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ABSTRACT

The rates of the reaction of chlorine gas with uranium tetrachloride dissolved in the LiCl-KCl eutectic have been studied in a wetted rod contactor. The reaction was studied at temperatures from 400°C to 700°C, UCl_4 concentrations of 1-3 w/o, and chlorine partial pressures of 0.25 to 1 atm. The production of UCl_6 appears to be limited by the equilibrium of the reaction UCl_4 (sol'n) + Cl_2(g) = UCl_6 (sol'n) at the interface and by U^{+4} diffusion in the liquid phase.

High temperature non-aqueous 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 of 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 UF_4-NaF-ZrF_4 melt was sprayed into a quiescent atmosphere of fluorine gas. Two possible rate-controlling steps were considered: the diffusion of UF_4 in the fused salt to the interface, and transfer by diffusion-convection of the product UF_6 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:

$$UCl_4(sol'n)+Cl_2(g) = UCl_6(sol'n) \qquad (1)$$

The reaction was carried out between gaseous chlorine and UCl_4 dissolved in the fused eutectic LiCl-KCl mixture (59 mole % LiCl). The eutectic melts at 350°C and experiments were carried out in the range of 400-700°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 Cl_2 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 1-4 hours, 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 NaOH solution for analysis. No measurable quantity of chlorine could be detected; hence the solubility of atmospheric pressure chlorine in the LiCl-KCl eutectic at 400 or 500°C is less than 4×10^{-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 w/o UCl_4. 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 one hour. 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 Fig. 1 can be expressed by

$$\ln K = 3.11 - 3250/T \qquad (2)$$

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 UCl_5 was not considered in the intepretation 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 HCl (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 Fig. 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 whose stem is 3.5 mm inner diameter. 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 HCl 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 CO_2 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:

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

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 Eq. (3) applies.

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 CO_2 to the air. Flow rates were measured by timing the effluent rate. The results are shown in Fig. 3. The theoretical slope from Eq. (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 few centimeter reduction 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 Eq. (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 Cl_2 in the fused salt and the low partial pressure of UCl_4, reaction (1) occurs only at the salt-gas interface. The interfacial concentration, C_i, of Eq. (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 UCl_6 remains in the liquid phase; (3) gas phase resistance to mass transfer is negligible; (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 Cl_2 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 Eq. (3) can then be written as:

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

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 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 UCl_4 from a bulk concentration of C_4 to a zero interfacial concentration and that of Cl_2 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 UCl_4 from the liquid to the surface under a constant driving force (C_4-0) is:

$$\overline{N}_\ell = \frac{2}{\sqrt{\pi}} \left(\frac{D_\ell u_s}{L} \right)^{1/2} C_4 \tag{5}$$

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 (i.e. a moving plane). The length-average molar flux of Cl_2 from the gas phase to the surface under a constant driving force (p-0) is:

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

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

$$\frac{\overline{N}_g}{\overline{N}_\ell} = \frac{0.75}{RT} \left(\frac{D_g}{D_\ell} \right)^{1/2} \left(\frac{p}{C_4} \right) \tag{7}$$

The following are typical of our experiments: a 2 w/o solution of UCl_4 in the fused LiCl-KCl eutectic and a 50% Cl_2-argon gas phase at 600°C; $D_\ell \approx 1.7\times10^{-5}$ cm^2/sec, $D_g \approx 0.47$ cm^2/sec. With these figures, the ratio of Eq. (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 minutes. With the rod in place, a small amount of molten salt was poured into the upper chamber of the contactor (Fig. 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 HCl gas for 15 minutes. This method of purification of the LiCl-KCl eutectic is similar to that employed by Gruen and McBeth.[7] Sufficient solid UCl_4 salt was added to give a ~2 w/o solution. After ~10 additional minutes of sparging with HCl, all of the UCl_4 had dissolved, forming a clean dark green solution with no sediment.

HCl 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 HCl had occurred. The 6% of U^{+6} was probably due to UO_2Cl_2

present in the as-received salt, which analyzed 92% U^{+4}. All gases were dried by passing through 1 liter of $CaSO_4$ at flow rate less than 0.1 CFH. The resulting contact time of > 20 minutes 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 re-seated and the chlorine flow to the lower chamber initiated. After ~1 minute, the rod was raised slightly and adjusted to a reasonable flow rate (10-12 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 minutes, the flow rate was ~3 cc/min.

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 HCl solution, for dissolution and analysis by the method outlined in the appendix.

Temperatures were varied from 400-700°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 w/o UCl_4 in the feed solution. At 600°C, however, runs at 1 and 3 w/o were conducted in a pure chlorine atmosphere, and at 2 w/o UCl_4, gas phases of 50% Cl_2-Ar, 25% Cl_2-Ar and 50% Cl_2-He were investigated.

RESULTS

The data obtained at 600°C are shown in Figs. 4 and 5 in which $\overline{C}^*$ of Eq. (4) is plotted against $1/Q^{2/3}$ as suggested by Eq. (3). The scatter

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

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 $\overline{C}^*$. Figure 4 indicates that there is no significant difference in the extent of conversion, as measured by $\overline{C}^*$, when the UCl_4 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 $\overline{C}^*$ of Eq. (4) is the appropriate concentration variable.

Figure 5 shows the effect of diluting the chlorine with inert gases. According to the theory, the variation of $\overline{C}^*$ 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 Fig. 4 for pure chlorine. The measurements at reduced chlorine partial pressures are not on 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 of the gas mixtures can be estimated from the equilibrium data for pure chlorine if the fraction of pentavalent uranium is known. The ordinates of Fig. 5 for the gas mixtures was based upon the assumption that all product is U^{+6}. If the product had been assumed to be all U^{+5}, Table II in the appendix shows that the equilibrium U^{+4} fractions are reduced. This would have the effect on Fig. 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 Fig. 5 at p = 0.5 atm in helium and argon diluents. If the gas phase resistance were important, the diffusion coefficient of Cl_2 in the carrier gas should have affected the overall conversion. The diffusivity of Cl_2 in helium is

roughly three times that than in argon. Even though the gas phase mass transfer coefficient depends upon the square root of the diffusion coefficient, the effect would have been noticable 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 the Henry's law constant of the volatile species. 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 UCl_6 in the fused salt. According to the assumption of chemical equilibrium at the interface, 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 UCl_6 transfer to the liquid is given in Eq. (5) with C_4 replaced by C_{6eq}, which denotes the constant UCl_6 concentration at the interface. The rate

at which UCl_6 transfers to the gas phase is given by Eq. (6), with p now designating the equilibrium partial pressure generated by a liquid phase concentration of C_{6eq}. The ratio of UCl_6 transferred to the gas and liquid phases is given by Eq. (7), in which the ratio (p/C_4) is now the Henry's law constant of UCl_6 in the salt. The limit of detectability of uranium loss from solution is ~ 1% or $\bar{N}_g/\bar{N}_\ell \leq 0.01$. Assuming the diffusivity of UCl_6 in Cl_2 to be ~1/4 of that of argon in Cl_2, the maximum value of the Henry's law constant is ~ $6X10^{-3}$ atm/(mole/lit), or on a mole fraction basis, 0.2 atm. By extrapolation of the low temperature data in Refs. 11 or 12, the vapor pressure of UCl_6 at 600°C is between 10 and 500 atm. The maximum activity coefficient of U^{+6} in the melt is between $2X10^{-2}$ and $4X10^{-4}$, 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 Eq. (3) is a function of the transport properties of the melt and the geometry of the rod. The diffusivity of U^{+4} in the LiCl-KCl 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 $D_\ell = 0.49X10^{-5}$ cm^2/sec, $\rho = 1.67$ gm/cc, $\mu = 4.7$ cp. 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 Fig. 4 with the coefficient of $1/Q^{2/3}$ in Eq. (3) is presented in Table I.

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 $\sqrt{D_\ell/\nu^{1/6}}$, 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 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 Eq. (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 I 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 build up 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 HCl. However, if reaction (1) is reversible, some of the UCl_6 formed in the reaction section could decompose to UCl_4 and Cl_2 in the process of drop formation and fall through HCl. This effect was noted in the CO_2 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 I and Fig. 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 Fig. 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 O_2 contaminant of the bottle of pure Cl_2 would be the same as in the bottles of the gas mixtures. Secondly, the salt solution took on a distinct yellow tinge after long chlorine spargings in the equilibration experiments. This is just the color of UO_2Cl_2 dissolved in the eutectic. Third, Gruen and McBeth[7] have examined the absorption spectrum of uranium solutions in LiCl-KCl 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 O_2 as the oxygenating agent rather than Cl_2 is provided by the lack of uranium volatilization in the kinetic experiments. This effect may have been due to the formation of non-volatile UO_2Cl_2 rather than UCl_2. 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 Cl_2 sparging rate in the equilibration experiments was ~ 0.1CFH, or, ~ 50 cc/min. If X_{O_2} is the mole fraction of O_2 impurity in the chlorine, this corresponds to a feed rate of ~ $2X10^{-3}$ X_{O_2} mole O_2/min. The fused salt contained ~ 2gm of UCl_4 per change. At 600°C, about 40% of this was U^{+6}, which corresponds to $2X10^{-3}$ mole of U^{+6}. The time required to produce $2X10^{-3}$ mole of UO_2Cl_2 at an oxygen feed rate of $2X10^{-3}X_{O_2}$ 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 ~ 1%, and nearly two hours would be required to attain the equilibrium U^{+4} ratio if UO_2Cl_2 was the sole product. In practice, it was observed that the U^{+4} ratio dropped

to its equilibrium value within 5-10 min. This comparison strongly suggests that the primary oxidizing agent in the equilibrium experiments was Cl_2, not O_2.

Finally, to assess the effect of oxygen on the oxidation of U^{+4} in the kinetic experiments, a run was made at 600°C with a reactant gas consisting of 20% O_2 in HCl. After contact with this gas in the wetted rod contactor, the salt remained clean and precipitate-free. The results indicated that a 20% O_2 gas produced approximately the same equilibrium U^{+4} fraction or 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 characterstics 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, UO_2Cl_2 formation is probably suppressed by the reaction:

$$UCl_4(sol'n) + O_2(g) = UO_2Cl_2(sol'n) + Cl_2(g) \qquad (8)$$

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 UCl_4 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 to exhibit 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 indication 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 surface reaction at the interface.[3] These features may permit the wetted rod contactor to be used in investigations of gas-liquid reactions in which the surface kinetics are sufficiently slow to constitute the rate-limiting step.

Table I. Comparison of experimental and theoretical slopes. Data for pure Cl_2--initial uranium concentration of 2 w/o

Temperature (°C)	Slope $(cc/sec)^{2/3}$ 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

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NOMENCLATURE

a	rod radius, cm
C_0	Total uranium concentration in salt, gm mole/lit
$\bar{C}$	average outlet liquid concentration, gm mole/lit
D	diffusion coefficient, cm^2/sec
g	acceleration of gravity, cm/sec^2
K	equilibrium constant for reaction (1), atm^{-1}
K_1	equilibrium constant for reaction (A-1), $atm^{1/2}$
L	length of rod. cm
$\bar{N}$	molar flux averaged over length of rod, gm mole/cm^2sec
N_{sc}	Schmidt Number
p	chlorine partial pressure, atm
Q	liquid flow rate down rod, cm^3/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

GREEK LETTER

ν	kinematic viscosity of liquid, cm^2/sec

SUBSCRIPTS

i	gas-liquid interface
0	inlet conditions
eq	at equilibrium
eq(1 atm)	denotes equilibrium results obtained with pure chlorine gas at 1 atmosphere

4	UCl_4
5	UCl_5
6	UCl_6
ℓ	liquid phase
g	gas phase
ox	oxidized species in salt

SUPERSCRIPT

*	dimensionless quantity defined in text
'	denotes apparent UCl_4 or UCl_6 concentration obtained by analysis

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FIGURE CAPTIONS

Fig. 1. Equilibrium constant of reaction (1), measured with pure chlorine in 2 w/o UCl_4 solution. UCl_5 production neglected.

Fig. 2 Quartz wetted rod contactor.

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

Fig. 4 UCl_4 chlorination in wetted rod contactor--pure chlorine, 600°C.

Fig. 5 Effect of chlorine partial pressure on UCl_4 chlorination--600°C, 2 w/o UCl_4.

APPENDIX - ANALYTICAL PROCEDURE

In addition to UCl_4 and UCl_6, 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 HCl gas and which analyzed as U^{+6}; and UCl_5, formed by the reaction:

$$UCl_6(sol'n) = UCl_5(sol'n) + \frac{1}{2} Cl_2(g) \qquad \text{(A-1)}$$

Before contact with chlorine gas, the uranium solution in the fused salt (which had been treated with HCl) contained U^{+4} and the oxidized species:

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

As a result of contact with chlorine, some of the initial U^{+4} was converted to U^{+5} and U^{+6}:

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

The frozen salt sample was dissolved in an aqueous HCl solution, which results in disproportination of the U^{+5} to equal amounts of U^{+4} and U^{+6}.

Part of the solution was treated with $FeCl_3$, which oxidized U^{+4} and U^{+6}. Back titration of the Fe^{+2} with $K_2Cr_2O_7$ gave the apparent U^{+4} content, which is related to the original concentration of UCl_4 and UCl_5 in the frozen sample by:

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

The remainder of the aqueous solution was first passed through a lead column to reduce all of the oxidized species, then analyzed for U^{+4} as described above. This procedure yielded the total uranium content of the sample (C_0).

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_{40}/C_0 ratio of 0.92. After dissolution of the salt in HCl- treated fused salt followed by an additional 10 mm of sparging with HCl gas, the C_{40}/C_0 ratio was 0.942±0.001, averaged over 17 determinations. Since the uranium-free KCl-LiCl mixture showed essentially no apparent U^{+4} or U^{+6} when analyzed, the 6-8% of oxidized impurities originated with the as-received salt, and was probably UO_2Cl_2 formed by contact with air.

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

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

The fraction of U^{+4} in the frozen salt can be obtained from Eqs. (A-2) to (A-5) as:

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

Similarly, the fraction of U^{+6} in the frozen salt is:

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

<u>Equilibrium of Reaction (1):</u>

The Equilibrium constant of Reaction (1) is:

$$K = \frac{C_6}{C_4 p} \qquad \text{(A-8)}$$

using Eqs. (A-6) and (A-7), this is:

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

In order to obtain values of K from the equilibrium measurements, all of the chlorinated UCl_4 was assumed to have produced UCl_6 (i.e., $K_1=0$). Since the equilibrium determinations were performed only with p = 1 atm, Eq. (A-9) reduces to:

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

These results are plotted in Fig. 1.

Kinetic Experiments

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

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

The concentration variable $\bar{C}^*$ obtained from the measured U^{+4} fractions is independent of the U^{+5}/U^{+6} 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^{+5}.

For kinetic experiments at reduced chlorine partial pressures, however, the ratio $(C_4'/C_0)_{eq}$ has not been measured and must be estimated for the equilibrium data obtained at 1 atmosphere of Cl_2. Equation (A-9) is first solved for $(C_4'/C_0)_{eq}$ in terms of K, K_1, and p. The equilibrium constant K is eliminated by use of Eq. (A-9) once again with p = 1 and

$(C_4'/C_0)_{eq}$ equal to the measured values in pure Cl_2. The result is:

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

Equation (A-12) provides a means of calculating the equilibrium U^{+4} fraction required in Eq. (A-11) for reduced chlorine partial pressures. These estimates, however, require a value of K_1, the effect of which is shown in Table II.

Table II. Effect of UCl_5 on U^{+4} Equilibrium at Reduced Chlorine Pressures

$T = 600°C$; $(C_4'/C_0)_{eq(1\ atm)} = 0.612\ C_{40}/C_0 = 0.942$

p	$(C_4'/C_0)_{eq}$	
	$K_1 = 0$	$K_1 = \infty$
1	0.612	0.612
0.5	0.742	0.647
0.25	0.831	0.691

The limit $K_1 = 0$ assumes the product to be entirely U^{+6}; $K_1 = \infty$ denotes production of U^{+5} only. The analysis of the kinetic data shown in Fig. 5 is based upon $K_1 = 0$.

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