive. The  $\text{UO}_x\text{C}_{1-x},\text{C}$  electrode became less and less negative and finally became positive with respect to the  $\text{UZn}_{8.5},\text{Zn}(\ell)$  electrode. The length of time for this to occur depended on the amount of oxygen present in the carbide, on the container material of the carbide electrode, and on previous heat treatment of the carbide samples. It took 66 hours for an electrode of the oxycarbide L-1 (Table 15) contained in graphite to become positive with respect to the  $\text{U}_2\text{Zn}_{17},\text{Zn}(\ell)$  electrode. When the same uranium oxycarbide as well as samples L-2 and L-3 were contained in copper, the resulting electrode was still negative with respect to the  $\text{U}_2\text{Zn}_{17},\text{Zn}(\ell)$  electrode and still

increasing after 175 hours. For this reason these experiments were discontinued and stable EMF readings were not observed. As indicated above the low initial negative potentials suggested that some free uranium might be present in the carbide. Therefore, samples L-5b, 6, 7 and 8 were annealed in graphite crucibles under argon at  $800^{\circ}\text{C}$  for 60 hours. Samples L-5b and L-6, which were of about the same composition as L-2 and L-3, were enclosed in graphite containers and the resulting electrodes were positive with respect to the  $\text{U}_2\text{Zn}_{17}, \text{Zn}(\ell)$  electrode and stable in 30 hours.

When a uranium oxycarbide sample of high oxygen content such as L-7, L-8 and L-4 was utilized in the  $\text{UO}_x\text{C}_{1-x}, \text{X}$  electrode, the EMF between the carbide electrode and the  $\text{U}_2\text{Zn}_{17}, \text{Zn}(\ell)$  electrode was very high initially with the  $\text{UO}_x\text{C}_{1-x}$  electrode being positive. The EMF decreased somewhat in the first four or five hours but the EMF was usually stable in 6-12 hours. It was necessary to wait about 12 hours for the EMF between the  $\text{U}-\text{UO}_x\text{C}_{1-x}, \text{C}$  or  $\text{U}_2\text{Zn}_{17}, \text{Zn}(\ell)-\text{UO}_x\text{C}_{1-x}, \text{C}$  electrodes to become stable after a temperature change of about  $50^{\circ}\text{C}$  when the carbide had a low oxygen content ( $\text{UO} < 0.50$ ) and about three hours when the carbide had a higher oxygen content. The EMF between the  $\text{U}-\text{UZn}_{8.5}, \text{Zn}(\ell)$  electrodes became stable within

ten minutes after a constant temperature was reached.

The results of measurements on cell 17 are shown graphically in Figure 17. Results for cell 19 are shown graphically in Figure 18. The potentials of Figure 18 may be employed to calculate the chemical potential of uranium in the oxycarbide phase.

It is also possible to evaluate the thermodynamic properties of oxygen-free uranium monocarbide from these data. Isotherms for 500°, 600°, 700°, and 750°C were taken on Figure 18 and the resulting potentials are plotted versus mole fraction UO in Figure 19. Extrapolation of these curves to zero mole percent UO yields the chemical potential of uranium in oxygen-free uranium monocarbide at the temperature of each isotherm. The resulting intercepts are plotted versus temperature on Figure 20. The equation of the line of Figure 20 is  $E = 0.2445 + 2.75 \times 10^{-5}T$  where  $E$  is the potential in volts and  $T$  is the temperature in °K. This equation represents the EMF observed with oxygen-free uranium monocarbide in the hypothetical cell



The extrapolation of the curves shown in Figure 19 to zero mole percent UO to obtain the free energy of formation

Figure 17. Electromotive force measurements between the U-UZn<sub>8.5</sub>Zn electrodes as represented in cell 17 (U/LiCl-KCl-UCl<sub>3</sub>/UZn<sub>8.5</sub>Zn). Data shown in Table 16

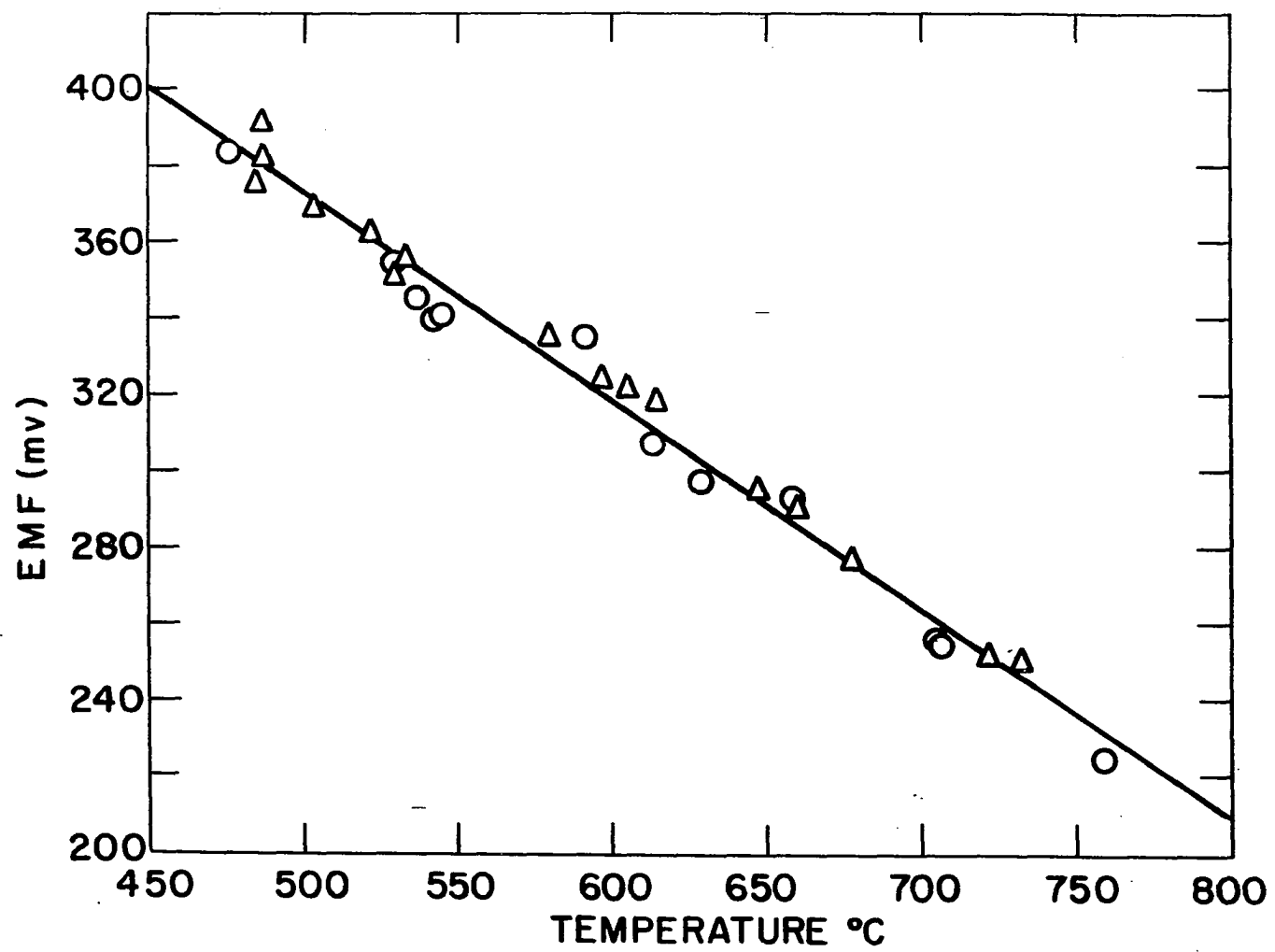




Figure 18. Electromotive force between  $\text{U-UO}_x\text{C}_{1-x}, \text{C}$  electrodes as represented in cell 19 ( $\text{U/LiCl-KCl-UCl}_3/\text{UO}_x\text{C}_{1-x}, \text{C}$ ). Data are shown in Table 17

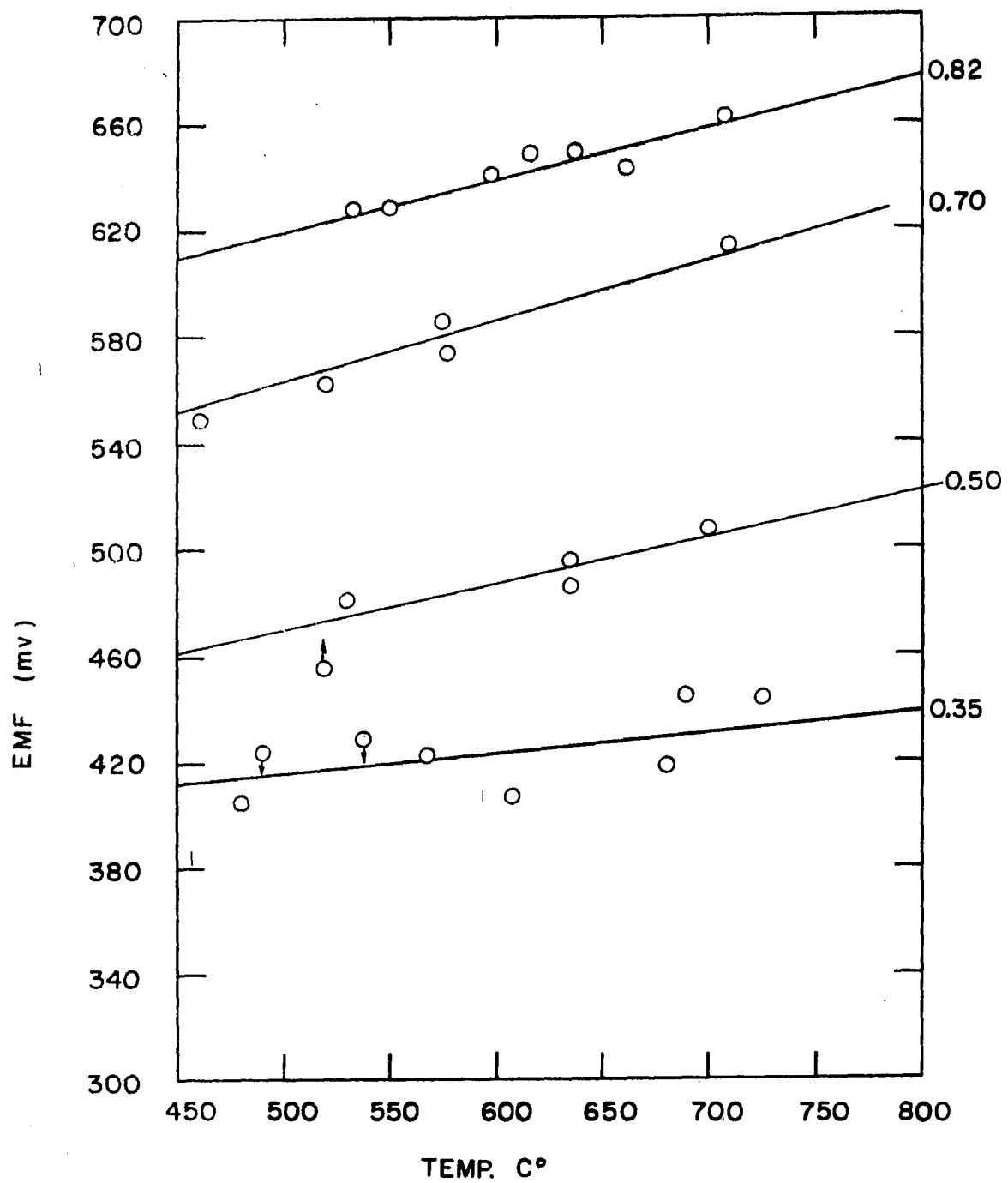


Figure 19. Electromotive force measurements between  
U- $\text{UO}_x\text{C}_{1-x}$ ,C electrodes versus mole % UO  
in  $\text{UO}_x\text{C}_{1-x}$ .

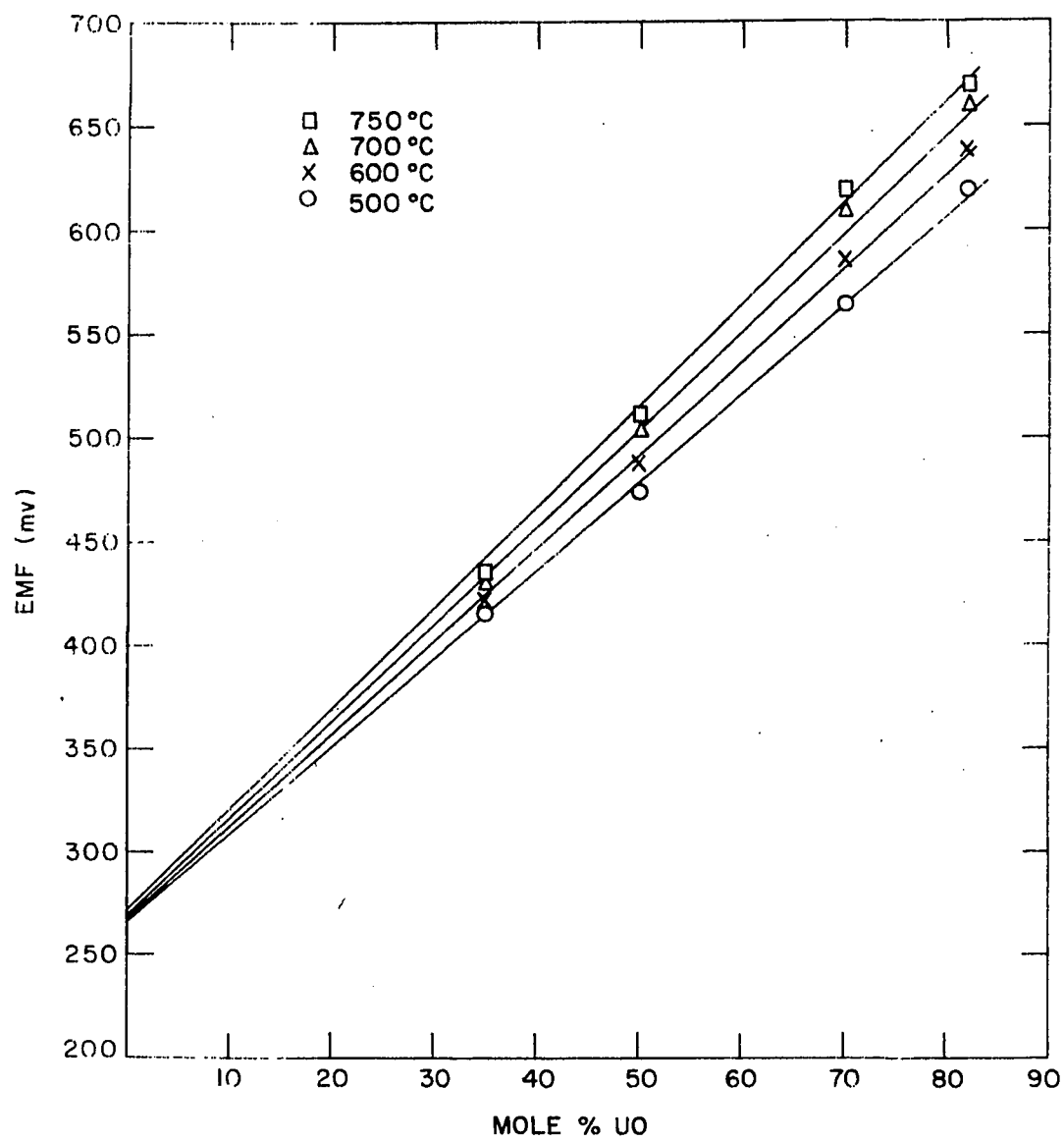
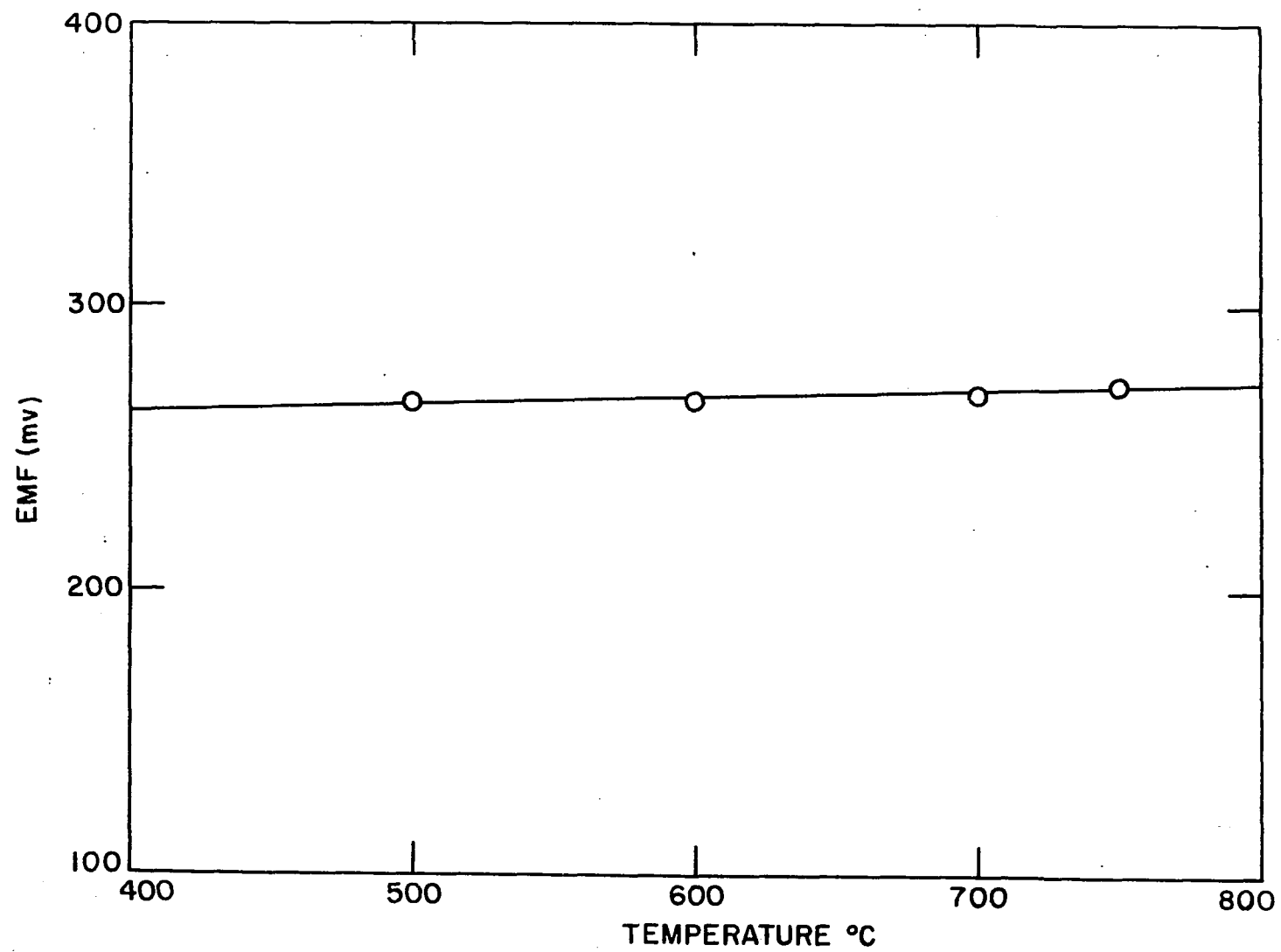
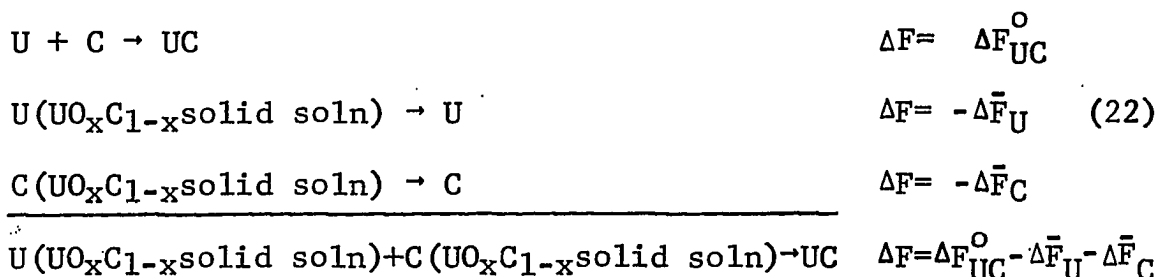


Figure 20. Electromotive force between U-UC,C electrodes versus temperature. The values are the intercepts obtained by extrapolating the isotherms to zero mole % UO in Figure 19



of uranium monocarbide is justified by considering the equations



where  $\Delta \bar{F}_{\text{U}}$  and  $\Delta \bar{F}_{\text{C}}$  represent the partial molar free energy of uranium and carbon respectively in the uranium oxycarbide phase. The oxycarbide samples were contained in graphite in all investigations except L-4. The EMF data measured between the L-4 oxycarbide electrode and the uranium zinc electrode coincided with the data obtained for the L-8 oxycarbide electrode which was contained in graphite. Therefore in all investigations the activity of carbon was equal to unity which defines  $\Delta \bar{F}_{\text{C}}(\text{UO}_x\text{C}_{1-x}) = 0$ . Furthermore as the oxygen concentration approaches zero the free energy of reaction of Equation 22 approaches zero. At zero mole fraction UO,  $\Delta \bar{F}_{\text{U}}(\text{UO}_x\text{C}_{1-x}\text{solid soln}) = \Delta F_{\text{UC}}^{\text{O}}$ . The overall electrode reaction is then shown by Equation 21.

Since  $\Delta F = -n\mathcal{F}E$  where  $n$  is the number of electrons transferred, three, and  $\mathcal{F}$  is Faraday's Constant, the free energy of formation of oxygen-free uranium monocarbide can be

calculated from the equation of the curve shown in Figure 20  
to be

$$\Delta F_{UC}^O = -16,915 - 1.90T. \quad (23)$$



## CONCLUSIONS

It is impossible to separate the effects of impurities from the measurement of properties in the uranium-carbide system. The role of oxygen and nitrogen in measurement of lattice parameter, equilibrium phases and thermodynamic properties has been the subject of considerable discussion in the recent literature (7,21,41). There has been wide variation in the reported values of these properties in the past five years. The accepted value of  $a_0$  for the monocarbide has risen from 4.952 to 4.961 (41). The reported free energy of formation of uranium dicarbide has been changed from -39 Kcal/mole U to -24 Kcal/mole U at 1750°C in five years (41). The pure uranium dicarbide is considered to be unstable below 1750°C although the tetragonal  $UO_xC_{2-x}$  phase can be stabilized at lower temperatures. In Vienna (21), a panel of experts stated that "The equilibrium diagram of the pure U-C binary system has yet to be established in detail and can only be established under conditions where oxygen and nitrogen are reduced to negligible proportions, since it is now clear that oxygen and nitrogen play a considerable part in controlling the appearance of various phases.". They add "Owing to kinetic effects, annealing times, to attain equilibrium at low

temperatures, may have to be pushed beyond the limit of normal investigation and the demand for purity may be prohibitive." This indicates that anyone dealing with carbides at low temperatures must consider his material as part of the U-C-O-N system. The fact that oxygen will cause the uranium carbide lattice to be considerably more stable is expected and was found to be the case in this investigation. The effect of nitrogen was not intentionally explored here. However, the free energy of formation of UN is reported as about -50,000 Kcal/mole U at 700°C (19) so nitrogen would influence the stability of the carbide phase. The nitrogen composition of the carbides utilized in this investigation was never as high as ten per cent of the oxygen composition so its effect was ignored.

It has been reported that the formation of  $U_2C_3$  is prohibited by impurities (35) and that it decomposes to an oxygen stabilized tetragonal " $UC_2$ " phase according to the reaction



when oxygen is present. When no oxygen or nitrogen is present and the temperature is below 1700°C, Reaction 24 proceeds to the left and uranium dicarbide decomposes to the sesquicarbide and graphite. However the uranium dicarbide phase has also

been shown to decompose at low temperatures into a face centered monocarbide phase according to the reaction



This was observed first in 1949 (28) in uranium dicarbide samples prepared by reaction of  $\text{UO}_2$  with graphite above  $2400^\circ\text{C}$  in an induction furnace. When the resulting carbides were slowly cooled, a uranium monocarbide type compound precipitated even when a large amount of excess graphite was present. This precipitation of the uranium monocarbide from the dicarbide lattice was interpreted by a panel in Vienna (21) to be due to nitrogen stabilization of the uranium monocarbide phase. However there was no nitrogen available in the system studied by Wilhelm et al. (28). Furthermore, Accary (38) noted that the uranium dicarbide phase of a uranium monocarbide-uranium dicarbide alloy disappeared when the alloy became richer in oxygen. Therefore it seems that both oxygen and nitrogen will cause the tetragonal uranium dicarbide phase to decompose to the face centered monocarbide phase. This is further substantiated by the fact that the dicarbide is not found with a high oxygen content or the phase is not formed in conditions where high contamination is probable. At Argonne (42) a uranium carbide phase has been precipitated at

800°C by the addition of excess graphite to a Zn-Mg solution containing 10 wt pct uranium. The precipitated carbide phase analyzed from 0.4 to 1.0 wt pct oxygen and was always a uranium monocarbide type phase. These experiments were exactly analogous to experiments WCR-1-109 and 91 and WCR-2-21, except that the experiments reported in this investigation involved a pure zinc solution. When methane was added to the Mg-Zn solution containing uranium, uranium sesquicarbide was precipitated. This indicates that the source of oxygen contamination was the powdered graphite. Graphite is a possible source of oxygen in all experiments in which graphite containers are used. In summary, the nature of the uranium carbide phase in equilibrium with carbon at low temperatures is determined by the oxygen and nitrogen contamination present in the carbide phase. At very low levels of contamination,  $U_2C_3$  is the stable phase; at slightly higher levels of contamination  $UC_2$ , an impurity stabilized tetragonal uranium dicarbide phase is present and at high concentration of oxygen,  $UO_xC_{1-x}$ , a face-centered uranium monocarbide type phase is the stable phase.

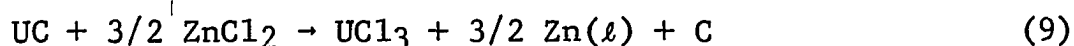
The uranium-oxygen-carbon system has been investigated by Stoops et al. (43) at 1800°C and the solubility limit of oxygen in the uranium monocarbide phase was found to be

$\text{UO}_{0.25}\text{C}_{0.75}$ . This is possible at  $1800^{\circ}\text{C}$  where the solubility limit of oxygen in any carbide phase will be lower than at lower temperatures. However there has been evidence at Ames Laboratory that a uranium oxycarbide phase of approximate composition  $\text{UO}_{0.50}\text{C}_{0.50}$  has been formed by reaction of  $\text{UO}_2$  and graphite at  $2000^{\circ}\text{C}$  (44). Also an experiment involving the equilibration of uranium and  $\text{UO}_2$  in the presence of a small amount of carbon produced a uranium oxycarbide phase of approximate composition  $\text{UO}_{0.88}\text{C}_{0.12}$  (37). Furthermore, the proposed phase diagram of Stoops et al. (43) places  $\text{UO}_2$  in equilibrium with  $\text{UC}_2$  and carbon at  $1800^{\circ}\text{C}$ . It is very unlikely that  $\text{UO}_2$  and carbon are in equilibrium at  $1800^{\circ}\text{C}$ . In fact it is doubtful that  $\text{UO}_2$  and  $\text{UC}_2$  can exist in equilibrium at  $1800^{\circ}\text{C}$ .

Namba et al. (36) showed that the substitution of oxygen for carbon in uranium monocarbide would proceed to a composition of  $\text{UO}_{0.80}\text{C}_{0.20}$  at  $1600^{\circ}\text{C}$ . He was able to attain a composition of  $\text{UO}_{0.67}\text{C}_{0.33}$  at  $1750^{\circ}\text{C}$ . The compacts prepared in this report indicate that the solubility limit of oxygen in the monocarbide at  $1575^{\circ}\text{C}$  is between 0.70 and 0.82 mole fraction  $\text{UO}$ .

The stabilization of the uranium carbide lattice by this

oxygen solubility is apparent in the results obtained in the equilibration of the monocarbide with zinc and with a KCl-LiCl-ZnCl<sub>2</sub>/zinc system. In the equilibrations of monocarbide with zinc, the absence of UC<sub>2</sub> or U<sub>2</sub>C<sub>3</sub> was noted and although reversal of the reaction appeared to occur at some temperature between 725 and 800°C, with only carbide phase above 725°C and predominantly U<sub>2</sub>Zn<sub>17</sub> below 725°C, there was a significant amount of carbide phase remaining at all temperatures in the 540-725°C range. In the latter equilibrations with the KCl-LiCl eutectic salt present, the addition of ZnCl<sub>2</sub> was expected to lead to complete oxidation of the carbide at relatively low levels of ZnCl<sub>2</sub> in the salt. Considering the reaction to be



and with the carbide and zinc both present in nearly pure form or unit activity at equilibrium, the ratio

$$K_N = \frac{N_{\text{UCl}_3}}{(N_{\text{ZnCl}_2})^{3/2}}$$

should be a constant in dilute salt solutions where Henry's Law is valid. It should be noted that the same ratio applies if the carbide reacting with the zinc is UC<sub>2</sub> or UC<sub>1.5</sub>. A constant value for this  $K_N$  was not observed. This observation implied that the activity of uranium in the carbide phase was variable and not a constant as had been initially supposed.

The  $K_N$  should also be very temperature dependent due to differences in the free energy of formation of  $UCl_3$ ,  $ZnCl_2$  and the uranium carbide at different temperatures. However, the oxygen composition of the carbide phase changes so rapidly during the latter portion of the oxidation that this temperature dependence can not be detected. For instance if the oxygen solubility of the oxycarbide lattice was 0.50 at saturation instead of 0.75 as predicted, the calculated behavior of  $K_N$  with moles  $ZnCl_2$ /mole UC as shown in Figure 16 would not be discernibly modified. The constant  $K_N$  portion of the curve would start at a moles  $ZnCl_2$ /mole UC ratio of 1.55 instead of 1.64. The rest of the curve would be identical. Therefore, the  $K_N$  did not appear to be temperature dependent in these equilibrations.

None of the foregoing discussion was concerned with the effect of nitrogen on the uranium carbide lattice. The uranium monocarbide and mononitride are completely soluble (45). Stoops (43) reports that the oxycarbide is also completely soluble with uranium mononitride. Therefore nitrogen contamination would almost certainly have affected the equilibria investigated. However, as mentioned previously, the nitrogen composition was never more than 10% and usually less than 5%

of the oxygen composition. Consideration of the relative free energies of formation of the uranium oxides and nitrides indicates that the oxygen should have a larger stabilizing effect on the uranium monocarbide lattice than the nitrogen. Nevertheless, a comprehensive study of the U-O-C-N system as a function of temperature and pressure is needed before accurate predictions and calculations on the uranium carbides can be made. It is also possible that the thorium carbides are similarly affected. An investigation of these systems will require an extensive project and a maximum of cooperation and sharing of knowledge between researchers.



## SUMMARY

A liquid zinc phase was equilibrated with uranium monocarbide at temperatures ranging from 540 to 800°C. The uranium monocarbide reacted with the liquid zinc at temperatures below 725°C to form a uranium-zinc compound and an oxygen enriched uranium monocarbide phase. There was no reaction between the carbide and zinc phase at 800°C. This indicates that the standard free energy of formation of uranium monocarbide is equal to the free energy of formation of  $\text{UZn}_{0.5}$  at about 725°C or approximately -18,500 Cal/mole U. Neither  $\text{UC}_2$  nor  $\text{U}_2\text{C}_3$  was ever observed as a product of the uranium monocarbide-zinc reaction.

The uranium monocarbide phase was also equilibrated in a  $\text{LiCl-KCl-ZnCl}_2$ /zinc system between 580 and 802°C. The resulting salt phase was analyzed for uranium and zinc and the mole fraction ratio  $K_N = N_{\text{UCl}_3} / (N_{\text{ZnCl}_2})^{3/2}$  was determined. This ratio, which should be constant at a constant temperature, was found to be a function of the moles  $\text{ZnCl}_2$ /moles UC charged. When  $K_N$  was greater than 20, the uranium in the zinc phase was present as an oxygen-rich uranium monocarbide; when the  $K_N$  was less than 15 the uranium was present as  $\text{UO}_2$ . This  $K_N$  range usually occurred at about three wt pct  $\text{ZnCl}_2$  in the salt.

The uranium in the uranium carbide charged was never completely oxidized although  $\text{ZnCl}_2$  concentrations in the salt as high as 28 wt pct and  $K_N$ 's as low as 0.21 were reached.

These results indicated that the uranium monocarbide lattice was being stabilized by oxygen.

An EMF cell of the type  $\text{U/LiCl-KCl-UCl}_3/\text{UO}_x\text{Cl}_{1-x}, \text{C}$  was utilized to investigate the increase in chemical potential of uranium in the uranium oxycarbide phase as a function of oxygen composition from 0.35 to 0.82 mole fraction  $\text{UO}$  and temperature from 460 to 760°C. Extrapolation of the data obtained to zero oxygen concentration was shown to yield the free energy of formation of  $\text{UC}$  as a function of temperature. The equation obtained is  $\Delta F_{\text{UC}}^{\text{O}} = -16,915 - 1.90T$ .

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## APPENDIX

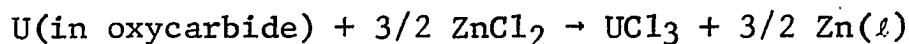
Calculations of the equilibrium ratios  $N_{\text{UCl}_3}/(N_{\text{ZnCl}_2})^{3/2}$  as a function of  $\text{ZnCl}_2$  added to a  $\text{KCl-LiCl}$ /zinc system containing oxygen contaminated uranium monocarbide.

The calculations outlined below are based on the following observations and conditions.

(a) The initial uranium monocarbide has the stoichiometry  $\text{UO}_{0.08}\text{C}_{0.92}$ .

(b) The equilibrium carbide phase in liquid zinc at  $700^\circ\text{C}$  is  $\text{UO}_{0.2}\text{C}_{0.8}$ .

(c) Oxidation of the carbide with  $\text{ZnCl}_2$  proceeds according to the reaction



and leads to a still higher oxygen content in the oxycarbide. At the composition  $\text{UO}_{0.75}\text{C}_{0.25}$  the dioxide  $\text{UO}_2$  is one of the reaction products.

(d) It is assumed that the initial charge consists of 12.2 moles of  $\text{LiCl-KCl}$  eutectic salt, one mole of  $\text{UO}_{0.08}\text{C}_{0.92}$ , and zinc in excess of the amount required to form the compound  $\text{UZn}_{8.5}$ . The total amount of salt affects the equilibrium ratio of  $\text{UCl}_3$  to  $\text{ZnCl}_2$  in the salt as may be seen from consideration of the above reaction and the ratio

$$K_N = \frac{N_{UCl_3}}{(N_{ZnCl_2})^{3/2}} = \frac{n_{UCl_3} n_t^{1/2}}{(n_{ZnCl_2})^{3/2}}$$

where  $N$  represents mole fraction,  $n$  represents actual number of moles and  $n_t$  represents the total moles of salt.

The above ratio of salt to uranium is roughly the ratio used in the batch equilibrations carried out in sealed tantalum and graphite containers, the data of which are shown in Figure 14.

In order to increase the oxygen content of the oxycarbide phase from  $UO_{0.08}C_{0.92}$  to  $UO_{0.20}C_{0.80}$ , which is the oxycarbide phase in equilibrium with liquid zinc, it is necessary to remove 60 per cent of the uranium in the  $UO_{0.08}C_{0.92}$  phase. Assuming that all of the oxygen in the initial uranium oxycarbide remains in the oxycarbide phase, the oxycarbide in equilibrium with zinc will be  $U_{0.40}O_{0.08}C_{0.32}$  which corresponds to a composition of  $UO_{0.20}C_{0.80}$ . Since 1.5 moles of  $ZnCl_2$  are required to oxidize one mole of uranium, 0.90 moles of  $ZnCl_2$  will be necessary to oxidize all of the uranium in the uranium-zinc phase. With  $UZn_{8.5}$  and carbide in the zinc phase there will be zero degrees of freedom at constant temperature and pressure. Consequently the composition of the zinc liquid, the zinc compound, the carbide, and the value of  $K_N$  will not

change on the addition of  $\text{ZnCl}_2$  until one of the phases (in this case  $\text{UZn}_{8.5}$ ) disappears. The  $K_N$  can be calculated from thermodynamic data to be approximately  $10^5$  at  $700^\circ\text{C}$ . Therefore, the concentration level of  $\text{ZnCl}_2$  in the salt phase during this step of the oxidation will be very low.

When the uranium-zinc compound phase is exhausted, the  $\text{ZnCl}_2$  will further react with the uranium oxycarbide phase. This reaction proceeds until a composition  $\text{UO}_{0.75}\text{C}_{0.25}$  is attained. In order to increase the oxygen content of the oxycarbide phase from  $\text{UO}_{0.20}\text{C}_{0.80}$  to  $\text{UO}_{0.75}\text{C}_{0.25}$ , 73.33 per cent of the uranium must be removed from the  $\text{UO}_{0.20}\text{C}_{0.80}$  phase, or an additional 0.2933 moles of uranium must be oxidized. This step in the oxidation requires 0.440 moles of  $\text{ZnCl}_2$ . The total remaining oxycarbide phase is  $\text{U}_{0.1066}\text{O}_{0.08}\text{C}_{0.0266}$  which corresponds to a stoichiometry  $\text{UO}_{0.75}\text{C}_{0.25}$ . When this oxycarbide composition is attained,  $\text{UO}_2$  is produced on further reaction and  $K_N$  attains a constant value of approximately 20. The total moles of  $\text{ZnCl}_2$  remaining in the salt phase may be calculated from the reaction

$$K_N = \frac{n_{\text{UCl}_3} n_t^{\frac{1}{2}}}{(n_{\text{ZnCl}_2})^{3/2}} = 20$$

or

$$20 = \frac{(0.8933)(12.2 + 0.8933 + n_{\text{ZnCl}_2})^{\frac{1}{2}}}{(n_{\text{ZnCl}_2})^{3/2}},$$

which yields  $n_{\text{ZnCl}_2} = 0.298$ . Therefore the total number of moles of  $\text{ZnCl}_2$  added in order to obtain the oxygen saturated oxycarbide phase is  $0.90 + 0.33 + 0.298 = 1.638$  moles.

The  $K_N$  will again remain constant until one of the phases disappears, in this case the 0.1066 moles of oxygen saturated oxycarbide which is oxidized to give 0.0666 moles of  $\text{UCl}_3$  and  $\text{UO}_2$ . This will require 0.10 moles  $\text{ZnCl}_2$ . In order to keep the  $K_N$  constant during this step in the oxidation additional  $\text{ZnCl}_2$  must accumulate in the salt. The total number of moles of uranium in the salt  $\text{N}_{\text{UCl}_3}$  is now  $0.8933 + 0.0666 = 0.96$ . Since  $K_N$  is still 20, the total moles of  $\text{ZnCl}_2$  in the salt may be calculated from the relation

$$20 = \frac{(0.96)(12.2 + 0.96 + n_{\text{ZnCl}_2})^{\frac{1}{2}}}{(\text{N}_{\text{ZnCl}_2})^{3/2}}.$$

Solution of this equation yields  $n_{\text{ZnCl}_2} = 0.314$ . Therefore, the total number of moles of  $\text{ZnCl}_2$  necessary to convert one mole of  $\text{UO}_{0.08}\text{C}_{0.92}$  to  $\text{UO}_2$  in this system is  $0.90 + 0.44 + 0.10 + 0.314 = 1.754$  moles.

The oxide  $\text{UO}_2$  is very stable and is not oxidized by  $\text{ZnCl}_2$  so that any further  $\text{ZnCl}_2$  added will simply accumulate in the salt. This means that the  $K_N$  will decrease according to the relation

$$K_N = \frac{(0.96)(12.2 + 0.96 + n_{\text{ZnCl}_2})^{\frac{1}{2}}}{(n_{\text{ZnCl}_2})^{3/2}} .$$

The effect of the additional  $\text{ZnCl}_2$  on the total number of moles is small so  $K_N$  actually decreases as  $(n_{\text{ZnCl}_2})^{3/2}$ .