ELECTROCHEMICAL BEHAVIOUR OF PLUTONIUM ION IN LiCl-KCL EUTECTIC MELTS

J. Serp, R.J.M. Konings, R. Malmbeck, J. Rebizant, C. Scheppler and **J-P. Glatz**
European Commission, JRC, Institute for Transuranium Elements,
Postfach 2340, D-76125 Karlsruhe, Germany

Abstract

This work presents a study on the electrochemical properties of $PuCl_3$ in a molten LiCl-KCl eutectic, at a temperature range of 733-833 K. Transient electrochemical techniques, such as cyclic voltammetry and chronopotentiometry, on inert metallic tungsten and molybdenum working electrodes have been used in order to investigate the reduction mechanism and transport parameters. The results show that Pu^{3+} is reduced to Pu metal by a single step mechanism and that the diffusion coefficient of Pu^{3+} ion is $D_{Pu^{3+}} \sim 2.10^{-5}$ cm^2/s at 733 K. In addition the standard potential (-2 796 V at 733 and vs. Cl_2/Cl^- reference electrode) and free enthalpy of formation for the Pu(III)/Pu(0) system have been measured and compared to thermodynamic data in order to estimate the activity coefficient of Pu^{3+} in the molten LiCl-KCl eutectic.

Introduction

Partitioning and transmutation (P&T) concepts are studied worldwide as they offer the possibility to reduce the long-term radiotoxicity of the nuclear waste. Essential for P&T concepts are the efficient recovery and multi-recycling of actinides. Pyrochemical separation processes for the recovery of uranium and to some extent for plutonium have been investigated for decades and are nowadays well known. The application to the reprocessing of metallic fuel from the EBR-II reactor is probably the best known process. [1] At present there is an increasing interest in the application of pyrochemical separation techniques in which also the minor actinides are recycled and burned by fission in dedicated reactors. As the fuel in such reactors will contain significant quantities of (minor) actinides, possibly also in inert (U free) matrices, and reach high burn-ups, pyrochemical separation techniques offer advantages compared to hydrochemical techniques. The high radiation stability of the salt solvent and the resulting shorter cooling times are reasons why pyrochemical techniques are better suited for the reprocessing and recycling of actinides from these type of fuels.

Electrorefining is the most common pyrochemical separation process used for nuclear fuels. The actinides are separated from the bulk of fission products by electrotransport in a molten salt electrolyte, i.e. uranium onto a solid cathode and plutonium and minor actinides into a liquid Cd cathode. [2] Additional systems for the separation of Pu and MA are now being developed such as electrotransport into different molten metal cathodes (for example Bi) and deposition or co-deposition of Pu onto different solid cathodes. The aim is to optimise the separation efficiency and to minimise the content of Ln´s in the product fraction. For this type of research, it is important that an accurate set of thermo and electrochemical data for all actinides is investigated. [3-5] In this work, we therefore report on the electrochemical investigation of Pu in a LiCl-KCl eutectic melt. A combination of transient electrochemical techniques such as cyclic voltammetry and chronopotentiometry has been applied in order to investigate valency, mechanisms of reduction and diffusion coefficients of Pu in molten chloride salt. In addition, some thermodynamic properties have been calculated and compared to reference thermodynamic data for Pu trichlorides for the calculation of the activity coefficient of Pu^{3+} in molten LiCl-KCl salt.

Experimental

The electrochemical experiments, storage and handling of all chemicals were carried out in a glovebox in purified Ar atmosphere (<1 ppm of water and oxygen). The glovebox is equipped with a well type oven in which the experimental set-up can moved up and down by means of a lifting system. The electrodes, thermocouple and a stirrer are positioned through a water-cooled flange, which supports the Al_2O_3 or quartz crucible used in the electrochemical cell. The electrolytic bath consisting of Pu^{3+} dissolved in LiCl-KCl eutectic (Aldrich 99.99%) was prepared by oxidising Pu-metal (ITU stock material, low Am content) introduced in a molten Bi phase in the bottom of the crucible by adding $BiCl_3$ to the salt phase. The redox reaction (1) obtained is described below:

$$Pu^0_{Bi-phase} + Bi^{3+}_{salt-phase} \Leftrightarrow Pu^{3+}_{salt-phase} + Bi^0 \tag{1}$$
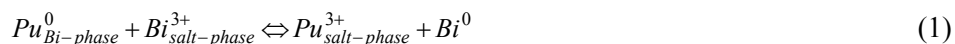
The electrochemical techniques used, i.e. cyclic voltammetry and chronopotentiometry, was carried out in an electrochemical cell having a three electrode set-up and a PAR 273 potentiostat with EG&G M270 electrochemical software. Inert working electrodes were prepared using 1 mm metallic W or Mo wires and inserted approximately 5 mm into the bath. The surface area could be determined after each experiment by measuring the immersion depth of the electrode. The reference electrode used was an Ag/LiCl-KCl-AgCl (1wt.%) prepared in a PYREX glass tube and the auxiliary electrode a 1 mm Mo wire bent into the shape of a spiral.

Samples (about 100 mg) were taken from the salt phase, dissolved and diluted in nitric acid. The concentration of Pu was determined by ICP-MS analysis and by HPGe γ counting. [6,7]

Results and discussion

Diffusion coefficient

The cyclic voltammogramms obtained at the W working electrode in a solution of PuCl$_3$ (8,3.10^{-5} mol.cm^{-3}) in LiCl-KCl eutectic salt are shown on Figure 1 (cf. [8,9]). A single cathodic peak I$_c$ is clearly associated with a sharp anodic peak I$_a$. It can thus be concluded that the electroreduction of Pu(III) ions proceeds via one step process (peak I$_c$ at -1,76V vs. Ag/AgCl 1wt.%). Peak I$_a$ corresponds to the reoxidation of the metal deposit formed during the cathodic sweep at the W working electrode. At lower concentrations of Pu^{3+}, a second smaller cathodic peak (E$_p$~-1,5 V) peak has been observed which is attributed to underpotential deposition of Pu on the tungsten electrode. [9]
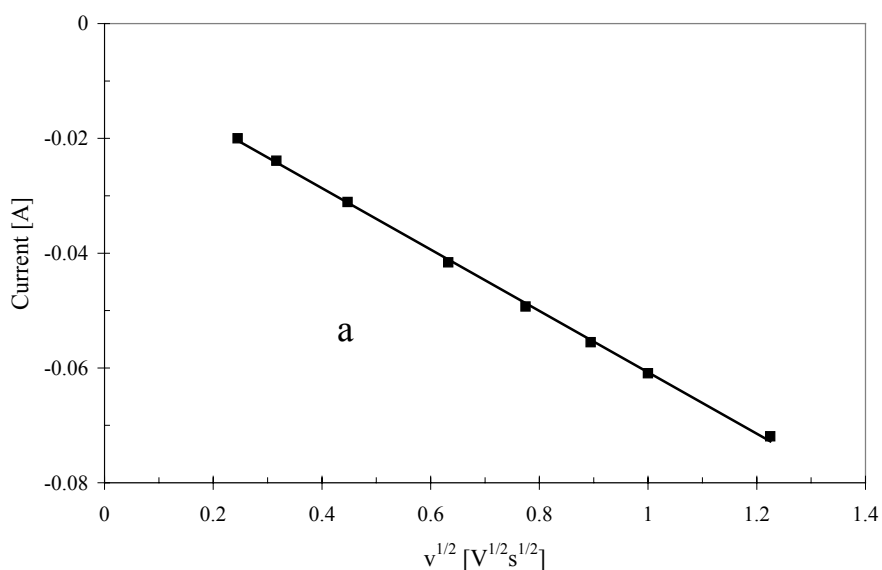
Figure 1. **Cyclic voltammogramms obtained for Pu^{3+} in LiCl-KCl eutectic salt**
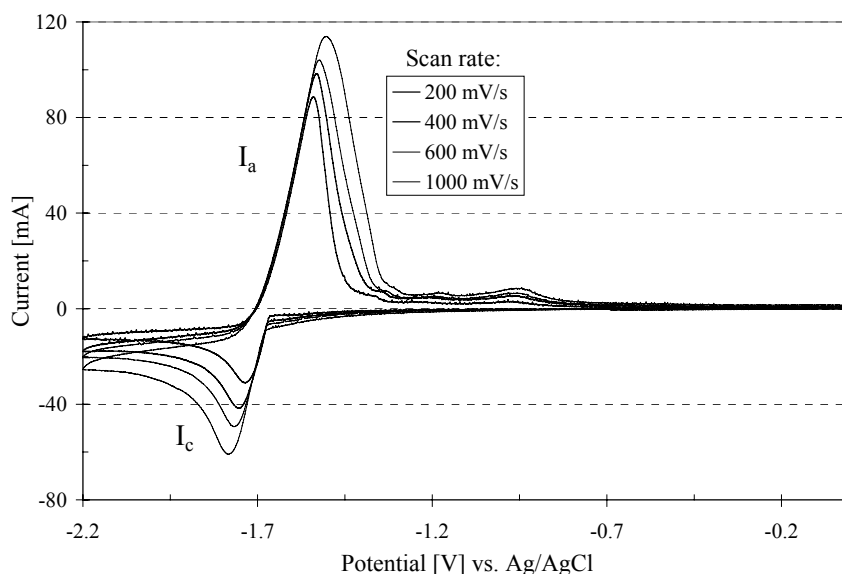
[Pu^{3+}] = 8.3·10^{-5} mol·cm^{-3},.W working electrode (S = 0.2 cm^2).
Temperature = 733 K. Reference electrode Ag/AgCl 1 wt.%.

The current of the peak I$_c$ is directly proportional to the square root of the polarisation rate, v [mV/s], which is shown in Figure 2. Moreover, up to a polarisation rate of 200 mV/s the value of the peak potential E$_p$ is constant and independent of the polarisation rate. According to the theory of linear sweep voltammetry, [10] the electrode process, for scan rates <200 mV/s, is thus reversible and controlled by the rate of mass transfer. For higher scan rates (v>200 mV/s), the cathodic peak potential is shifted negatively, indicating that the system becomes quasi-reversible. [11]

Figure 2. **The dependencies of peak currents (a) of the deposition process
on the polarisation rate**

$[Pu^{3+}] = 8.3 \cdot 10^{-5}$ mol·cm^{-3}. W working electrode (S = 0,2 cm^2).
Temperature = 733 K. Reference electrode Ag/AgCl 1wt.%.

For cyclic voltammetry, the diffusion coefficient of Pu(III) species was calculated (Table 1) at low scan rates (v <200 mV/s) using the Berzins and Delahay equation for reversible systems, controlled by diffusion, [12] assuming that the number of electrons exchanged in the reduction process involved in peak I_c equals 3:

$$\frac{I_P}{\sqrt{v}} = 0,61(nF)^{3/2}(RT)^{-1/2} AD^{1/2}C_{Pu(III)} \tag{2}$$

where I_p is the peak cathodic current (A), S is the electrode area (cm^2), $C_{Pu(III)}$ is the bulk concentration of the electroactive species (mol·cm^{-3}), D is the diffusion coefficient (cm^2·s^{-1}), v is the potential sweep rate (V·s^{-1}), and n the number of electrons involved in the reaction.

In addition, the linear potential sweep data were transformed according to the convolution principle, [11] into a form resembling a steady-state voltammetric curve. Typical semi-integrals for voltammetric curves at low scan rates, see Figure 3, indicate that the m* value is constant for v<200 mV/s. According to the theory of convolution, [13,14] the diffusion coefficient of Pu(III) is obtained (Table 1) using equation (3):

$$m^* = - nFS \, C_{Pu(III)}D^{1/2} \tag{3}$$

where n is the number of electrons, S is surface area of the working electrode (cm^2), m* is the maximum of the semi-integral of the voltammetry current.

Figure 3. **Semi-integrals of cyclic voltammetric curves**
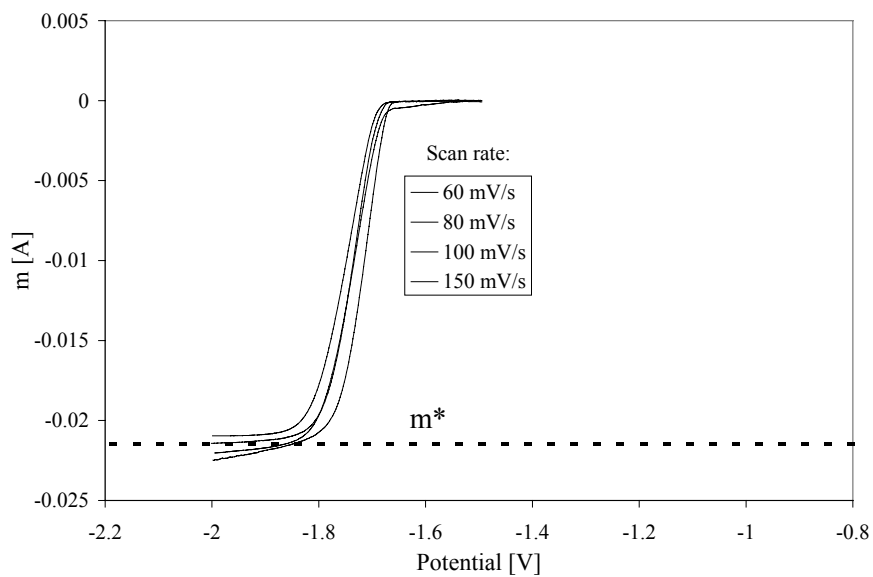
PuCl$_3$ concentration: $1,2.10^{-4}$ mol.cm^{-3}.
W working electrode: W (s = 0,15 cm^2).
Temperature: 733 K. Reference electrode Ag/AgCl 1 wt.%.

A typical chronopotentiogramm for the electroreduction of Pu(III) to Pu(0) in LiCl-KCl eutectic at a tungsten electrode in this case for a current of 30 mA, is shown in Figure 4. Several different current densities were used and the plot of $i\tau^{1/2}$ versus i, yielded a straight line as shown in Figure 5. In addition, the chronopotentiometric curves did not shift in negative direction with increasing current density.

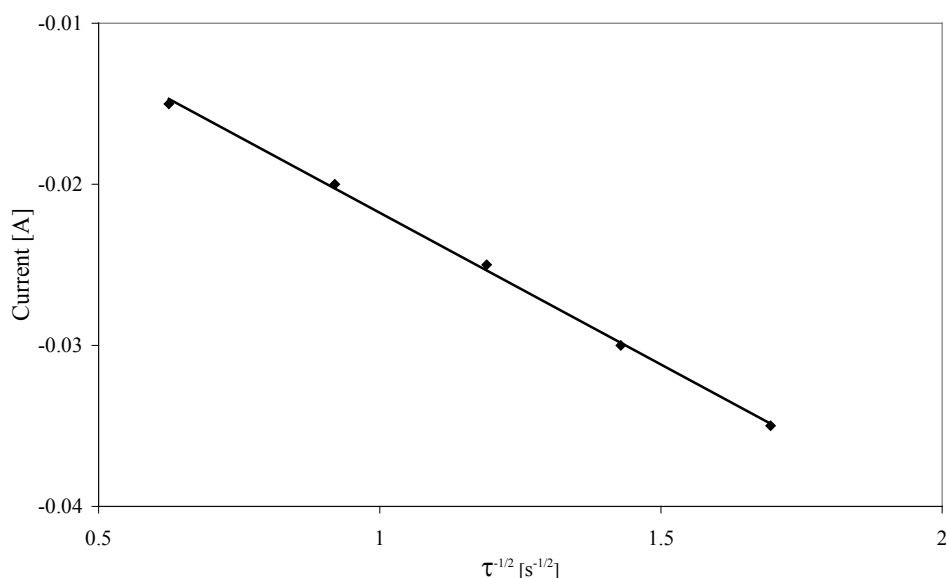Figure 4. **Chronopotentiogramm of PuCl$_3$+LiCl-KCl eutectic**
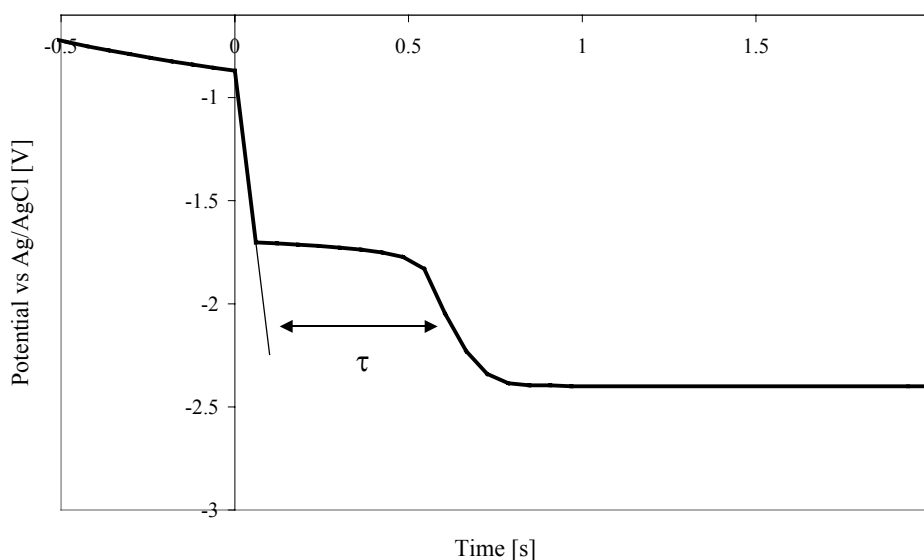
[Pu^{3+}] concentration: $8.3·10^{-5}$ mol·cm^{-3}. W working electrode (S = 0.2 cm^2).
Temperature = 733 K. Reference electrode Ag/AgCl 1wt.%, I = -30 mA.

On the basis of these results, the electrochemical reduction of Pu(III) can be considered as a reversible and diffusion controlled process [15] and the diffusion coefficient of Pu(III) in the LiCl-KCl eutectic can be calculated (Table 1) using the Sand equation: [11]

$$i\sqrt{\tau} = \frac{nFC_{Pu(III)}s\sqrt{\pi D}}{2} = \text{constant} \tag{4}$$

Figure 5. **The dependence of current vs $\tau^{-1/2}$**

PuCl$_3$ concentration: $8,3.10^{-5}$ mol.cm^{-3}. W working electrode: W (s = 0,2 cm^2).
Temperature: 733 K. Reference electrode Ag/AgCl 1wt.%.

Table 1. **Diffusion coefficient of Pu^{3+} in LiCl-KCl at 733 K**

	Pu^{3+} [mol/cm^3]	Diffusion coefficient, $10^5 \cdot D_{Pu3+}$ [cm$^2 \cdot$s^{-1}]
Cyclic voltammetry	$8.3 \cdot 10^{-5}$	1.5
Convolution	$8.6 \cdot 10^{-5}$ $1.2 \cdot 10^{-4}$	1.3 1.6
Chronopotentiometry	$8.6 \cdot 10^{-5}$ $1.2 \cdot 10^{-4}$	1.85 1.7

Apparent standard potential

By applying the Nernst equation in the case of the formation of a metallic deposit, logarithm analysis of semi-integral curves allows to calculate the number of electrons exchanged as well as the standard potential of the studied redox couple [13] according to:

$$E = E^0_{Pu(III)/Pu(0)} + \frac{RT}{nF}\ln\frac{a_{PuCl_3}}{a_{Pu(0)}} + \frac{RT}{nF}\ln(\frac{m*-m}{m*}) \tag{5}$$

where a_{PuCl_3} and $a_{Pu(0)}$ are the activity coefficient of PuCl$_3$ and pure plutonium metal, respectively. The chronopotentiometric curve for a reversible electroreduction with formation of an insoluble

metallic deposit, assuming the activity of the pure metal is 1, can be described [16] by the following equation:

$$E(t) = E^0_{Pu(III)/Pu(0)} + \frac{RT}{nF}\ln\left(a_{PuCl_3}\right) + \frac{RT}{nF}\ln(\frac{\sqrt{\tau}-\sqrt{t}}{\sqrt{\tau}}) \tag{6}$$

where τ is the transition time (s). By introducing the apparent standard potential, E^{*0}, for the Pu(III)/Pu(0) redox couple as:

$$E^{*0}_{Pu(III)/Pu(0)} = E^0_{Pu(III)/Pu(0)} + \frac{RT}{nF}\ln\gamma_{PuCl_3} \tag{7}$$

Equations 5 and 6 can be rewritten to:

$$E = E^{*0}_{Pu(III)/Pu(0)} + \frac{RT}{nF}\ln X_{PuCl_3} + \frac{RT}{nF}\ln\frac{m^*-m}{m^*} \tag{8}$$

$$E = E^{*0}_{Pu(III)/Pu(0)} + \frac{RT}{nF}\ln X_{PuCl_3} + \frac{RT}{nF}\ln\frac{\sqrt{\tau}-\sqrt{t}}{\sqrt{\tau}} \tag{9}$$

Plots of the electrode potential versus $\ln(\frac{m^*-m}{m^*})$ or $\ln(\frac{\sqrt{\tau}-\sqrt{t}}{\sqrt{\tau}})$ are linear and the slopes (RT/nF) agree very well with a three-electron exchange process. Knowing the mole fraction of $PuCl_3$, the apparent standard potential can be obtained from Eqs. 7 and 8. It was calculated for two mole fractions and three different temperatures and the results are listed in Table 2. All measurements were done at plutonium concentration levels where Henry´s law applies (i.e. $a_{PuCl_3} = \gamma_{PuCl_3} \cdot c_{PuCl_3}$ thus γ_{PuCl_3} is constant) and the correction to infinite dilution ($X_{PuCl_3} \to 0$) [17] can be neglected.

The apparent standard potential is obtained in mole fraction scale versus the Ag/AgCl (1 wt.% = X_{AgCl} = 0.0039) reference electrode. For conversion to the scale of a Cl_2/Cl^- reference electrode, unit activity coefficient and unit activity of the pure metal are assumed for the AgCl and Ag, respectively. [4] The potential of the reference electrode can then be defined as:

$$E_{AgCl} = E^0_{AgCl} + \frac{RT}{nF}\ln X_{AgCl} \tag{10}$$

where, for X_{AgCl} = 0.0039 = 1 wt.%, the difference between E_{AgCl} and E^0_{AgCl} is –0.3505 V. At low concentrations of AgCl in LiCl-KCl eutectic, the value of E^0_{AgCl} relative to the Cl_2/Cl^- is given by Fusselman et al.: [4]

$$E^0_{AgCl} = -1.0910 + 0.0002924 \cdot T(K) \tag{11}$$

At T = 733K, Eq. 11 yields a standard potential E^0_{AgCl} of -0,877 V vs. Cl_2/Cl^- and Eq. 10 yields the potential of the reference electrode E_{AgCl} to –1,226 V vs. Cl_2/Cl^-.

The average apparent standard potential obtained at 773 K is $E^{*0}_{Pu(III)/Pu(0}$ = –2.769 V and this value is in very good agreement with the standard potential given by Roy et al. [18] $E^0_{Pu(III)/Pu(0}$ =–2.775 V obtained from emf measurement.

Table 2. **Apparent standard potentials and Gibbs free energy of formation of $PuCl_3$**

T (K)	X_{PuCl3}	E^{*0} vs Ag/AgCl		E^{*0} vs Cl_2/Cl^-		$\Delta G^{\infty}_{PuCl_3}$ kJ/mole	Average $\Delta G^{\infty}_{PuCl_3}$ kJ/mole
733	$1,662.10^{-3}$	CV	-1.5715	CV	-2,7975	- 809,9	- 809,5
		CP	-1.5629	CP	-2,7889	- 807.4	
	$3,03.10^{-3}$	CV	-1.5804	CV	-2,8064	- 812.4	
		CP	-1.5664	CP	-2,7924	- 808.4	
773	$1,662.10^{-3}$	CV	-1,5336	CV	-2,7699	- 801.9	- 801,9
		CP	-1,5312	CP	-2,7675	- 801.2	
	$3,03.10^{-3}$	CV	-1,5432	CV	-2,7695	- 802.8	
		CP	-1,5327	CP	-2,769	- 801.6	
823	$3,03.10^{-3}$	CV	-1,4961	CV	-2.7416	- 793.7	- 792,1
		CP	-1,4865	CP	-2,7302	- 790.4	

The standard free energy of formation, $\Delta G^{\infty}_{PuCl_3}$ at infinite dilution is calculated according to:

$$\Delta G^{\infty}_{PuCl_3} = nFE^{*0}_{Pu(III)/Pu(0)} \qquad (12)$$

A plot of the average $\Delta G^{\infty}_{PuCl_3}$ as a function of temperature shows a linear dependence. A least square fit of the free standard energy versus temperature data can then be expressed by the following equation:

$$\Delta G^{\infty}_{PuCl_3} = \Delta H^{\infty}_{PuCl_3} - T\ \Delta S^{\infty}_{PuCl_3} \qquad (13)$$

from which values of enthalpies ($\Delta H^{\infty}_{PuCl_3}$) and entropies ($\Delta S^{\infty}_{PuCl_3}$) of formation, at infinite dilution, are obtained. These are in good agreement with thermodynamic data obtained in previous emf measurements. [18]

$$\text{This work:}\quad \Delta G^{\infty}_{PuCl_3} = 0.200 - 956.6 \cdot T \qquad (14)$$

$$\text{From [18]}\quad \Delta G^{0}_{PuCl_3} = 0.2039 - 960.6 \cdot T \qquad (15)$$

The Gibbs energy of formation of $PuCl_3$ in the supercooled liquid state has been calculated from the data in Table 3, which shows the thermodynamic data from two different sources, the OECD-NEA chemical thermodynamic database [19] and the ITU material property database f-MPD. [20] The differences between the two sources are marginal, though most of them are estimated. Only the enthalpy of formation and the melting point are based on experimental measurements. The ITU data have been obtained from a comparison to the lanthanide(III) halides, [21] for which a thorough analysis has been made.

Activity coefficient of $PuCl_3$ in the LiCl-KCl, γ_{PuCl3}, has been calculated from the difference between the Gibbs free energy at infinite dilution from the electrochemical measurements and the Gibbs free energy of formation in the supercooled state (sc):

$$RT \ln \gamma_{MCl_n} = \Delta G^{\infty}_{MCl_3} - \Delta G^{0}_{MCl_3 (sc)} \qquad (16)$$

The activity coefficients obtained are shown in Table 4. The values differ significantly depending on the source of the data for the sc state. This shows the need for more accurate thermochemical data for pure $PuCl_3$.

Table 3. **The thermochemical data for PuCl₃**

	NEA-TDP [19]	f-MPD [20]
$\Delta_f H^o$(298.15 K) / kJ mol^{-1}	-956.6 ± 1.8	-956.6 ± 1.8
S^o(298.15 K) / J K^{-1} mol^{-1}	161.7 ± 3.0	161.4 ± 3.0
C_p(sol) / J K^{-1} mol^{-1}	91.35+24.0·10^{-3} (T/K)+ 2.4·10^{-5}(T/K)$^{-2}$	91.412+37.16·10^{-3}(T/K)+ 0.274·10^{-5}(T/K)$^{-2}$
T_{fus} / K	1041 ± 2	1041 ± 2
$\Delta_{fus} H^o$ / kJ mol^{-1}	55 ± 5	49 ± 3
C_p(liq) / J K^{-1} mol^{-1}	145 ± 15	144 ± 10

Table 4. **The derived activity coefficients of PuCl₃ in LiCl-KCl eutectic**

T/K	NEA-TDP		f-MPD		
	$\Delta_f G^o$(T) / kJ mol^{-1}	γ^o(T)	$\Delta_f G^o$(T) / kJ mol^{-1}	γ^o(T)	γ^o(T) [18]
733	-775.1	3.5·10^{-3}	-786.2	9.5·10^{-3}	2.3·10^{-3} (723K)
773	-767.9	5.0·10^{-3}	-777.8	1.2·10^{-2}	4.1·10^{-3}
823	-759.0	7.9·10^{-3}	-767.3	1.6·10^{-2}	-

Conclusion

The electrochemical behaviour of PuCl₃ has been investigated in molten LiCl-KCl eutectic. It has been shown that Pu^{3+} is reduced to Pu metal by a single step mechanism and that the diffusion coefficient of Pu^{3+} ion is $D_{Pu^{3+}}$ ~2.10^{-5} cm^2/s at 733 K. The apparent standard potential and $\Delta G^\infty_{PuCl_3}$ have been measured using transient electrochemical techniques (CV, CP) and are in agreement with results obtained by previous emf measurements. This proves that transient techniques, as well, can be used for the determination thermochemical data. The activity coefficient of PuCl₃ in LiCl-KCl, γ_{PuCl3}, has been calculated from the difference between the Gibbs free energy at infinite dilution from the electrochemical measurements and the calculated Gibbs free energy of formation in the supercooled state (sc). The values differ significantly depending on the source of the data for the sc state. This shows the need for more accurate thermochemical data for pure PuCl₃.

REFERENCES

[1] J.J. Laidler *et al.* (1997), *Development of Pyroprocessing Technology* Prog. Nucl. Energy, 31(1/2), 131.

[2] T. Nishimura *et al.* (1998), *Development of an Environmentally Bening Reprocessing Technology – Pyrometallurgical Reprocessing Technology,* Prog. Nucl. Energy, 32(3/4), 381.

[3] Y. Sakamura *et al.* (1998), *Measurement of Standard Potentials of Actinides (U,Np,Pu,Am) in LiCl-KCl Eutectic Salt and Separation of Actinides from Rare Earths by Electrorefining,* J. Alloys Compd., 271-273, 592.

[4] S.P. Fusselman *et al.* (1999), *Thermodynamic Properties for Rare Earths and Americium in Pyropartitioning Process Solvents,* J. Electrochem. Soc., 146(7), 2573.

[5] R.J.M. Konings, R. Malmbeck, J. Serp (2001), *Critical Evaluation of Fundamental Data for a Pyrochemical Partitioning Process, Actinides-2001*, Hayama, Japan (in press).

[6] S. Abousahl *et al.* (2002), *Radiometric Assay Techniques for the Control of Minor Actinides in Advanced Nuclear Fuel Cycles, 24th ESARDA* Annual Meeting, Workshop on Safeguards and Nuclear Material Management, Luxembourg.

[7] S. Abousahl *et al.* (2002), *Radiometric Analytical Methods for the Pyrochemical Partitioning Process,* 43th INMM Annual Meeting Orlando, Florida 23-27 June.

[8] M. Iizuka *et al.* (2001), *Behaviour of Plutonium and Americium at Liquid Cadmium Cathode in Molten LiCl-KCl Electrolyte,* J. Nucl. Mater., 299, 32.

[9] O. Shirai *et al.* (1998), *Electrochemical Behaviour of Actinide Ions in LiCl-KCl Eutectic Melts,* J. Alloys Compd., 271-273: p. 685-688.

[10] R.S. Nicholson, I. Shain (1964), Anal. Chem., 36, 706.

[11] A.J. Bard, L.R. Faulkner (1980), *Electrochemical Methods, Fundamentals and Applications,* Wiley, New York.

[12] G. Mamantov, D.L. Manning, J.M. Dale (1965), J. Electroanal. Chem., 9, 253.

[13] M. Goto, K.B. Oldham, (1973), Anal. Chem., 45(12), 2043.

[14] A.M. Martinez *et al.* (2000), *Chemical and Electrochemical Behaviour of Chromium in Molten Chlorides,* J. Electroanal. Chem., 493**,** 1.

[15] Z. Galus (1976), *Fundamentals of Electrochemical Analysis,* Ellis Horwood, London.

[16] P. Chamelot (1994), Thesis, Université Paul Sabatier.

[17] O. Knacke, J. Krahe, F. Müller (1966), *Aktivität von UCl3 in der Eutektischen Schmeltze LiCl-KC,* Z. Phys. Chem. (Munich), 50**,** 91.

[18] J.J. Roy *et al.* (1996), *Thermodynamic Properties of U, Np, Pu and Am in Molten LiCl-KCl Eutectic and Liquid Cadmium,* J. Electrochem. Soc., 143(8), 2487.

[19] R.J. Lemire *et al.* (2001), *Chemical Thermodynamics of Neptunium and Plutonium,* Elsevier, Amsterdam.

[20] *The ITU Material Property Data Base for f-Elements and Compounds, f-MPD*, http://www.jrc.cec.eu.int. (from 91.01.2003).

[21] R.J.M. Konings, A. Kovács in *The Handbook on Physics and Chemistry of Rare Earths*, ed. K.A. Gschneidner Jr, J-C.G. Bünzli, and V.K. Pecharsky, (in press).