

# Reaction of Chlorine and Uranium Tetrachloride in the Fused Lithium Chloride-Potassium Chloride Eutectic

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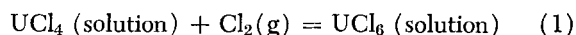
The rates of the reaction of chlorine gas with uranium tetrachloride dissolved in the lithium chloride-potassium chloride eutectic have been studied in a wetted-rod contactor. The reaction was studied at temperatures from 400° to 700°C., uranium tetrachloride concentrations of 1 to 3 wt. %, and chlorine partial pressures of 0.25 to 1 atm. The production of uranium hexachloride appears to be limited by the equilibrium of the reaction  $UCl_4$  (solution) +  $Cl_2$  (g) =  $UCl_6$  (solution) at the interface and by  $U^{+4}$  diffusion in the liquid phase.

High-temperature nonaqueous reprocessing of spent fuel from nuclear reactors has received considerable attention in recent years, and in some instances can compete favorably with the standard aqueous methods. In a typical volatility process, separation of uranium and plutonium from fission products and cladding materials is effected by producing the volatile hexahalide of the heavy elements by contact with the halogen gas. The halides of the fission product metals are generally not appreciably volatile and remain behind (8).

While considerable thermochemical information on high-temperature metal-halogen systems has been accumulated, very little is known about the kinetics of these reactions in fused salts. The overall rate of conversion of a lower to a higher halide depends upon the interaction of the appropriate chemical and physical equilibria and the diffusional and chemical rates. The only pertinent work in this area is the fluoride volatility study by workers at the Argonne National Laboratory (5) in which a uranium tetrafluoride-sodium fluoride-zirconium tetrafluoride melt was sprayed into a quiescent atmosphere of fluorine gas. Two possible rate controlling steps were considered: the diffusion of uranium tetrafluoride in the fused salt to the interface, and transfer by diffusion-convection of the product uranium hexafluoride from the interface to the bulk gas phase. Both of these mechanisms predicted essentially complete removal of uranium from the salt, but the observed removal never exceeded 30%. It was concluded that the rate was limited by chemical kinetics.

The fluoride volatility reaction is the most interesting from an application standpoint, but the corrosion and toxicity problems require elaborate safety precautions. Consequently, the analogous chlorine system was chosen since chlorine is somewhat more manageable than fluorine.

The purpose of this study was to investigate the diffusional and chemical rate phenomenon associated with the reaction:



The reaction was carried out between gaseous chlorine and uranium tetrachloride dissolved in the fused eutectic lithium chloride-potassium chloride mixture (59 mole % lithium chloride). The eutectic melts at 350°C. and experiments were carried out in the range of 400° to 700°C. At these temperatures the pure hexachloride is volatile and, depending upon the conditions of the reaction, may appear either as a gaseous or a dissolved species.

## EQUILIBRIUM STUDIES

To assist in interpreting the kinetic data, the solubility of chlorine in the fused salt eutectic at 400° and 500°C. was measured by the technique developed at Oak Ridge (1). Chlorine was sparged into a stainless steel tank containing 500 cc. of the molten salt for 1 to 4 hr., after which some of the saturated solution was transferred to a stripping tank through a freeze valve. Dissolved chlorine was removed from the melt in the second tank by sparging with argon and absorbed in a sodium hydroxide solution for analysis. No measurable quantity of chlorine could be detected; hence the solubility of atmospheric pressure chlorine in the lithium chloride-potassium chloride eutectic at 400° or 500°C. is less than  $4 \times 10^{-9}$  g.-mole/cc., which is the limit of detectability of the analytical technique. This result indicates that the chlorination reaction must take place at the gas-liquid interface, since neither reactant is soluble in the other phase.

The equilibrium of reaction (1) was studied by sparging pure chlorine gas into a fused salt melt containing 2

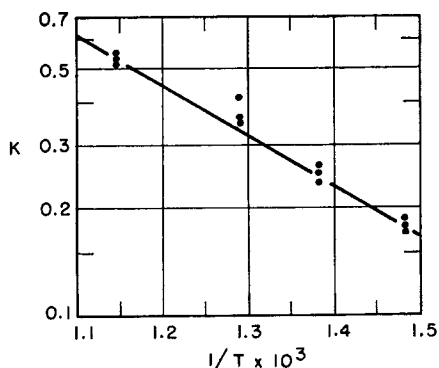


Fig. 1. Equilibrium constant of reaction (1), measured with pure chlorine in 2 wt. % uranium tetrachloride solution. Uranium pentachloride production is neglected.

wt. % uranium tetrachloride. Approximately 50 cc. of the melt was held in a Pyrex test tube in a resistance furnace. The mixture was sampled periodically by dipping a small glass cup into the melt and allowing the liquid to freeze under the chlorine atmosphere.

Three samples at each temperature were taken for spargings which lasted approximately 1 hr. Some volatilization of uranium was noted: at 400°C. the total uranium content decreased by ~30% during an hour; at 600°C. over 50% of the uranium was volatilized. However, while the removal of uranium was a relatively slow process, the fraction of the uranium present as  $U^{+4}$  appeared to equilibrate with greater speed. All the samples taken at a particular temperature showed the same  $U^{+4}$  fraction (usually to within 1%) and permitted determination of the equilibrium constant of reaction (1) by the method outlined in the Appendix. The results shown in Figure 1 can be expressed by

$$\ln K = 3.11 - 3,250/T \quad (2)$$

The reaction is endothermic, with a heat of 6.4 kcal./mole, and does not go to completion: at 400°C. equilibrium  $U^{+4}$  fraction is 0.800, while at 600°C. it is 0.612. Details of the analytical technique are given in the Appendix. Production of uranium pentachloride was not considered in the interpretation of the equilibrium measurements.

#### TESTING OF THE WETTED-ROD CONTACTOR

The primary criterion in selecting a contacting device in which to study the kinetics of reaction (1) was knowledge of the hydrodynamics of the gas and liquid phases. If the velocity distributions in both phases are known, the associated diffusion problems can be solved. Diffusional resistances can be theoretically extracted from overall rate measurements, and any chemical kinetic limitation can be uncovered.

The device had to be simple and resistant to the corrosive effects of molten salts. It is difficult to use valves and transfer lines with fused salts because valve packing is rapidly attacked and transfer lines are susceptible to freezing. A laminar jet device was attempted first, but because of the high surface tension of the salt (~100 dynes/cm.), a jet could not be formed. A wetted-wall column was discarded because of the relatively large quantities of liquid required and the mechanical intricacies of the feed and outlet systems. The system could not be constructed of metal, because the extremely corrosive nature of hot chlorine and fused salt saturated with hydrochloric acid (required to stabilize  $U^{+4}$  in solution) caused rapid attack of even nickel.

Consequently, an all-quartz wetted-rod contactor of the type depicted in Figure 2 was chosen. The apparatus

consists of an upper chamber into which the salt is charged, a lower chamber in which the melt is contacted with chlorine, and a collector at the bottom. The central rod is provided with a tapered ground fitting to effect a gas and liquid seal between the two chambers. Raising the rod slightly allows the salt to flow smoothly down the rod. The end of the 3-mm. diameter rod terminates in a section of a funnel with a 3.5-mm. I.D. stem. It was found by trial and error that a 0.25-mm. annulus was sufficient to maintain a liquid level at the top of the stem and thus provide a gas seal between the chlorine section and the collecting section. The outlet stem was bathed in hydrogen chloride gas to prevent oxidation of the  $U^{+4}$  by contact with air.

Visual examination of the flow of both water and the fused salt down the rod showed that a smooth, thin film could be obtained on a clean rod. No rippling was observed, but periodically a disturbance was initiated about half way down and would quickly move to the bottom. To insure that the flow pattern on the rod was that of a falling liquid film in laminar flow and to assess the effect of the disturbance noted, the system was tested by absorbing carbon dioxide into water.

The theory of liquid phase transfer in a wetted-rod device is identical to that developed for wetted-wall columns (4). The average outlet concentration is related to the geometry of the system and the flow rate by

$$\bar{C}^* = \frac{\bar{C} - C_i}{C_0 - C_i} = 1 - [3^{1/3} 2^{7/6} \pi^{1/6} g^{1/6}] \frac{\sqrt{D_i L} a^{2/3}}{v^{1/6} Q^{2/3}} \quad (3)$$

This relation requires an interfacial concentration  $C_i$  which is constant along the length of the rod. It further assumes a diffusion rate sufficiently slow to permit the film to be approximated by a medium of infinite depth moving at the surface velocity. This assumption is invoked in nearly all falling film studies; its validity has been examined by Emmert and Pigford (4). Since the film thickness is small compared to the rod diameter, the cylindrical surface has been approximated by a flat plane, to which Equation (3) applies.

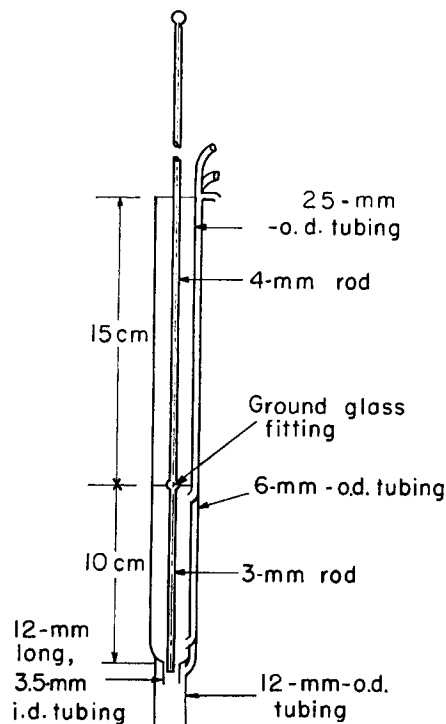


Fig. 2. Quartz wetted-rod contactor.

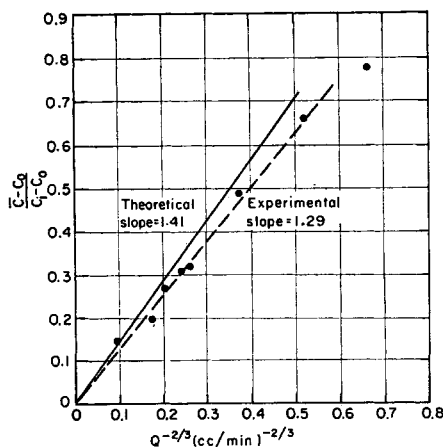


Fig. 3. Carbon dioxide desorption in wetted-rod contactor, 25°C.

Carbon dioxide in the lower chamber was absorbed by water flowing down the rod from the upper chamber. Samples were taken with a hypodermic syringe inserted in the outlet tube, to prevent desorption of carbon dioxide to the air. Flow rates were measured by timing the effluent rate. The results are shown in Figure 3. The theoretical slope from Equation (3) is 1.41. The experimental slope is 1.29, or 8.5% below theoretical. This discrepancy is probably due to a stagnant film near the bottom end of the rod which reduces the effective length of the rod. This effect has been noted previously in wetted-wall columns, and generally results in a reduction of a few centimeters in the length of contact (9). The deviation of the point at 79% saturation is probably due to the failure of the infinite depth approximation inherent in Equation (3) (3, 4). The results demonstrate that the falling film model applies as well to the wetted rod as to the wetted-wall column, and that the small amount of rippling observed does not significantly affect the mass transfer.

Because of the insolubility of chlorine in the fused salt and the low partial pressure of uranium tetrachloride, reaction (1) occurs only at the salt-gas interface. The interfacial concentration  $C_i$  of Equation (3) can be replaced by the equilibrium  $U^{+4}$  concentration if the following restrictions are satisfied: (1) the diffusivities of  $U^{+4}$  and  $U^{+6}$  in the liquid are equal; (2) the product uranium hexachloride remains in the liquid phase; (3) gas phase resistance to mass transfer is negligible; and (4) the reaction attains equilibrium at the interface. Assumptions 1 and 2 are sufficient to insure that the total uranium concentration is everywhere equal to its initial value (3). Since by assumption 3 the interfacial partial pressure of chlorine is equal to its known bulk value, the interfacial concentration of  $U^{+4}$  is constant along the length of the rod and can be computed from the equilibrium constant of reaction (1). The dimensionless concentration variable in Equation (3) can then be written as

$$\bar{C}^* = \frac{\bar{C}_4 - C_{4eq}}{C_{40} - C_{4eq}} = \frac{\bar{C}_4/C_0 - (C_4/C_0)_{eq}}{C_{40}/C_0 - (C_4/C_0)_{eq}} \quad (4)$$

Experimental verification of assumptions 2 and 3 will be discussed later. The method of obtaining the variable  $\bar{C}^*$  from the measured  $U^{+4}$  fractions is discussed in the Appendix.

#### GAS PHASE RESISTANCE

In the preceding development, the gas phase resistance was assumed negligible in comparison to the liquid phase resistance. While this assumption cannot be assessed for the general case, the liquid and gas phase resistances can

be compared for a rapid, irreversible surface reaction. In this case, either the liquid or gas phase concentration must be zero at the interface, since the two reactants cannot coexist. We will compute the average transfer rates of uranium tetrachloride from a bulk concentration of  $C_4$  to a zero interfacial concentration and that of chlorine from a partial pressure of  $p$  to zero interfacial partial pressure. The component which exhibits the slowest transfer rate will be depleted at the surface and constitute the rate controlling step.

The length-average molar flux of uranium tetrachloride from the liquid to the surface under a constant driving force ( $C_4 - 0$ ) is:

$$\bar{N}_l = \frac{2}{\sqrt{\pi}} \left( \frac{D_l u_s}{L} \right)^{1/2} C_4 \quad (5)$$

In reference 3 the gas phase hydrodynamic and diffusion equations have been solved by the momentum integral method for the case of a moving rod whose radius is much greater than the gas phase boundary-layer thickness (that is, a moving plane). The length-average molar flux of chlorine from the gas phase to the surface under a constant driving force ( $p - 0$ ) is:

$$\bar{N}_g = 0.843 N_{Sc}^{1/8} \left( \frac{u_s D_g}{L} \right)^{1/2} \frac{p}{RT} \quad (6)$$

For a gas phase Schmidt number of unity, the ratio of these maximum driving force transfer rates is

$$\frac{\bar{N}_g}{\bar{N}_l} = \frac{0.75}{RT} \left( \frac{D_g}{D_l} \right)^{1/2} \left( \frac{p}{C_4} \right) \quad (7)$$

The following are typical of our experiments: a 2 wt. % solution of uranium tetrachloride in the fused lithium chloride-potassium chloride eutectic and a 50% chlorine-argon gas phase at 600°C.;  $D_l \approx 1.7 \times 10^{-5}$  sq.cm./sec.,  $D_g \approx 0.47$  sq.cm./sec. With these figures, the ratio of Equation (7) is 10, which indicates that the gas phase contributes ~10% to the overall resistance and the reaction is liquid phase diffusion controlled.

#### EXPERIMENTAL PROCEDURE

The quartz rod was cleaned with hot chromic acid followed by soaking in molten salt for 15 min. With the rod in place, a small amount of molten salt was poured into the upper chamber of the contactor (Figure 2) and was allowed to run down the rod. The rod was quickly lifted out of the chamber to ascertain that complete wetting was occurring. This could be verified by noting that the adhering salt froze uniformly over the rod. The rod was inserted and 50 cc. of the molten salt were poured into the upper chamber. With the rod seated in its ground joint, no leakage of the salt to the lower chamber occurred. The molten salt was purified by bubbling with anhydrous hydrogen chloride gas for 15 min. This method of purification of the lithium chloride-potassium chloride eutectic is similar to that employed by Gruen and McBeth (7). Sufficient solid uranium tetrachloride salt was added to give a ~2 wt. % solution. After ~10 additional min. of sparging with hydrogen chloride, all of the uranium tetrachloride had dissolved, forming a clean dark-green solution with no sediment.

Hydrogen chloride flow to the collector outlet tube and the inner chamber was begun. The rod was raised slightly and a blank sample collected for analysis. The blank runs analyzed 94%  $U^{+4}$  in all cases, indicating that no detectable oxidation of the  $U^{+4}$  by oxygen or water vapor contaminants in the hydrogen chloride had occurred. The 6% of  $U^{+6}$  was probably due to uranyl chloride present in the as-received salt, which analyzed 92%  $U^{+4}$ . All gases were dried by passing through 1 liter of calcium sulfate at flow rate less than 0.1 cu. ft./hr. The resulting contact time of >20 min. was sufficient to reduce the water content of the gases to a point which did not sensibly affect the uranium in the fused salt. Gruen and McBeth (7)

have noted that even traces of water vapor produce a purple uranium oxide precipitate.

After the blank had been collected the rod was resealed and the chlorine flow to the lower chamber initiated. After ~1 min. the rod was raised slightly and adjusted to a reasonable flow rate (10 to 12 cc./min.). As the salt level in the upper chamber fell, the flow rate decreased. At the end of the run, which lasted about 5 min., the flow rate was ~3 cc./min. The flow rate decreased in an exponential manner with a half life of approximately 150 sec. According to the theory of a falling liquid film, the surface velocity of the liquid was approximately 8 cm./sec. at the beginning of the experiment and 4 cm./sec. at the end. The maximum contact time between the liquid and the reactant gas is approximately 2 sec. Since this figure is two orders of magnitude smaller than the decay half life of the flow rate, the assumption of quasi steady state transfer is valid despite the variation of the flow rate during an experiment.

In the interim, five samples of the outlet salt were collected in 1-cc. glass cups. The time required to fill the cup was measured to give the flow rate. The cup was immediately inserted into a flask containing an aqueous hydrogen chloride solution for dissolution and analysis by the method outlined in the Appendix.

Temperatures were varied from 400° to 700°C. The temperature in the lower chamber was within 10°C. of the desired temperature over the entire length of the rod.† Most experiments were conducted in pure chlorine and 2 wt. % uranium tetrachloride in the feed solution. At 600°C., however, runs at 1 and 3 wt. % were conducted in a pure chlorine atmosphere, and at 2 wt. % uranium tetrachloride, gas phases of 50% chlorine-argon, 25% chlorine-argon, and 50% chlorine-helium were investigated.

## RESULTS

The data obtained at 600°C. are shown in Figures 4 and 5 in which  $\bar{C}^*$  of Equation (4) is plotted against  $1/Q^{2/3}$ , as suggested by Equation (3). The scatter of the data is primarily due to the necessity of measuring the three  $C_4/C_0$  ratios (each of which consists of two analyses) required for each  $\bar{C}^*$ . Figure 4 indicates that there is no significant difference in the extent of conversion, as measured by  $\bar{C}^*$ , when the uranium tetrachloride concentration is varied by a factor of three. This is in accord with the assumption inherent in the analysis that the overall rate is diffusion controlled and that  $\bar{C}^*$  of Equation (4) is the appropriate concentration variable. The apparent curvature exhibited by the points in Figure 4 is believed to be due to scatter of the data, since similar plots for the six other temperatures studied showed no constant curvature.

Figure 5 shows the effect of diluting the chlorine with inert gases. According to the theory, the variation of  $\bar{C}^*$

† Temperature profiles in the lower chamber at a particular furnace power level were measured with argon flowing and the central rod removed.

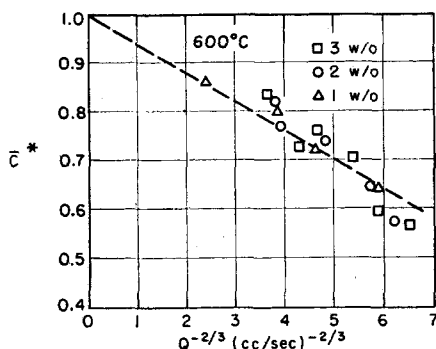


Fig. 4. Uranium tetrachloride chlorination in wetted-rod contactor, pure chlorine, 600°C.

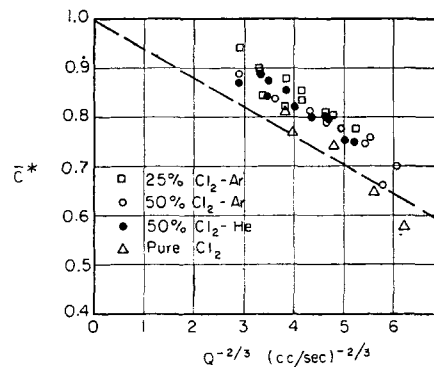


Fig. 5. Effect of chlorine partial pressure on uranium tetrachloride chlorination, 600°C., 2 wt. % uranium tetrachloride.

with  $Q$  should be independent of chlorine partial pressure, the effect of which is embedded in the ratio  $(C_4/C_0)_{eq}$ . The results for 25 and 50% diluent chlorine mixtures are indistinguishable but lie above the line of Figure 4 for pure chlorine. The measurements at reduced chlorine partial pressures are not as firm a basis as those in pure chlorine, since only for the latter was the equilibrium  $U^{+4}$  fraction measured. As shown in the Appendix the equilibrium  $U^{+4}$  fraction for the gas mixtures can be estimated from the equilibrium data for pure chlorine if the fraction of  $U^{+5}$  is known. The ordinates of Figure 5 for the gas mixtures were based upon the assumption that all product is  $U^{+6}$ . If the product had been assumed to be all  $U^{+5}$ , Table 2 in the Appendix shows that the equilibrium  $U^{+4}$  fractions are reduced. This would have the effect in Figure 5 of raising all of the points for the gas mixture, thus increasing the discrepancy with the pure chlorine results.

The calculation which indicated a negligible gas phase resistance is verified indirectly by the agreement between the results shown in Figure 5 at  $p = 0.5$  atm. in helium and argon diluents. If the gas phase resistance were important, the diffusion coefficient of chlorine in the carrier gas should have affected the overall conversion. The diffusivity of chlorine in helium is roughly three times that in argon. Even though the gas phase mass transfer coefficient depends upon the square root of the diffusion coefficient, the effect would have been noticeable if gas phase resistance were significant.

In all kinetic experiments the total uranium concentration of the outlet liquid remained constant, indicating that no volatilization of higher uranium chlorides occurred. This seems somewhat unexpected at first, since the very name volatility process implies removal of gaseous uranium halides. However, volatilization is assured only if the entire bulk liquid phase contains an equilibrium ratio of  $U^{+4}$  to  $U^{+6}$ . When, as in our experiments, the liquid phase is only partially saturated with  $U^{+6}$ , the disposition of the  $U^{+6}$  depends upon the gas and liquid phase resistances and Henry's law constant of the volatile species. By assuming both physical and chemical equilibrium at the interface, the experimental observation of no uranium loss from the solution permits an estimate of the Henry's law constant for uranium hexachloride in the fused salt. According to the assumption of chemical equilibrium at the interface, the  $U^{+4}$  fraction at the surface is a function of the chlorine partial pressure only, and is thus independent of position down the rod. If the diffusivities of  $U^{+4}$  and  $U^{+6}$  are equal, and if no uranium volatilizes, the total uranium concentration is independent of both axial and radial location in the liquid film. These two requirements imply that  $U^{+6}$  concentration at the surface is also independent of distance down the rod. The  $U^{+6}$

transfers from the interface (where it is created) to the bulk of the gas and liquid phases by length-independent driving forces, and the transfer rates can be described by relations applicable to simple mass transfer. The average rate of uranium hexachloride transfer to the liquid is given in Equation (5) with  $C_4$  replaced by  $C_{6eq}$ , which denotes the constant uranium hexachloride concentration at the interface. The rate at which uranium hexachloride transfers to the gas phase is given by Equation (6), with  $p$  now designating the equilibrium partial pressure generated by a liquid phase concentration of  $C_{6eq}$ . The ratio of uranium hexachloride transferred to the gas and liquid phases is given by Equation (7), in which the ratio  $(p/C_4)$  is now the Henry's law constant of uranium hexachloride in the salt. The limit of detectability of uranium loss from solution is  $\sim 1\%$  or  $\bar{N}_g/\bar{N}_l \leq 0.01$ . By assuming the diffusivity of uranium hexachloride in chlorine to be  $\sim 1/4$  of that of argon in chlorine, the maximum value of the Henry's law constant is  $\sim 6 \times 10^{-3}$  atm./ (mole/liter), or on a mole fraction basis, 0.2 atm. By extrapolation of the low-temperature data in references 11 or 12, the vapor pressure of uranium hexachloride at 600°C. is between 10 and 500 atm. The maximum activity coefficient of  $U^{+6}$  in the melt is between  $2 \times 10^{-2}$  and  $4 \times 10^{-4}$ , which is reasonable in view of the considerable complexing of uranium by chloride ions (6).

Equation (3) permits the data to be compared directly to the theoretical predictions. The coefficient of  $1/Q^{2/3}$  in Equation (3) is a function of the transport properties of the melt and the geometry of the rod. The diffusivity of  $U^{+4}$  in the lithium chloride-potassium chloride eutectic has been measured by Thalmeyer et al. (13) and the density and viscosity data are also available (10, 2). Typical values at 400°C. are  $D_l = 0.49 \times 10^{-5}$  sq.cm./sec.,  $\rho = 1.67$  g./cc., and  $\mu = 4.7$  centipoise. The rod radius  $a = 0.15$  cm. and the length  $L = 9.2$  cm. A comparison of the slopes of the lines such as that in Figure 4 with the coefficient of  $1/Q^{2/3}$  in Equation (3) is presented in Table 1.

The agreement is satisfactory at low temperatures, where the experimental slopes are somewhat greater than theory. At higher temperatures, however, the experimental slopes are considerably smaller than the theoretical values. Whereas the experimental slopes are nearly temperature independent, the theoretical slopes exhibit the activation energy of  $\sqrt{D_l/\nu}^{1/6}$ , which is 5.0 kcal./mole. It should be noted that the amount of reaction increased with temperature: at  $Q = 6$  cc./min., the ratio  $\bar{C}_4/C_0$  decreased during reaction from 0.942 to 0.908 at 400°C. and from 0.942 to 0.854 at 700°C. However the equilibrium ratio  $(C_4/C_0)_{eq}$ , which fixes the driving force, also decreased, dropping from 0.800 at 400°C. to 0.535 at 700°C. As a result the dimensionless concentration of Equation (4) was the same at both temperatures. Although the conversion increased with temperature, it did

not increase as rapidly as predicted by the temperature variation of the equilibrium and the transport properties.

## DISCUSSION

Although the data were analyzed with the assumption of chemical equilibrium at the interface, the discrepancies in Table 1 cannot be attributed to a chemical rate restriction at the interface; the deviations became greater as the temperature increased, which would require a negative activation energy for the chemical step.

A more reasonable cause is the inequality of the diffusion coefficients of  $U^{+4}$  and  $U^{+6}$  in the salt. Because of the extensive complexing of uranium ions, which probably occurs in chloride salts (6), the diffusivity of  $U^{+6}$  is probably less than that of  $U^{+4}$ . This would result in a buildup in the total uranium concentration at the interface, and the  $U^{+4}$  concentration at the surface would be larger than if the total uranium concentration remained at the bulk value. With a greater  $U^{+4}$  concentration at the interface, the driving force for diffusion is reduced, and the overall conversion correspondingly less.

Another possible source of the observed deviation is a systematic error introduced by the method of sampling. The samples were collected by placing a small cup at the bottom of the tube surrounding the funnel stem from which the effluent salt dropped. To avoid oxidation, this tube was flushed continually with anhydrous hydrogen chloride. However, if reaction (1) is reversible, some of the uranium hexachloride formed in the reaction section could decompose to uranium tetrachloride and chlorine in the process of drop formation and fall through hydrogen chloride. This effect was noted in the carbon dioxide absorption studies and required sampling by a hypodermic syringe before contact with air. Unfortunately, the high melting point and corrosive nature of the fused salt prevented sampling by this method.

Another possible source of the discrepancies noted in Table 1 and Figure 5 is the contamination of the chlorine gas with oxygen. It is conceivable that traces of oxygen in the reactant gases and not the chlorine were primarily responsible for the increase of the oxidation state of the uranium.

The discrepancies in Figure 5 between the results for pure chlorine and the gas mixtures could be attributed to this cause. If most of the uranium oxidation were due to oxygen, then the basis upon which the equilibrium  $U^{+4}$  fractions were calculated for the gas mixtures is in error; there is no reason to expect that the fraction of oxygen contaminant of the bottle of pure chlorine would be the same as in the bottles of the gas mixtures. Second, the salt solution took on a distinct yellow tinge after long chlorine spargings in the equilibration experiments. This is just the color of uranyl chloride dissolved in the eutectic. Third, Gruen and McBeth (7) have examined the absorption spectrum of uranium solutions in lithium chloride-potassium chloride after prolonged sparging with chlorine. They found that when  $U^{+4}$  was the starting material, there was no change in the spectrum. From this they concluded that the higher valence uranium chlorides are unstable in the fused salt at 400°C. However, in our equilibrium experiments, it was noted that at 400°C. the equilibrium  $U^{+6}$  fraction is 0.2, and the preponderance of  $U^{+4}$  may have swamped the  $U^{+6}$  spectrum. In addition, prolonged sparging by chlorine does not continually build up more  $U^{+6}$ ; after several minutes, the uranium concentration decreases due to volatilization, while the fraction  $U^{+4}$  remains constant.

Finally, evidence for oxygen as the oxygenating agent rather than chlorine is provided by the lack of uranium volatilization in the kinetic experiments. This effect may have been due to the formation of nonvolatile uranyl

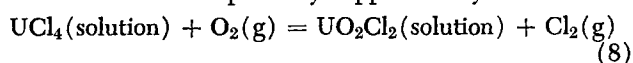
TABLE I. COMPARISON OF EXPERIMENTAL AND THEORETICAL SLOPES. DATA FOR PURE CHLORINE—INITIAL URANIUM CONCENTRATION OF 2 WT. %

Temperature, °C.	Slope (cc./sec.) <sup>2/3</sup>	
	Theoretical	Experimental
400	0.043	0.055
450	0.055	0.063
500	0.069	0.054
550	0.083	0.050
600	0.097	0.057
650	0.114	0.055
700	0.132	0.049

chloride rather than uranium chloride. However, the lack of uranium loss could also be explained by assigning low, but not unreasonable, activity coefficients to  $U^{+6}$  in the fused salt. Moreover, considerable volatilization was observed during the equilibrium experiments.

In addition to the observed loss of uranium during chlorine sparging, there are other reasons for rejecting the hypothesis of considerable oxygen reaction with the  $U^{+4}$ . The first is the amount of oxygen required to produce the increase in uranium valence observed in the equilibrium measurements. The chlorine sparging rate in the equilibration experiments was  $\sim 0.1$  cu.ft./hr., or,  $\sim 50$  cc./min. If  $X_{O_2}$  is the mole fraction of oxygen impurity in the chlorine, this corresponds to a feed rate of  $\sim 2 \times 10^{-3} X_{O_2}$  mole oxygen/min. The fused salt contained  $\sim 2$  g. of uranium tetrachloride per charge. At  $600^\circ\text{C}$ . about 40% of this was  $U^{+6}$ , which corresponds to  $2 \times 10^{-3}$  mole of  $U^{+6}$ . The time required to produce  $2 \times 10^{-3}$  mole of uranyl chloride at an oxygen feed rate of  $2 \times 10^{-3} X_{O_2}$  mole/min. (assuming all the oxygen introduced reacts) is  $1/X_{O_2}$  min. A reasonable upper limit for the oxygen impurity in the chlorine is  $\sim 1\%$ , and nearly 2 hr. would be required to attain the observed  $U^{+4}$  ratio if uranyl chloride was the sole product. In practice, it was observed that the  $U^{+4}$  ratio dropped to its equilibrium value within 5 to 10 min. This comparison strongly suggests that the primary oxidizing agent in the equilibrium experiments was chlorine, not oxygen.

Finally, to assess the effect of oxygen on the oxidation of  $U^{+4}$  in the kinetic experiments, a run was made at  $600^\circ\text{C}$ . with a reactant gas consisting of 20% oxygen in hydrogen chloride. After contact with this gas in the wetted-rod contactor, the salt remained clean and precipitate free. The results indicated that a 20% oxygen gas produced approximately the same equilibrium  $U^{+4}$  fraction as pure chlorine at the same temperature: at a salt flow rate of 0.1 cc./sec., the  $U^{+4}$  fraction in the outlet salt was 0.85 for pure chlorine and 0.83 for 20% oxygen. Since the diffusional characteristics in the two cases are nearly equivalent, the equality in the outlet  $U^{+4}$  fraction reflects a corresponding equality in the equilibrium interfacial  $U^{+4}$  fractions generated by the two reactant gases. If the oxygen mole fraction is 1% instead of 20%, its oxidizing power would be roughly comparable to a 5% chlorine gas and would not contribute appreciably to the increase in uranium valency in the kinetic experiments. Moreover, when the oxygen is a contaminant in chlorine gas, uranyl chloride formation is probably suppressed by the reaction:



In sum, the unequal diffusivity and sampling error effects are the most reasonable sources of the discrepancies between theory and experiment at high temperatures. Nevertheless, the order of magnitude agreement between predicted and observed conversion suggests that the rate of chlorination of uranium tetrachloride in a fused salt by elemental chlorine is controlled by liquid phase diffusion of  $U^{+4}$  and an equilibrium restriction imposed by reaction (1) at the interface.

The wetted-rod device developed for this study was found to be simple to operate, sturdy enough to resist corrosion by the reactants, and exhibits diffusional characteristics theoretically predicted by falling film flow. The theoretical and experimental results indicated that the overall rate is not affected by a gas phase resistance. Although the surface boundary condition for the diffusion equation of the falling film was one of chemical equilibrium in this study, the analytical solution has also been obtained for a slow, reversible first order reaction at the interface (3). These features may permit the wetted-rod contactor to be used in investigations of gas-liquid reac-

tions in which the surface kinetics are sufficiently slow to constitute the rate limiting step.

#### ACKNOWLEDGMENT

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#### NOTATION

$a$	= rod radius, cm.
$C_0$	= total uranium concentration in salt, g.-mole/liter
$\bar{C}$	= average outlet liquid concentration, g.-mole/liter
$D$	= diffusion coefficient, sq.cm./sec.
$g$	= acceleration of gravity, cm./sec. <sup>2</sup>
$K$	= equilibrium constant for reaction (1), atm. <sup>-1</sup>
$K_1$	= equilibrium constant for reaction (A-1), atm. <sup>1/2</sup>
$L$	= length of rod, cm.
$\bar{N}$	= molar flux averaged over length of rod, g.-mole/(sq.cm.) (sec.)
$N_{Sc}$	= Schmidt number
$p$	= chlorine partial pressure, atm.
$Q$	= liquid flow rate down rod, cc./sec.
$R$	= gas constant
$T$	= temperature, °K.
$u_s$	= surface velocity of liquid film, cm./sec.
$X_{O_2}$	= mole fraction oxygen impurity in chlorine
$\nu$	= kinematic viscosity of liquid, sq.cm./sec.
$\rho$	= liquid density, g./cc.
$\mu$	= liquid viscosity, centipoise

#### Subscripts

$i$	= gas-liquid interface
0	= inlet conditions
eq	= at equilibrium
eq(1 atm.)	= equilibrium results obtained with pure chlorine gas at 1 atm.
4	= uranium tetrachloride
5	= uranium pentachloride
6	= uranium hexachloride
$l$	= liquid phase
$g$	= gas phase
ox	= oxidized species in salt

#### Superscripts

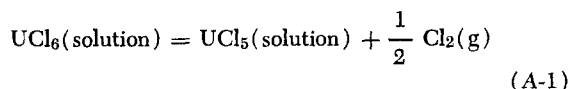
*	= dimensionless quantity defined in text
'	= apparent uranium tetrachloride or uranium hexachloride concentration obtained by analysis

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APPENDIX—ANALYTICAL PROCEDURE

In addition to uranium tetrachloride and uranium hexachloride, the salt samples collected in the equilibrium and kinetic studies contained two other species: an oxidized species which could not be removed by prolonged sparging with hydrogen chloride gas and which analyzed as U<sup>+6</sup>; and uranium pentachloride formed by the reaction:



Before contact with chlorine gas, the uranium solution in the fused salt (which had been treated with hydrogen chloride) contained U<sup>+4</sup> and the oxidized species

$$C_0 = C_{40} + C_{ox} \quad (\text{A-2})$$

As a result of contact with chlorine, some of the initial U<sup>+4</sup> was converted to U<sup>+5</sup> and U<sup>+6</sup>:

$$C_0 = C_4 + C_5 + C_6 + C_{ox} \quad (\text{A-3})$$

The frozen salt sample was dissolved in an aqueous hydrogen chloride solution, which results in disproportionation of the U<sup>+5</sup> to equal amounts of U<sup>+4</sup> and U<sup>+6</sup>.

Part of the solution was treated with ferric chloride, which oxidized U<sup>+4</sup> and U<sup>+6</sup>. Back titration of the Fe<sup>+2</sup> with potassium dichromate gave the apparent U<sup>+4</sup> content, which is related to the original concentration of uranium tetrachloride and uranium pentachloride in the frozen sample by

$$C_4' = C_4 + \frac{1}{2} C_5 \quad (\text{A-4})$$

The remainder of the aqueous solution was first passed through a lead column to reduce all of the oxidized species and then analyzed for U<sup>+4</sup> as described above. This procedure yielded the total uranium content of the sample (C<sub>0</sub>).

The uranium tetrachloride used in these experiments was obtained from the Oak Ridge National Laboratory. When analyzed in this manner the raw salt showed a C<sub>40</sub>/C<sub>0</sub> ratio of 0.92. After dissolution of the salt in hydrogen chloride-treated fused salt, followed by an additional 10 min. of sparging with hydrogen chloride gas, the C<sub>40</sub>/C<sub>0</sub> ratio was 0.942 ± 0.001, averaged over seventeen determinations. Since the uranium-free potassium chloride-lithium chloride mixture showed essentially no apparent U<sup>+4</sup> or U<sup>+6</sup> when analyzed, the 6 to 8% of oxidized impurities originated with the as-received salt, and was probably uranyl chloride formed by contact with air.

From the equilibrium constant of reaction (A-1) the ratio of U<sup>+5</sup> to U<sup>+6</sup> in the fused salt is fixed by the temperature and chlorine partial pressure:

$$\left(\frac{C_5}{C_6}\right) = \frac{K_1}{\sqrt{p}} \quad (\text{A-5})$$

$$\left(\frac{C_4'}{C_0}\right)_{\text{eq}} = \left(\frac{C_{40}}{C_0}\right) \frac{\left[1 + K_1 \left(1 - \frac{1}{2} \sqrt{p}\right)\right] \left(\frac{C_4'}{C_0}\right)_{\text{eq}(1 \text{ atm.})} - \frac{1}{2} K_1 (1 - \sqrt{p}) \left(\frac{C_{40}}{C_0}\right)}{\left[(1-p) + K_1 (1 - \sqrt{p})\right] \left(\frac{C_4}{C_0}\right)_{\text{eq}(1 \text{ atm.})} + \left[p - K_1 \left(\frac{1}{2} - \sqrt{p}\right)\right] \left(\frac{C_{40}}{C_0}\right)} \quad (\text{A-12})$$

The fraction of U<sup>+4</sup> in the frozen salt can be obtained from Equations (A-2) to (A-5) as

$$\frac{C_4}{C_0} = \frac{C_4'}{C_0} \left(\frac{1 + K_1/\sqrt{p}}{1 + K_1/2\sqrt{p}}\right) - \left(\frac{K_1/2\sqrt{p}}{1 + K_1/2\sqrt{p}}\right) \frac{C_{40}}{C_0} \quad (\text{A-6})$$

Similarly, the fraction of U<sup>+6</sup> in the frozen salt is

TABLE 2. EFFECT OF URANIUM PENTACHLORIDE ON U<sup>+4</sup> EQUILIBRIUM AT REDUCED CHLORINE PRESSURES  
T = 600°C.; (C<sub>4</sub>'/C<sub>0</sub>)<sub>eq(1 atm.)</sub> = 0.612; C<sub>40</sub>/C<sub>0</sub> = 0.942

p	K <sub>1</sub> = 0	(C <sub>4</sub> '/C <sub>0</sub> ) <sub>eq</sub>	K <sub>1</sub> = ∞
1	0.612		0.612
0.5	0.742		0.647
0.25	0.831		0.691

$$\frac{C_6}{C_0} = \left(\frac{C_{40}}{C_0} - \frac{C_4'}{C_0}\right) / (1 + K_1/2\sqrt{p}) \quad (\text{A-7})$$

Equilibrium of Reaction (1)

The equilibrium constant of reaction (1) is

$$K = \frac{C_6}{C_{4p}} \quad (\text{A-8})$$

With Equations (A-6) and (A-7), this is

$$Kp = \frac{C_{40}/C_0 - (C_4'/C_0)_{\text{eq}}}{(1 + K_1/\sqrt{p})(C_4'/C_0)_{\text{eq}} - (K_1/2\sqrt{p})(C_{40}/C_0)} \quad (\text{A-9})$$

In order to obtain values of K from the equilibrium measurements, all of the chlorinated uranium tetrachloride was assumed to have produced uranium hexachloride (that is, K<sub>1</sub> = 0). Since the equilibrium determinations were performed only with p = 1 atm., Equation (A-9) reduces to

$$K = \frac{C_{40}/C_0}{(C_4'/C_0)_{\text{eq}(1 \text{ atm.})}} - 1 \quad (\text{A-10})$$

These results are plotted in Figure 1.

Kinetic Experiments

The primary variable in the analysis of the kinetic experiments is the dimensionless concentration defined by Equation (4). For kinetic and equilibrium experiments performed at the same temperature and chlorine partial pressure, substitution of Equation (A-6) into Equation (4) yields

$$\bar{C}^* = \frac{\bar{C}_4'/C_0 - (C_4'/C_0)_{\text{eq}}}{C_{40}/C_0 - (C_4'/C_0)_{\text{eq}}} \quad (\text{A-11})$$

The concentration variable  $\bar{C}^*$  obtained from the measured U<sup>+4</sup> fractions is independent of the U<sup>+5</sup>/U<sup>+6</sup> ratio in the chlorinated product, provided that reaction (A-1) is at equilibrium at the interface. The kinetic results at 1 atm. chlorine pressure are valid despite the presence of U<sup>+5</sup>.

For kinetic experiments at reduced chlorine partial pressures, however, the ratio (C<sub>4</sub>'/C<sub>0</sub>)<sub>eq</sub> has not been measured and must be estimated for the equilibrium data obtained at 1 atm. chlorine. Equation (A-9) is first solved for (C<sub>4</sub>'/C<sub>0</sub>)<sub>eq</sub> in terms of K, K<sub>1</sub>, and p. The equilibrium constant K is eliminated by the use of Equation (A-9), once again with p = 1 and (C<sub>4</sub>'/C<sub>0</sub>)<sub>eq</sub> equal to the measured values in pure chlorine. The result is

Equation (A-12) provides a means of calculating the equilibrium U<sup>+4</sup> fraction required in Equation (A-11) for reduced chlorine partial pressures. These estimates, however, require a value of K<sub>1</sub>, the effect of which is shown in Table 2.

The limit K<sub>1</sub> = 0 assumes the product to be entirely U<sup>+6</sup>; K<sub>1</sub> = ∞ denotes production of U<sup>+5</sup> only. The analysis of the kinetic data shown in Figure 5 is based upon K<sub>1</sub> = 0.

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