

Thermodynamics Properties of plutonium in CaCl₂ and in gallium at 1073K

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Pyrochemical separations from molten salts media with metal solvent by liquid/liquid extraction or electrorefining are commonly used for the reprocessing of nuclear spent fuels and Pu [1-2]. Many studies have been carried out on Pu in LiCl-KCl [3]. Consequently, the standard potential of Pu(III)/Pu in CaCl₂ has been studied at 1073K. An electrochemical study has been performed on liquid Ga with dilute Pu at 1073K to obtain activity coefficients. Then, a comparison of several metal phases based on activity coefficient of cerium and Pu and consequences on separation efficiency is proposed.

Figure 1 shows a typical cyclic voltammogram of Pu(III) in CaCl₂ at 1073K on tungsten electrode. With the background cyclic voltammogram, we can see that one well-defined system (Ia/Ic) appears near the calcium chloride reduction (IIc). The value of the Pu(III)/Pu redox potential has been estimated from the results of cyclic voltammetric studies. The obtained results have been summarized in Table 1 and compared to those previously determined.

An electrochemical study has been performed on liquid Ga with dilute Pu at 1073K. In order to obtain characteristic potential ($E_{i=0}$), chrono-amperograms have been determined and are reported on $I=f(E)$ curves at various time on figure 2 in CaCl₂ at 1073K. The redox systems Ia and IIa on figure 2 are attributed to the oxidation of Pu into Pu trichloride and to the oxidation of Ga metal into Ga trichloride. The activity coefficient of Pu in liquid Ga can be calculated with the following relation:

$$\Delta E = -\frac{2.3RT}{3F} \log(\gamma_{Pu_{Ga}} * x_{Pu_{Ga}}) \quad (1)$$

with ΔE the difference potential of galvanic cell (Pu(in Ga)/PuCl₃(in molten chloride)//Pu(s)), $\gamma_{Pu_{Ga}}$ the activity coefficient of Pu and $x_{Pu_{Ga}}$ the molar fraction of Pu in liquid Ga. The results are reported on Table 2. The activity coefficients of Pu obtained with two molten chlorides are of the same order and that confirms that the coefficient activity of Pu in Ga is independent of selected molten chlorides.

The consequence on the electrochemical selectivity by using our present results on Pu in liquid Ga and the published values [6] for Al, Bi and Cd on cerium and Pu have been calculated. By using the Nernst relation, the electrochemical selectivity between Pu and Ce ($\Delta E_{(Pu-Ce)M}$) in a molten chloride depends on the ratio of their activity coefficient in metal (for the same oxidation state). For a high temperature, the use of liquid Ga is better than Al, Bi and Cd. At a low temperature (around 873K) we have seen that the electrochemical selectivity between Pu and Ce in Cd decreases and in Al increases, for Bi it is slightly the same. The activity coefficient of Pu in liquid Ga at low temperature is not available yet, so we can not conclude for Ga at this temperature.

To conclude, in CaCl₂, the standard potential of Pu(III)/Pu is close to the reference state PuCl₃/Pu_{liq}.

Electrochemical measurements demonstrated that a selective extraction of Pu dissolved in Ga by anodic oxidation is easy. The deposition of Pu on a liquid Ga cathode is possible with a careful control of cathode potential to prevent metal chloride melt reduction. Activity coefficient of Pu in Ga has been deduced from electrochemical studies. By comparing with other solvent liquid metal such as Cd, Bi, Al, Ga seems to be the most favorable for Pu/Ce separation. For economic reasons, Al appears to be good choice for large-scale applications.

References:

1. J.P. Ackerman, *Ind. Eng. Chem. Res.*, **29** (1991) 141
2. L. J. Mullins, LA-2666, (1962)
3. L. Martinot, "Handbook on the Physics and Chemistry of the Actinides", ed. by A. J. Freeman, Elsevier, (1991)
4. R. Benz, *J. Phys. Chem.*, **65** (1961) 1056
5. O.V. Skiba, Report NIIAR-P-118, (1971)
6. V. A. Lebedev, *Selectivity of Liquid Metal Electrodes in Molten Halides*, Metallurgiya, Chelyabinsk, (1993)

Salt	Skiba <i>et al.</i>	R. Benz <i>et al.</i>	This work
NaCl-KCl	-2.585 [5]		-2.54
NaCl	-2.513 [5]	-2.393 [4]	
KCl	-2.605 [5]	-2.381 [4]	
CaCl ₂			-2.51

Table 1: Values of standard potential of Pu(III)/Pu at 1073K, (V/Cl₂(1 atm)/Cl, mole fraction scale)

Salt	$X_{Pu_{Ga}}$	ΔE (in V)	$\log(\gamma_{Pu_{Ga}})$
CaCl ₂	0.0129	0.65	-7.5±0.5
NaCl-KCl	0.0137	0.66	-7.2±0.5

Table 2: Values of molar fraction ($X_{Pu_{Ga}}$) of metal Pu in liquid Ga and its corresponding ΔE and $\log(\gamma_{Pu_{Ga}})$

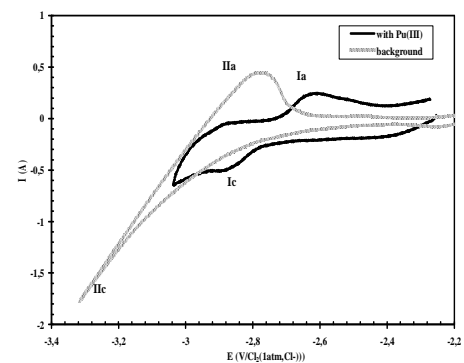


Figure 1: Cyclic voltammogram for Pu trichloride in CaCl₂ at 1073K, scan rate 0.1V/s, $x_{PuCl_3}=1.1 \cdot 10^{-3}$

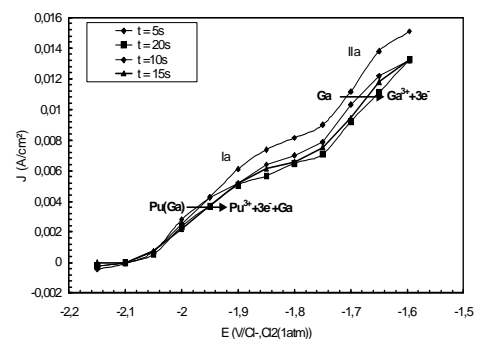


Figure 2: Intensity-potential curve in CaCl₂ at 1073K obtained from chronoamperograms, $x_{Pu_{Ga}}=0.0129$, $x_{PuCl_3}=0.0011$