Dissolution of Uranium Metal into Molten LiCl-KCl-UCl$_4$

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A study has been made on the kinetics of dissolution of uranium metal into molten LiCl-KCl eutectic with some UCl$_4$ as an oxidizing agent under static and dynamic conditions at temperatures ranging from 400° to 500°C. The static dissolution rates have been determined by the weight losses of the metal, and were shown to obey a first order kinetic equation. The measurements of the dynamic dissolution rates have been carried out by a rotating disc method, and the concentration changes were measured by an emf method. The dynamic dissolution rates were also confirmed to follow a first order kinetic equation, and were proportional to the $1/2$ power of rotating speeds. The dissolution process is concluded to be controlled by the diffusion of U(IV). The activation energies were $9.3 \pm 1.0$ kcal/mol for the static dissolution and $6.6 \pm 0.6$ kcal/mol for the dynamic dissolution. These values are compared with the value of $7.43$ kcal/mol of the activation energy for the diffusion coefficients of U(IV) determined in the previous work. The differences between the values could be explained by the temperature dependence of the thickness of the diffusion layer.

1 Introduction

Since the high temperature non-aqueous fuel reprocessing technique has been developed, kinetics of the process have become important. While relatively much information on the chemical equilibria for the process has been accumulated, little work has been reported on the kinetics of the transfer process in the non-aqueous system. Dissolution of solid metal into molten salt is one of the fundamental processes associated with the pyrochemical reprocessing of spent reactor fuels, and its kinetic study is important from theoretical and practical points of view.

The over-all rate of dissolution is governed by the relative magnitudes of two separate rates, i.e., the rate of the surface reaction, and the rate of the introduction or removal of reactants by diffusion in the liquid.

The general expression for the rate of dissolution or heterogeneous reaction has been derived by Berthoud$^1$, that is,

$$C_t = C^* \left[ 1 - \exp(-KSt/V) \right]$$

(1)

where $C_t$: solute concentration at time $t$, $C^*$: the saturation concentration of solute, $S$: the surface area of the solid, $V$: the volume of liquid, $D$: the diffusion coefficient of the solute, $\delta$: the thickness of the diffusion boundary layer, $K_s$: the rate constant of the surface reaction, $K$: the over-all rate constant.

When the surface reaction is rate-controlling as the slowest process, $K$ equals $K_s$, and when the diffusion process is rate-controlling, $K$ equals $D/\delta$.

In the present paper, a study on the kinetics of dissolutions of solid uranium metal into molten LiCl-KCl eutectic with some UCl$_4$, as oxidizing agents is described. The study was carried out in two different manners; the static dissolution in which a U disc was hung down and dissolved in the molten salt, and the dynamic dissolution in which a U disc was rotated in the melt. The fused salt system was chosen because of its importance in pyrochemical reprocessing, and of a convenience for the analysis. The dissolution proceeds due to the following reaction.

$$\text{U} + 3\text{UCl}_4 \rightarrow 4\text{UCl}_4$$

The free energy changes and the equilibrium
Table 1 Standard free energy changes and equilibrium constants for the reaction
U + 3 UCl → 4 UCl₃ in LiCl-KCl eutectic melt

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>(-dG°) (Hcal/mol)</th>
<th>(K_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>60.4</td>
<td>3.6 (\times) 10¹⁵</td>
</tr>
<tr>
<td>450</td>
<td>60.2</td>
<td>1.4 (\times) 10¹⁸</td>
</tr>
<tr>
<td>500</td>
<td>59.9</td>
<td>8.1 (\times) 10¹⁶</td>
</tr>
<tr>
<td>600</td>
<td>59.7</td>
<td>6.6 (\times) 10¹⁵</td>
</tr>
</tbody>
</table>

Constants for the reaction (3) in LiCl-KCl eutectic melt were calculated from the emf data described in the previous report and listed in Table 1 at various temperatures.

2 Experimental

2.1 Materials

Uranium metal discs with a diameter of 8 mm and a length of 6 mm were used. These samples were fabricated from reactor grade uranium metal and supplied by the Power Reactor and Nuclear Fuel Development Corporation. The nominal impurities in the sample were:

- B < 0.1, Cd < 0.2, Co < 5, Fe < 86,
- Mn < 13, Ni < 35, Si < 36, C < 720,
- N < 20, Ag < 0.2, Cu < 7, Al < 14,
- Cr < 17, Mg < 16, V < 10, Zn < 50 (in ppm)

Before use, it was polished with emery paper, etched with nitric acid, washed with alcohol and acetone, and then dried.

UCl₃ was prepared from uranium metal shavings by three step reactions of hydrogenation, hydrochlorination and chlorination as described in the previous report. The produced crude UCl₃ was purified by vacuum distillation at 600°C for 2 hr. Purifications of LiCl-KCl eutectic and AgCl-LiCl-KCl for a reference electrode have been described in the previous report. The content of AgCl in the reference electrode was determined to be 1.29 mol %.

2.2 Apparatus and procedures

1: Static dissolution

(1) Static dissolution

The solidified solvent salt and UCl₃ powder were weighed and loaded in a pyrex crucible in a dry-box. After the crucible had been placed in the cell, and a thermocouple sheath and a U disc in a Pt basket coated by pyrex-glass hung down with a brass chain and a Pt wire had been placed in position, the whole assembly was evacuated. Fig. 1 shows the apparatus for the static dissolution. The cell was then filled with purified Ar and heated until the salt melted. The temperature was controlled at predetermined level, then the U disc was immersed in the melt. After a certain duration of time for dissolution, the U disc and the thermocouple sheath were lifted up to the upper portion of the cell. The gate valve was shut, and the disc was removed from the cell and quickly cooled in n-hexane. The disc was washed with water to remove the included salt, washed with alcohol and acetone, dried and then weighed precisely. The dissolution rate was determined from the weight losses of the disc against the dissolution time. After the disc was replaced, the upper portion of the cell was evacuated, and then filled with purified Ar. The gate valve was opened and the disc hung down through the valve into the melt for successive dissolutions.
During the dissolution, the melt was stirred with a magnetic stirrer in order to reduce the effects of natural convection. The dissolution was, therefore, not strictly static.

(2) Dissolution with a rotating disc

The U disc was fitted into a micarex casing to form a uniformly dissolving plane, as shown in Fig. 2. The apparatus for the rotating disc method is shown in Fig. 3. The micarex casing was connected with the bottom of the stainless steel shaft of 16 mm in diameter inserted into the cell through an O-ring seal. The shaft was coupled with the upper shaft of 30 mm in diameter, which was supported by two radial ball bearings and driven by a D.C. motor (125 Wp) at a speed ranging from 400 to 1600 rpm. The rotating speed was controlled by a servomechanical controller and measured by a photoelectric-tube tachometer. The cell assembly for the rotating disc method was equipped with a 5 mm square Pt foil indicator electrode, a silver-silver chloride reference electrode, a pyrex tube thermocouple well, a pyrex tube for introducing purified Ar into the cell, and the shaft with the rotating disc.

LiCl–KCl eutectic salts and UCl₃ were weighed in a dry-box, and melted in the cell under Ar atmosphere. Before the dissolution started, the cell had been held at predetermined temperature for further 1 hr to establish an equilibrium between the electrodes and the melts. The disc was rotated, and the cell was lifted up together with the furnace by a jack until the disc was immersed just below the melt surface. Then the dissolution started.

The dissolution rate was determined by measuring the potential change of the indicator electrode against the reference electrode with time. The potential change was recorded with a pen-recorder.

3 Results

3.1 Static dissolution rate

The static dissolution rates of the U discs into UCl₃–LiCl–KCl melt were determined isothermally at temperatures ranging from 400°C to 500°C. Fig. 4 shows the weight loss vs. time curves at various temperatures.

The dissolution rates could be expressed by
the first order kinetic equation. Fig. 5 shows
the plots of $\log \left( \frac{w^t}{w^0 - w^t} \right)$ against time,
where $w^t$ is the weight loss of the U disc at
time $t$, and $w^0$ is the extrapolated value of $w^t$
for $t$ to infinity. The plots show straight
lines, and the dissolution rate constants $K$
are derived from the slopes.

Fig. 6 shows a plot of $\log K$ against $1/T$. The
activation energy of the dissolution $\Delta H_k$ is
obtained to be $9.3 \pm 1.0$ kcal/mol from Fig. 6.

3.2 Determination of the dynamic
dissolution rate

The dynamic dissolution rate was obtained
from the emf changes for the couple of U
(IV)/U(III) in LiCl-KCl. By assuming the first
order kinetics for the dynamic dissolution, the
concentrations of UCl$_4$ and UCl$_2$ in the melt
was expressed as follows:

$$C_{U(IV)} = \frac{4}{3} C_{U(IV)} [1 - \exp(-KSt/V)] \quad (4)$$
$$C_{U(III)} = C_{U(IV)} \exp(-KSt/V) \quad (5)$$

where, $C_{U(IV)}$ and $C_{U(III)}$ are the concentrations
of UCl$_4$ and UCl$_2$ at time $t$, and
$C_{U(IV)}$ is the initial concentration of UCl$_4$, and was about $2 \times 10^{-3} M$ in this experiment. By introducing eqs.
(4) and (5) into the Nernt equation, one
obtains for the potential at time $t$,

$$E_t = E^0 + \frac{RT}{F} \ln \left( \frac{3}{4} \frac{f_{U(IV)}}{f_{U(III)}} \exp(-KSt/V) \right)$$

where, $E_t$: the potential of the indicator electrode at time $t$, $E^0$: the standard potential for
the couple of U(IV)/U(III), $f_{U(III)}$, $f_{U(IV)}$: activity coefficients. As the concentrations were
low, the activity coefficients are considered to be
constant. Rearrangement of the equation leads to

$$E_t = E^0 - \frac{RT}{F} K't - \frac{RT}{F} \ln \left( \frac{1 - \exp(-K'S)}{1 - \exp(-K'S/t)} \right)$$

where, $E_o = E^0 + (RT/F) \ln (3/4)$, $E^0$: standard
redox potential of the couple U(IV)/U(III) in
LiCl–KCl eutectic salt, $K'$: apparent rate constant and equals $(S/V) K$.

The theoretical $E$-$t$ curve expressed by eq. (7) is shown in Fig. 7. When $t$ approaches to infinity, the second term in the right hand side of eq. (7) diminishes and the curve gradually approaches a line with a slope of $(RT/F) K'$ and with an intercept $E_a$. Then $K$ can be obtained from the slope.

To confirm the relations, $E_a$ was plotted against “reducing time” $K't$, for various rotating speeds at 450°C, as shown in Fig. 8. The plots are well on the theoretical curve, and the equation (7) holds for the dynamic dissolution. The standard redox potential of the couple U(IV)/U(III) was calculated from the intercepts $E_a$. The obtained value is 0.61 ± 0.01 V against Ag–AgCl reference electrode at 450°C, and agrees well with the value 0.595 V against Ag–AgCl obtained in the previous work.2

Thus, the assumption of the first order kinetics for the dynamic dissolution is justified.

3.3 Dynamic dissolution rate with the rotating disc

The dynamic dissolution rates for the rotating U disc were determined at rotating speeds ranging from 400 to 1600 rpm and at temperatures ranging from 400° to 500°C.

For the rotating disc method, by assuming the diffusion kinetics for the dissolution, $K$ is expressed as follows5.

$$K = 0.62 D^{1/5} \nu^{-1/6} \omega^{1/2} \quad (8)$$

where, $D$: the diffusion coefficient of solute, $\nu$: the kinematic viscosity of solution, $\omega$: the angular velocity of the rotating disc.

Fig. 9 shows the relationships between $K$ and $\omega^{1/2}$ for various temperatures. The plots show that $K$ is proportional to $\omega^{1/2}$, and that the
dissolution is controlled by diffusion. The plots of log $K$ vs. $1/T$ are shown in Fig. 10. The activation energies for the dissolution at rotating speeds 600, 800, and 1,000 rpm almost equal each other within the values of $6.6 \pm 0.6$ kcal/mol.

4 Discussion

4.1 Mechanism of the dissolution

From the results of the dynamic dissolution, it is concluded that the process is controlled by diffusion, so that Nernst’s theory is applicable. According to Nernst, the amount of material dissolved per unit time $Q$ is expressed as follows:

$$Q = D (C^a - C_t) S/\delta$$

(9)

Equation (9) expresses the fundamental point of Nernst’s theory, namely, that the liquid closely adjacent to the surface of the dissolving solid is always saturated. The rate of the dissolution is determined by the rate of diffusion between the saturated layer and the bulk of the solution.

For the dissolution associated with a chemical reaction such as eq. (3), it is reasonable to postulate the existence of an equilibrated layer closely adjacent to the solid surface in place of the saturated layer.

From the data of the equilibrium constants for the reaction (3) presented in Table 1, it is concluded that the concentration of U(IV) in the equilibrated layer is extremely low compared with that of U(III) in the layer and can be taken as zero. Fig. 11 shows the concentration distributions of U(III) and U(IV) near the U metal surface schematically.

The amount of U(IV) reaching the U disc surface per unit time is therefore expressed as follows,

$$Q_{U(IV)} = D_{U(IV)} C_{U(IV)} S/\delta.$$  

(10)

that is,

$$-V \frac{dC_{U(IV)}}{dt} = D_{U(IV)} C_{U(IV)} S/\delta.$$  

(11)

The concentration of U(IV) at time $t$ is expressed as,

$$C_{U(IV)}(t) = C_{U(IV)} \exp(-D_{U(IV)} St/\delta).$$  

(12)

This is the same as eq. (5). From eq. (3), the weight loss of the U disc is,

$$W_t = \frac{M_U}{3 V} \int_0^t Q_{U(IV)} dt.$$  

(13)

where $M_U$: molecular weight of U. By introducing eqs. (10) and (12) into (13) and integrating, one obtains,

$$W_t = W_0 \left\{ 1 - \exp \left( - \frac{D_{U(IV)} S}{\delta V} t \right) \right\}.$$  

(14)

Thus, for the weight loss of the U disc, the first order kinetic equation is derived by Nernst’s theory.

The dissolution rate constant $K$ is represented as,

$$K = D_{U(IV)}/\delta.$$  

(15)

Equation (15) expresses that this dissolution process is controlled by the diffusion of U(IV).

From eq. (15), $\delta$ can be calculated. For static dissolution, $\delta$ is about $2 \times 10^{-3}$ cm at 450°C. This agrees with the empirical order of magnitude $10^{-3} - 10^{-4}$ cm. For dynamic dissolution, at 450°C, $\delta$’s are 6.8, 5.6, 4.7 and $4.4 \times 10^{-4}$ cm at 400, 600, 800 and 1,000 rpm, respectively.

4.2 Comparison of the activation energies for the dissolution with that for the diffusion

Provided that the thickness of the diffusion layer $\delta$ is independent of temperature, from eq. (15), activation energies for the dissolution should coincide with that for the diffusion of U(IV).

For the case of the static dissolution, a comparison of $\Delta H_K$ with $\Delta H_D$ (U(IV)) is made in Fig. 6, where $\Delta H_D$ (U(IV)) is the activation energy for the diffusion of U(IV). From Fig. 6, $\Delta H_K$ is determined to be 9.3 ± 1.0 kcal/mol, while $\Delta H_D$ (U(IV)) is 7.3 kcal/mol from the data obtained in the previous work. The difference between $\Delta H_K$ and $\Delta H_D$ (U(IV)) can be
accounted for the change of $\delta$ with temperature. The conditions of the dissolution were almost static, but the melt was stirred by a magnetic stirrer in order to reduce the effects of natural convection. Under such a condition, the thickness of the diffusion boundary layer $\delta$ is generally expressed as follows;

$$\delta \propto (\nu/U)^n$$  \hspace{1cm} (16)

where $U$ is relative velocity of the solid and liquid, the exponent $n$ varies according to whether the flow is laminar ($n=0.5$) or turbulent ($n=0.2$). Therefore, $\delta$ depends on temperature by $\nu$. By taking account the dependence of $\delta$ on temperature, the activation energy for the dissolution is expressed as follows;

$$\Delta H_k = \Delta H_D(U(IV)) - n\Delta H_\nu$$  \hspace{1cm} (17)

where $\Delta H_\nu$ is the activation energy for $\nu$. When equals 0.2, the value of the right hand side of eq. (17) becomes 8.8 kcal/mol, and this agrees with the experimental value of 9.3 ±1.0 kcal/mol.

For dynamic dissolution with rotating disc, $\Delta H_k$ can be derived from eq. (8) as follows.

$$\Delta H_k = |4\Delta H_D(U(IV)) - \Delta H_\nu|/6$$  \hspace{1cm} (18)

The value of $\Delta H_k$ calculated from eq. (18) is 6.1 kcal/mol, and this agrees with the experimental value 6.6±0.6 kcal/mol.

5 Conclusion

1) The studies on the dissolution of U metal into LiCl-KCl-UCl$_3$ by the reaction of U+3 UCl$_3$ →4UCl$_4$ have been carried out in both static and dynamic conditions at 400°-500°C. The dissolution process was expressed by a first order kinetic equation.

2) The dynamic dissolution rates with the rotating disc were proportional to the 1/2 power of rotating speeds, and the dissolution process was controlled by the diffusion of U(IV).

3) The activation energy for the static dissolution rate was considerably large compared with that for the diffusion coefficients of U(IV), but the difference can be explained by the temperature dependence of the thickness of the diffusion layer.

4) For the dynamic dissolution, the value of the activation energies agreed well with the calculated value from Levich's equation.

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References:


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3) M. KANNO, S. YAMAGAMI, This Journal 43, 131 (1975).

