NOTATION

g = acceleration due to gravity
r = radius from center of mandrel to center of tube
v = mean velocity in neutral position
ρ = density in neutral position
θ = angle subtended by liquid film at tube center
ϕ = angle subtended with the vertical by mark M at tube center

Subscripts

g = gas phase
l = liquid phase

Superscript

= inverted position

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Uranium Chlorination in Fused Salts

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In a recent publication (*1*), the kinetics of the chlorination of uranium tetrachloride in the fused lithium chloride–potassium chloride 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. The results of this model are incorporated in the following expression:[†]

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

where the theoretical value of the parameter S is

$$S = 12.4\,\frac{\sqrt{D_l L}\,a^{2/3}}{\nu^{1/6}} \tag{2}$$

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 reference *1*, however, the data were analyzed by plotting the dimensionless concentration $\overline{C}^*$ against $1/Q^{2/3}$, which effectively forces $\overline{C}_4/C_0$ to pass through the value C_{40}/C_0 at $1/Q^{2/3}$ equal to zero. If the data are plotted according to Equation (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, 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 focusing on the slopes of plots of $\overline{C}_4/C_0$ vs. $1/Q^{2/3}$ in the flow rate range in which the data were obtained. According to Equation (1), division of the measured slopes by the driving force $[C_{40}/C_0 - (C_4/C_0)_{\text{eq}}]$ should yield the geometry and property dependent parameter S, the theoretical value of which is given by Equation (2). This has been done for the data obtained with pure chlorine reactant gases, taking $C_{40}/C_0 = 0.942$ and $(C_4/C_0)_{\text{eq}}$ directly from the equilibrium measurements. The results of this method of data analysis are shown in Figure 1 and are compared to the theoretical values of S computed from Equation (2) (these are given in the second column of Table 1 in reference *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 Equation (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 reference *1*, this discrepancy may also be due to the fact that the equilibrium U(IV) fractions were not

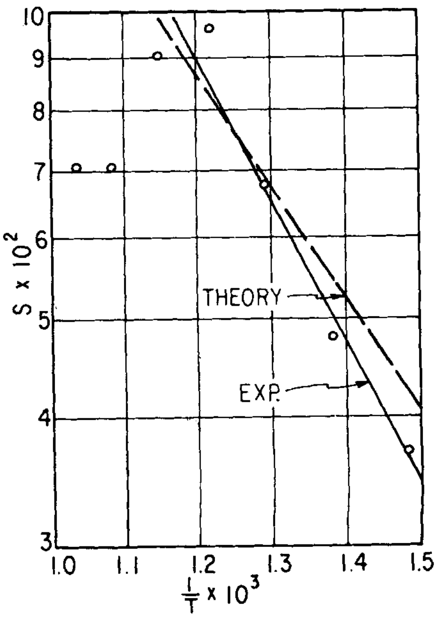

Fig. 1. Comparison of experimental results with diffusion-equilibrium model.

[†] Equation (1) is a combination of Equations (3) and (4) of reference *1*.

measured at temperatures above 600°C. but were estimated by Equation (2) of reference *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 Figure 5 of reference *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 Equation (1) of reference *1*, is in error. This conclusion is substantiated by the observation (for which we are indebted to Leo Brewer) that the measured reaction entropy of 6.2 entropy units (eu) is much larger than the entropy change for the standard state reaction (—31.3 eu). Since the difference of 37.5 eu is far in excess of what would be expected from excess entropies of solution of uranium tetrachloride and uranium hexachloride, it appears that the increase in the uranium valency observed in the equilibrium experiments cannot be attributed to a simple chlorination reaction. Several possible sources of this discrepancy are discussed in reference 2.

According to the development in the Appendix of reference *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.

ACKNOWLEDGMENT

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NOTATION

a = rod radius, cm.
$\bar{C}_4/C_0$ = U(IV) fraction in outlet salt
C_{40}/C_0 = U(IV) fraction in feed salt
$(C_4/C_0)_{eq}$ = U(IV) fraction in salt at equilibrium
$\bar{C}^*$ = $[(\bar{C}_4/C_0) - (C_4/C_0)_{eq}]/[(C_{40}/C_0) - (C_4/C_0)_{eq}]$
D_l = diffusivity of U(IV) in salt, sq.cm./sec.
L = length of rod, cm.
Q = salt flow rate down rod, cc./sec.
ν = kinematic viscosity of salt, sq.cm./sec.

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A Modified Redlich-Kwong Equation for Helium from 30° to 1,473° K.

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The original Redlich-Kwong equation is modified for helium by setting $B = 0.06372\ T_c/P_cT$ for $30° \lesssim T \lesssim 1.473°K$. This modified equation represents the compressibility factors of each of seventy-six isotherms tested in this temperature range to less than 1% average deviation.

Numerous investigators (*3, 11, 14 to 16, 20, 21, 23* to *25*) have used the virial equation of state to represent the experimental compressibility factors for helium. Mann (*12*) used a seventeen-constant, modified Benedict-Webb-Rubin equation. McCarty and Stewart (*13*) developed a six-constant equation explicit in volume. Dodge (*4*) used special reduced conditions for fitting the helium data on a generalized compressibility chart. Redlich (*18*) suggested the use of the pseudocritical values, $T_c = 12.2°K.$ and $P_c = 7.8$ atm., in conjunction with a recent work (*17*).

The original Redlich-Kwong (*19*) equation of state is

$$P = RT/(V - b) - a/T^{1/2}V(V + b) \quad (1)$$

or

$$Z = 1/(1 - h) - (A^2/B)h/(1 + h) \quad (2)$$

where

$$Z = PV/RT \quad (3)$$

$$A^2 = a/R^2T^{2.5} = 0.4278\ T_c^{2.5}/P_cT^{2.5} \quad (4)$$

$$B = b/RT = 0.0867\ T_c/P_cT \quad (5)$$

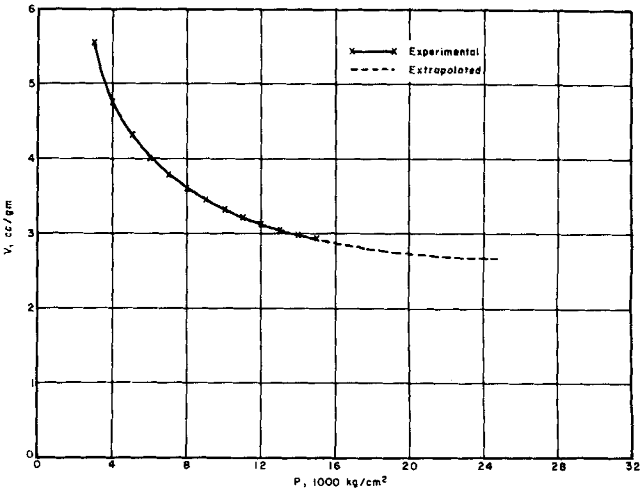

Fig. 1. Bridgman's (*1*) data extrapolated to constant volume.

$$h = b/V = BP/Z \quad (6)$$

In this investigation the experimental critical values of helium, that is, $T_c = 5.2°K.$, $P_c = 2.26$ atm., were used.

This paper concerns the adjustment of the coefficient 0.0867 in Equation (5) to produce good agreement be-