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THE STABILITY OF URANIUM TRIFLUORIDE
PART II. STABILITY IN MOLTEN FLUORIDE SOLUTION

G. Long and F. F. Blankenship

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THE STABILITY OF URANIUM TRIFLUORIDE
PART II. STABILITY IN MOLTEN FLUORIDE SOLUTION

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ABSTRACT

The equilibrium quotient, Q^R, for the reaction

$$\tfrac{1}{2}H_{2(g)} + UF_{4(d)} \rightleftharpoons UF_{3(d)} + HF_{(g)}$$

has been measured in a series of molten mixtures of LiF and BeF_2 containing from 26 to 42.4 mole % BeF_2 and up to 5 mole % UF_4. Over the temperature range 724 to 950°C the data are represented by the expression

$$\log_{10} Q^R = \log_{10} \frac{x_{UF_3}}{x_{UF_4}} \frac{p_{HF}}{p_{H_2}^{\frac{1}{2}}}$$

$$= 4.00 - 9.33\ (10^3/T) + 3.77\ x_{UF_4} + 2.09\ (x_{BeF_2} - 0.30)$$

By combining these data with those for the reduction of pure UF_4, values for the activity coefficient of UF_4 and the disproportionation quotient of UF_3 are derived.

INTRODUCTION

The relative stability in a molten fluoride solvent of UF_4 and UF_3 is of technological significance in the operation of reactor fueled with molten fluorides.[1] It determines both the extent of corrosion of container metals (M):

$$M_{(s)} + xUF_{4(d)} = MF_{x(d)} + xUF_{3(d)} \qquad (1)$$

and the extent of disproportionation of the UF_3 (either produced by corrosion or deliberately added to minimize it):

$$4UF_{3(d)} \rightleftharpoons 3UF_{4(d)} + U^{o}_{(s)} \qquad (2)$$

This may be regarded as a special case of the reverse of reaction (1), with $MF_x = UF_3$. Knowing the difference in free energies of formation of UF_4 and UF_3 in molten fluoride solvent, combined with corresponding data for

MF_x, the position of equilibria such as 1 and 2 may be readily calculated. As in the case of pure phases[2] an experimentally convenient technique is the measurement of the partial pressure of HF produced when the dissolved UF_4 is reduced in a stream of hydrogen:

$$\tfrac{1}{2}H_{2(g)} + UF_{4(d)} \rightleftharpoons UF_{3(d)} + HF_{(g)} \qquad (3)$$

For this reaction an equilibrium quotient, Q^R, expressed in terms of the mole fractions, x, of the dissolved species and the partial pressure, p, of the gaseous reactants may be defined:

$$Q^R = (x_{UF_3}/x_{UF_4})\ (p^{\frac{1}{2}}_{HF}/p_{H_2})\ \text{atm.}^{\frac{1}{2}} \qquad (4)$$

The value of the constant for the pure materials[1] is, however, small. Furthermore, it might be expected that, since UF_4 has a smaller, more highly charged cation and a lower melting point, it would have a smaller activity coefficient than UF_3 in a molten fluoride solvent. It is therefore possible that the value of Q^R might be such that the equilibrium pressure of HF at measurable concentrations of UF_3 would be immeasurably small.

An estimate of the value of Q^R may be obtained by combining available equilibrium quotients for two reactions, firstly, Q^C for the corrosion of metal M by UF_4 (equation 1):

$$Q^C = (x_{UF_3}/x_{UF_4})^x x_{MF_x}$$

and secondly, Q^M for the reduction of metal fluoride MF_x by hydrogen (analogous to equation 3).

For measurements at the same temperature in the same solvent and for a given metal M^o these two quotients may be combined to give the required quotient, Q^R, for the hydrogen reduction of UF_4 in solution, $Q^R = (Q^C \cdot Q^M)^{\frac{1}{2}}$.

Available data which fulfil the requirements of common metal and

and solvent are summarized in Table 1.

Table 1. Estimates of the Hydrogen Reduction Quotient (Q^R) for UF_4 in Various Salt Mixtures from the Quotients for Metal Corrosion (Q^C) and Metal Fluoride Reduction (Q^M)

Melt Composition	Temperature (°C)	Metal	Q^M [a]	Q^C [b,c]	$Q^R = (Q^M \cdot Q^C)^{\frac{1}{2}}$ x 10^4
$NaF-ZrF_4$ (53-47 mole %)	600	Cr	$\sim 10^{-5}$	$1.3 10^{-4}$	~ 0.4
	600	Fe	$9.6 10^{-2}$	$2.0 10^{-6}$	4.4
	800	Cr	$6.4 10^{-4}$	$2.9 10^{-4}$	4.3
	800	Fe	2.54	$6.0 10^{-7}$	12
$LiF-BeF_2$ (62-38 mole %)	800	Cr	$4.4 10^{-4}$	-	1.7
(48-52 mole %)	800	Cr	-	7.10^{-5}	

[a] C. M. Blood, Solubility and Stability of Structural Metal Difluorides in Molten Fluoride Mixtures, ORNL-CF-61-5-4 (1961).

[b] F. F. Blankenship et al., Aircraft Nuclear Propulsion Project Quarterly Progress Report for Period Ending June 30, 1957, ORNL-2340, p. 133

[c] C. M. Blood, Aircraft Nuclear Propulsion Project Quarterly Progress Report for Period Ending December 31, 1957, ORNL-2440, p. 76.

The values of Q^R so derived are promising, suggesting that measurable pressures of HF should be obtained at temperatures in the region of 800°C (e.g., $p_{HF} \sim 2.10^{-3}$ atm. when $x_{UF_3}/x_{UF_4} = 0.1$).

EXPERIMENTAL

The equipment for the purification of hydrogen and helium, the metering of HF into the hydrogen, the analysis of HF and the control and measurement of temperature were as previously described.[2]

The welded nickel reaction vessel is shown in Figure 1. The depth of the gas inlet tube could be varied with the system at temperature by means of a Teflon gland, so that the completeness of reaction in the single pass of hydrogen could be established. Since most of the reaction presumably occurs while the bubble of hydrogen rises through the melt, rather than at the free surface, the contact time at a given dip-tube depth is roughly constant, independent of gas flow rate. It is therefore, not feasible, as in solid-gas reactions, to determine the equilibrium conditions by varying the flow and extrapolating to zero flow rate. Furthermore the completeness of reaction could not be checked by observing the effect of introducing HF into the hydrogen inlet gas, since this procedure would seriously impair the accuracy of the mass-balance calculations necessary to determine the concentration of the UF_3. It was found, however, that the HF concentration was independent of depth of immersion when this exceeded 1 cm., indicating that equilibrium was achieved at the normal working depth of 5 cm.

The melt temperature was recorded by means of an Inconel-sheathed chromel-alumel thermocouple, calibrated to $\pm$ 0.1°C, which was inserted down the gas inlet tube. The output of the thermocouple was measured to $\pm$ 0.01 mV (~0.25°C) and recorded continuously on a Leeds and Northrup "Azar" millivolt recorder. Temperature scans along the dip line showed that the total variation in temperature through the melt was less than 0.5°C.

Gas was normally passed through the melt at a flow rate within 3 ml/min of a standard 18 ml/min. Observations on a water bubbler showed that at this flow rate problems arising from carry-over of droplets would not arise. Consideration of the vapour pressure data showed that purging could be

carried out for several hours at a temperature as high as 950°C without undue loss of BeF_2 by volatilization.

No provision was made for sampling the melt for subsequent determination of the UF_3 content. The conventional technique of drawing a sample through a sintered frit of copper or nickel is suspect in this application. The high area of clean metal surface in contact with a small amount of UF_3 is believed to promote disproportionation by alloy formation with the uranium. Furthermore, the anticipated concentrations of UF_3 were low, near the limit of analytical detection, so that the errors in the determination would be high. Consequently the UF_3 content of the melt was inferred from the total evolution of HF from the system. Possible interfering reactions which might invalidate this procedure are discussed below.

Measurement of the Equilibrium Quotient Q^R

The equilibrium quotient (Equation 2) for the hydrogen reduction reaction of UF_4 may be expressed in terms of those quantities which are measured when pure hydrogen is passed through a melt containing UF_4:

$$Q^R = \frac{M_{UF_3}}{M^o_{UF_4} - M_{UF_3}} \quad \frac{P_{HF}}{P_{H_2}} \quad P_{H_2}^{\frac{1}{2}} \tag{5}$$

where

P_{H_2} is the pressure of hydrogen (atm)

$M^o_{UF_4}$ is the total amount of UF_4 initially present (millimoles)

M_{UF_3} is the total amount of UF_3 present (millimoles)

(P_{HF}/P_{H_2}) is the ratio of partial pressures of HF and H_2.

Experimentally the concentration of HF in the outlet stream was determined by measuring the volume of wet hydrogen at the laboratory temperature

passing out of the sampler while a given volume of standard NaOH solution was neutralized. Appropriate corrections were applied for the vapour pressure of water, the laboratory temperature and atmospheric pressure. Since at the pressures and temperatures employed HF behaves as a perfect gas the measured concentration is readily converted to the required partial pressure ratio (P_{HF}/P_{H_2}). The total amount of UF_3 produced (M_{UF_3}) was calculated by mass balance from the total amount of HF evolved up to the time when the measurement of the ratio (P_{HF}/P_{H_2}) was made.

The anticipated variation in HF concentration with time may be derived as follows. By mass balance, when a volume (dV, l) of hydrogen at a pressure of 1 atm. passes through the melt the change in UF_3 content (dM_{UF_3}, millimole) is given by

$$dM_{UF_3} = \frac{P_{HF}}{2.24\ 10^{-2}}\ dV$$

substituting for P_{HF} from Equation 4 and integrating gives

$$P_{HF} = \left(\frac{1.12\ 10^{-2}\ Q^{R}\ M_{UF_4}}{V}\right)^{\frac{1}{2}}\ \text{atm.}$$

where V (l) is the total volume of gas passed.

The pressure of HF is seen to vary with $V^{-\frac{1}{2}}$, so that at a given temperature the rate of production of UF_3 falls as the experiment proceeds. In order to achieve the required concentrations of UF_3 in a reasonable time it was therefore necessary to operate at successively higher temperatures, returning to the lower temperatures for further equilibrium determinations.

Interfering Reactions

Since the UF_3 concentration in the solution was to be determined by measuring the total evolution of HF, it was essential that the amount of HF involved in any reactions giving rise to an uptake or generation of HF should be

negligible compared with the amount of HF (up to a maximum of about 10 millimoles) expected from the reduction of UF_4. The several possibilities are:

(1) Reversible uptake and release by the vessel and pipework.

(2) Reaction with oxide in the melt.

(3) Reduction of other reducible impurities (e.g., NiF_2) in the melt.

(1) Uptake by the Metal System

The materials of construction of the pipework and reaction vessel were chosen so that thermodynamically there should be no separation of pure corrosion-product phase with the HF/H_2 ratios anticipated. Tests on the pipework alone showed that this was indeed the case. With an unused nickel reaction vessel, however, irreversible uptake of HF occurred at elevated temperatures (~1000°C) and slight fumes, presumably arising from SiF_4, were observed in the outlet sampler. Exhaustive tests showed that after such pre-treatment the subsequent uptake and release of HF under the conditions of the experiments was small compared with the amount of HF produced by the reduction of the UF_4.

(2) Reaction With Oxide Ion

Possible reactions are:

$$O^{2-} + 2HF \rightleftharpoons H_2O + 2F^- \qquad (6)$$

$$O^{2-} + HF \underset{\text{low } P_{HF}}{\overset{\text{high } P_{HF}}{\rightleftharpoons}} OH^- + F^- \qquad (7)$$

Measurements of the equilibrium (7) have shown[3] that provided the oxide concentration of the melt is less than ~ 100 ppm loss of HF by this reaction at temperatures in excess of 700°C is negligible. Conversely, any moisture in the purge gases is quantitatively converted to oxide and HF. In order

that the amount of HF generated from any moisture in the hydrogen be small compared with the measured HF pressures the moisture content must be maintained as less than approximately 10 ppm ($\equiv 2.10^{-5}$ atm HF). At this level the buildup of oxide in the melt during a run (100 l H_2 passed into approximately 100 g melt) is also negligibly small (< 10 ppm).

Formation of hydroxide is, however, more restrictive. Reaction (7) in effect substantially increases the otherwise negligible solubility[4] of HF in pure melt, and makes the stripping of a melt by helium down to low outlet HF concentrations a long, tedious process. Reaction (6) was used to render the melts free of oxide, HF at a high concentration (about 1,000 $\mu m/\ell$) in hydrogen being passed through the melt at 550°C until no further loss of HF was noted. At this point sparging with helium rapidly brought the outlet HF concentration down to a low level.

(3) Reduction of Impurities

Analysis showed that initially the melt contained 100 to 200 ppm of potentially reducible impurities (difluorides of Fe, Ni, and Cr). If the HF evolved in their reduction were ascribed to the production of UF_3 an error of up to 1 millimole (~ 10% of the total UF_3 produced) would be introduced. However, from the equilibrium quotients for the reduction of these fluorides (Table 1) it was concluded that no significant reduction of CrF_2 would occur over the whole range of the experimental conditions employed. On the other hand, FeF_2 and NiF_2 would be almost completely reduced by passing hydrogen through the melt at 650°C until the outlet concentration of HF fell to < 100 ppm. A correction for the small amount of UF_3 produced under these conditions was readily made using values of the reduction constant for UF_4 extrapolated from measurements at higher

temperatures. At temperatures in excess of 650°C the partial pressure of HF resulting from the reduction of UF_4 increases. The calculations show that some loss of HF due to reoxidation of Fe could be expected, upsetting the mass balance until such time as the HF concentration had fallen, with increasing concentration of UF_3, to the point where all the FeF_2 was reduced again to metal.

These preliminary considerations were borne out experimentally firstly by reduction experiments, described below, performed on a melt free of UF_4 and secondly by the values of the reduction quotient Q^R obtained at low concentrations of UF_3, (high concentrations of HF). Here the observed values of Q^R were only obtained at a given temperature after the partial pressure of HF had fallen below the value for which the estimates showed that FeF_2 was reduced to the metal.

Experimental Procedure

The experimental procedure, adopted in view of the above considerations, was as follows: the degreased and pickled reaction vessel was heated to 750°C under vacuum for approximately 12 hours and in a hydrogen stream at the same temperature for approximately one hour. Hydrogen fluoride at a partial pressure of approximately 2.10^{-2} atm was introduced into the hydrogen and the temperature raised to 1000°C for 6 hours. During this treatment the outlet concentration of HF, initially $\sim 5.10^{-3}$ atm, slowly rose to the inlet value, and fumes of SiF_4 ceased to be observed in the outlet sampler. Finally residual and physically adsorbed HF were swept out by helium.

The charge ($\sim$ 80 g) of Be-purified $LiF-BeF_2$ salt was finely powdered in a dry-atmosphere box and introduced into the vessel through a long-

stemmed funnel. After pumping at 400°C the charge was melted and heated to 550°C under a hydrogen/HF atmosphere ($P_{HF} \sim 5.10^{-2}$ atm.), the dip line introduced and sparging continued until only a small (< 5%) loss in HF concentration was estimated from the known equilibrium constant for the oxide-HF reaction[3] to be less than 2 ppm. On subsequent helium sparging the HF recovered corresponded to that contained in the dead volumes of the equipment and dissolved in the melt. The observed final concentration of HF (~ 10 ppm) corresponded with the observed water content of the helium.

When the helium was replaced by hydrogen at 650°C a sharp rise in the HF concentration occurred, this arising from the reduction of both UF_4 and impurity fluorides. Reduction was continued until the outlet HF concentration fell to ~ 10^{-4} atm. Using the extrapolated value of the UF_4 reduction constant the amount of UF_3 produced in this stage was calculated (~ 0.1 millimole). All further evolution of HF at higher temperatures was ascribed solely to the production of UF_3.

For the run proper, the system was brought to the lowest chosen temperature, the total evolution of HF continuously determined and the concentration of HF determined at intervals. When the partial pressure of HF fell to such a value that the rate of production of UF_3 became small, the temperature was raised by about 50°C and the process repeated. As the UF_3 concentration was built up at the higher temperature the system was occasionally cooled to within ± 3°C of some previous operating temperature and the concentration of HF determined. An appropriate correction (rarely exceeding 5%) was applied to the observed HF concentration to allow for the small differences between the actual and nominal temperature. Whenever the temperature was changed sufficient time was allowed for the HF

concentration to establish the new equilibrium value. Several measurements were made at intervals to ensure that equilibrium had indeed been achieved. Normally constant values of the equilibrium quotient were obtained after about half an hour, but at the lowest temperatures, where the HF concentration was approaching the limit set by the solvent, longer periods were required. Here it was convenient to leave the equipment running overnight before measurement.

As part of the preparation for Experiment 2 a series of hydrogen reduction experiments were carried out on the solvent alone, before the addition of UF_4, in order to determine the amount, if any, of HF resulting from the reduction of either impurities or the solvent itself. Some reduction was indeed observed, but the amounts of HF involved were trivial compared with those arising from the reduction of UF_4.

Five reduction experiments were carried out; in three of these the solvent composition was held constant at 66 mole % LiF, 34 mole % BeF_2, while the initial concentration of UF_4 was 1.60, 3.34, and 5.06 mole % respectively. For the remaining two experiments the UF_4 content was held at 5.0 mole % while the LiF content of the solvent was 72.6 mole % and 55.3 mole %. New reaction vessels were used for Experiments 1 and 2, while for the remaining experiments the required compositions were obtained by adding to the reaction vessel for Experiment 3: UF_4, Experiment 4: LiF and UF_4, and for Experiment 5: BeF_2 and UF_4. The normal pretreatment with HF ensured that any oxide introduced with the added components was removed and the UF_3 produced in the previous experiment was completely reconverted to UF_4.

EXPERIMENTAL RESULTS

Reduction of Solvent by Hydrogen

As a preliminary to Experiment 2 the HF resulting from the hydrogen reduction of the solvent alone was measured at a series of temperatures. The melt was rendered oxide-free by treatment with HF at 550°C and stripped of HF with helium to an outlet concentration of < 10 ppm (0.5 μ mole/l). The evolution of HF with time was then followed after the helium had been replaced by hydrogen. The procedure was repeated at successively higher temperatures. At each temperature the introduction of hydrogen brought about an increase in the concentration of HF. This dropped to a steady value over a period of hours. The observations are summarized in Table 2.

Table 2. HF Arising from Hydrogen Reduction of Purified Solvent ($LiF-BeF_2$, 66-34 mole %)

Temperature (°C)	HF Concentration (micromole/l) Initial	Final	Time (hr)	Total HF Evolved (micromole)
600	24	2-3	10	100
800	22	8	1½	20
950	32	22	1½	30

The high evolution of HF at 600°C presumably arises from easily reducible impurities (NiF_2, FeF_2), and in a normal run this is evolved during the purification stages. At the higher temperatures no reduction of the solvent will occur until the concentration of HF arising from the

reduction of the UF_4 falls below the initial concentration of HF quoted in Table 2. As the reduction of UF_4 proceeds beyond this point and the outlet concentration of HF falls, an error in the calculated production of UF_3 will be introduced to an extent approximating to the total evolution of HF from the solvent. Above 600°C this is clearly small compared with the total evolution (approximately 10 millimoles) arising from the reduction of UF_4. The limiting final concentration of HF arising from the solvent does impose a limit, albeit not very restrictive, on the lowest HF concentration measurable at each temperature. In practice it was found that at the higher concentration of UF_3, where the observed HF concentration fell to a value approaching the limiting value at each temperature, equilibration was very slow, several hours' purging being necessary before consistent values of Q^R were obtained.

Reduction of UF_4 in $LiF-BeF_2$ Melts

The results for the five experiments are presented in Figures 2 to 6. Here the values of Q^R calculated by Equation 6 at each temperature are plotted as a function of the percentage conversion of UF_4 to UF_3. The order in which the measurements were made is clearly apparent in these figures. Each point represents the mean of between four and six determinations of the concentration of HF, the standard deviation in the titrations being in the range 1 to 2%.

In general the values of Q^R are independent of the extent of conversion to UF_3 over the range studied. The spread of the data is somewhat greater than the standard deviations in the titrations, and this reflects the small day-to-day variations in other parameters, such as temperature. The mean

values of Q^R at each temperature, with standard deviations, are presented in Table 3. For each solvent composition the individual values of Q^R were fitted by the method of least squares to an expression of the form

$$\log_{10} Q^R = A + B/T \quad .$$

Values of A and B with the derived enthalpy and entropy changes for the reaction are also summarized in Table 3. The values of Q^R on a logarithmic scale are plotted against the reciprocal of the absolute temperature in Figure 7.

DISCUSSION

Inspection of Figure 7 shows that, at a solvent composition of around 66 mole % LiF, 34 mole % BeF_2 the effect on Q^R of changing either the UF_4 or BeF_2 content is slight. This is illustrated in Figures 8 and 9. Here the interpolated values of $\log_{10} Q^R$ at the mean temperature of the experiments (860°C) are plotted, in Figure 8, against the initial concentration of UF_4, with constant solvent composition and, in Figure 9, against the BeF_2 content of the solution, the UF_4 concentration being held constant at 5.0 mole %. At this temperature $\log_{10} Q^R$ is a linear function of the UF_4 concentration, while over a limited range of concentrations (25 to 35 mole % BeF_2) the dependence on BeF_2 concentration may be assumed to be linear within experimental error. The observed values of Q^R at 860°C may therefore be represented by the expression

$$\log_{10} Q^R = \log_{10} Q_0^R - 0.238 + 3.77\, x_{UF_4} + 2.09\, [x_{BeF_2} - 0.30] \qquad (5)$$

where x_{UF_4} and x_{BeF_2} are respectively the mole fractions of UF_4 and BeF_2 present in the solution and Q_0^R is the reduction quotient for a hypothetical melt containing 30% BeF_2 and no UF_4.

Table 3. Values of the Equilibrium Quotient, Q^R, the Parameters of the Expression $\log_{10} Q(atm^{\frac{1}{2}}) = A + B/T$ and the Derived Values of ΔH and ΔS

Experiment No.	Initial Composition of Solution (mole %)		Temp. (°C)	$10^5\ Q^R$ ($atm^{\frac{1}{2}}$)	$10^5\ \sigma$ ($atm^{\frac{1}{2}}$)	A	-B (°K)	ΔS (cal/deg.mole)	ΔH (kcal/mole)
1	LiF	62.7	724	0.78	0.08	4.255	9.357	19.5	42.9
	BeF_2	32.3	772	1.99	0.08	±0.090	±0.10	±0.4	±0.5
	UF_4	5.0	831	5.9	0.4				
			881	14.5	0.4				
			948.5	39.3	0.7				
2	LiF	65.0	774	1.61	0.07	4.350	9.581	19.9	43.4
	BeF_2	33.4	824	3.93	0.15	±0.12	±0.14	±0.6	±0.6
	UF_4	1.6	879	11.2	0.4				
			949.5	32.4	0.5				
3	LiF	63.8	824	4.9	0.1	3.895	9.000	17.8	41.2
	BeF_2	32.8	879	12.3	0.3	±0.081	±0.10	±0.4	±0.5
	UF_4	3.4	949.5	34.1	0.7				
4	LiF	69.0	774	1.54	0.03	4.244	9.490	19.4	43.4
	BeF_2	26.0	824	3.8	0.2	±0.118	±0.13	±0.5	±0.6
	UF_4	5.0	879	10.6	0.2				
			949.5	29.9	0.6				
5	LiF	52.6	724	3.9	0.2	3.998	8.403	18.29	38.5
	BeF_2	42.4	774	9.3	0.6	±0.207	±0.24	±1.0	±1.1
	UF_4	5.0	824	21.8	1.5				
			879	52.2	1.2				
			949.5	133	4.0				
Hypothetical Standard Solution (see text)	LiF	70.0				4.233	9.329	19.4	42.7
	BeF_2	30.0				±0.063	±0.081	±0.3	±0.4
	UF_4	0.0							

In addition, the data of Experiments 1 to 4 can all be adequately represented by a single value (42.7 kcal/mole) for the heat of reaction, as illustrated in Figure 7. The apparent exception is Experiment 3, where the point at 949.5°C is low, but only by an amount comparable with the deviations of points in other experiments at other temperatures. The deviation can therefore be considered fortuitous and no significance can be attached to the fact that the value of ΔH for this experiment, with measurements at only three temperatures, differs from the average ΔH by twice the standard deviation.

Values of Q_0^R calculated by means of equation 5 from the set of values of Q^R in each solution, are plotted on a logarithmic scale against the reciprocal of the absolute temperature in Figure 10, and parameters A and B and the heat and entropy changes summarized in Table 3. The mean deviation of the points from the least-squares line is 3% in Q_0^R, and it is therefore concluded that the expression

$$\log_{10} Q^R = 4.00 - 9.33\ (10^3/T) + 3.77\ x_{UF_4} + 2.09\ (x_{BeF_2} - 0.30) \qquad (6)$$

adequately describes the experimental data. The expression only strictly applies for UF_4 concentrations up to 5 mole % in a solvent containing 66 mole % LiF and for variations in solvent composition at a constant 5.0 mole % UF_4. Nevertheless the changes in Q^R are so small that equation 6 can probably be applied to any solution containing up to 10 mole % of UF_4 and between 25 and 35 mole % of BeF_2 without introducing errors of greater than 10% in Q^R. Furthermore equation 6 may be applied to solutions containing ZrF_4 as well as UF_4, using $x_{ZrF_4} + x_{UF_4}$ in place of x_{UF_4}. The ions Zr^{4+} and U^{4+} are so similar in size that, at least over a small concentration range, they are expected to have similar effects on the solvent

properties of the mixture.[5]

Activity Coefficient of UF_4

The ratio of the activity coefficients of UF_4 and UF_3, referred to the pure crystalline solids, is obtained directly from the ratio of the equilibrium (Q^R) in solution and the equilibrium constant (K^R) for the reduction of pure UF_4:[2]

$$\gamma_{UF_4}/\gamma_{UF_3} = Q^E/K^R$$

The value of γ_{UF_3} can be deduced from the solubility data of Shaffer[6] for UF_3 in the MSRE solvent, of composition LiF 65.0, BeF_2 29.2, ZrF_4 5.0, and UF_4 0.8 mole %. Since the solubility of UF_3 is low, Henry's law may be assumed, so that

$$\log_{10} \gamma_{UF_3} = -\log_{10} x^{sat}_{UF_3} = -1.62 + 3.77\ (10^3/T)$$

Assuming that ZrF_4 and UF_4 have a comparable influence on solvent properties, the value of Q^R in a solvent of the above composition is calculated from equation 6 to be given by:

$$\log_{10} Q^R = 4.20 - 9.23\ (10^3/T)$$

The free energy change for the hypothetical reduction of UF_4 to give pure UF_3 is given[2] by

$$\Delta F^R_T = 32.7 - 17.6\ (T/1000)\ \text{kcal mole}^{-1}$$

so that $\log_{10} K^R = -\Delta F^R_T/2.30\ RT = 3.96 - 7.16\ (10^3/T)$

hence $\log_{10} (\gamma_{UF_4}/\gamma_{UF_3}) = \log_{10} Q^R - \log_{10} K^R = +0.24 - 2.07\ )10^3/T)$

and $\log_{10} \gamma_{UF_4} = \log_{10} (\gamma_{UF_4}/\gamma_{UF_3}) + \log_{10} \gamma_{UF_3} = -1.38 + 1.70\ (10^3/T)$

Values of $\gamma_{UF_4}/\gamma_{UF_3}$, γ_{UF_3} and γ_{UF_4} at 500 and 700°C are listed in Table 4. Also included in the table are the estimated activity coefficients of UF_4 in a similar solvent containing ~ 1 mole % UF_4,[7] and in a solution containing

~ 25 mole % UF_4. The latter were derived from the solubility of UF_4 in a solvent of the same $LiF:BeF_2$ ratio as the MSRE solvent, the data being obtained from the ternary phase diagram.[8]

Table 4. Activity Coefficients of UF_3 and UF_4 in MSRE Solvent Referred to the Pure Crystalline Solids

Temp. (°C)	$\gamma_{UF_4}/\gamma_{UF_3}$	γ_{UF_3}	γ_{UF_4} Ref. 7 (~1 M % UF_4)	γ_{UF_4} This work (6M% UF_4 + ZrF_4)	γ_{UF_4} Phase diagram (~25 M % UF_4)
500	0.0036	1800	1.1	6.5	9
700	0.013	190	0.6	2.5	2.5

The values of γ_{UF_4} show the anticipated trend with respect to both composition and temperature. Furthermore the small values of the ratio $\gamma_{UF_4}/\gamma_{UF_3}$ confirms the assumption that the small size and high charge of UF_4 would result in UF_3 being less stable in a molten fluoride solvent than in the pure state.

Disproportionation of UF_3

The quotient (Q^D) for the disproportionation of UF_3 is calculated for the MSRE solvent by means of equation 3. Substituting the expressions for $\log_{10} Q^R$ and $\log_{10} \gamma_{UF_4}$ quoted above, and for the free energies of formation of UF_4 and HF:

Substituting ΔF_T^f (UF) = -448.5 + 67.4 T (Reference 9)

and ΔF_T^f (HF) = -65.17 - 1.02 T (from data of Reference 10)

gives $\log Q^D = -0.64 - 0.52\ (10^3/T)$ in MSRE solvent.

For the disproportion of pure UF_3, $\gamma_{UF_4} = 1.0$ and K^R is obtained from

reference 1, giving

$$\log K^D = -0.03 - 3.04\ (10^3/T)$$

The low temperature coefficient for the disproportionation in solution is noteworthy, the negative temperature coefficient of $\log K^D$ being almost balanced by the strong positive coefficient of $\log \gamma_{UF_3}$.

It is of interest to estimate the activity of uranium (a_u) in equilibrium with a solution in which a certain fraction (f) of the initial UF_4 content ($x^o_{UF_4}$) is converted to UF_3:

$$a_u = (Q^D)^4\ x^o_{UF_4} \cdot f^4/(1 - f)^3$$

Calculated values of the uranium activity at 1000°K for an MSRE solution initially containing 1 mole % of UF_4 are listed in Table 5 along with the value for a mixture of pure UF_4 and UF_3. These figures demonstrate the lower stability of UF_3 in solution compared with the pure material; to maintain equal amounts of the two species in solution a uranium activity of $1.1\ 10^{-7}$ is required, compared with 5.10^{-14} for the pure material. Nevertheless UF_3 is still sufficiently stable in solution for almost quantitative (> 99%) conversion of UF_4 to UF_3 to be achieved by the reaction with uranium metal. In addition, fairly high concentrations of UF_3 can be tolerated before UF_3 reacts with graphite, to produce uranium carbide. The activities at 1000°K of uranium in UC_2 and UC, calculated from the free energies of formation[9] are 5.10^{-7} and 3.10^{-5} respectively. Thus 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.

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Table 5. Calculated Activities of Uranium in Equilibrium with MSRE Solvent Initially Containing 1 mole % of UF_4 at 1000°K ($Q^D = 7.10^{-2}$)

Percent conversion of UF_4 to UF_3	99.5	99	95	90	80	50	30	10
Uranium Activity[a]	>1.0	$1.3\ 10^{-1}$	$1.6\ 10^{-3}$	$1.5\ 10^{-4}$	$1.1\ 10^{-5}$	$1.1\ 10^{-7}$	5.10^{-9}	3.10^{-11}

[a] cf a_u for pure UF_4:UF_3 mixture 5.10^{-14}

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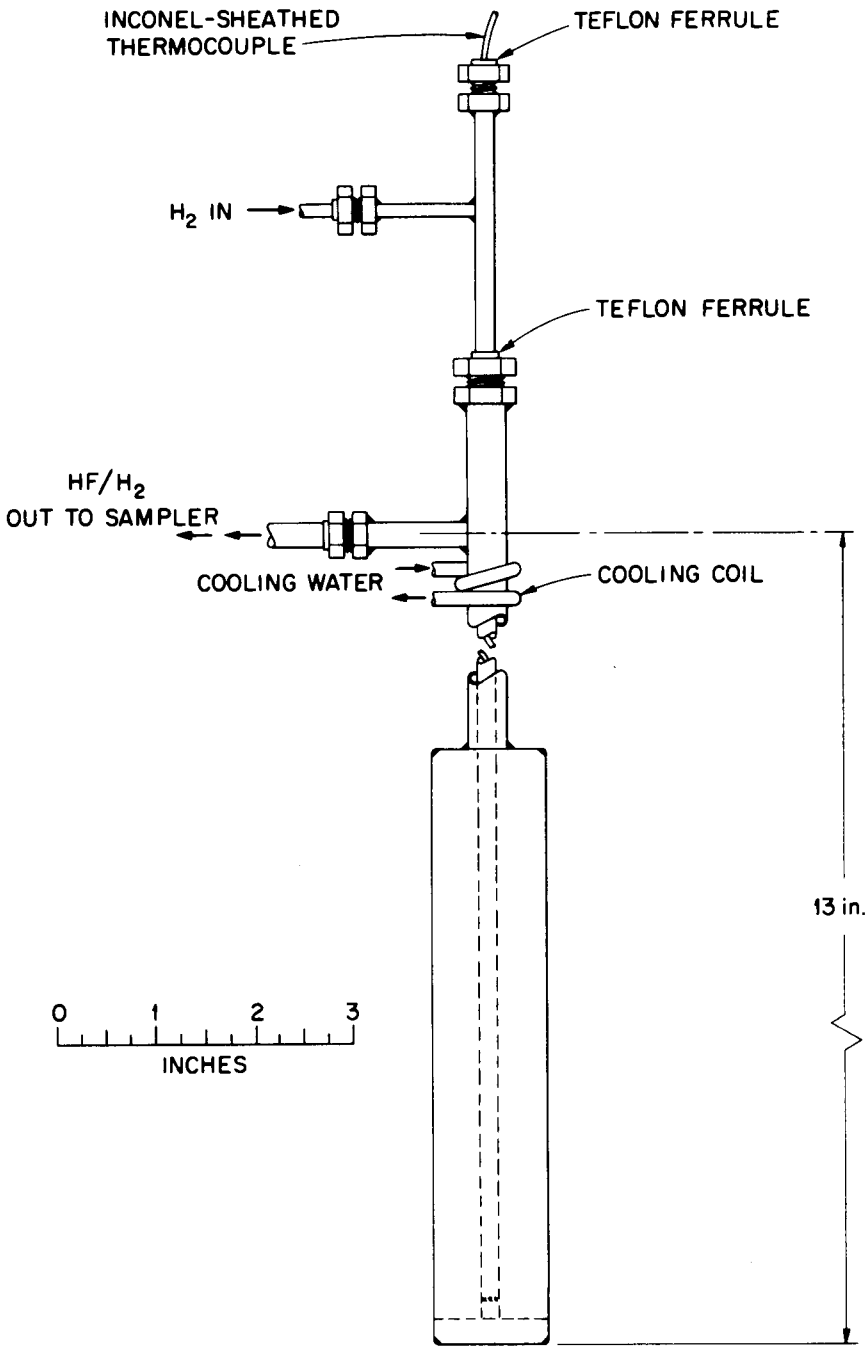

Fig. 1. Reaction vessel for the hydrogen reduction of UF_4 in a molten fluoride solvent.

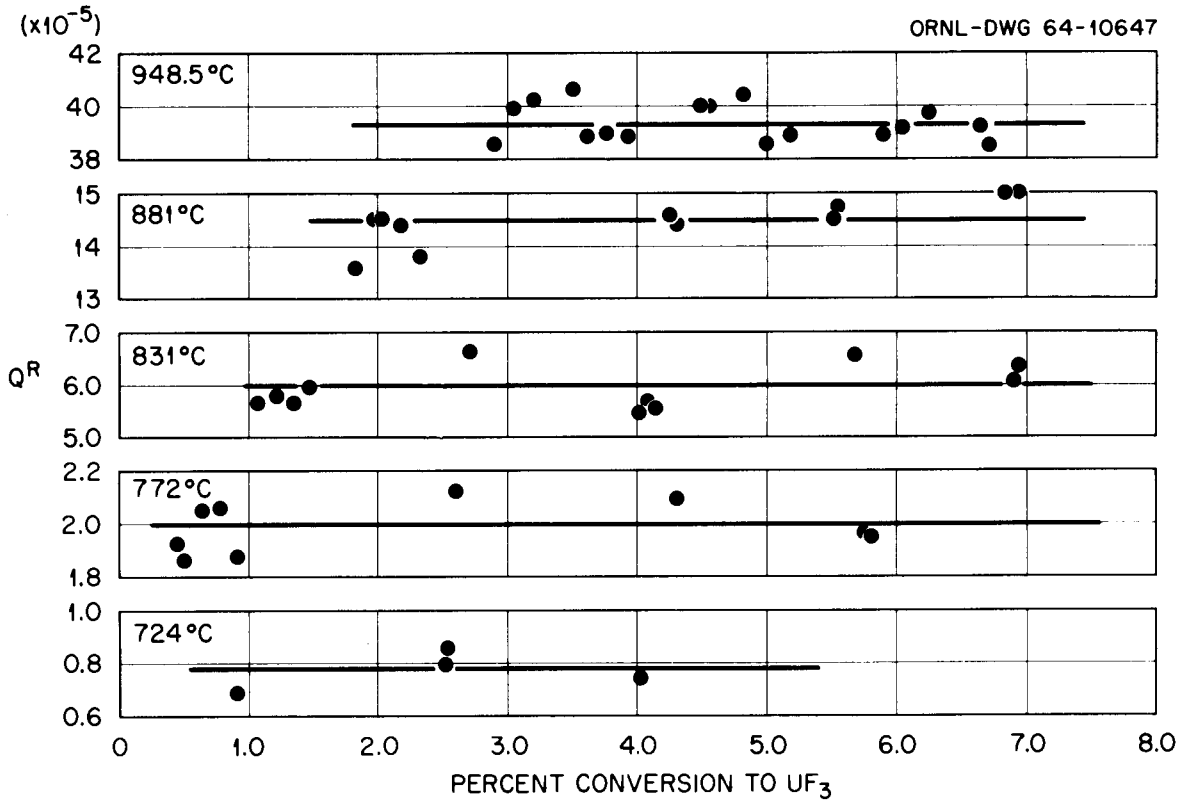

Fig. 2. Plot of equilibrium quotient, Q^R, as a function of percent conversion to UF_3. Experiment 1; LiF: 62.7, BeF_2: 32.3, UF_4: 5.0 mole %.

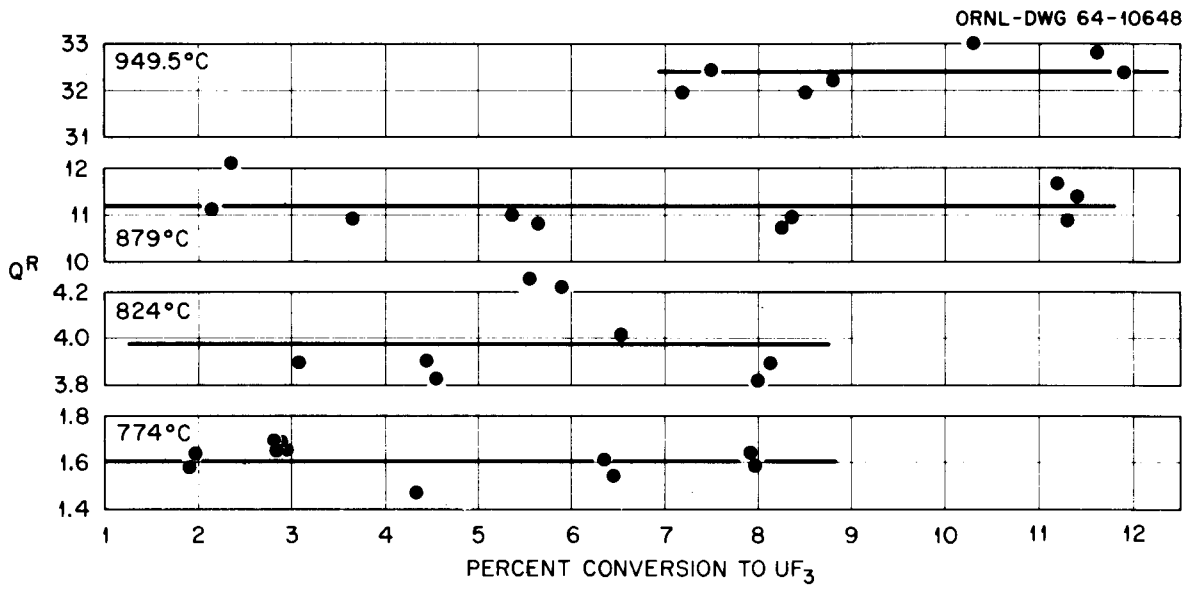

Fig. 3. Plot of equilibrium quotient, Q^R, as a function of percent conversion to UF_3. Experiment 2; LiF: 65.0, BeF_2: 33.4, UF_4: 1.6 mole %.

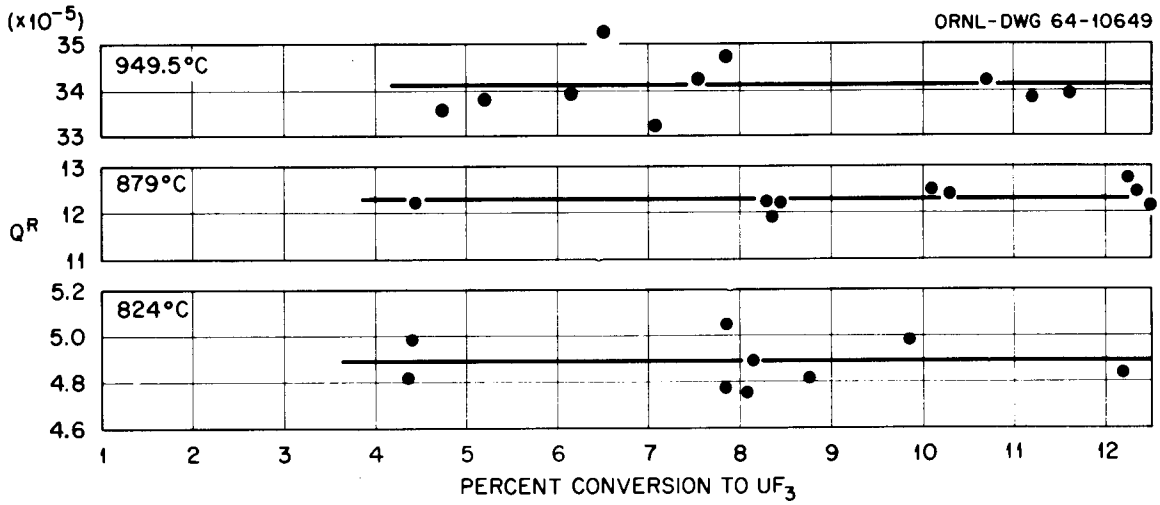

Fig. 4. Plot of equilibrium quotient, Q^R, as a function of percent conversion to UF_3. Experiment 3; LiF: 63.8, BeF_2: 32.8, UF_4: 3.4 mole %.

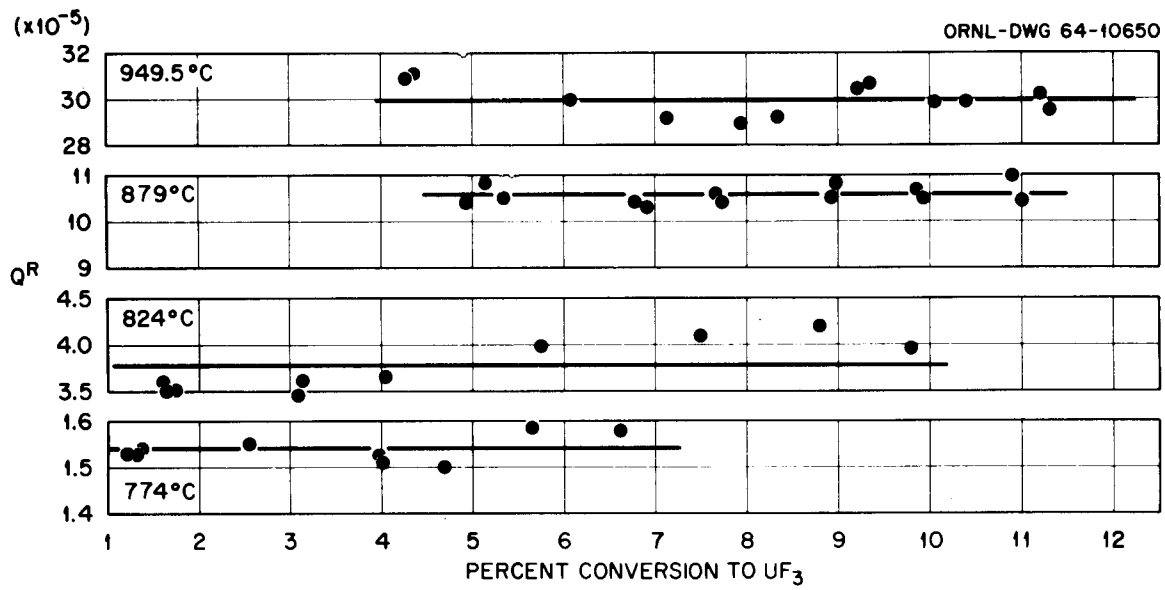

Fig. 5. Plot of equilibrium quotient, Q^R, as a function of percent conversion to UF_3. Experiment 4; LiF: 69.0, BeF_2: 26.0, UF_4: 5.0 mole %.

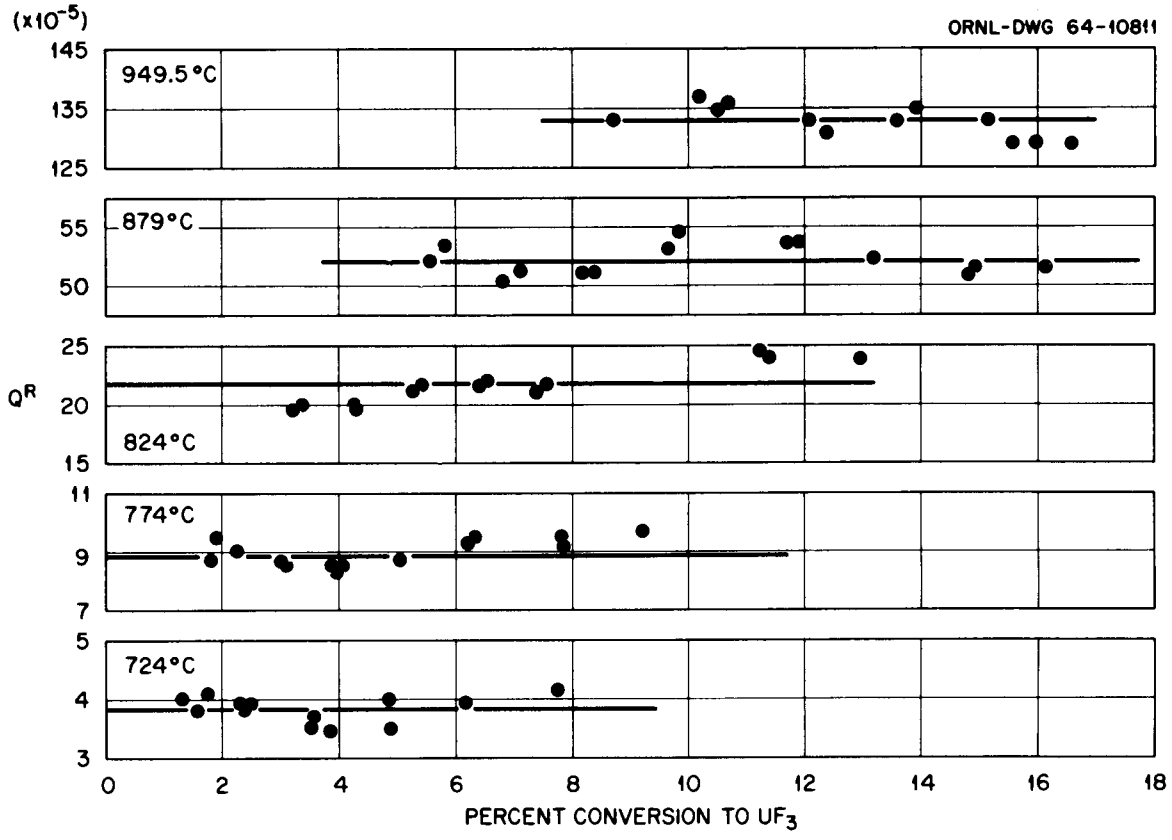

Fig. 6. Plot of equilibrium quotient, Q^R, as a function of percent conversion to UF_3. Experiment 5; LiF: 52.6, BeF_2: 42.4, UF_4: 5.0 mole %.

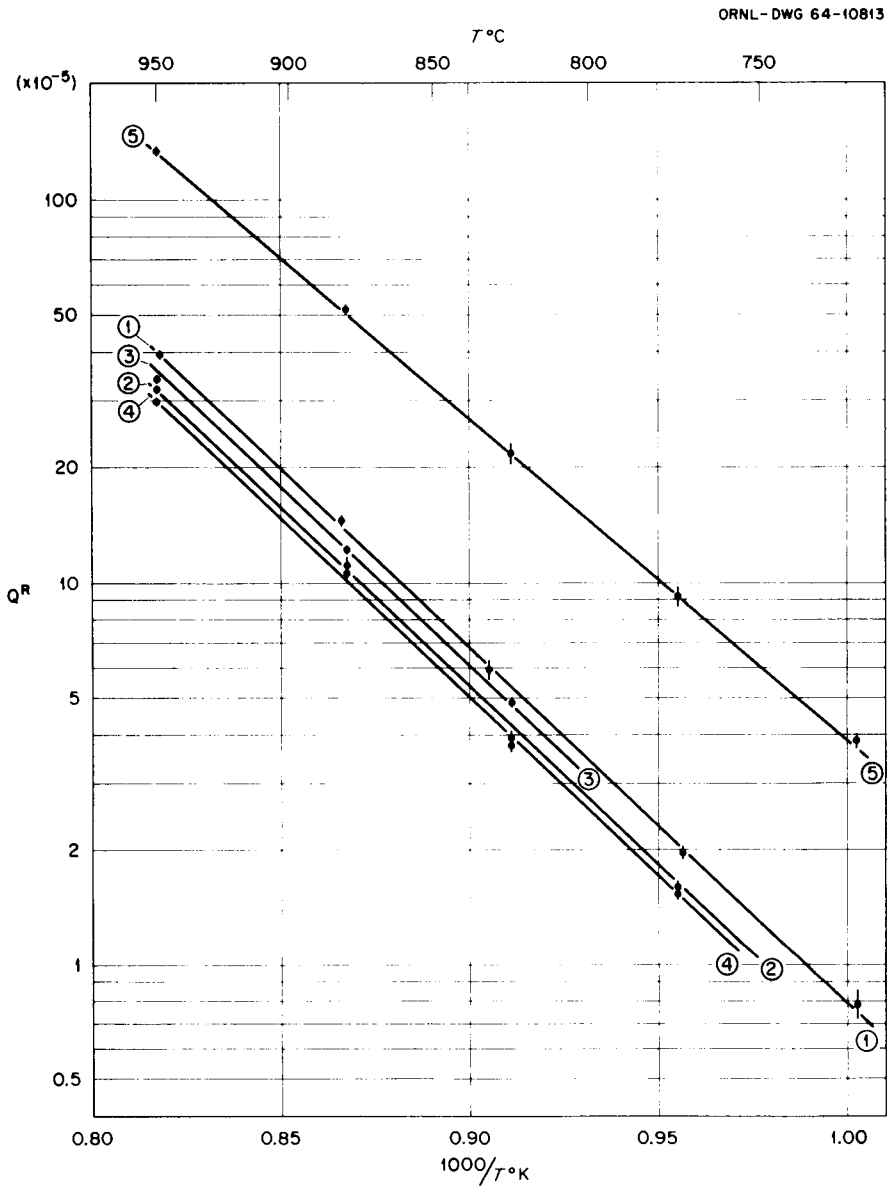

Fig. 7. Plot of $\log_{10} Q^R$ versus $10^3/T^oK$ for the hydrogen reduction of UF_4 in various solutions (plots numbered according to Table 3).

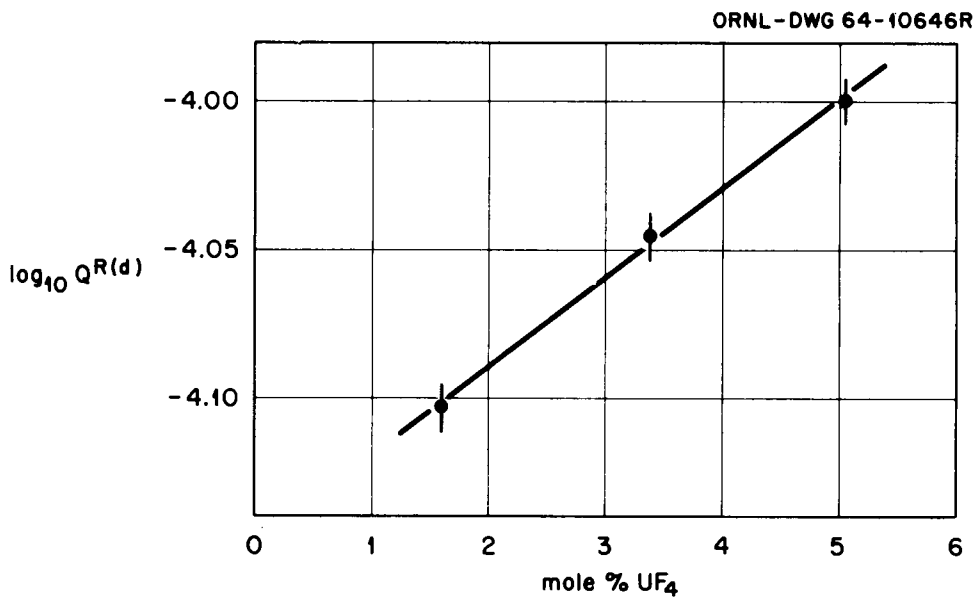

Fig. 8. Effect on Q^R at 860°C of varying the initial UF_4 concentration, with constant solvent composition (66 mole % LiF, 34 mole % BeF_2).

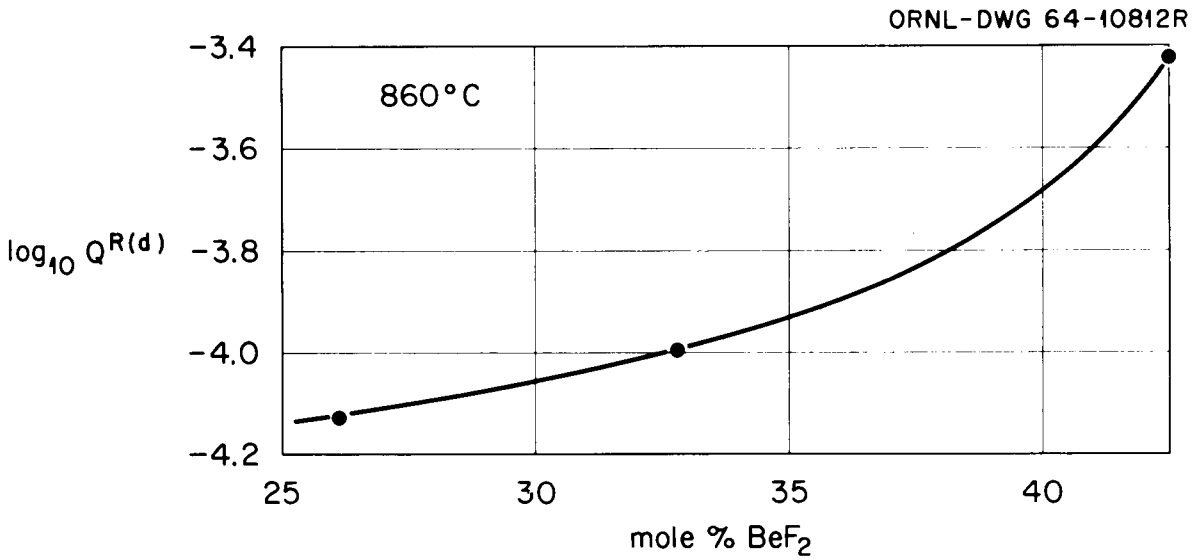

Fig. 9. Effect on Q^R at 860°C of varying the BeF_2 content of the solution, with constant UF_4 concentration (5.0 mole %).

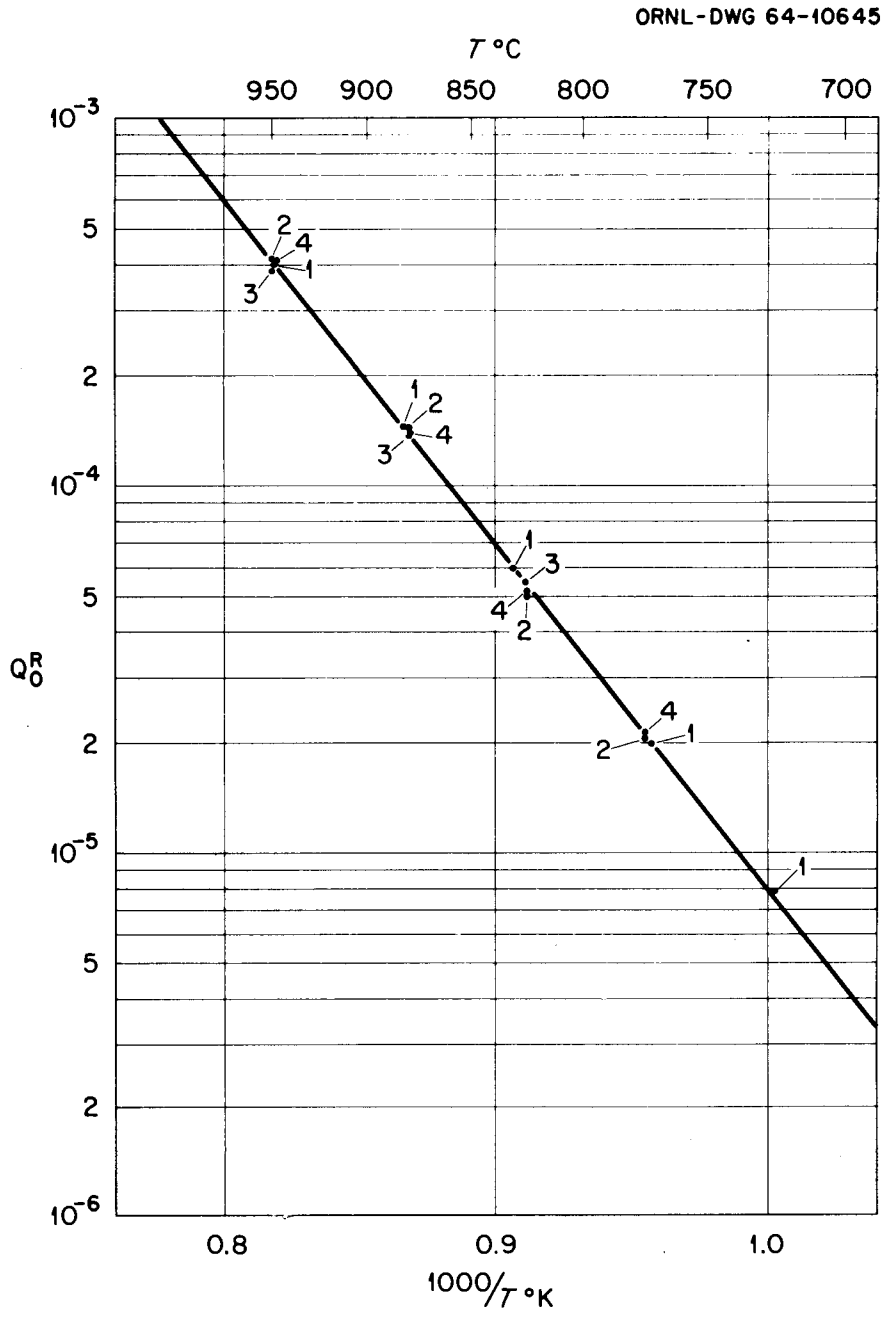

Fig. 10. Plot of $\log_{10} Q_o^R$ versus $10^3/T^oK$.

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