OXIDATION-REDUCTION POTENTIAL OF THE SYSTEM $\mathrm{U}^{3+}/\mathrm{U}^{4}$ IN MOLTEN $\mathrm{NaCl}–\mathrm{KCl}$

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Abstract

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OXIDATION-REDUCTION POTENTIAL OF THE SYSTEM U^{3+}/U^{4+} IN MOLTEN NaCl—KCl

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The oxidation-reduction potential of the system U^{3+}/U^{4+} characterizes not only the equilibrium between metallic uranium and its trivalent and tetravalent ions in the melt, but also the residual current during the electrolysis of uranium tetrachloride in molten chlorides of alkali metals, caused by the reduction of U^{4+} to U^{3+}. There are two papers in the literature ([1,2]) in which the oxidation-reduction potential of uranium was determined in a molten eutectic mixture of LiCl—KCl, at temperatures of 600°C. Unfortunately, the measurements were carried out not with one, but with different, and moreover metallic, reference electrodes: silver ([1]) and platinum ([2]). This circumstance makes comparison of the results of the published studies difficult and greatly complicates their thermodynamic interpretation. But even allowing for possible errors in recalculating the potential values to any one reference electrode, considerable discrepancies are obtained between them. Thus, from the work of Tschebyatovskii and Kish ([1]) it follows that, recalculated to the platinum reference electrode at 450° in molten LiCl—KCl ([3]),

$$E^0_{U^{3+}/U^{4+}} = -0.813 \text{ V},$$

whereas according to the direct measurements of Hill, Parano, and Osteryoung ([2]), under the same conditions,

$$E^0_{U^{3+}/U^{4+}} = -1.25 \text{ V}.$$

As can be seen, the discrepancy reaches 0.44 V.

Fig. 1. Cell. 1 –quartz test tube, 2 –porcelain sleeves, 3 –thermocouple, 4 –Pt and Mo electrode, 5 –alumina crucible with Mo suspension, 6 –electrolyte under investigation, 7 –metallic uranium, 8 –NaCl—KCl melt, 9 –chlorine reference electrode, 10 –quartz tube for charging uranium.

We measured the oxidation-reduction potential U^{3+}/U^{4+} at higher temperatures, 690—810°, in a molten equimolar mixture of NaCl—KCl. A chlorine electrode, which is reversible with respect to the electrolyte under investigation, was chosen as the reference electrode. We used a method, previously tested by

Fig. 2. Curves of potentiometric titration with metallic uranium. 1 — experiment No. 13, 2 —experiment No. 7, 3 —experiment No. 6

Figure 1: Fig. 2. Curves of potentiometric titration with metallic uranium. 1 —experiment No. 13, 2 —experiment No. 7, 3 —experiment No. 6

us on the system Ti^{2+}/Ti^{3+} ([4]), of potentiometric titration of UCl_4 in molten NaCl—KCl with metallic uranium. It made it possible to avoid errors associated with the difficulties of accurately determining in the melt the concentration ratios of tetravalent and trivalent uranium, owing to the high reactivity of the latter.

The cell in which the measurements were carried out is shown schematically in Fig. 1. The chlorine reference electrode was located in a separate quartz test tube with an opening closed by an asbestos diaphragm. The indicator elec-

···electrode, which acquired the potential of the U^{3+}/U^{4+} system, was a platinum or molybdenum wire, which was rotated in order to stir the electrolyte. The latter was prepared by melting an equimolar mixture of chemically pure sodium and potassium chlorides under vacuum. Uranium tetrachloride was obtained by chlorinating its dioxide with vapors of carbon tetrachloride and was purified by 2-3-fold sublimation in vacuum. In individual experiments, the electrolyte contained from 0.6 to 9.6 wt. % U. After evacuation, the gas space above the salt mixture was filled with pure argon. The cell was placed in a preheated furnace, held until the specified temperature was reached, which was maintained constant within $\pm 1^{\circ}$, then metallic uranium was immersed in the melt and, with continuous stirring of the electrolyte, the potential of the indicator electrode was measured every minute. The measurement results, plotted against time, give distorted potentiometric titration curves; with time the latter become increasingly stretched out, since, as the concentration of tetravalent uranium in the melt decreases, the rate of the heterogeneous reduction reaction

$$3U^{4+}_{melt} + U_T = 4U^{3+}_{melt}$$

falls. Nevertheless, inflections were observed on all the curves obtained, corresponding to the attainment of equality of the concentrations of U^{4+} and U^{3+} in the electrolyte. This is seen especially clearly on the differential curves, the most typical of which are shown in Fig. 2.

Fig. 2. Curves of potentiometric titration with metallic uranium. 1 —experiment No. 13, 2 —experiment No. 7, 3 —experiment No. 6

In the case of a molybdenum indicator electrode, one more inflection appeared on the curves, lying at more positive potentials, about −1 V. Under the same conditions, it was absent on a platinum electrode. Evidently,

Table 1

Experiment No.	Temp., °C	Concentration of uranium in the initial melt, U, wt. %	Concentration of uranium in the initial melt, $[U^{4+}]$	Indicator-electrode material	e.m.f.	Experiment No.	Temp., °C	Concentration of uranium in the initial melt, U, wt. %	Concentration of uranium in the initial melt, $[U^{4+}]$	Indicator-electrode material	e.m.f.
1	698	1.77	$5.0 \cdot 10^{-3}$	Mo	1.432	9	715	5.55	$1.7 \cdot 10^{-2}$	Mo	1.422
2	701	4.75	$1.4 \cdot 10^{-2}$	Mo	1.423	10	720	2.24	$6.5 \cdot 10^{-3}$	Mo	1.414
3	701	9.6	$2.8 \cdot 10^{-2}$	Mo	1.423	11	740	2.10	$6.0 \cdot 10^{-3}$	Pt	1.404
4	708	7.92	$2.3 \cdot 10^{-2}$	Mo	1.416	12	786	4.21	$1.2 \cdot 10^{-2}$	Pt	1.377
5	714	1.52	$4.3 \cdot 10^{-3}$	Mo	1.418	13	790	0.6	$1.7 \cdot 10^{-3}$	Pt	1.376
6	714	7.95	$2.3 \cdot 10^{-2}$	Pt	1.416	14	802	1.86	$5.3 \cdot 10^{-3}$	Mo	1.376
7	705	1.98	$5.7 \cdot 10^{-3}$	Mo	1.428	15	805	2.86	$8.1 \cdot 10^{-3}$	Pt	1.372
8	715	2.14	$6.1 \cdot 10^{-3}$	Mo	1.416						

it was associated with dissolution of molybdenum through the reaction:

$$\mathrm{Mo_t} + 3\mathrm{U^{4+}_{melt}} = \mathrm{Mo^{3+}_{melt}} + 3\mathrm{U^{3+}_{melt}}.$$

Table 1 gives, for different temperatures and concentrations of tetravalent uranium in the initial melts, the values of the cell emf corresponding to the inflection points of the potentiometric titration curves. After subtracting the thermal emf between the cell electrodes (C–Mo or C–Pt), they give the sought values of the oxidation-reduction potential $E^0_{U^{3+}/U^{4+}}$ relative to the chlorine reference electrode. The corresponding points, plotted (Fig. 3) as a function of temperature, fit well on a straight line described by the empirical equation

$$E^0_{U^{3+}/U^{4+}} = -1.906 + 4.83 \cdot 10^{-4} T \pm 0.003 \text{ V}.$$

Fig. 3. Temperature dependence of the oxidation-reduction potential of the U^{3+}/U^{4+} system

Figure 2: Fig. 3. Temperature dependence of the oxidation-reduction potential of the U^{3+}/U^{4+} system

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Despite the fact that the ionic-mole concentration of uranium in the initial melts changed by almost a factor of 17 (from $1.7 \cdot 10^{-3}$ to $2.8 \cdot 10^{-2}$), the value of $E^0_{U^{3+}/U^{4+}}$ remained constant within the possible measurement errors. This indicates that salt mixtures of the investigated compositions UCl_3—UCl_4—NaCl —KCl behave as ideal solutions.

The oxidation-reduction potential U^{3+}/U^{4+} in a NaCl—KCl melt is considerably more positive than the potential Th^{2+}/Th^{4+}. At 1000°K the potential difference reaches

$$E^0_{U^{3+}/U^{4+}} - E^0_{Th^{2+}/Th^{4+}} = 0.517 \text{ V}.$$

From the previously found ([5]) value

$$E^0_{Th^{2+}/Th^{4+}} = -1.945 - 0.95 \cdot 10^{-4} T \text{ V}$$

in the NaCl—KCl melt relative to the chlorine reference electrode, one can find expressions for the equilibrium constant of the reaction

$$2U^{4+}_{melt} + Th^{2+}_{melt} \rightleftarrows 2U^{3+}_{melt} + Th^{4+}_{melt}$$

$$\lg K = \lg \frac{[Th^{4+}][U^{3+}]^2}{[Th^{2+}][U^{4+}]^2} = 5.82661 + \frac{391}{T}.$$

It follows from this that, for example, at 1000°K, reduction in the melt of 99% of U

$$\left(\frac{[U^{3+}]}{[U^{4+}]} = 99\right)$$

is accompanied by reduction of only 0.6% of Th

$$\left(\frac{[Th^{2+}]}{[Th^{4+}]} = 0.0061\right).$$

From measurements of the equilibrium potentials of uranium in the NaCl–KCl melt ([6]), it was established that

$$E^0_{U/U^{3+}} = -3.010 + 6.65 \cdot 10^{-4} T \text{ V}$$

relative to the chlorine reference electrode. This makes it possible to calculate, from the equality

$$E^0_{U^{3+}/U^{4+}} = 4E^0_{U/U^{4+}} - 3E^0_{U/U^{3+}},$$

the value of the standard electrode potential U/U^{4+}:

$$E^0_{U/U^{4+}} = -2.734 + 6.14 \cdot 10^{-4} T \text{ V}.$$

Since the value $E^0_{U/U^{4+}}$ is given relative to a reversible chlorine electrode, it can be used directly for calculations of thermodynamic quantities characterizing the state of uranium tetrachloride in a NaCl–KCl melt. If it is assumed that solutions of UCl_4 in this melt behave as ideal solutions at concentrations corresponding essentially to mixtures of the congruently melting compound K_2UCl_6 ([7]) with NaCl and excess amounts of KCl, then the decomposition voltage of UCl_4 at an ionic-mole uranium concentration $[U^{4+}] = 0.2$ is

$$\varepsilon_{\text{decomp}} = -E^0_{U/U^{4+}} - 0.496 \cdot 10^{-4} T \lg 0.2,$$

$$\varepsilon_{\text{decomp}} = 2.734 - 5.79 \cdot 10^{-4} T \text{ V}.$$

This quantity is a direct measure of the change in the isobaric potential in the reaction of formation of uranium tetrachloride from the elements in a melt of the given composition:

$$U_t + 2Cl_{2g} = UCl_{4\,\text{melt}},$$

$$\Delta Z = -4F\varepsilon_{\text{decomp}} = -252\,206 + 53.41T \text{ cal/mol},$$

whence the heat and entropy of this reaction are:

$$\Delta H_{UCl_{4\,\text{melt}}} = -252\,206 \text{ cal/mol},$$

$$\Delta S_{UCl_{4\,\text{melt}}} = -53.41 \text{ cal/deg} \cdot \text{mol}.$$

From the thermodynamic data available in the literature (7), one may calculate the change in the isobaric potential in the reaction of formation from the elements of pure liquid uranium tetrachloride:

$$\Delta Z_2 = -233\,561 + 49.34T \text{ cal/mol.}$$

Thus it is seen that mixing liquid uranium tetrachloride with the NaCl–KCl melt is accompanied by a considerable change in the isobaric potential, equal to:

$$\Delta Z_{\text{mix}} = \Delta Z_1 - \Delta Z_2 = -18\,645 + 4.07T \text{ cal/mol.}$$

This indicates the formation in the molten mixture UCl_4–NaCl–KCl of stable complex anions:

$$U^{4+}_{\text{melt}} + 6Cl^{-}_{\text{melt}} \rightarrow UCl^{2-}_{6\,\text{melt}}.$$

This reaction proceeds with the evolution of heat $\Delta H = -18.6$ kcal/g-ion and with a small decrease in the entropy of the system $\Delta S = -4.07$ e.u., owing to some ordering in the mutual arrangement of ions in the melt.

Knowing the values of $E^0_{U/U^{3+}}$ and $E^0_{U/U^{4+}}$, one can obtain expressions for the change in isobaric potential and the equilibrium constant of the reaction

$$3U^{4+}_{\text{melt}} + U_t \rightleftarrows 4U^{3+}_{\text{melt}}$$

$$\Delta Z = -276\,744\left(E^0_{U/U^{4+}} - E^0_{U/U^{3+}}\right) = -76\,381 + 14.11T \text{ cal},$$

$$\lg K = \lg \frac{[U^{3+}]^4}{[U^{4+}]^3} = \frac{120000}{1.984T}\left(E^0_{U/U^{4+}} - E^0_{U/U^{3+}}\right) = -3.0845 + \frac{16690}{T}.$$

In contrast to thorium dichloride (5), uranium trichloride in the NaCl–KCl melt is stable over the entire accessible temperature interval (its disproportionation to UCl_4 and U should begin at temperatures above 5000°).

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Note: Figure translations are in progress. See original paper for figures.