SOME ASPECTS OF THE CHEMISTRY OF THE ACTINIDES IN CHLORIDE MELTS [1]

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Abstract

It is now possible to recognize the main outlines of the chemical behavior of the actinides in molten chloride systems. Topics discussed are: oxidation states, apparent standard potentials, disproportionation equilibria, identification of complex ionic species from spectroscopic and electrochemical measurements, as well as from phase equilibria.

I. Introduction

The solution chemistry of the actinides had been studied almost exclusively in "room temperature" solvents such as water, the most ubiquitous liquid. However, the nature of water sets serious limitations on the types of chemical reactions which can be carried out in this solvent. For example, its 100° liquid range at atmospheric pressure imposes severe temperature constraints. The chemical stability of water is relatively low, particularly with respect to the reduction of hydrogen ions. Of particular importance for actinide chemistry is the relative ease with which water can be decomposed radiolytically.

In attempting to overcome the limitations of water as a solvent, and in order to explore a wider range of actinide solution chemistry, a large number of "non-aqueous" solvent systems have been investigated. Actinide chemistry has been extensively studied in the last 15 years in fused salt systems which comprise a particularly extensive and unique class of inorganic solvents. [2-4] Many fused salt mixtures, such as the LiCl-KCl eutectic mixture have wide liquid ranges (400°-1400°C), vapor pressures below 1 atmosphere, and extraordinary chemical stability. The molten alkali halides, for example, are very stable particularly with respect to reduction and are not decomposed by radiation. The latter property makes them attractive as solvent media for the highly radioactive actinide elements such as macroscopic amounts of the transcurides.

The study of the chemical reactions of the actinides in fused salts is of scientific interest primarily because of the possibilities offered by these unusual high
temperature solvents for exploring new chemical phenomena. Topics to be discussed in this paper include the oxidation states of the actinides; the relative strengths of anionic complexes; apparent standard potentials and disproportionation equilibria; identification of complex ionic species from spectroscopic, and electrochemical measurements, as well as from phase equilibrium data.

II. Oxidation States

Oxidation states of the actinides have been characterized using absorption spectrophotometric as well as electrochemical techniques. The oxidation states which have been definitely established in LiCl-KCl eutectic are Th(IV); U(III,IV,V,VI); Np(III,IV,V,VI); Pu(III,IV,V,VI); Am(III); and Cm(III). The U(V,VI), Np(V,VI) and Pu(V,VI) states appear to exist only in the form of the oxygenated MO_2^+ or MO_2^{+2} ions. Lower valent states of Th appear not to be stable in LiCl-KCl eutectic.

The spectra in LiCl-KCl eutectic of the oxygenated ions UO_2^{2+}, NpO_2^+ and of the tripositive ions U^{3+}, Np^{3+}, Pu^{3+}, Am^{3+} can be correlated quite well with spectra in aqueous hydrochloric acid solutions. The solvent medium appears to affect the spectra of these ions in only minor ways. The spectrum of Am^{3+} reproduced in Fig. 1 exemplifies this situation. [2]

On the other hand, the spectra of the tetrapositive ions U^{4+}, Np^{4+} and Pu^{4+} in chloride melts are quite different from their aqueous solution spectra and show pronounced changes even on varying the cation composition of a chloride melt. [2]

These observations may be understood on the basis of the following considerations. The spectra of NpO_2^+ and PuO_2^{2+} have been interpreted on the basis of a model which postulates that the molecular field of the metal-oxygen bonds overwhelms both the spin-orbit coupling and the electrostatic interaction between the two unpaired 5f electrons. [5] The triatomic oxygenated molecule ions determine the essential features of the spectra so that other less strongly bound ligands exert only minor effects on the spectra of these ions.

On the other hand, the spectra of U^{3+}, Np^{3+}, Pu^{3+} and Am^{3+}, are essentially "rare-earth like" in that they can be understood on the basis of a crystalline field which is small compared to the spin-orbit interaction and, also,
very much smaller than the electrostatic repulsion between the 5f electrons. With these ions therefore, one finds not unexpectedly, that the spectra are perturbed in only relatively minor ways even by quite drastic environmental changes. [2]

The oxygenated and the tripositive actinide cations represent extremes in that the first group exists in the form of an extremely stable complex ion whose spectrum is essentially wholly determined by the invariant molecular constitution of the complex itself. The spectra of the tripositive ions which are present in solution in the form of labile complexes are virtually unaffected by changes in the constitution of the complex because of the weak interaction of ligand fields with the shielded 5f electrons.

Intermediate between these two groups stand the tetrabivalent ions U4+, Np4+ and Pu4+. It is these ions which show large spectral changes due to changes in coordinating groups. These ions therefore are important probes for structural investigations of melts, and their spectra will be referred to again in a later section of the paper dealing with complex ions of the actinides.

There has been some controversy about the oxidation states of thorium in chloride melts since Smirnov et al. [6-8] reported evidence for the formation of ThCl2 in fused chloride salts, via the reaction Th + ThCl4 = 2ThCl2 or Th4+ + Th = 2Th2+. Work by Chiotti and Parry [9] also indicated that lower valence states of Th exist in LiCl-KCl eutectic in contact with liquid Zn.

On the other hand, Inman et al. [10] found, on anodic dissolution of thorium in a eutectic mixture of KCl-LiCl salt, a value of 3.7-4.5 for the number of electrons given up per gram-atom of thorium. Gruen et al. [11] reviewed the chemistry of the actinide elements in fused KCl-LiCl eutectic and interpreted Inman et al.'s results as indicating a 4+ oxidation state for thorium. They also reported that thorium did not react with a ThCl4-KCl-LiCl salt contained in a single-crystal sapphire crucible at 500°C. A similar experiment carried out with NaCl-KCl eutectic and ThCl4, contained in a platinum crucible at 730-800°C, showed no reaction of thorium with the salt and therefore negative evidence for lower oxidation states of Th. [12]

In a more recent study of the Th-ThCl4 system [13] in the temperature range 300-1100°C no evidence was found for the presence of lower-valent chlorides such as ThCl2 or
ThCl₃. Finally, emf data on cells of the types Th/KCl-LiCl-ThCl₄/KCl-LiCl-AgCl/Ag and Th/KCl-LiCl-ThCl₄/ThZn₈.₅,Zn have been obtained. [14] These data show that the oxidation state of Th is +4 in the LiCl-KCl eutectic. It appears that some of the literature data on the existence of lower valent thorium chlorides in fused salt can be explained on the basis of contamination by ThO₂ whilst other evidence, based on the slope of emf data composition plots, can be misleading if the composition dependence of the activity coefficient of ThCl₄ is not taken into account.

III. Apparent Standard Potentials

In spite of the experimental difficulties associated with determining emf's of cells involving solutions of actinides in molten salts at elevated temperatures, measurements of apparent standard potentials have been obtained as shown in Table I. The temperature dependence of the apparent standard potential generally decreases with increasing temperature thus giving a negative temperature coefficient. The concentration dependence of the potentials can be related to the activity coefficients of the actinide halides in the molten salt solutions and deviation of solute behavior from ideality can therefore be evaluated. The electrochemical data thus have become an important source of information on the stability constants of chloride complexes, a topic to be discussed more fully in a later section.

The data listed in Table I have involved emf measurements in concentration cells, although some data are available on redox potentials in formation cells. [15,16] For the most part Ag⁺/Ag and Cl₂/carbon reference electrodes were used. Actinide ion concentrations have been in the range 10⁻²⁻¹⁻⁰⁻⁴ mole fraction. Such low metal ion concentrations necessitate extreme salt purity and control of inert atmospheres in the cells to prevent concentration changes due to reactions with unwanted impurities. A low solute concentration is, of course, desirable to justify the assumption that the junction potential term in the Nernst equation can be neglected. [17]

IV. Oxidation-Reduction and Disproportionation Equilibrium

The U(III), U(IV) and U(VI) oxidation states were identified spectrophotometrically by Gruen and McBeth [30] and the U(V) state by Adams et al. [31,32] It was found that Al as well as U metal reduces U(IV) to U(III) while
Mg metal reduces U(III) to U(0) in LiCl-KCl. Landresse and Duyckaerts [33] found that hydrogen gas in contact with a solution of U(VI) in LiCl-KCl results first in the reduction to U(V) according to the equation

$$\text{UO}_2^{2+} + \frac{1}{2}H_2 + Cl^- \rightarrow \text{UO}_2^+ + HCl$$  \hspace{1cm} (1)

Prolonged contact with $H_2$ gives a further reduction to $\text{UO}_2$:

$$\text{UO}_2^+ + \frac{1}{2}H_2 + Cl^- \rightarrow \text{UO}_2 + HCl$$  \hspace{1cm} (2)

Above $500^\circ C$, hydrogen gas reduces U(IV) to U(III):

$$\text{U}(IV) + \frac{1}{2}H_2 + Cl^- \rightarrow \text{U}(III) + HCl$$  \hspace{1cm} (3)

The reaction of oxygen with U(IV) was studied by Molina [34] who found that

$$\text{U}(IV) + O_2 + Cl^- \rightarrow \text{UO}_2(VI) + Cl_2$$  \hspace{1cm} (4)

This reaction has been restudied [33] with the result that $\text{UO}_2(V)$ does not appear as an intermediate species.

The disproportionation reaction, which can be given the general formulation

$$2\text{UO}_2(V) + nHCl \leftrightarrow \text{UO}_2(VI) + \text{U}(IV) + 2W + nCl^-$$  \hspace{1cm} (5)

has been studied spectrophotometrically. [33] In equation (5) $W$ represents $H_2O$, $H_3O^+$ or $OH^-$ and the equilibrium constant was written by Landresse and Duyckaerts [33]

$$K = \frac{[\text{UO}_2(VI)][\text{U}(IV)][W]^2}{[\text{UO}_2(V)]^2P^nHCl}$$  \hspace{1cm} (6)

Substituting in (6), $[W] = 2[\text{U}(IV)]$ gives

$$L = \frac{[\text{UO}_2(VI)][\text{U}(IV)]^3}{[\text{UO}_2(V)]^2}; \hspace{0.5cm} K = \frac{[\text{UO}_2(VI)][\text{U}(IV)]^3}{[\text{UO}_2(V)]^2P^nHCl}$$  \hspace{1cm} (7)

From which one obtains

$$n\log P_{HCl} = \log L - \log \frac{1}{4}K$$  \hspace{1cm} (8)

However, the concentrations of $H_2O$, $H_3O^+$ and $OH^-$ are strongly dependent on HCl pressure. Furthermore, the autoprotolysis equilibrium $[H_3O^+][OH^-]/[H_2O]^2$ was found to be quite large, $K \approx 10^3$. Therefore, the data analysis becomes complicated and earlier results have had to be revised in light of later data. A study of equilibrium (5) as a function of temperature and solvent composition has shown that the principal species, $W$, is $H_3O^+$ in the NaCl-KCl-MgCl ternary; In 70% LiCl-30% KC1, W is primarily $H_2O$ and in 55% LiCl-45% CsCl, W appears to be well represented by $OH^-$ in equilibrium (5).
A log $P_{\text{HCCl}}$ (mm) vs log$L$ plot of the disproportionation reaction in various molten salt solvents shows that the extent of disproportionation given by the value of $L$ is in the order of the inverse charge density of the solvent cations Cs$^+$ < K$^+$ < Li$^+$ < Mg$^{2+}$. The lower the charge density, the greater the tendency for UO$_2$(V) to disproportionate to U(IV) and U(VI). [33]

The effect of complex formation in molten salts on the chemical activity of ionic species has been observed in a wide variety of measurements [4]. Suffice it to say here, that the changes in the disproportionation equilibrium of UO$_2$(V) are most readily accounted for on the basis of complex ion formation. The complex ionic species UCl$_6^{3-}$ and chlorocomplexes of UO$_2$(VI) in fused salts were first identified on the basis of spectrophotometric and chromatographic measurements. [30,36,37] Stromatt showed that the stability of UO$_2$(VI) is enhanced in solvents with low cation charge density. [38] Similarly, Morrey was able to show that the stability of UCl$_6^{3-}$ in alkali metal chloride melts is a marked function of cation composition and increases with decreasing cationic charge density. [39] On the other hand, it is known from work on aqueous solutions that the actinide MO$_2$(V) ions are very weak complex formers [40] so that the stability of UO$_2$(V) may in fact depend only to a minor extent on solvent composition. Therefore, the observed changes of five or six orders of magnitude in the disproportionation equilibrium constant $L$ as a function of solvent composition are most easily rationalized on the basis of increasing stability of the chlorocomplexes of UO$_2$(VI) and U(IV) with decreasing cationic charge density.

The Np(III), Np(IV) and NpO$_2$(V) oxidation states were identified spectrophotometrically and on the basis of these studies the complex ionic species NpCl$_6^{3-}$ and NpO$_2^{+}$ were found to exist in the LiCl-KCl eutectic. [30,36,37,44] Evidence for the existence of NpO$_2$(VI) in LiCl-KCl eutectic was obtained in voltammetric studies [41] where two polarographic waves were found suggestive of a similar situation observed in the polarographic reduction of UO$_2$(VI). [42,43]

The oxidation-reduction reaction

$$\text{NpO}_2^{(V)} + 4\text{HCl} \rightarrow \text{Np}^{(IV)} + 2\text{H}_2\text{O} + \frac{1}{2}\text{Cl}_2 + 3\text{Cl}^-$$  \hspace{1cm} (9) 

has been studied spectrophotometrically [29] as a function of H$_2$O, HCl and Cl$_2$ partial pressures and as a function of temperature. Plots of ln [Np(IV)]/[NpO$_2$(V)], a quantity obtained from the spectrophotometric data vs
ln $[P^2H_2O^{1/2}Cl_2]/[P^4HCl]$ gave straight lines with unit slope as required theoretically thus confirming the postulated stoichiometry. Extrapolation of these curves to the origin yielded the following values of $\ln K x 10^6$ (in units of atm$^{-3/2}$) -11.60 (450°C); -12.19 (500°C); -12.38 (550°C); -12.80 (600°C). Increasing the temperature causes a shift of the equilibrium to the left favoring the formation of $\text{NpO}_2(V)$.

The Pu(III) and Pu(IV) oxidation states and the PuCl$_6^{2-}$ ion were identified spectrophotometrically in LiCl-KCl eutectic. [44] It had been determined that the reaction

$$\text{Pu(IV)} + \text{Cl}^- \rightarrow \text{Pu(III)} + \frac{1}{2}\text{Cl}_2$$

occurs in the melt reversibly being shifted to the right with increasing temperature. Recent work [35] has confirmed these results in all their essentials. In addition it was found that if one treats a solution of Pu(IV) with a Cl$_2$-O$_2$ gas mixture, one obtains absorption spectra characteristic of PuO$_2$(V) and PuO$_2$(VI). The principal bands of PuO$_2$(V) are at 770, 780, 875, 990, 1122, 1300 and 2070 nm and those of PuO$_2$(VI) at 1012, 1390 and 1448 nm. The spectrum of PuO$_2$(V) resembles that in 0.2 M HClO$_4$ at 25°C while that of PuO$_2$(VI) in LiCl-KCl is similar to the spectrum of the PuO$_2$Cl$_4^{2-}$ ion which has been identified in nitromethane solutions at 25°C. [46]

The PuO$_2$(V) and PuO$_2$(VI) states are unstable in LiCl-KCl eutectic and PuO$_2$ precipitates tend to form in such solutions. A maximum in the intensity of the V and VI spectra is reached in treating a solution of Pu(III) and Pu(IV) with a mixture of 33% O$_2$-67% Cl$_2$. Subsequently the intensities of the V and VI spectra diminish with the formation of a PuO$_2$ precipitate. If at the time the Pu(V) and Pu(VI) spectra have reached maximum intensity one switches to a N$_2$-Cl$_2$ mixture, the PuO$_2$(V) intensity is found to increase slightly to the detriment of the Pu(VI) intensity as the N$_2$ partial pressure is increased and vice versa. This observation was used to assign the spectral bands to the two species respectively. The experimental observations were rationalized on the basis of the following chemical equilibria by Landresse and Duyckaerts [35]

$$2\text{Pu(III)} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{Pu(IV)} + \text{O}^2-$$

(11)

$$\text{Pu(IV)} + 2\text{O}_2^- \rightarrow \text{PuO}_2^{2+}$$

(12)

$$\text{Pu(IV)} + \text{O}_2 + 2\text{Cl}^- \rightarrow \text{PuO}_2(\text{VI}) + \text{Cl}_2$$

(13)

$$\text{PuO}_2(\text{VI}) + \text{Cl}^- \rightarrow \text{PuO}_2(V) + \frac{1}{2}\text{Cl}_2$$

(14)
PuO$_2$(V) + Cl$^-$ + PuO$_2^{+}$ + $\frac{1}{4}$Cl$_2$ \hspace{1cm} (15)

Potential diagrams for various redox couples vs pO$_2$ (pO$_2$ = -log[O$_2^-$]) have been set up for uranium [47], neptunium [28] and plutonium [28,35,48]. In the LiCl-CsCl eutectic, the redox potentials of the various plutonium couples change in such a way with respect to the LiCl-KCl eutectic as to indicate stabilization of the Pu(IV) and PuO$_2$(VI) states relative to PuO$_2$(V). This may be interpreted, in a manner similar to the situation found in the uranium system, as due to preferential complexation of the (IV) and (VI) oxidation states to form the ions PuCl$_6^{2-}$ and PuO$_2$Cl$_4^{2-}$ which is favored in melts of high Cl$^-$ activity.

V. Complex Ions of the Actinides in Molten Chlorides

The importance of the relative stabilities of complex ionic species in determining the basic chemistry of the actinides in fused chloride systems is amply documented in the discussions of the previous sections of this paper. Oxidation states, disproportionation equilibria, redox potentials, precipitation behavior, reactions with various melt constituents and gases in equilibrium with melts all are determined to a considerable extent by variations in the chloride ion activity of the melt and the ensuing ability of Cl$^-$ to enter into the formation of anionic actinide chlorocomplexes.

Information on the stoichiometries, stabilities and structures of actinide chlorocomplexes have come from a wide variety of investigations including electronic and vibrational spectroscopic studies; emf measurements; voltammetry, chronopotentiometry and conductance measurements; phase equilibria including metal-salt, salt-salt, and salt-vapor equilibria, as well as studies of the extraction and distribution of actinides between immiscible salt-salt and metal-salt systems. [4] Space does not permit a thorough review of the topic here. The salient results on the identification of actinide anionic complexes is however contained in Table II which lists those species that have been identified, the chief method used in their identification and the appropriate literature references.
Table I. Apparent Standard Potentials of Actinides vs. Cl$_2$/2Cl$^-$ Reference Electrode in LiCl-KCl Eutectic at 450°C.

| Actinide Couple    | $E_{app}^0$ (volt) | References |
|--------------------|-------------------|------------|
| Th$^{4+}$/Th$^0$   | 2.30              | 14         |
| U$^{3+}$/U$^0$     | 2.53              | 10,18-21   |
| U$^{4+}$/U$^0$     | 2.27$^*$          | 20-24      |
| U$^{4+}$/U$^{3+}$  | 1.47              | 21-24      |
| U$^{6+}$/U$^{4+}$  | 0.50              | 21         |
| Np$^{3+}$/Np$^0$   | 2.34              | 25         |
| Np$^{4+}$/Np$^0$   | 2.15$^*$          | 25         |
| Np$^{4+}$/Np$^{3+}$| 1.59              | 26         |
| NpO$_2^+$/NpO$_2^+$| -0.12             | 28         |
| NpO$_2^+/NpO_2^-_2| -0.22 (400°C)     | 29         |
| Pu$^{3+}$/Pu$^0$   | 2.01              | 27,61      |
| Pu$^{4+}$/Pu$^0$   | 1.52$^*$          | --         |
| Pu$^{4+}$/Pu$^{3+}$| 0.05 (400°C)     | 28,35,48   |
| Am$^{3+}$/Am$^0$   | 1.90              | 62         |
| Cm$^{3+}$/Cm$^0$   | 1.78              | 63         |
| Cl$_2/2$Cl$^-$     | 0.00              |            |

$^*$Calculated from the relationship

$$ E_{app}^0 (M^{4+}/M^0) = \frac{E_0}{4} (M^{4+}/M^{3+}) + \frac{3}{4} E_{app}^0 (M^{3+}/M^0) $$
| Complex Ion | System          | Temp. (°C) | Method     | Ref. |
|------------|----------------|------------|------------|------|
| UCl$^{4-}$ | NaCl/KCl       | 700        | chronopot. | 50   |
| UCl$^{5-}$ | LiCl/LCl, Alk. Cl | 450-550 | emf        | 10,51|
| UCl$^{6-}$ | NaCl, Alk. Cl  | 700-845    | vap. press.| 53   |
| UCl$^{5-}$ | KCl/CuCl       | 180        | distribution | 54 |
| UCl$^{6-}$ | KCl/CuCl, KCl/AlCl$_3$ | 180 | distribution | 54 |
| UCl$^{6-}$ | KCl/UCl$_4$    | 450-750    | conductivity | 56 |
| UO$_2$Cl$_{3-}$ | LiCl-KCl | 650 | spectroscopy | 31,32 |
| UO$_2$Cl$_{4-}$ | KCl/AlCl$_3$ | 625 | distribution | 55 |
| NpCl$_{6-}$ | LiCl/KCl      | 500        | spectroscopy | 44   |
| PuCl$_{6-}$ | Alk. Cl       | ---        | phase diagr. | 59,60|
| PuCl$_{6-}$ | LiCl/KCl, KCl/AlCl$_3$ | 500 | spectroscopy | 44 |
| Pu$_2$Cl$_{4-}$ | LiCl/KCl | 450 | spectroscopy | 46   |
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Absorption spectra of Am(III) in 11.6 M HCl and LiCl-KCl eutectic at 400°C

**Figure 1**

Absorption spectra of Am(III) in 11.6 M HCl and LiCl-KCl eutectic at 400°C

1.7

1.5

Optical Density

Wavelength in m/μ

0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8

400 500 600 700 800 900