Determination Of Partial Molar Excess Gibbs Energy Of $ThCl_4$ In LiCl-KCl Eutectic Using Electromotive Force Measurements

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Abstract:

Electromotive force measurements on $Th^{4+}|Th$ couple in molten LiCl-KCl eutectic in the temperature range 673-798 K were carried out to derive standard electrode potential, partial molar Gibbs energy of formation and activity coefficientof $ThCl_4$ and compared with that of other actinide chlorides. Low activity coefficient of $ThCl_4$ is suggestive of formation of strong complexes in LiCl-KCl eutectic similar to that seen in other actinide chlorides.

Keywords: Molten salt, standard electrode potential, Gibbs energy, activity coefficient

1. Introduction

Electrochemical studies on the redox behaviour of $ThCl_4$ in molten LiCl-KCleutectichave been carried out earlier in our laboratory. This included the determination of standard electrode potential of $Th^{4+}|Th$ couple using various transient methods [1] and evaluation of electrode kinetics parameters like exchange current density using DC polarization techniques [2]. The above studies on thorium are further extended in the present work by determining the partial Gibbs energy of formation and activity coefficient of $ThCl_4$ in LiCl-KCl eutectic using galvanic cell measurements. Thisstudy is aimed at investigating the complexation behaviour of thorium by estimating its partial excess Gibbs energy in LiCl-KCl eutectic.

2. Experimental

2.1. Preparation of electrolyte and electrodes

LiCl-KCl-$ThCl_4$ electrolyte was prepared by equilibration of thorium metal (obtained from BARC, Mumbai) with cadmium chloride in molten LiCl-KCl eutectic at 773 K for 30 h inside Ar atmosphere glove box.Preparation of Th electrode is discussed elsewhere and is shown in Figure 1 [2].All experiments were carried out in inert atmosphere in the temperature range 678-798 K. Details on loading of electrochemical cell assembly are discussed elsewhere [2]. Electromotive force and temperature were recorded using Agilent 34970A data acquisition system.



Figure 1: Th electrode used in galvanic cell measurements.

3. Results and Discussions

Equilibrium potential $E^{eq}_{Th^{4+}|Th}$ between $Th^{4+}|Th$ and $Ag^{+}|Ag$ reference electrode in LiCl-KCl-$ThCl_4$ electrolyte was measured by constructing the following galvanic cell:

from the linear fit were found to be −1178.2±11.7 kJ mol^{-1} and 266.3±15.8 J K^{-1} mol^{-1}, respectively. Partial molar excess Gibbs energy of $ThCl_4$ in LiCl-KCl eutectic can be estimatedfrom the following expression where the supercooled liquid state of $ThCl_4$ is chosen as reference state:

$$\overline{G^{salt}_{Th^{4+}}} - G^{sc\,liq.}_{Th^{4+}} = O\overline{G^{ex}_{Th^{4+}}} = RT\ln\psi_{Th^{4+}} = RT[\ln a_{Th^{4+}} - \ln x_{Th^{4+}}] \quad (5)$$

The temperature dependence of partial molar excess Gibbs energy is therefore given by:

$$O\overline{G^{ex}_{Th^{4+}}}\left(Jmol^{-1}\right) = -(53963 \pm 4863) + (35.1 \pm 6.7)T(K) \quad (6)$$

Here, partial molar excess enthalpy and partial molar excess entropy of $ThCl_4$ in LiCl-KCl eutectic were -53963 ± 4863 J mol^{-1} and 35.1± 6.7 J K^{-1} mol^{-1}, respectively. The activity coefficient of $ThCl_4(\psi_{4+})$ wasestimated using Equation 5 and was found to be in the range of

4.5×10^{-3} to 1.5×10^{-2}in the measured temperature range. These values are in close agreement with those estimated by Chiotti et al. [4], Yang et al. [5] and Casseyre et al. [6]. For all practical purposes, activity coefficient of $ThCl_4$can be considered similar to that of UCl_3, $PuCl_3$, $NpCl_3$ and $AmCl_3$ [7-8]. The complexation behaviour of thoriumtherefore is also expected to be similar [4,6] to that of other actinides in the melt.

4. Conclusions

Galvanic cell measurements were carried out in the present work to measure partial molar Gibbs energy of formation of $ThCl_4$ in LiCl-KCl eutectic and compared with that of other actinides chlorides. Partial molar excess Gibbs energy of $ThCl_4$ was estimated from emf data to calculate activity coefficient of $ThCl_4$, which was found to be close to that of other actinide chlorides. The low values of activity coefficient indicate formation of stable complexes of thorium in LiCl-KCl melt, which are also similar in stability as that of uranium, plutonium and minor actinides like Np and Am.

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Nomenclature

$E^{eq}_{Th^{4+}|Th}$: Equilibrium potential of Th^{4+}|Th couple

$E^{\circ}_{Ag^{+}|Ag}$: Standard electrode potential of Ag^{+}|Ag couple (*vs.* $Cl^{-}|Cl_2$)

$E^{\circ}_{Th^{4+}|Th}$: Standard electrode potential of Th^{4+}|Th couple (*vs.* $Cl^{-}|Cl_2$)

x_{AgCl}: Mole fraction of AgCl

x_{ThCl_4}: Mole fraction of $ThCl_4$

$\overline{G^{salt}_{Th^{4+}}}$: Partial molar Gibbs energy of $ThCl_4$

$G^{sc.liq.}_{Th^{4+}}$: Molar Gibbs energy of supercooled $ThCl_4$ liquid

$O\overline{G^{ex}_{Th^{4+}}}$: Partial molar excess Gibbs energy of $ThCl_4$

R: Universal gas constant (8.31452 J $mol^{-1}K^{-1}$)

T: Temperature in K

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