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OPERATED BY UNION CARBIDE CORPORATION • FOR THE U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The equilibrium of dilute UF_3-UF_4 molten fluoride solutions in contact with graphite and UC_2:

$$3UF_4 + UC_2 \rightleftarrows 4UF_3 + 2C$$

has been studied as a function of temperature (370-700°C), melt composition and atmospheric contamination. Equilibrium quotients, $Q = (UF_3)^4/(UF_4)^3$ for the reaction were determined by measuring the UF_3 and UF_4 concentrations spectrophotometrically. The solvents used were primarily LiF-BeF_2 mixtures. Results from this solvent system were related to the reactor solvents LiF-BeF_2-ZrF_4(65.6-29.4-5 mole %) and LiF-BeF_2-ThF_4(72-16-12 mole %). It has been found that the equilibrium quotient is very sensitive to both temperature and solvent changes increasing as either the temperature increases or the alkali-metal fluoride content of the solvent decreases.

INTRODUCTION

The relative stability of dilute UF_3-UF_4 molten fluoride solutions contained in graphite is of practical importance to Molten Salt Breeder Reactors, MSBR, in which these solutions are used as nuclear fuels. Because the reactors contain a large amount of graphite in the core serving as a neutron moderator, reaction of UF_3 with graphite:

$$4UF_{3(d)} + 2C \rightleftarrows 3UF_{4(d)} + UC_2{}^{*} \qquad (1\text{-}1)$$

to form UF_4 and uranium dicarbide has long been recognized[1] as a major factor limiting the amount of UF_3 which can be maintained in solution.

Although typical fuel mixtures consist essentially of 1 mole % $U^{235}F_4$ or less in a solution of LiF and BeF_2, the ease of UF_4 reduction to UF_3 by the chromium in the metal containment vessel**

$$2UF_{4(d)} + Cr^{o} \rightleftarrows 2UF_{3(d)} + CrF_{2(d)} \qquad (1\text{-}2)$$

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* The subscript "d" indicates that the component is in solution.

**Hastelloy N, a nickel-based alloy containing Cr, Fe and Mo has been used[2] to fabricate the metal containment vessel for the Molten Salt Reactor Experiment, MSRE.

necessitates the consideration of UF_3 chemistry as well. The effect of the corrosion reaction of Eq. 1-2 is to leach chromium from the structural metal and cause it to appear in solution as CrF_2.

In order to minimize the corrosion, the equilibrium of Eq. 1-2 is shifted to the left by reducing a small percentage (approximately 1%) of the UF_4 to UF_3 through the addition of beryllium metal:[3]

$$2UF_{4(d)} + Be^{o} \rightleftarrows 2UF_{3(d)} + BeF_2 \tag{1-3}$$

Although a small amount of UF_3 is beneficial in reversing the corrosion mechanism, it produces complications due to possible reaction via Eq. 1-1 and the resulting undesirable formation of an insoluble uranium carbide. Reference to "UF_3 stability" in this paper will therefore mean specifically the equilibrium concentration of UF_3 relative to UF_4 as determined by Eq. 1-1.

This equilibrium has never been experimentally measured despite the fact that it is the major factor in determining UF_3 stability for molten salt reactor systems. Although they used indirect means, Long and Blankenship[4] are the only investigators who have attempted to measure the equilibrium. Since their work is the basis on which all previous estimates of UF_3 stability have been made, it will be reviewed in detail, with the equilibrium expressions in fractional coefficients as used by the authors. They studied the reduction of UF_4 (both pure solid phase UF_4 and in molten fluoride solution) with hydrogen:

$$\frac{1}{2}H_2 + UF_4 \rightleftarrows UF_3 + HF \tag{1-4}$$

and determined the equilibrium quotients for the above reduction:

$$Q^R = \frac{X_{UF_3}}{X_{UF_4}} \frac{P_{HF}}{P_{H_2}^{1/2}} = K^R \frac{\gamma_{UF_4}}{\gamma_{UF_3}} \tag{1-5}$$

by measuring HF and H_2 ratios evolved from a reaction vessel containing UF_4 and UF_3. From the solid-phase UF_4 reduction they obtained equilibrium constants, K^R, for the reduction. These, combined with the equilibrium quotient, Q^R, for the dilute solutions and the activity coefficient for UF_3, γ_{UF_3}, obtained from solubility data, enabled them to calculate the activity coefficient for UF_4, γ_{UF_4}, in the molten fluoride solution. By combining the free energy expression for Eq. 1-4 with one for the decomposition of UF_3 into UF_4 and U^o:

$$UF_{3(d)} \rightleftarrows \frac{3}{4}UF_{4(d)} + \frac{1}{4}U^o \qquad (1\text{-}6)$$

they obtained an expression for the equilibrium quotient, Q^D, of Eq. 1-6, in terms of the equilibrium quotient for Eq. 1-4, Q^R, and the activity coefficients of UF_4 and HF. (c.f. p 18, Ref. 4, part II). Using free energies of formation for UC_2 and UC from Rand and Kubachewski,[5] which were acceptable at the time, they estimated uranium activities in the carbides and concluded that solutions in which up to 60% of the initial 1 mole % of UF_4 is converted to UF_3 are expected to be stable in the presence of graphite. In addition they concluded that temperature and solvent changes should have little effect on the equilibrium mechanism of Eq. 1-1 since they found no significant effect from them on the H_2 reduction mechanism of Eq. 1-4.

In view of the significance of Eq. 1-1 to Molten Salt Reactor Technology, a closer examination of it is clearly warranted. The development of spectrophotometric techniques for the study of molten fluorides and the realization of solvent effects on molten fluoride chemistry, have given impetus to the study. We have already identified[6] UC_2, as the stable uranium carbide phase in equilibrium with UF_3-UF_4 solutions in graphite. The object of this report is to describe the effects of temperature, solvent, and atmospheric contamination on the equilibrium. Both the forward and the back reaction of Eq. 1-1 in the reference solvent system LiF-BeF_2 have been followed. The data in the reference solvent system have been related to practical reactor solvents such as the Molten Salt Reactor Experiment, MSRE, solvent, LiF-BeF_2-ZrF_4 (65.6-29.4-5 mole %) and the proposed Molten Salt Breeder Reactor, MSBR, solvent, LiF-BeF_2-ThF_4 (72-16-12 mole %). Our findings are compared with earlier observations which have not been reviewed before.

EXPERIMENTAL

Equilibrium quotients for the back-reaction* (Eq. 3-2) were determined by measuring UF_3 and UF_4 concentrations spectrophotometrically with a Cary Model 14-H recording spectrometer. The sample system consisted of a controlled temperature, inert atmosphere furnace shown in Fig. 2-1 which held a diamond-windowed graphite spectrophotometric cell.[7] Molten fluoride salt solutions and reagent uranium carbides were contained in this cell. Absorption spectra of the molten salt solution were measured against an air reference. Net spectra due to UF_3 and UF_4 were determined by subtracting independently determined solvent blank spectra using standard digital computer techniques. Spectra were measured in the near infra-red and visible regions from 4000 to 33000 cm^{-1}. The absorption spectra of UF_3 and UF_4 served as the primary means of monitoring these components in solution as a function of temperature, time, and solvent composition.

Materials - Molten salt solvent compositions were prepared by mixing calculated amounts of the pure component fluoride salts. Optical quality crystal fragments from the Harshaw Chemical Co. was the source of LiF. Beryllium fluoride was prepared by vacuum distillation[8] from a large special purchase supplied by the Brush Beryllium Co. The water-clear, glass-like product contained no spectrographically detectable cation impurities, but was exceedingly hydroscopic and had to be stored under very anhydrous conditions. Uranium tetrafluoride was taken from a laboratory purified spectroscopic standard which contained less than 10 ppm of total cation impurities. Thorium tetrafluoride was part of a special purchase from the National Lead Co. which contained no greater than 100 ppm in any cation impurities.

Storms and coworkers of the Las Alamos Scientific Laboratory supplied each of the uranium carbides used in this study and supplied the following analysis:

Uranium dicarbide - UC_2** wt % C = 8.83 or 75.74 mole % C
O_2 = 200 ppm

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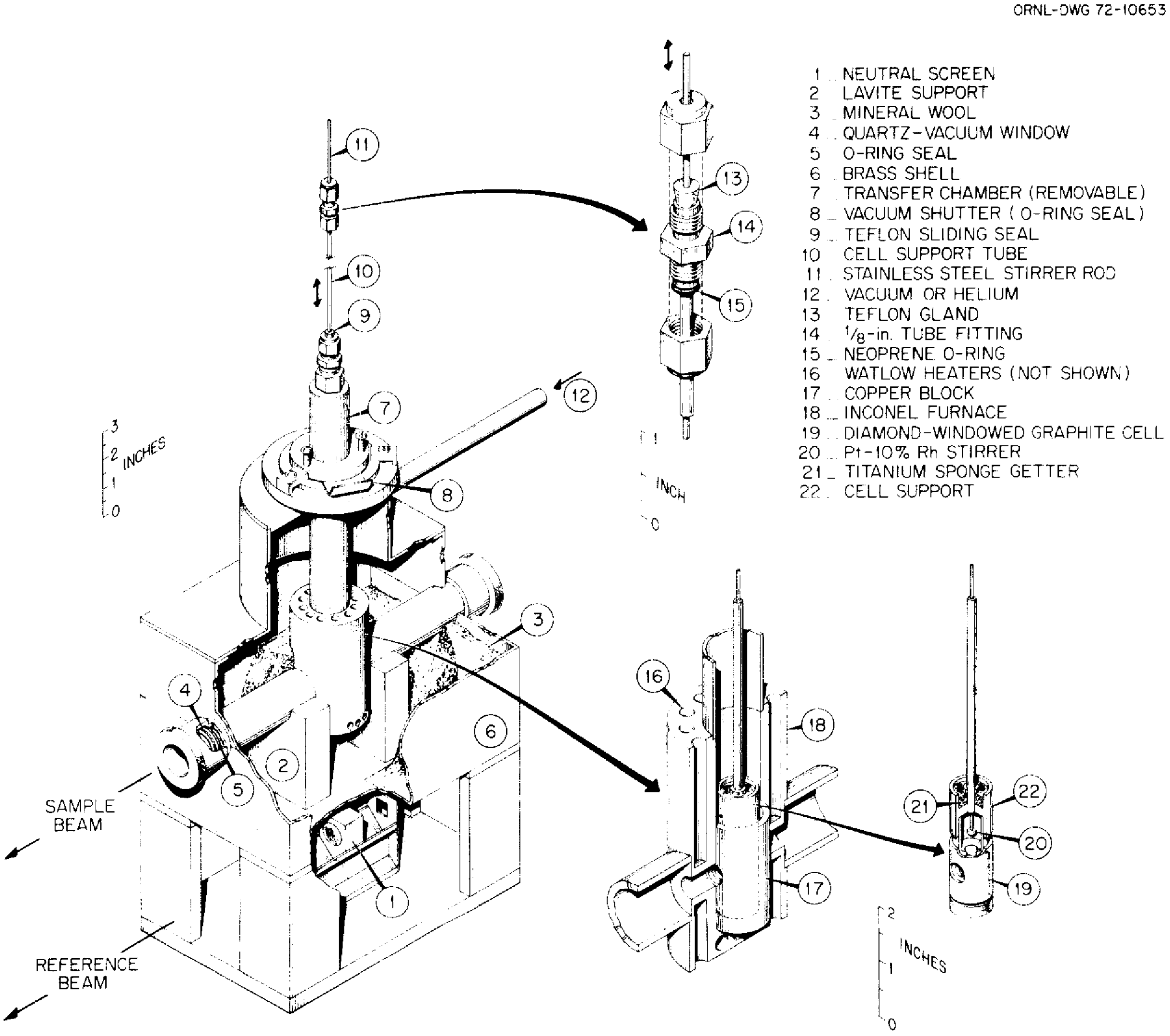
*See Results and Discussion Section for an explanation of why the back-reaction was measured.

**Although uranium dicarbide is a substoichiometric compound,[13] it will be identified as UC_2 in this paper.



2-1 High Temperature Furnace System for Absorption Spectra of Molten Fluorides.

crystal lattice by X-ray $a = 3.5251 \pm 0.0005Å$
$c = 5.9962 \pm 0.0008Å$

Uranium sesquicarbide - U_2C_3 wt % C = 6.99 or 59.83 mole % C
$O_2 = 50$ ppm

crystal lattice by X-ray $a = 8.0889 \pm 0.0009Å$

These high purity carbides were received as lusterous gray-black granules which ranged in size from 1/2 to 1 mm^3. They were shipped sealed in glass ampules and stored in a helium filled dry box. Exposure to even the dry box conditions was kept to the absolute minimum needed for weighings and cell loadings.

Procedure - Even though the reagent salts were quite free of cation impurities, they were not free of oxides and H_2O to the degree needed. All compositions were therefore treated while molten at 600°C for oxide removal by sparging for several hours with reagent HF gas or HF-H_2 gas mixtures.[9] Residual HF was then stripped from the melt with He prior to cooling. Clean portions of the recovered salt "button" were then crushed and used to charge the spectrophotometer cell, by weighing out the fluorides in a helium drybox which was maintained at a water vapor content < 0.1 ppm and at an O_2 content < 2 ppm. Between 0.5 and 0.6 gm of salt solvent made a convenient cell loading to which was added from 5 to as much as 100 mg of the uranium carbide under study. Poco AXF-5Q1 grade graphite[10] spectrophotometric cells were used which were purified after fabrication by heating in an H_2 gas stream to 1000°C and then flushed free of H_2 with He. Subsequent dry box handling and loading techniques have been discussed earlier.[11] A "dash pot" stirrer made from platinum-10% rhodium (see Fig. 2-1) was used to hasten the attainment of equilibrium which is otherwise dependent largely on diffusion. It proved to be a great aid in shortening the time needed to reach equilibrium. We observed a small but temporary loss of transmission directly after stirring in some cases which was equal to 0.15 absorbance units at 4000 cm^{-1}. We have assumed this recoverable loss to be caused by the temporary suspension of fine particles which later settle. Whole grains of the carbide were used after early attempts to increase the surface area by crushing caused the carbide to collect at the window and interfere with the optical transparency of the cell. A large excess of the solid carbide phase was always maintained in the cell. On some occasions, the experimental sequence was interrupted and additional uranium carbide was added to demonstrate that an excess was indeed present. No change was observed in the concentrations of UF_3 or UF_4 in the homogeneous solutions as a result of these additions.

Spectral Measurements - Molar concentrations of dissolved UF_3 and UF_4 were determined simultaneously in solution at a series of temperatures above the melting point by measuring optical densities at 9174 and 11360 cm^{-1}. These wave numbers represent the maximum absorbance values for dissolved UF_4 and UF_3 respectively in the near infra-red region as shown in Figs. 2-2 and 2-3. The strong UF_3 absorption in the visible region from 16000 to 33000 cm^{-1} was in general too intense to be useful since the solutions studied had initial UF_4 molarities in the range of 0.04 to 0.10. Figures 2-2 and 2-3 show that for spectra of pure UF_4 and UF_3 there is a contribution from each at the most sensitive absorbance region of the other member. Stated differently, the absorbance at 9174 cm^{-1} in a mixed solution is primarily due to UF_4, but not entirely so. This condition is solved uniquely for the contriburion from each species by the solution of a set of simultaneous linear equations equal to number to the number of components in the system which contribute to the net spectra, in our case 2.

Using Beer's law

$$-\log I/I_o = A_\nu = (\varepsilon_\nu)_T (M)_T \ell \qquad (2\text{-}1)$$

where

I = measured optical intensity of the sample

I_o = measured optical intensity of the reference solvent

A = total absorbance at a given frequency, ν.

$(\varepsilon_\nu)_T$ = molar absorption coefficient at ν and temperature T

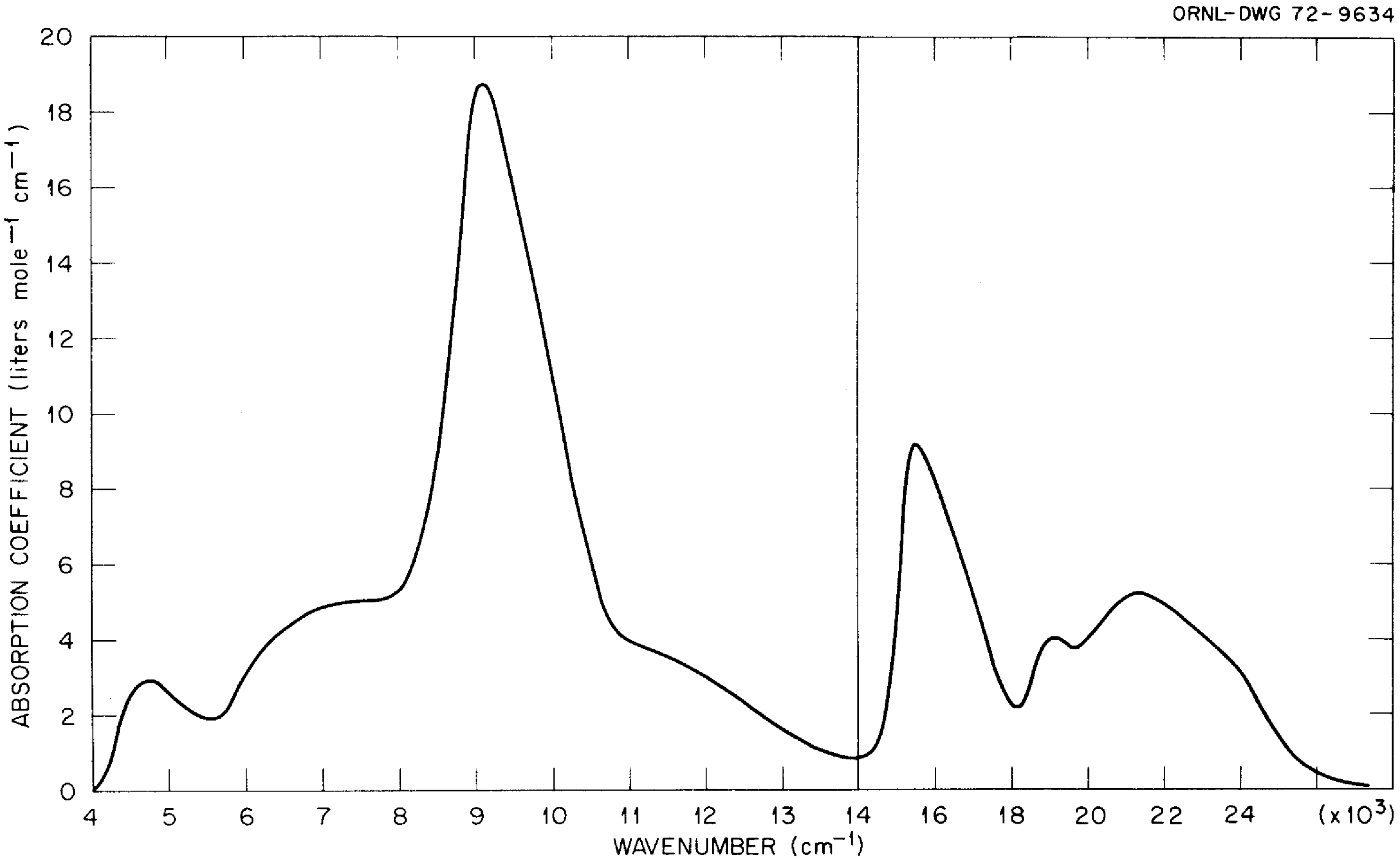
$(M)_T$ = molarity of component in solution

ℓ = cell path length = 0.635 cm

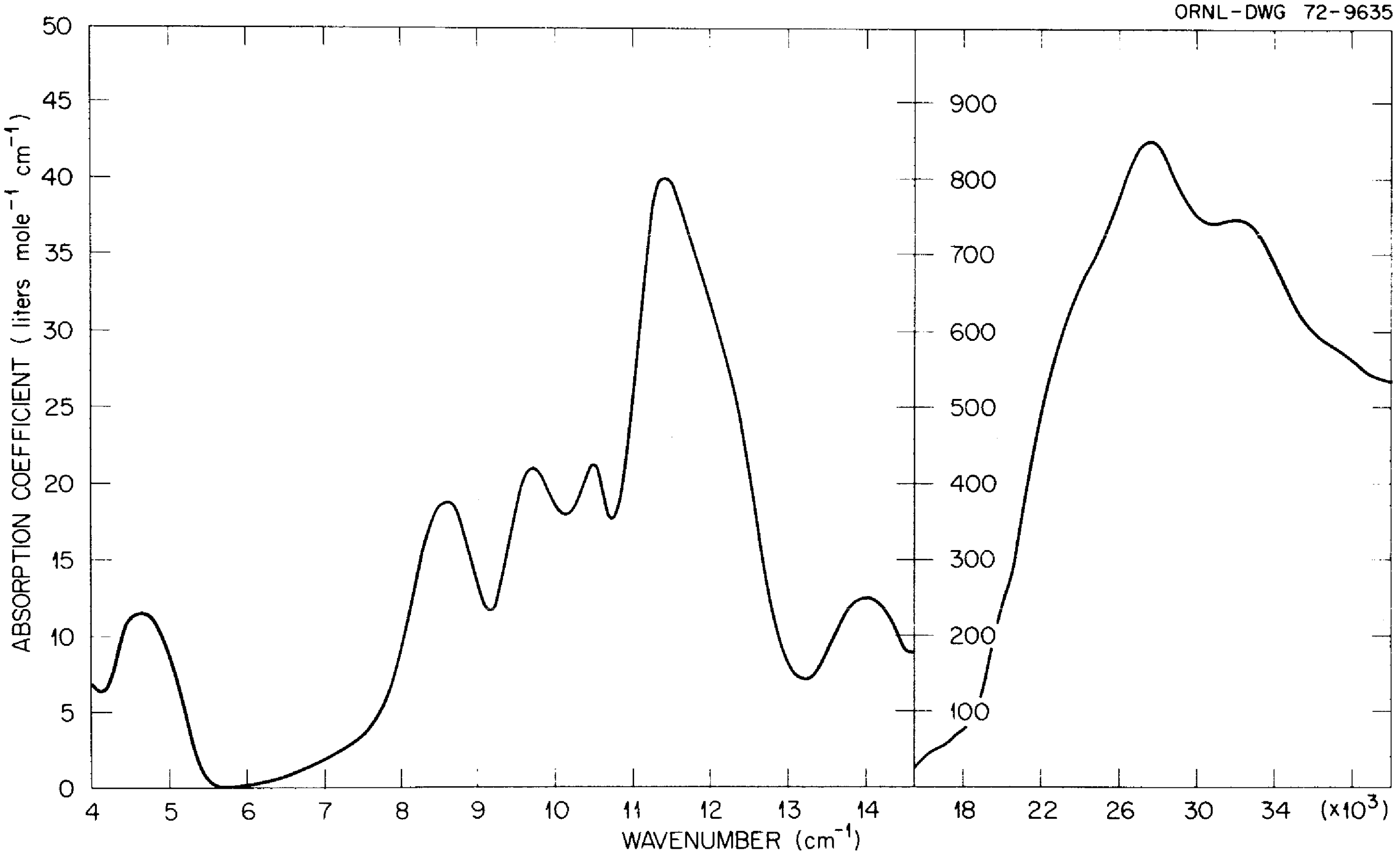
The following set of equations are sufficient to determine the separate molar concentrations in a mixed solution at a particular temperature.

$$A_{\nu 1} = A^3_{\nu 1} + A^4_{\nu 1} = \varepsilon^4_{\nu 1}(M_4)_T\ell + \varepsilon^3_{\nu 1}(M_3)_T\ell \qquad (2\text{-}2)$$

$$A_{\nu 2} = A^3_{\nu 2} + A^4_{\nu 2} = \varepsilon^4_{\nu 2}(M_4)_T\ell + \varepsilon^3_{\nu 2}(M_3)_T\ell \qquad (2\text{-}3)$$



2-2 UF_4 Spectrum (approximately 1 mole %) in $LiF\text{-}BeF_2\text{-}ThF_4$ (72-16-16 mole %) at 575°C.



2-3 UF_3 Spectrum (approximately 0.3 mole %) in LiF-BeF_2 (66-34 mole %) at 600°C.

where:

$1 = 9174\ \mathrm{cm}^{-1}$
$2 = 11360\ \mathrm{cm}^{-1}$
$3 = \mathrm{UF_3}$ component
$4 = \mathrm{UF_4}$ component

Solving Eqs. (2-2) and (2-3) simultaneously for $(M_4)_T$ and $(M_3)_T$ gives the desired molarities since $A_{\nu 1}$ and $A_{\nu 2}$ are measured and the ε values are known from previous calibrations.

$$(M_4)_T = \frac{(\varepsilon^4_{\nu 2}\ A_{\nu 1} - \varepsilon^3_{\nu 1}\ A_{\nu 2})}{\ell(\varepsilon^3_{\nu 2}\varepsilon^4_{\nu 1} - \varepsilon^3_{\nu 1}\varepsilon^4_{\nu 2})} \qquad (2\text{-}4)$$

$$(M_3)_T = \frac{(\varepsilon^4_{\nu 1}\ A_{\nu 2} - \varepsilon^4_{\nu 1}\ A_{\nu 1})}{(\varepsilon^3_{\nu 2}\varepsilon^4_{\nu 1} - \varepsilon^3_{\nu 1}\varepsilon^4_{\nu 2})} \qquad (2\text{-}5)$$

Because spectra were recorded versus a neutral screen in the reference beam (see Fig. 2-1) it was always necessary to subtract a solvent spectrum, or blank, which was independently determined for each experimental spectrum, to get the net absorbance due to species in solution.

Analyzing composite spectra required making calibrations for ε with solvent melts containing a known concentration of pure $\mathrm{UF_4}$ and $\mathrm{UF_3}$. Values of ε are reduced with increasing temperature because of two effects: the change of molarity caused by thermal expansion and temperature effects on the absorption spectra themselves.

Changes in molarity due to temperature changes were adjusted by using S. Cantor's data[12] for the molal volume of various fused fluoride salts and assuming that the molal volumes are additive to within ± 3% according to the following general relations:

$$N_T[x_1(\nu_1)_T + x_2(\nu_2)_T \text{------}] = 1000\ \mathrm{ml} \qquad (2\text{-}6)$$

$$(M_1)_T = N_T\ x_1 \qquad (2\text{-}7)$$

where

N_T = moles per liter of solution at temperature T
x_1 = mol fraction of component #1
$(\nu_1)_T$ = molar vol of 1 at temperature T in cc/mole
$(M_1)_T$ = molarity of 1 in moles/l at temperature T

Molar absorptions were first measured for pure UF_4 solutions at various temperatures using a known concentration and at molarities adjusted for expansion. Measured values of $(\varepsilon^4_{\nu 1})_T$ and $(\varepsilon^4_{\nu 2})_T$ are recorded in Table 2-1.

A corresponding calibration was performed for pure UF_3 under identical conditions. This was most easily achieved by adding an excess of a reducing agent. Both zirconium and uranium metal were used for this purpose, they react as shown in Eqs. (2-8) and (2-9).

$$Zr + 4UF_4 \rightleftarrows 4UF_3 + ZrF_4 \tag{2-8}$$

$$U + 3UF_4 \rightleftarrows 4UF_3 \tag{2-9}$$

The effect on the properties of the solutions caused by the production of ZrF_4 in Eq. 2-8 was very small and hence neglected for these dilute solutions. When uranium was used concentrations had to be increased by 1/3 over those calculated for UF_4 in the initial solutions as shown in Eq.(2-9). Pure UF_3 solutions in contact with graphite result in the loss of uranium from solution by the formation of UC_2 as shown in Eq. (1-1). Fortunately this reaction is rather slow under the conditions that we have studied, and it was possible to correct for this loss by measuring absorbances as a function of time to determine the rate of loss (dA_ν/dT), and correcting for the loss by extrapolating back to zero time. Reducing UF_4 with uranium does not result in a loss of UF_3 from solution. The addition of Eq. (1-1) and (2-9) results in the cyclic conversion of U and C to UC_2 with no net change of UF_3 concentration in solution as shown in Eq. (2-10).

$$4UF_3 + 2C \rightarrow 3UF_4 + UC_2 \tag{1-1}$$

$$\underline{3UF_4 + U \rightarrow 4UF_3} \tag{2-9}$$

$$U + 2C \rightarrow UC_2 \tag{2-10}$$

An alternate approach to determining the molar absorption coefficients (ε_ν) for UF_3 in solution has also been used. Since UF_4 solutions are more stable than UF_3 solutions under our experimental conditions, the calibration results for UF_4 are more reliable and associated with less error than are those for UF_3. Using this fact the uncertainty associated with the UF_3 calibration can be reduced by measuring the absorption spectrum of a mixture

Table 2-1

Molar Absorption Coefficients for Molten Fluoride Solutions of UF_4 and UF_3

Solution in Mole %	L_2B Solvent: $LiF \cdot BeF_2$ (66.7-33.9)				LB Solvent: $LiF \cdot BeF_2$ (48-52)				MSBR Solvent: $LiF \cdot BeF_2 \cdot ThF_4$ (72-16-12)			
Spectra	UF_3		UF_4		UF_3		UF_4		UF_3		UF_4	
Molar Absorption Coefficient	ε_{11360}	ε_{9170}	ε_{11360}	ε_{9170}	ε_{11360}	ε_{9170}	ε_{11360}	ε_{9170}	ε_{11360}	ε_{9170}	ε_{11360}	ε_{9170}
Temperature °C												
370					44.2	7.6	3.1	18.4				
400					43.2	7.8	3.1	17.8				
450	46.0	10.0	3.90	18.7	41.7	8.1	3.1	16.9				
500	44.2	10.0	3.85	17.9	40.1	8.4	3.1	16.0	58.5	14.5	2.80	19.2
550	41.7	10.0	3.80	17.1	38.5	8.6	3.1	15.1	56.8	14.5	2.70	18.2
600	39.0	10.0	3.75	16.3	36.9	8.9	3.1	14.2	55.0	14.5	2.65	17.2
650	36.2	10.0	3.70	15.4	35.3	9.2	3.1	13.3	53.3	14.5	2.55	16.2
700	33.5	10.0	3.65	14.8	33.7	9.4	3.1	12.4	51.6	14.5	2.50	15.2
750	30.7	10.0	3.60	14.1					49.9	14.5	2.40	14.5
800									48.0	14.5	2.35	13.8

of UF_3 and UF_4 where the UF_3 is generated by partially reducing a dilute UF_4 solution of known concentration. (The reductant chosen for partial reduction was UC_2.) The spectrum is then converted to digital form along with a UF_4 reference spectrum. Using iterative computer techniques, varying amounts of the UF_4 spectrum (i.e., k x (UF_4 spectrum) where k is the coefficient which is varied in the iteration process) are subtracted until the resulting spectrum visually matches that of previously measured (uncalibrated) UF_3 spectra. When a match is found for a particular value of k, the concentration of UF_3 in solution and thus the absorption coefficient can be calculated knowing the total amount of UF_4 before reduction. Comparison of ε values by this method with the total reduction method showed agreement within a 5% uncertainty.

In Table 2-1, absorption coefficients are listed for the various solutions and temperature ranges that have been studied. Values were taken from smoothed functions which within the limits of our precision are a linear function of temperature.

RESULTS AND DISCUSSION

An equilibrium expression such as the one written in Eq. 1-1 implies that certain criteria are valid: (1) The equilibrium expression should include all reactants and products which are involved in the reaction and these components should combine in the stoichiometry indicated by the expression. (2) The entire process must be reversible.

Before quantitative data for the equilibrium in Eq. 1-1 were measured, the above criteria were examined in the following manner: The equation represents a heterogeneous equilibrium between a molten-fluoride solution of UF_3 and UF_4 and two solid phases, UC_2 and graphite. The identification of the UF_3 and UF_4 was made by the characteristic absorption spectrum of each component in the near-infrared and visible regions (4000–33000 cm^{-1}). The identification of these two solute components is well established because their absorption spectra have been thoroughly documented.[11] In view of the extensive spectroscopic work which has preceded, there is no spectral evidence for any cations in the solution other than U^{+3}, U^{+4}.

The solid phase components, UC_2 and graphite, exhibit no measurable solubility in molten fluorides. These phases were identified by their respective X-ray diffraction patterns. A serious anomally arises as a result of the UC_2 phase identification since its formation is contrary to the established phase diagram[13] for the U-C system which shows UC_2 to be metastable with respect to U_2C_3 and graphite at temperatures less than 1500°C. On the basis of the uranium-carbon phase diagram and the accepted free energies of formation for the uranium carbides at temperatures less than 1000°K, U_2C_3 should be the carbide phase which was identified. Nevertheless, UC_2 has been repeatedly shown to form at these temperatures and has been established as the stable carbide phase in the equilibrium of Eq. 1-1. The reader who is interested in the details of this identification is referred to an earlier paper.[6] In the present paper we have included a series of equilibration experiments where excess U_2C_3 was used to reduce UF_4 solutions via the back reaction of Eq. 1-1. Results are compared with similar experiments where UC_2 was used as a reductant.

One of the simplest and yet most convincing observations to offer for the equilibrium is that the stoichiometry of the soluble uranium fluoride species follows the four-to-three relationship of Eq. 1-1. When a solution of approximately 0.1 mole % UF_3 in LiF-BeF_2 is allowed to react with graphite it is observed that 4 moles of UF_3 form 3 moles of UF_4. For example, when a 0.068 molar solution of UF_3 was allowed to react via Eq. 1-1 to form UF_4, it was observed that under conditions where reaction was more than 99% complete, a 0.049 molar UF_4 solution resulted. If the process were merely one of UF_3 oxidation, then $4UF_3$ should form $4UF_4$. For example:

$$4UF_3(d) + 2MF_{2(d)} \rightleftarrows 4UF_{4(d)} + 2M \qquad (3\text{-}1)$$

where M is a metal such as Ni.

Finally the reversibility of the reaction was demonstrated by the reversible temperature dependence of the equilibrium. From a particular temperature at which the system had attained equilibrium and concentrations of UF_3 and UF_4 measured, the temperature could be repeatedly raised or lowered causing the relative concentrations of UF_3 and UF_4 to shift and attain equilibrium concentrations at these new temperatures. When the system was returned to the initial temperature, the original concentrations of UF_3 and UF_4 were reproduced. Quantitative aspects of the temperature dependence will be given in the following sections.

The criteria tests established the equilibrium process as written in Eq. 1-1. We found it more practical to measure the back reaction mechanism:

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

since, by intentionally adding excess UC_2, we could insure that the molten fluoride solution was always in contact with all the reactive solid phases. Furthermore, we could interrupt the equilibration and add fresh UC_2 to demonstrate that the original carbide had not been consumed or altered during the course of the reaction. This procedure also insured that more active reducing agents, including other uranium carbides, were not present.

An equilibrium quotient for Eq. 3-2 can be written:

$$Q = \frac{(UF_3)^4}{(UF_4)^3} \tag{3-3}$$

where UF_3 and UF_4 are expressed in mole fractions of the solution. Q is simply the reciprocal of the equilibrium quotient, Q', for the forward reaction of Eq. 1-1. The data in the following paragraphs will be presented as Q values in terms of the back reaction and should not be confused with forward action.

The effect of variables such as temperature, melt composition, carbide composition and atmospheric contamination on the equilibrium of Eq. 3-2 in the solvent system $LiF-BeF_2$ have been measured and are treated separately in the following sections. Since the equilibrium of Eq. 3-2 (also Eq.1-1) is the central theme of this paper, it will often be cited as simply "the equilibrium."

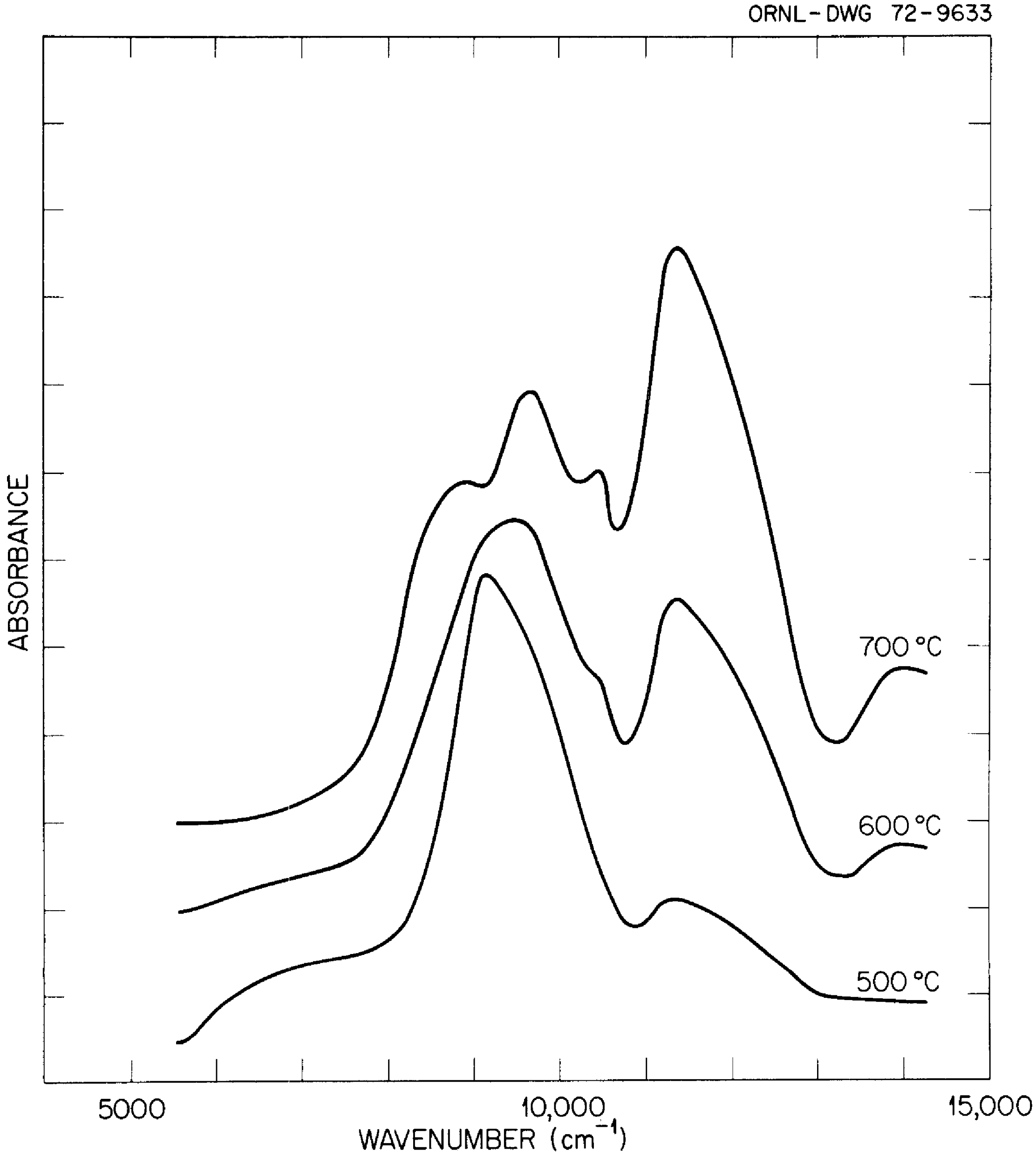
Effect of Temperature on the Equilibrium

Previous results[4] from the hydrogen reduction of UF_4 in molten fluoride solutions indicated that the temperature effect on the equilibrium of Eq. 1-1 should be small. However, when we measured the equilibrium by either the forward or the back reaction, we found it to be very sensitive to temperature. This can be seen qualitatively by examining the molten fluoride absorption spectra of Fig. 3-1 for equilibrium mixtures of dilute UF_3 and UF_4 in $LiF-BeF_2$ (66-34 mole %), in L_2B, over excess UC_2 at various temperatures. The spectra are due only to the UF_3 and UF_4 components of the solution. Therefore, by comparing these spectra with the spectra of pure UF_4 and pure UF_3 (Figs. 2-2 and 2-3 respectively), it can be seen that at 500°C, most of the uranium in solution is present as UF_4 whereas at 700°C, enough UF_3 is present to make the composite spectrum resemble that of Fig. 2-3. The composite spectrum at 600°C resembles neither of the two pure component spectra but instead an intermediate mixture of the two.

The quantitative aspects of these spectra were calculated by the procedure described in the experimental section. From absorption spectra such as those in Fig. 3-1 concentrations of UF_3 and UF_4 were determined in mole fractions and used in Eq. 3-3 to calculate equilibrium quotients, Q, at various temperatures. The data are presented in Table 3-1 along with Q values which are then presented in Fig. 3-2 as $\log_{10}Q$ versus $1/T_K$ (where T_K is the Kelvin temperature). At the top of the figure is shown the centigrade scale and at the right side of the figure, the equilibrium ratio,

$$R = \frac{[UF_3]}{[UF_3]+[UF_4]} \qquad (3-4)$$

where $[UF_3]$ and $[UF_4]$ are the concentrations in solution. (Note that the denominator of Eq. 3-4 represents the total uranium fluoride in solution.) These R values have been the customary manner in which UF_3-UF_4 concentrations are expressed within the MSRE program. The two lines drawn through the data points represent the experimental uncertainty of the data which arises mainly from the baseline error in the absorption spectra. Equilibria at various temperatures were approached from both the high (open circles) and low (closed circles) temperature direction. The system was initially held at ca. 50°C above the temperature desired until the UF_3 concentration had ceased to grow (UF_4 reacting with UC_2 via Eq. 3-2). Then the temperature was dropped 50° and the UF_3 concentration was allowed to fall by reaction of UF_3 with graphite until no further change could be detected. The equilibrium could be shifted repeatedly in this manner by varying the temperature of the system. The train of points at any given

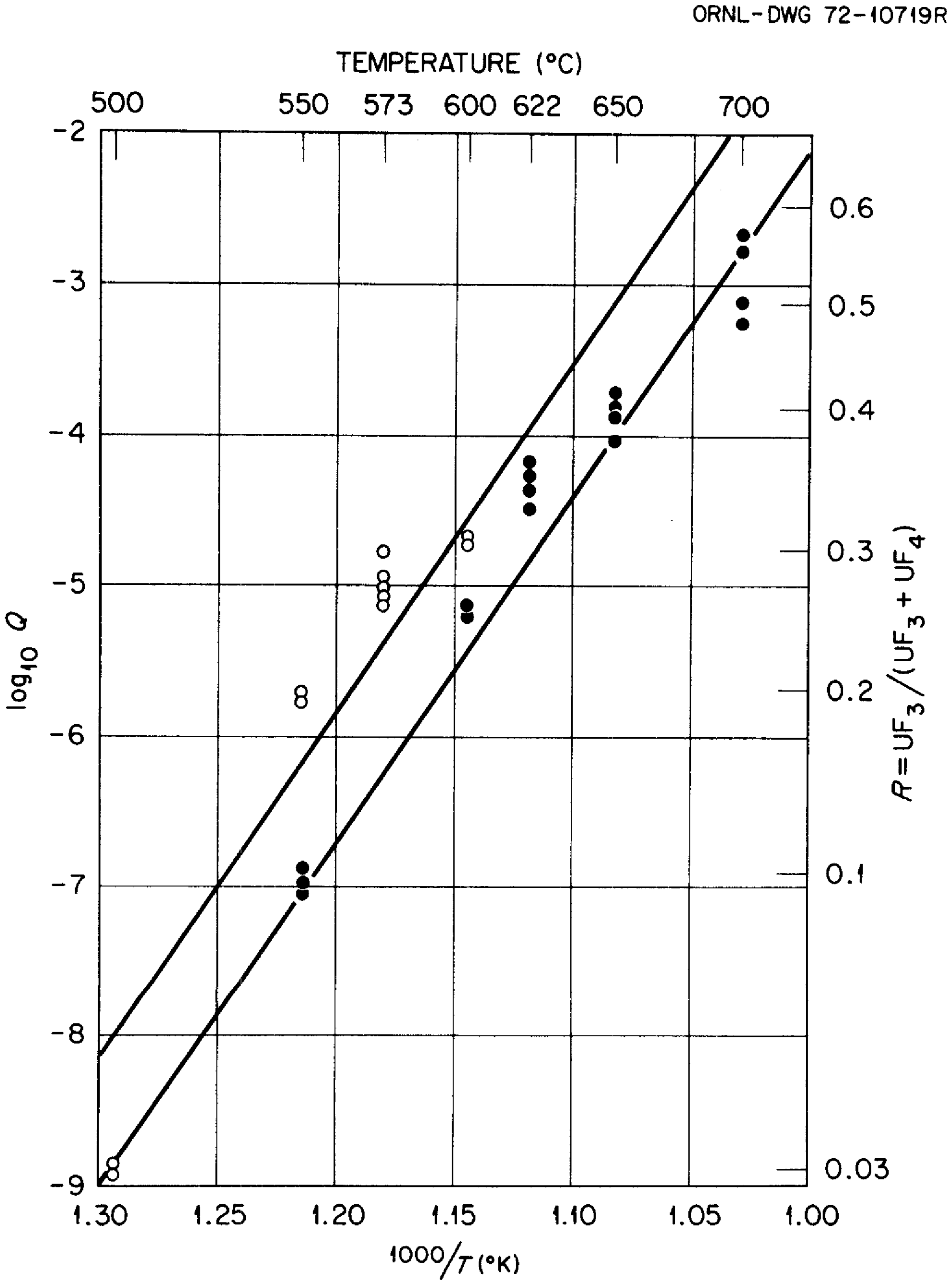


3-1 Spectra of Dilute UF_3-UF_4 Mixtures in LiF-BeF_2 (66-34 mole %) Showing Temperature Effect on the Equilibrium: $4UF_3 + 2C \rightleftarrows 3UF_4 + UC_2$.

Table 3-1

Typical Equilibrium data used in Figures 3-2 to 3-5 where Q and R are defined by Eqs. 3-3 and 3-4.

Run	Solvent	Carbide Phase	Temp (°C)	Measured Absorbance 11360 cm^{-1}	9170 cm^{-1}	Mole Fraction $UF_3(10^4)$	$UF_4(10^4)$	Q ($x10^8$)	R
1	L_2B	UC_2	500	0.130	0.515	0.264	7.25	0.128	0.035
2	L_2B	UC_2	550	0.217	0.505	0.804	7.22	11.12	0.10
3	L_2B	UC_2	600	0.485	0.517	2.76	6.68	1951.0	0.29
4	L_2B	UC_2	650	0.692	0.527	4.57	6.14	19080.0	0.43
5	L_2B	UC_2	700	1.305	0.780	9.83	7.60	212300.0	0.56
6	L_2B	U_2C_3	500	0.254	0.538	0.99	7.17	26.0	0.12
7	"	"	600	0.409	0.416	2.36	5.29	2070.0	0.31
8	"	"	700	1.083	0.567	8.29	4.74	443000.0	0.64
9	LB	UC_2	370	0.147	0.384	0.53	5.52	4.6	0.087
10	"	"	400	0.215	0.330	1.04	4.67	115.0	0.18
11	"	"	450	0.380	0.328	2.23	4.36	2950.0	0.34
12	"	"	500	0.482	0.274	3.09	3.21	27600.0	0.49
13	MSBR	UC_2	550	0.925	1.317	3.97	18.31	401.0	0.18
14	"	"	600	1.257	1.165	6.13	15.16	4050.0	0.29
15	"	"	650	2.575	1.433	14.0	14.32	129000.0	0.49



3-2 Equilibrium quotients, $Q = (UF_3)^4/(UF_4)^3$, versus temperature for $UC_2 + 3UF_{4(d)} \rightleftarrows 4UF_{3(d)} + 2C$ in the solvent LiF-BeF_2 (66-34 mole %).

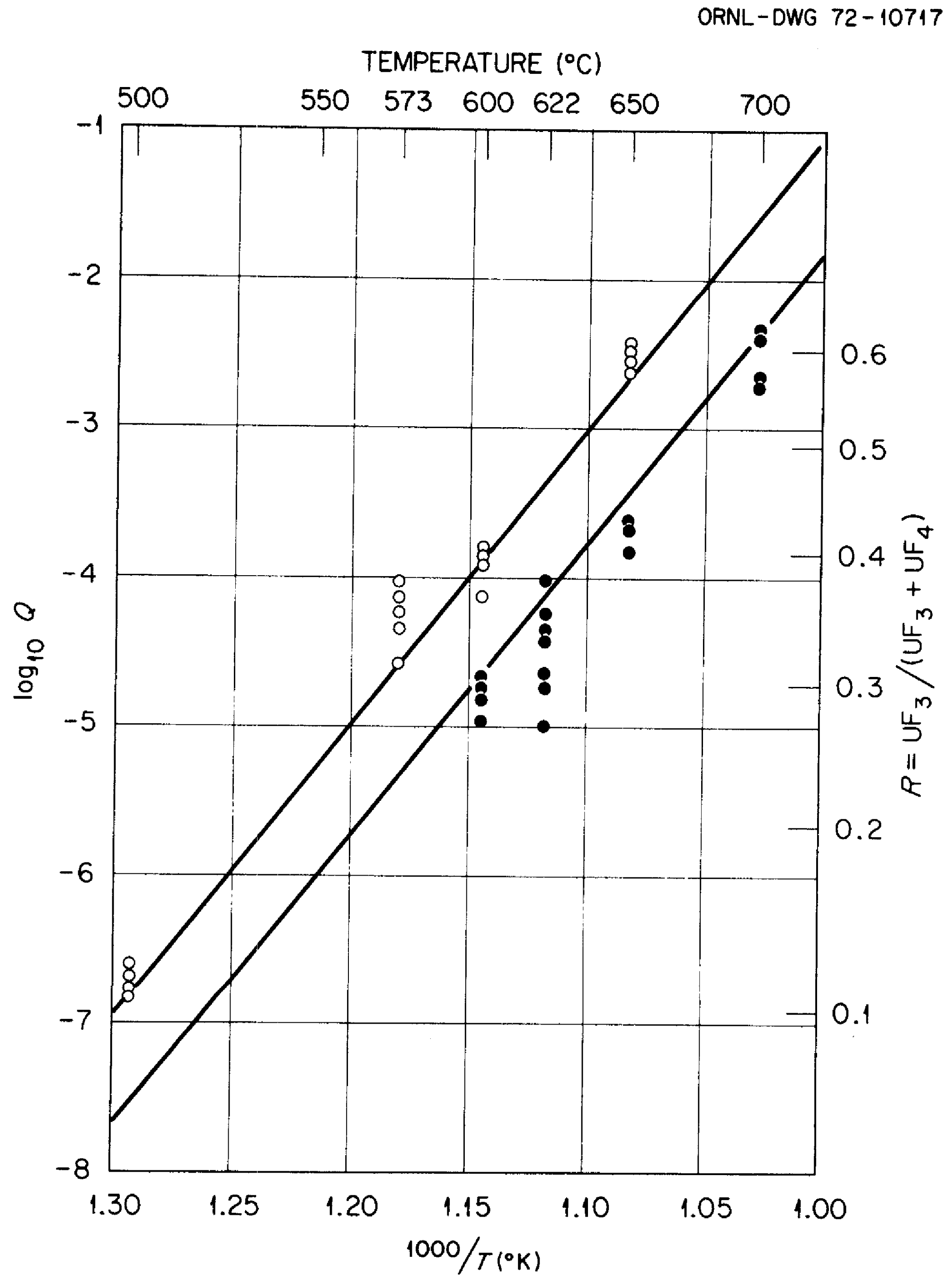
temperature represents the approach to equilibrium with only the lowermost (for open circles) and uppermost (for closed circles) being the best measured equilibrium value.

The large temperature effect on the equilibrium is exemplified by Fig. 3.2 where the quotient, Q, shifts by 10^6 in going from 500 to 700°C. In practical terms, this means that the concentration of UF_3 relative to the total uranium fluoride in solution is increased from ca. 5% at 500°C to ca. 60% at 700°C. The same large temperature effect on the equilibrium is found when U_2C_3 (in place of UC_2) is equilibrated with UF_4 solutions. These data are presented in Table 3-1 and the resulting Q values are plotted in Fig. 3-3. Here the Q values are greater at a given temperature than in Fig. 3-2 and therefore support the identification of UC_2 as the stable carbide phase of Eq. 1-1. Furthermore the U_2C_3 equilibration experiments demonstrate that the UF_3 stability in dilute fluoride solutions as well as the temperature effect on the equilibrium would not be far different from that presented in Fig. 3-2, even if the identification of UC_2 as the stable carbide phase of Eq. 1-1 were not correct.

The data of Fig. 3-2 can be used to calculate the change in enthalpy for the equilibrium. By defining the standard state of the solutes UF_3 and UF_4 as one mole percent in L_2B, their activity coefficients are unity and then the equilibrium quotients become equilibrium constants, K. The change in enthalpy, ΔH, for the reaction in the temperature range of 500-650°C can be calculated from the slope of the line in Fig. 3-2 using the expression:

$$\Delta H = -R \frac{d(\ln K)}{d(1/T)} \qquad (3\text{-}5)$$

where R is the gas constant. The value obtained for ΔH of Eq. 3-2 is 99.3 Kcal/mole which is surprisingly large in view of the enthalpy change calculated from enthalpies of formation for the pure, undiluted components at either 298° or 800°K. These values are given in Table 3-2 and yield ΔH^o = -10 Kcal/mole for the undissolved components of Eq. 3-2 at 298°K and ΔH^o = -12.90 Kcal/mole at 800°K. The process of solvation is not included in the calculation since no heats of solution for UF_3 and UF_4 are available. It should be noted that even the sign of the ΔH is different: We measure an endothermic process whereas a slightly exothermic process is expected.



3-3 Equilibrium quotients, Q = $(UF_3)^4/(UF_4)^3$, versus temperature for $1/2U_2C_3 + 3UF_{4(d)} \rightleftarrows 4UF_{3(d)} + 3/2C$ in the solvent $LiF\text{-}BeF_2$ (66-34 mole %).

Table 3-2

Enthalpy Data in (Kcal/mole)

Sources of the Data are from Tabulations referenced as Superscripts

	UC_2	UF_4	UF_3	C
ΔH^o_{298}	$-20(1)^{13}$	$-450(5)^{5}$	$-345(10)^{5}$	0
$H^o_{800}-H^o_{298}$	8.79^{13}	14.99^{14}	11.8^{15}	1.83^{16}

Table 3-3

Equilibrium Quotients, Q, and Ratios, R,

for

UF_3, UF_4 Solutions in Atmospheric Contaminated System

(Taken from Ref. 24)

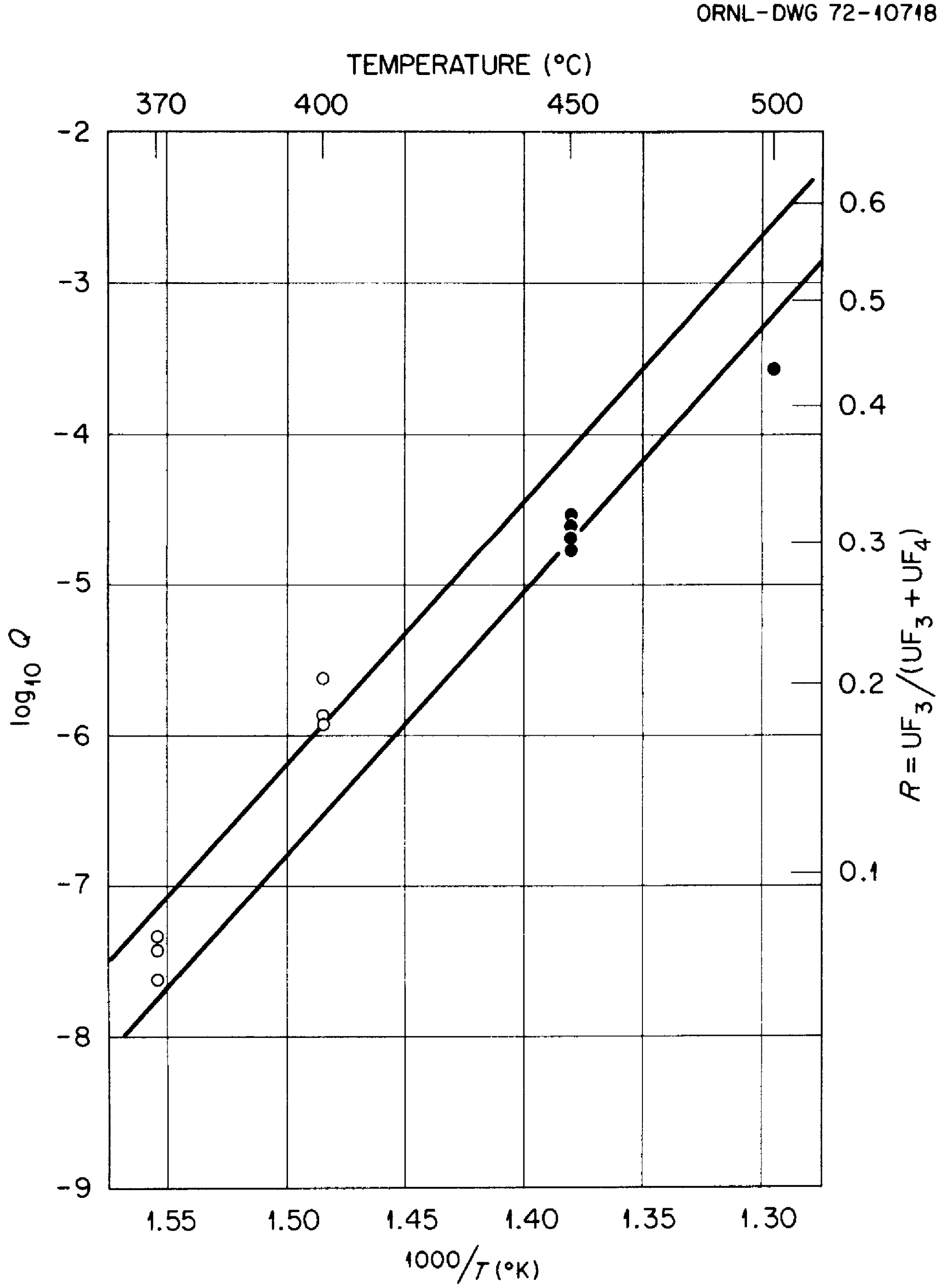
Solution (Mole %)	675°C		575°C	
$LiF-BeF_2$	R	Q	R	Q
66-34	.025	$2.7x10^{-10}$	.004	$1.8x10^{-13}$
48-52	.13	$3x10^{-7}$	.03	$6.2x10^{-10}$

Heats of solution could plausibly account for a large amount of the discrepancy since it is observed that the heat of solution for CeF_3 in L_2B (600-800°C) is 17 Kcal/mole whereas only 10 to 12 Kcal/mole is predicted.[17] From the enthalpy data, without the heats of solution, we can only conclude that the thermodynamic data is not adequate to predict the change in enthalpy for the reaction.

Effect of Solvent on the Equilibrium

In the same way that temperature shifted the equilibrium, changes in the solvent composition did also. The original purpose of this research was to demonstrate that changes in the fluoride ion concentration (which have already been shown to affect the coordination behavior of dilute UF_4 solutions[18]) might be related to shifts in redox equilibria as well. The effect of changing the solvent composition on the equilibrium is exemplified by comparing the equilibrium quotients, Q, for LiF-BeF_2 (48-52 mole %), LB, in Fig. 3-4 with those previously shown in Fig. 3-2 for the L_2B composition. At any given temperature (e.g., 500°C), Q is considerably larger in the LB composition than in the corresponding L_2B melt. Therefore the equilibrium of Eq. 3-2 is shifted to the right by increasing the concentration of BeF_2 in the solvent, i.e., by making the solvent more F^- deficient through the addition of a component which coordinates strongly with fluoride ions. The ratio, R, of Eq. 3-4 at 500°C has been increased from ca. 0.05 for the L_2B solvent to ca. 0.55 for the LB solvent (c.f. Figs. 3-2 and 3-4 at 500°C).

The magnitude of this change can be compared with that which is predicted from Baes' activity coefficients for M^{3+} and M^{4+} cations.[19] Realizing that the only difference in equilibrium quotients between the two melts is the ratio of the respective activity coefficients, γ, for UF_3 and UF_4 raised to the appropriate powers:



3-4 Equilibrium quotients, $Q = (UF_3)^4/(UF_4)^3$, versus temperature for $UC_2 + 3UF_{4(d)} \rightleftarrows 4UF_{3(d)} + 2C$ in the solvent $LiF-BeF_2$ (48-52 mole %).

$$K = Q_{L_2B} \frac{\left(\gamma_{UF_3}^{L_2B}\right)^4}{\left(\gamma_{UF_4}^{L_2B}\right)^3} = Q_{LB} \frac{\left(\gamma_{UF_3}^{LB}\right)^4}{\left(\gamma_{UF_4}^{LB}\right)^3} \qquad 3\text{-}6$$

where L_2B and LB denote the solvent systems. Since Baes defines all activity coefficients as unity in the reference composition, L_2B, then:

$$\frac{Q_{LB}}{Q_{L_2B}} = \frac{\left(\gamma_{UF_4}^{LB}\right)^3}{\left(\gamma_{UF_3}^{LB}\right)^4} \qquad 3\text{-}7$$

The right-hand term can be estimated from Baes' data at 600°C[19] where $\gamma_{UF_3} \approx \gamma_{CeF_3} = 0.7$ and $\gamma_{UF_4} \approx \gamma_{ThF_4} = 10$ by extrapolating to $LiF\text{-}BeF_2$ (48-52 mole %). By this procedure Q_{LB}/Q_{L_2B} is estimated to be 4×10^3.

From our data, Q_{LB}/Q_{L2B} at 600°C can be determined by extrapolating the double lines to 600°C and comparing this value, Q_{LB}, with the value, Q_{L2B}, read from Fig. 3-2. We find $Q_{LB}/Q_{L2B} \approx 5 \times 10^4$ agrees reasonably with the estimate from Baes' data. Even better agreement could be obtained if a non-linear extrapolation (which is suggested by the trend in the data of Fig. 3-4) is made. Furthermore, it should be noted that Baes' activity coefficients are only approximate for UF_3 since they are actually based on data for CeF_3. The comparison serves to show that the magnitude of the solvent effect is in reasonable agreement with previous data and consequently must be considered when estimating UF_3 stabilities in other molten fluoride solvent systems.

This leads then to the practical question, "What UF_3 stability is expected in the MSRE and the MSBR solvents?". In these ternary systems the relative measure of F^- concentration is more difficult to determine than in the binary system $LiF\text{-}BeF_2$ since there are two "acidic"* cations in each competing for fluoride ions. It is currently regarded that the MSRE solvent is more F^- deficient than L_2B and results of a previous electrochemical study of UF_3 stability by Manning[20] support this contention. Little

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*By "acidic" we mean, in the Lewis acid concept, the tendency to coordinate with F^-.

attention has been given to the UF_3 stability in MSBR solvents. We have first attempted to predict it and finally we have measured it directly.

Realizing the solvent effects on UF_3 stability arise from changes in the available free F^-, an attempt was made to estimate the F^- concentration in MSRE and MSBR solvents based on the earlier observation[18] that the coordination equilibrium of U^{4+} ions in LiF-BeF_2 solvents depended upon F^- according to:

$$UF_8{}^{4-} \rightleftarrows UF_7{}^{3-} + F^- \qquad 3\text{-}8$$

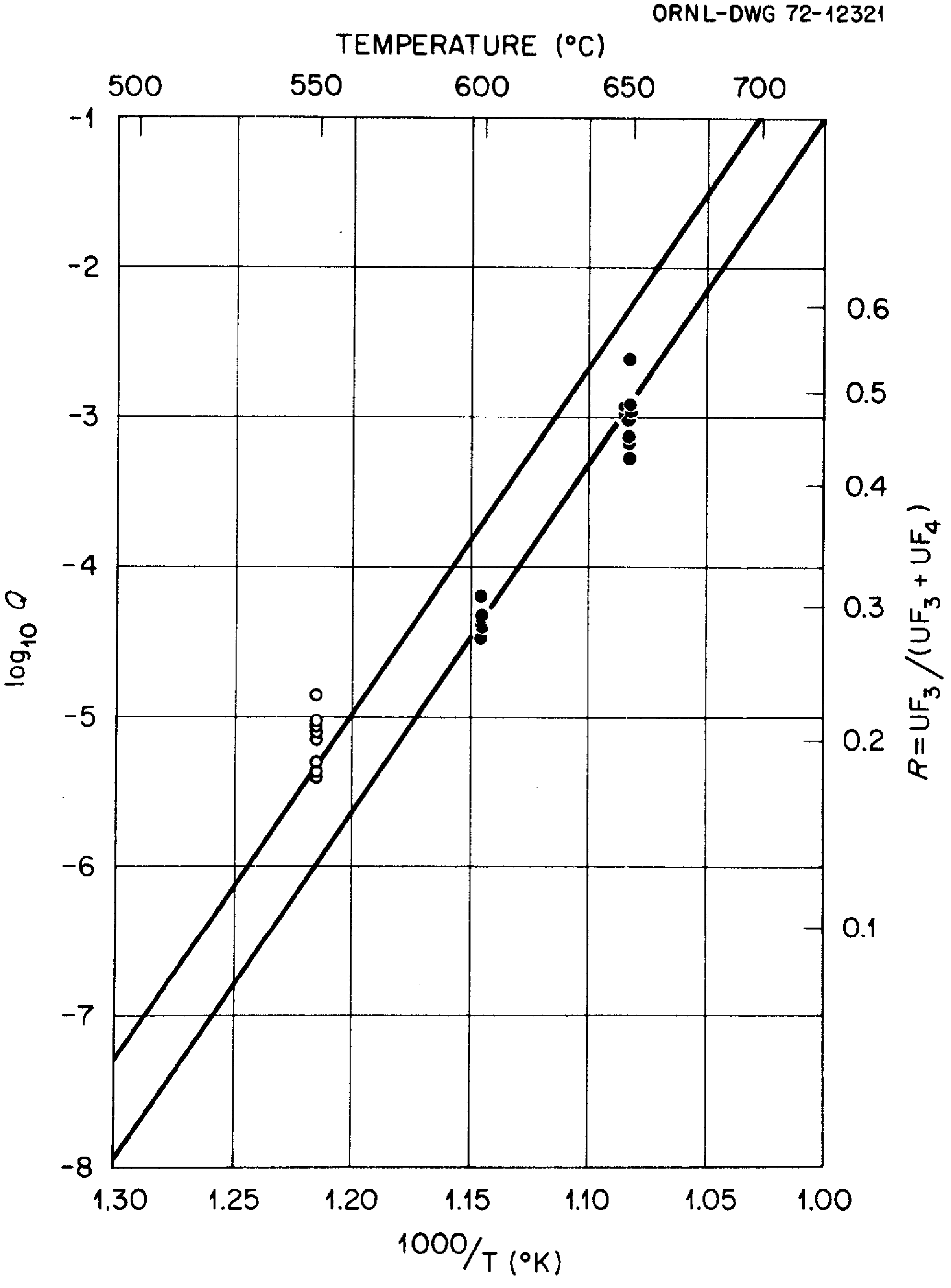
We have previously suggested[21] that the F^- could be measured by determining the concentration of $UF_8{}^{4-}$ and $UF_7{}^{3-}$ and then estimating the F^- concentration by Eq. 3-8. This method was found to work for LiF-BeF_2 solutions with BeF_2 concentrations of up to 52 mole % and for the MSRE solvent which is essentially a LiF-BeF_2 solvent.

The method then was used to estimate the F^- concentration in the MSBR solvent. Because the spectrum of UF_4 in this solvent was largely $UF_8{}^{4-}$, a F^- concentration greater than that in L_2B was suggested from Eq. 3-8. We concluded that the stability of UF_3 would be very much less than in L_2B, and in fact, some earlier UF_3 stability measurements[21] tended to support this conclusion.

In contrast to this viewpoint, were activity coefficient data by C. F. Baes[19] and BF_3 solubility data by S. Cantor[22] which suggested that the UF_3 should be slightly more stable in the MSBR solvent than in L_2B.

We examined this discrepancy by experimentally measuring the stability of UF_3 in the MSBR solution over excess UC_2 in the graphite spectrophotometric cell. The results are shown as $\log_{10}Q$ vs $1/T_K$ in Fig. 3-5 in the same form as that used for previous figures. These data show that UF_3 is more stable in MSBR than in L_2B. From the standpoint of reactor operations, concentration ratios, R, of UF_3 (c.f. Eq. 3-4) of up to 0.03 can be maintained safely down to the ca. 500°C freezing point of the solution.

The discrepancy in our earlier[21] predictions can only be rationalized by allowing a more complex coordination mechanism for the MSBR solvent than is described in Eq. 3-8. This probably involves U^{4+} which are fluoride bridged to neighboring Th^{4+} or Be^{2+} so that, through bridging, the



3-5 Equilibrium quotients, Q = $(UF_3)^4/(UF_4)^3$ versus temperature for $UC_2 + 3UF_{4(d)} \rightleftarrows 4UF_{3(d)} + 2C$ in the solvent $LiF-BeF_2-ThF_4$ (72-16-12 mole %).

coordination number (and accordingly by Eq. 3-8, the F^- concentration) appears much larger. There is some evidence for this in LiF-BeF_2 solvents where the BeF_2 concentration is greater than 52 mole %.[23]

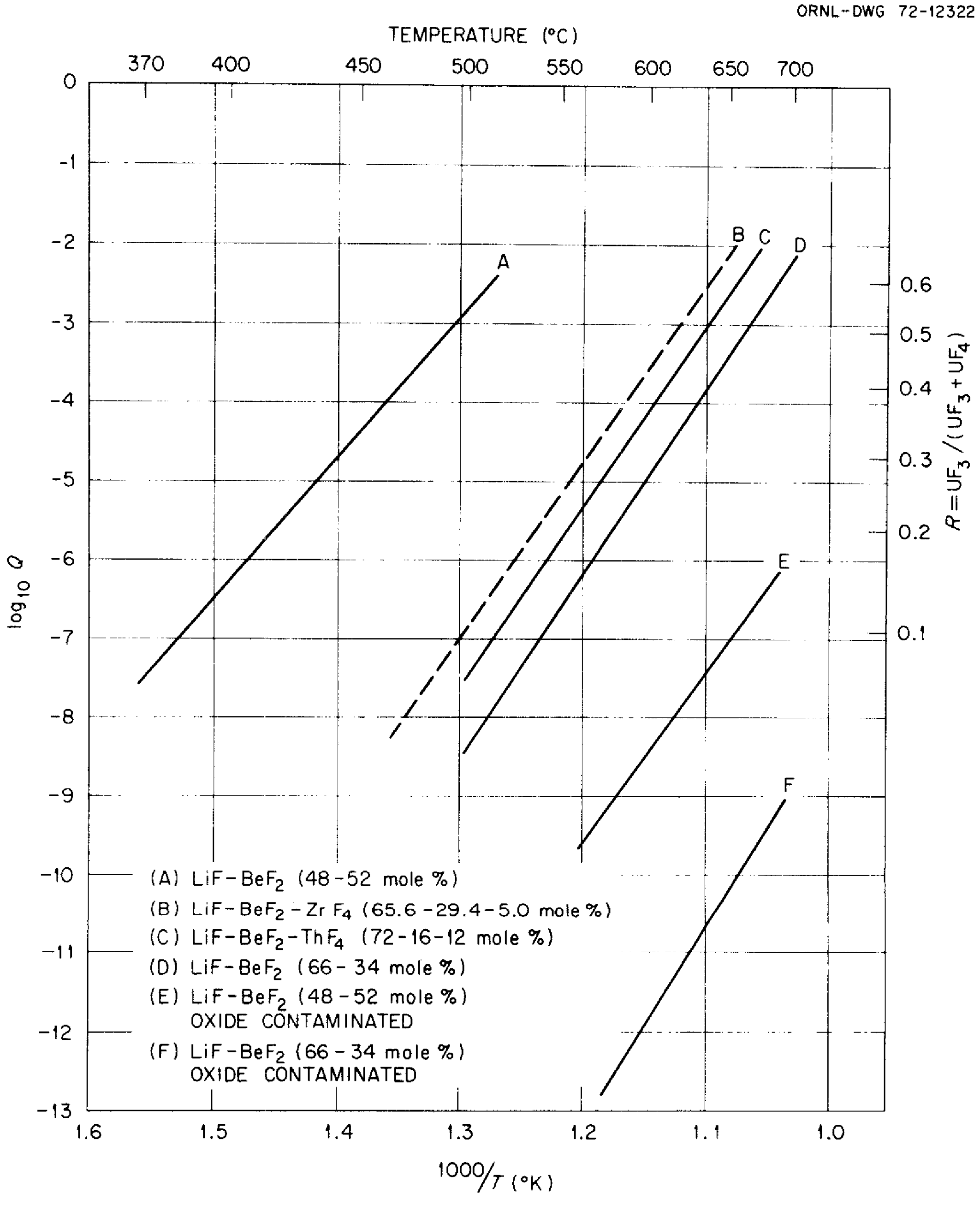
Effect of Atmospheric Contamination on the Equilibrium

In earlier attempts to measure the equilibrium quotients for Eq. 1-1, it was apparent that the equilibrium concentration of UF_3 in LiF-BeF_2 solvents was unusually low[24] compared with the present results. These results are presented in Table 3-3 and were measured by following the reaction of UF_3 in graphite with no uranium carbides added directly to the system. These reactions were always accompanied by the formation of UO_2 and other unidentified solid phases. However after various improvements were made which eliminated obvious signs of atmospheric contamination, such as UO_2 formation, the stability of UF_3 was greatly enhanced. We have subsequently concluded that these earlier measurements involved equilibria of UF_3 and UF_4 solutions in graphite and an oxy-carbide phase (as opposed to a pure carbide phase). It was never possible to identify the oxy-carbide phase by X-ray analysis despite the fact that the equilibria were very easy to reproduce from Eq. 3-2.

The effect of atmospheric contamination is clear -- it greatly reduces the stability of UF_3 and is therefore a major factor which cannot be ignored when considering UF_3 stability in molten fluoride solutions.

Effect of Temperature, Solvent and Contamination Compared

All of the effects of the variables have been collected to compare their relative importance and are shown in Fig. 3-6 as $\log_{10}Q$ vs T_K^{-1} in the same fashion as the previous figures but with a substantial reduction in scale. The effect of increasing temperature is similar in all cases, causing an increase in the stability of UF_3. There is no reason for the lines to be parallel to each other because they differ principally (except for the case of the atmospheric contamination) in the activity coefficients for UF_3 and UF_4 in the different solutions and these need not change proportionately for all solutions. Neither should it be necessary that the data be represented by straight lines, implying that ΔH for the reaction is constant. They are used here only because the data are insufficient to



3-6 A comparison of equilibrium quotients versus temperature for $UC_2 + 3UF_{4(d)} \rightleftarrows 4UF_{3(d)} + 2C$ in various solvent systems.

justify greater detail.

Decreasing the F^- concentration by the addition of BeF_2 is very beneficial in increasing UF_3 stability whereas atmospheric contamination causes the opposite and most disasterous effects on UF_3 stability.

Since the MSRE results do not come from our work, the MSRE line is broken. The stability of UF_3 in the MSBR solvent is between that of the MSRE solvent and L_2B. It is obvious that the region of greatest UF_3 stability is that of high temperature and low F^- concentration. We therefore suggest that little UF_3 could be maintained in F^- rich solvents such as LiF-NaF-KF (46.5-11.5-42.0 mole %) even if the reported K^+ reduction by UF_3(25) were not to occur. Conversely, the greater stability of pure UF_3(4) (i.e., not dissolved in a molten fluoride solvent) is explained by the absence of solvating F^-.

Other Considerations

If the thermodynamic data are sufficiently accurate then it should be possible to calculate the free energy change for Eq. 3-2 in the solvent LiF-BeF_2 (66-34 mole %) and then the equilibrium constant by:

$$\Delta G = -RT \ln K \tag{3-9}$$

The expressions for the free energy of formation are given in Table 3-4 for UC_2, UF_4 and UF_3 (where the latter two are for the standard state of

Table 3-4

Free Energies of Formation for Pure UC_2 and the Solutes UF_3 and UF_4 in LiF-BeF_2 (66-34 mole %) with standard deviations, σ, in Kcal/mole for relationship: $\Delta G = A + B\ (T_K/1000)$

Component	A	B	σ	Source
UC_2	-15.82	-8.2	-	Storms[13]
UF_3	-338.04	40.26	2	Baes[26]
UF_4	-445.92	57.85	2	Baes[26]

one mole percent each in L_2B). These free energy functions, when combined in the proper stoichiometric proportions yield a change of free energy for Eq. 3-2 of $\Delta G = 1.42-4.31\ (T_K/1000)$ with a significantly large combined standard deviation of $\pm$ 16 Kcal/mole. At 500°C, ΔG is -1.91 Kcal/mole and the equilibrium constant from Eq. 3-9 is 3.5. Since these are standard states for the UF_3 and UF_4 solutes, then Q is also equal to 3.5 and the ratio, R, of Eq. 3-4 is 0.89. (c.f. with $Q = 1.5 \times 10^{-9}$ and $R = 0.03$ in Fig. 3-2). Therefore, from the existing free energies of formation for the components of the reaction, practically all of a dilute UF_3 solution in contact with graphite should be stable. However, neither our results, nor those from any other investigators support this high a stability of UF_3.

A word of caution should be given at this point. It may seem obvious to demonstrate UF_3 stability via Eq. 1-1 by holding UF_3 solutions in graphite and allowing the UF_3 to react with graphite. Furthermore, it may be most convenient to generate a UF_3 solution by reducing a dilute UF_4 solution with a strong reductant such as Be, Zr, or U metal within the same graphite vessel that will be used for the stability measurement. We have observed that this results in the formation of mixtures of UC, U_2C_3 and UC_2 phases accompanied by the consumption of more reducing metal than is expected for the complete UF_4 reduction. The apparent anomaly is caused by the reversibility of Eq. 1-1 since as soon as UF_3 is formed in excess of its equilibrium concentration within the graphite vessel, it reacts with graphite forming uranium carbide phases and UF_4 in solution. The UF_4 is, in turn, reduced again by the excess reductant, forming more UF_3. An example of the process using Zr metal is:

$$4UF_4 + Zr \rightleftarrows 4UF_3 + ZrF_4 \qquad (3\text{-}10)$$

$$4UF_3 + xC \rightleftarrows 3UF_4 + UC_x \qquad (3\text{-}11)$$

so that the net reaction is:

$$UF_4 + Zr + xC \rightleftarrows ZrF_4 + UC_x \qquad (3\text{-}12)$$

This is one of the major reasons why we found it more practical to study the equilibrium by the back-reaction mechanism of Eq. 3-2. Although the UC and U_2C_3 phases do finally react leaving ultimately UC_2, we found that even for our small reaction system of less than 0.5 cc, it took an impractical length of time. Larger systems with smaller surface-to-volume ratios would take even longer.

The question of reaction times brings up the final point to be mentioned, that is, the kinetics involved in achieving the equilibrium of Eq. 1-1. Since UF_3 is reacting with graphite to form uranium carbides, the mechanism is obviously heterogeneous. It is considered by these authors far too difficult a mechanism to attempt to clearly describe; but if reaction rates are sought, the initial measurements should demonstrate that the mechanism is heterogeneous by varying the surface-to-volume ratios of the reacting system. We predict that the outcome of such a measurement will substantiate the heterogeneous mechanism. Another point of caution should be made. Since larger surface-to-volume ratios mean slower reaction rates, apparent high stabilities of UF_3 may appear whereas they actually involve metastable states of the equilibrium mechanism which include uranium carbide phases other than UC_2. These other carbides will ultimately be converted to UC_2 by the mechanism of Eq. 1-1; but, until the conversion is completed, the UF_3 ratio, R, will remain fixed at a high value.

The ultimate aim of the UF_3 stability study has been to describe conditions under which certain UF_3 ratios can be maintained in graphite. To demonstrate the validity of our measurements we mixed dilute UF_3 and UF_4 in the LB solvent so that the resulting solution had a UF_3 ratio, $R = 0.17$. The solution was maintained for a period of a week in the graphite spectrophotometric cell at 475°C with no loss of UF_3 or UF_4 from solution. (c.f. Fig. 3-4 which shows the maximum R at 475°C to be 0.40-0.45).

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