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In a recent publication, the kinetics of the chlorination of uranium tetrachloride in the fused LiCl-KCl eutectic were analyzed by a model based upon diffusion of U(IV) in a falling liquid film with a chemical equilibrium restriction at the interface.¹ The consequences of this model are incorporated in the following expression:[†]

$$\frac{\bar{C}_4}{C_0} = \frac{C_{40}}{C_0} - S \left[\frac{C_{40}}{C_0} - \left(\frac{C_4}{C_0} \right)_{eq} \right] \frac{1}{Q^{2/3}} \quad (1)$$

where the theoretical value of the parameter S is:

$$S = 12.4 \frac{\sqrt{D_1 L} a^{2/3}}{v^{1/6}} \quad (2)$$

Equation (1) predicts that a plot of the outlet U(IV) fraction against $1/Q^{2/3}$ should be a straight line with a slope equal to the parameter S times the driving force for diffusion and an intercept equal to the U(IV) fraction in the feed salt. In Ref. 1, however, the data were analyzed by plotting the dimensionless concentration $\bar{C}^*$ against $1/Q^{2/3}$, which effectively forces $\bar{C}_4/C_0$ to pass through the value C_{40}/C_0 at $1/Q^{2/3}$ equal to zero. If the data are plotted according to Eq. (1), on the other hand, it is found that the intercepts do not in general coincide with the measured value of C_{40}/C_0 ,

[†] Equation (1) is a combination of Eqs. (3) and (4) of Ref. 1. The nomenclature is that employed in Ref. 1.

but range from 0.93 at low temperatures to 1.02 at high temperatures.

The deviations of the intercepts from the predicted value are probably not significant, since the data were obtained in the range $3 < 1/Q^{2/3} < 6$ and extrapolation to $1/Q^{2/3} = 0$ is of dubious validity.

A more reliable interpretation of the data is obtained by focussing on the slopes of plots of $\bar{C}_4/C_0$ versus $1/Q^{2/3}$ in the flow rate range in which the data were obtained. According to Eq. (1), division of the measured slopes by the driving force $[C_{40}/C_0 - (C_4/C_0)_{eq}]$ should yield the geometry and property dependent parameter S, the theoretical value of which is given by Eq. (2). This has been done for the data obtained with pure chlorine reactant gases, taking $C_{40}/C_0 = 0.942$ and $(C_4/C_0)_{eq}$ directly from the equilibrium measurements. The results of this method of data analysis are shown in Fig. 1 and are compared to the theoretical values of S computed from Eq. (2) (these are given in the second column of Table 1 in Ref. 1). For temperatures between 400 and 600°C, the agreement is good; the activation energy of the experimentally determined parameter S is 6.2 kcal/mole, compared to the theoretical value of 5.0 kcal/mole. The absolute values of S are also quite close to those predicted by Eq. (2). This agreement further substantiates the original conclusion that the chlorination of uranium tetrachloride in this system is controlled by U(IV) diffusion in the salt phase, and that the measured equilibrium U(IV) fractions provide the correct driving force for mass transfer.

At 650 and 700°C, however, the experimental values fall considerably below both the theoretical and low temperature lines. In addition to the possible reasons discussed in Ref. 1, this discrepancy may also be due to the fact that the equilibrium U(IV) fractions were not measured at tem-

peratures above 600°C but were estimated by Eq. (2) of Ref. 1, which was based upon low temperature equilibrium measurements. Extrapolation of the equilibrium U(IV) fractions to chlorine partial pressures less than 1 atm. was equally unsuccessful, as evidenced by the deviations of the data for gas mixtures from those of pure chlorine in Fig. 5 of Ref. 1. The inability to extend the equilibrium data beyond the range in which measurements were made suggests that the extrapolation method, which was based upon the assumption that the reaction is that given by Eq. (1) of Ref. 1, is in error.

According to the development in the Appendix of Ref. 1, the preceding analysis of the kinetic results does not require detailed knowledge of the nature of the products involved in the reaction. Even if impurities such as oxygen or water vapor participated as gaseous reactants, the analysis would remain valid. All that is required is that an equilibrium U(IV) concentration be maintained at the gas-liquid surface on the rod, and that this concentration be the same as that measured in the equilibrium experiments. This condition is satisfied if the composition of the gas phase which generates the equilibrium distribution among the different oxidation states of the uranium in solution is the same in both the equilibrium and kinetic measurements. It is of interest, however, to examine the equilibrium data more carefully and attempt to identify the actual reaction.

If chlorine is the only oxidant, the reaction can be written as

or:

The standard state (uranium chlorides as solids) enthalpy and entropy changes are -10.0 kcal/mole and -15.3 eu for the pentachloride and -19.2 kcal/mole and -31.3 eu for the hexachloride.² The difference between the standard state enthalpy and entropy changes and those of the reaction in solution is given by:

$$\Delta H^\circ - \Delta H = \Delta \bar{H}(\text{UCl}_4) - \Delta \bar{H}(\text{UCl}_5 \text{ or } \text{UCl}_6) \quad (5)$$

or:

$$\Delta S^\circ - \Delta S = \Delta \bar{S}^e(\text{UCl}_4) - \Delta \bar{S}^e(\text{UCl}_5 \text{ or } \text{UCl}_6) \quad (6)$$

Although the heats and excess entropies of solution for the uranium chlorides involved in reactions (3) and (4) in the LiCl-KCl eutectic are not known, the dissolution of U(III) has been studied. For the process $\text{UCl}_3(\text{s}) = \text{UCl}_3(\text{sol'n})$, $\Delta \bar{H} = 12.7$ kcal/mole and $\Delta \bar{S}^e = 11.3$ eu in dilute solutions in the LiCl-KCl eutectic.³ Excess functions for dissolution of UCl_4 in the NaCl-KCl eutectic can be estimated from the data reported by Smirnov and Skiba⁴ and Rand and Kubaschewski² as $\Delta \bar{H} = -4.5$ kcal/mole and $\Delta \bar{S}^e = 8.0$ eu.

If the equilibrium data obtained here are assumed to represent reaction (4), Eq. (2) of Ref. 1 shows that the enthalpy of the reaction is 6.4 kcal/mole and the entropy is 6.2 eu. For reaction (3), the corresponding figures are 9.9 kcal/mole and 13.0 eu. The difference between the enthalpies of the reactions in solution and in the standard state is of the order of 25 kcal/mole. According to Eq. (5), this difference should be equal to the difference in the heats of solution of UCl_4 and the UCl_5 or UCl_6 products. This is a sizeable difference to be accounted for by heats of solution, but not impossible, in view of the variable magnitude and sign of the solution enthalpies observed for U(III) and U(IV) in fused salts.

Similarly, the 28 or 37 eu entropy difference between the solution and standard state reactions must equal the difference in the excess entropies of solution of the reactant and product uranium chlorides. Since the excess entropies of solution of both U(III) and U(IV) in fused salts appear to be on the order of 10 eu, differences of 28 or 37 eu can hardly be attributed to solution effects. It appears that the increase in the uranium valency observed in the equilibrium experiments reported here cannot be the result of a simple chlorination reaction. Although UCl_6 may not have accounted for a significant portion of the higher valence uranium in the fused salt, some must have been formed in the equilibrium experiments, since considerable volatilization was observed.

If oxygen impurities were present in the chlorine, uranyl chloride would have been formed by the reaction:

The standard state enthalpy and entropy changes for reaction (7) are -52.5 kcal/mole and -8.9 eu respectively.² In the NaCl-KCl eutectic, the corresponding figures are -52.0 kcal/mole and -15.2 eu.⁴ At 1000°K, the equilibrium constant of reaction (7) is approximately 10^8 and an oxygen impurity level in the feed chlorine of one part in 10^8 would have generated an equilibrium U(IV) fraction of $\frac{1}{2}$, which is typical of that observed in our equilibrium measurements.

However, the kinetic experiment performed at 600°C with a reactant gas consisting of 20% oxygen in HCl gave a slope of the plot of the outlet U(IV) fraction versus $1/Q^{2/3}$ nearly equal to that for pure chlorine at the same temperature. As discussed in Ref. 1, this indicates that the interfacial U(IV) fraction was approximately equal for the two reactant

gases (i.e., $(C_4/C_O)_{eq} \approx 0.6$). However, if reaction (7) were at equilibrium at the interface, an equilibrium constant of 10^8 would have reduced the U(IV) fraction to very close to zero for a gas containing 20% oxygen. Whether this represents a chemical kinetic restriction at the surface is not known, but in any case, the modest oxidation accomplished by the 20% oxygen in HCl gas mixture suggests that small oxygen impurity concentrations in the chlorine feed gas should have a minor effect on the measurements reported here. In addition, reaction (7) is exothermic by 52 kcal/mole, compared to the measured endothermicity of 6.4 kcal/mole obtained from the equilibrium measurements.

Water vapor impurities in the feed chlorine could have produced uranyl chloride by the reaction:

Based on the thermochemical properties of reaction (7) and the known equilibria of the HCl oxidation reaction,⁵ the enthalpy and entropy of reaction (8) in the NaCl-KCl eutectic are -25.0 kcal/mole and 13.9 eu. However, the equilibrium constant of this reaction is so large, that even small quantities of water vapor should have reduced the U(IV) fraction to zero. In addition, the enthalpy of reaction (8) differs from that observed in the equilibrium experiments by 31 kcal/mole.

None of the reactions discussed above satisfactorily account for the observed equilibrium. The simple chlorination reactions predict far different reaction entropies. The reactions involving water or oxygen are considerably more exothermic than the observed reaction, and also predict complete conversion of U(IV) to U(VI) at even trace concentrations. The observed thermochemical constants of the reaction may

represent a mixture of chlorination and oxidation reactions. A detailed study of the $U(IV) \rightleftharpoons U(VI)$ equilibrium in fused salt solutions, including the effects of oxygen and water, is required before the precise nature of the reaction can be determined.

Despite the uncertainty concerning the nature of the reaction, the kinetic data of Fig. 1 indicate that the reaction of UCl_4 in the fused $LiCl-KCl$ eutectic with chlorine gas is governed by diffusion of UCl_4 in the fused salt and by an equilibrium restriction on the interfacial $U(IV)$ fraction.

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Fig. 1. Comparison of experimental results with diffusion-equilibrium model.

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