

## Thermodynamics and separation factor of lanthanides and actinides in a “liquid metal-molten salt” system

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### Abstract

Separation of lanthanides and actinides can be achieved in a “molten chloride – liquid metal” system. Here thermodynamic properties and separation factor of lanthanum, praseodymium, neodymium and uranium were studied in a Me(alloy)/3LiCl-2KCl system at different temperatures. The influence of the elements nature on activity coefficients and separation factor was determined.

**Keywords:** Uranium, Lanthanum, Praseodymium, Neodymium, Alloys, Molten salts, Thermodynamic properties, Separation factor

### 1. Introduction

Pyrochemical separation processes in molten salt – liquid metal media are considered as a promising option for the future nuclear fuel cycles [1–3]. The major steps of the pyrochemical technology include electrorefining or reductive extraction in a molten chloride – liquid metal system for recovering actinides, including the minor actinides, from the spent metallic or nitride nuclear fuels and high level radioactive wastes [4, 5]. A strategy termed “Partitioning and Transmutation” (P&T) is currently being developed in several countries. The primary goal is achieving the maximum possible reduction of the nuclear waste radiotoxicity in the back end of the fuel cycle.

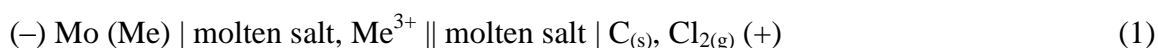
In terms of the efficiency of separating lanthanide (Ln) and actinide (An) elements, the following sequence of the low-melting metals was proposed: Al > Ga > Sn > Bi > In > Zn > Cd [6]. Cadmium is currently considered as the low-melting metal electrode for separating actinides and fission products in the pyrochemical spent nuclear fuel (SNF) reprocessing. This element has the advantages of compatibility with low-carbon steels and high vapor pressure at elevated temperatures but it is not efficient in separating lanthanides and actinides [7]. High melting point of aluminum (933.52 K) and low compatibility with the metallic construction materials limit its application in pyrochemical technologies utilizing chloride media. Gallium is next in the row and is considered as a prospective liquid metal electrode material. Ga, however, is a trace element, and therefore is rather expensive for the industrial application. Alloys of gallium with other elements, *e.g.* aluminum or indium, can be employed instead of pure Ga. Ga–In and Ga–Al eutectics contain 21.4 wt% In or 1.5 wt% Al, respectively, and are very prospective for reprocessing SNF.

The goal of the present work was analyzing the effect of various parameters on Ln/An thermodynamic properties and separation factors (SF) in a “chloride melt – liquid metal” system including temperature, the nature of the liquid metal alloy and the nature of lanthanides.

## 2. Experimental

The experiments were carried out at 723–823 K under dry argon atmosphere in an electrochemical cell with a three electrode setup. The electrochemical measurements were performed employing an AUTOLAB 302N potentiostat controlled by NOVA 1.11 software. Salt and metal mixtures of the required compositions were prepared from the individual components, LiCl (Aldrich, 99.99 %), KCl (99.9 %, certified purity), NdCl<sub>3</sub> (Aldrich, 99.99 %), PrCl<sub>3</sub> (99.9 %, certified purity), LaCl<sub>3</sub> (99.9 %, certified purity), Ga (99.99 %, certified purity), Al (A-999, 99.99 %). The following galvanic cells were used for measuring the electrode potentials of the

$E_{\text{Me(III)/Me}}^{**}$  (1) and alloys  $E_{\text{Me(Ga-Al)}}^{**}$  (2):



The lanthanides and uranium concentration in the chloride melts and metallic alloys were determined by ICP-MS.

### 3. Results and discussion

The value of the apparent standard redox potential was determined by potentiometry at zero current. The principle of the method was the following. The inert molybdenum electrode was polarized for a short time under potentiostatic conditions for depositing a small amount of the metal investigated on the working electrode surface. After switching off the polarizing current, the dependence of the potential vs. time was recorded. The potential value of horizontal plateau corresponded to the quasi-equilibrium potential of Me(III)/Me couple, where Me was La, Pr or Nd.

The value of the apparent standard redox potential of Me(III)/Me couple was calculated from the Nernst equation (3):

$$E_{Me(III)/Me} = E_{Me(III)/Me}^* + \frac{RT}{nF} \ln C_{Me^{3+}}, \quad (3)$$

$$E_{Me(III)/Me}^* = E_{Me(III)/Me}^{\circ} + \frac{RT}{nF} \ln f_{Me^{3+}}, \quad (4)$$

where  $E_{Me(III)/Me}$  is the quasi-equilibrium potential of the system, V;  $E_{Me(III)/Me}^*$  is the apparent standard redox potential of the system, V;  $n$  is the number of electrons exchanged;  $C_{Me^{3+}}$  is the mole fraction concentration of metal (La, Pr or Nd) ions; and  $f_{Me^{3+}}$  is the activity coefficient.

The experimental data were fitted to the following equations using the Origin Pro version 7.5 software:

$$E_{La(III)/La}^* = -(3.731 \pm 0.004) + (7.3 \pm 0.6) \cdot 10^{-4} T \pm 0.004 \quad V \quad (5)$$

$$E_{Pr(III)/Pr}^* = -(3.759 \pm 0.016) + (8.6 \pm 0.2) \cdot 10^{-4} T \pm 0.011 \quad V \quad (6)$$

$$E_{Nd(III)/Nd}^* = -(3.750 \pm 0.005) + (8.8 \pm 0.1) \cdot 10^{-4} T \pm 0.003 \quad V \quad (7)$$

The values of the apparent standard redox potential of Me(Ga–In) and Me(Ga–Al) alloys were calculated from the Nernst equation:

$$E_{Me(alloy)} = E_{Me(III)/Me}^0 + \frac{RT}{3F} \ln \frac{a_{Me^{3+}}}{a_{Me(alloy)}} \quad (8)$$

or

$$E_{Me(alloy)} = E_{Me(III)/Me}^0 + \frac{RT}{3F} \ln \frac{C_{Me^{3+}} \cdot f_{Me^{3+}}}{x_{Me(alloy)} \cdot \gamma_{Me(alloy)}} \quad (9)$$

The apparent standard potentials of the alloys were determined by potentiometry measurements at zero current employing the following technique. After preparing the alloys of the known composition, the potential-time dependences were recorded at different temperatures. The potential value of the horizontal part of the curve corresponded to the quasi equilibrium

potential of the alloy. In molten salts the activity coefficients of the solute species  $Me^{n+}$  are constant at concentrations below  $(3-5) \cdot 10^{-2}$  mole fraction [8]. For the dilute solutions of Me in the alloys, the activity coefficients are also constant [6]. To characterize the electrochemical behavior of the alloy the apparent standard potential of the alloy,  $E_{Me(alloy)}^{**}$ , was used:

$$E_{Me(alloy)} = E_{Me(alloy)}^{**} + \frac{RT}{3F} \ln \frac{C_{Me^{3+}}}{x_{Me(alloy)}}, \quad (10)$$

where  $E_{Me(alloy)}$  is the equilibrium potential of the alloy, V;  $E_{Me(alloy)}^{**}$  is the apparent standard redox potential of the alloy, V;  $n$  is the number of electrons exchanged;  $C_{Me^{3+}}$  is the mole fraction concentration of the metal ions in the solvent; and  $x_{Me(alloy)}$  is the atomic fraction concentration of metal in the alloy.

Temperature dependencies of the apparent standard potentials of metals in the alloys studied were fitted to the following equations using the Origin Pro version 7.5 software:

$$E_{La(Ga-In)}^{**} = -(2.906 \pm 0.003) + (5.7 \pm 0.6) \cdot 10^{-4} \cdot T \pm 0.002 \quad V \quad (11)$$

$$E_{Pr(Ga-In)}^{**} = -(3.061 \pm 0.025) + (7.9 \pm 0.3) \cdot 10^{-4} \cdot T \pm 0.016 \quad V \quad (12)$$

$$E_{Nd(Ga-In)}^{**} = -(2.895 \pm 0.009) + (5.8 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.005 \quad V \quad (13)$$

$$E_{U(Ga-In)}^{**} = -(2.508 \pm 0.006) + (3.8 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.003 \quad V \quad (14)$$

$$E_{La(Ga-Al)}^{**} = -(3.073 \pm 0.007) + (6.0 \pm 0.5) \cdot 10^{-4} \cdot T \pm 0.005 \quad V \quad (15)$$

$$E_{Pr(Ga-Al)}^{**} = -(3.121 \pm 0.017) + (7.1 \pm 0.5) \cdot 10^{-4} \cdot T \pm 0.011 \quad V \quad (16)$$

$$E_{Nd(Ga-Al)}^{**} = -(2.847 \pm 0.007) + (5.2 \pm 0.5) \cdot 10^{-4} \cdot T \pm 0.005 \quad V \quad (17)$$

$$E_{U(Ga-Al)}^{**} = -(2.715 \pm 0.006) + (5.1 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.003 \quad V \quad (18)$$

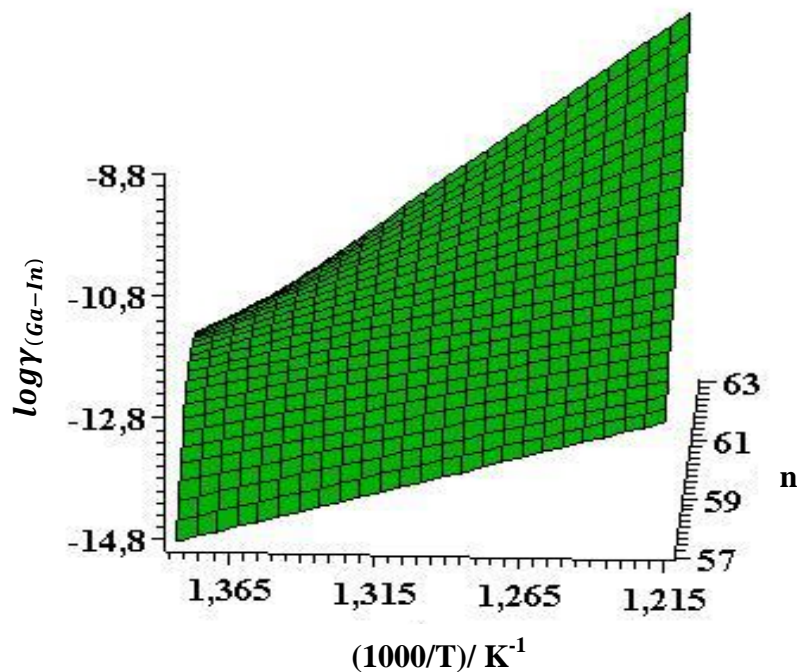
Newton interpolation polynomial expressions were obtained to develop three-dimensional  $\log \gamma - T - n$  and  $\log \theta - T - n$  graphs on the basis of the functional dependence of the apparent electrode potentials of the metals and alloys, temperature and the atomic number of the elements in the Periodic Table. The universal mathematical Maple 17 software was used for this purpose. The three-dimensional graphs obtained are presented in Figs. 1–4. The following expressions describe the three-dimensional graphs:

$$\log \gamma_{(Ga-In)} = (-3794.37 + 129.52n - 1.11n^2) \cdot \frac{1000}{T} + (4704.54 - 161.53n + 1.39n^2) \quad (19)$$

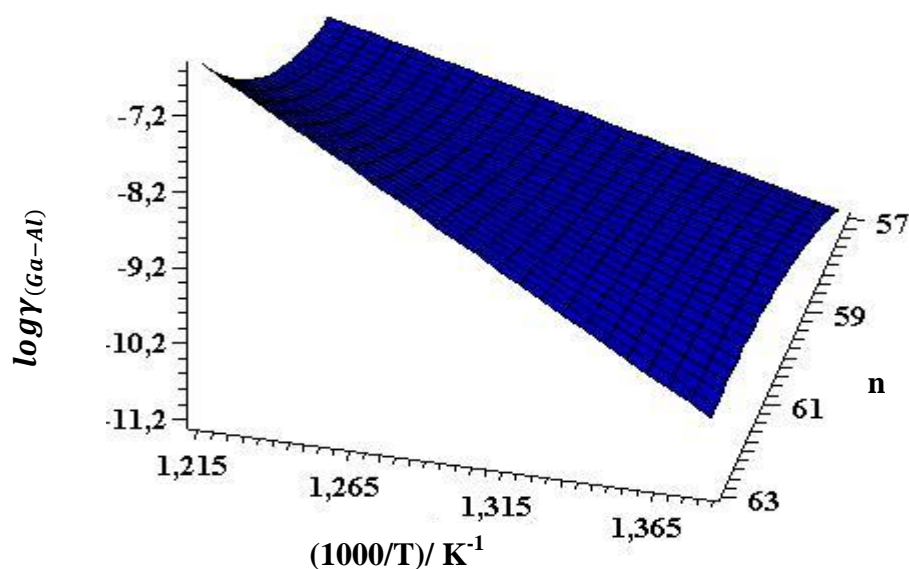
$$\log \gamma_{(Ga-Al)} = (-1784.33 + 61.22n - 0.53n^2) \cdot \frac{1000}{T} + (2322.02 - 80.32n + 0.695n^2) \quad (20)$$

$$\log \theta_{(Ga-In)} = (-4253.24 + 145.76n - 1.25n^2) \cdot \frac{1000}{T} + (5597.02 - 191.53n + 1.64n^2) \quad (21)$$

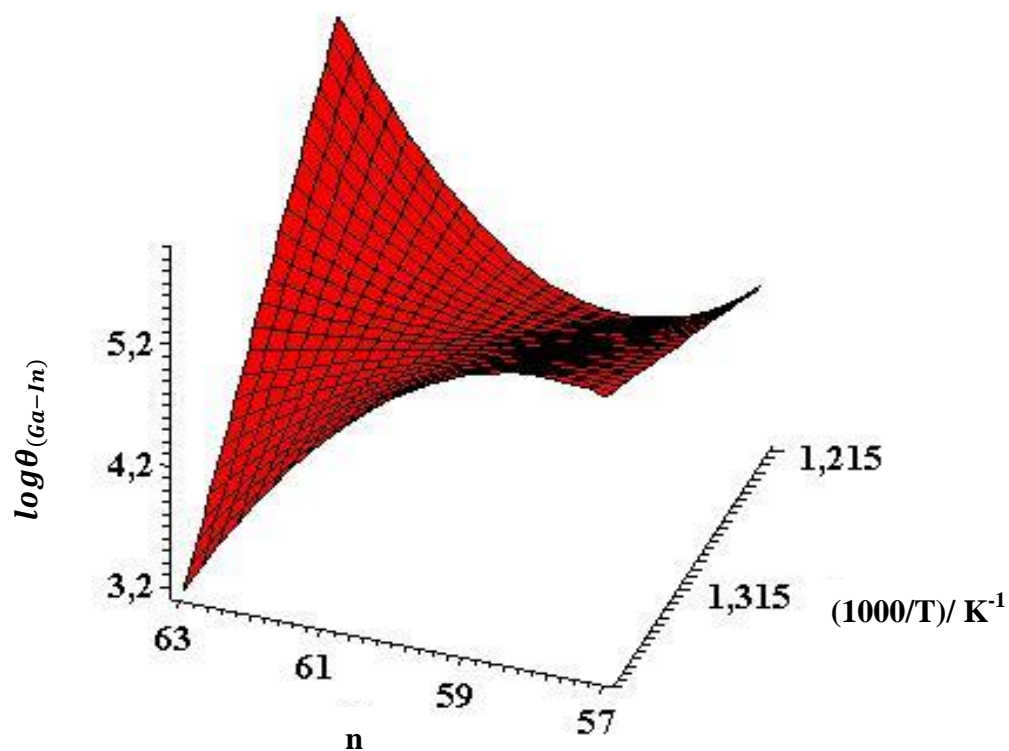
$$\log \theta_{(Ga-Al)} = (-2653.93 + 91.38n - 0.78n^2) \cdot \frac{1000}{T} + (3512.65 - 120.55n + 1.03n^2) \quad (22)$$



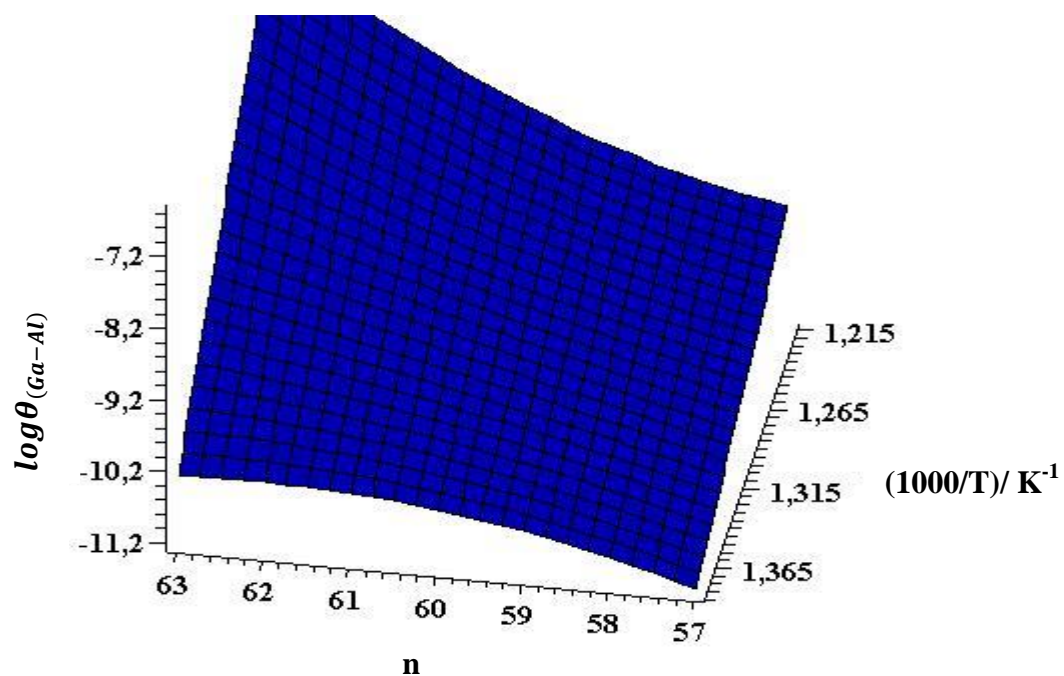
**Figure 1.** Three-dimensional  $\log \gamma_{\text{Me(Ga-In)}}$  -T- n graph for Me = La, Pr, Nd in fused Me(Ga-In)/3LiCl-2KCl system.



**Figure 2.** Three-dimensional  $\log \gamma_{\text{Me(Ga-Al)}}$  -T- n graph for Me = La, Pr, Nd in fused Me(Ga-Al)/3LiCl-2KCl system.



**Figure 3.** Three-dimensional  $\log\Theta_{\text{Me(Ga-In)}}$  - T - n graph for Me/U couples in fused Me(Ga-In)/3LiCl-2KCl system.



**Figure 4.** Three-dimensional  $\log\Theta_{\text{Me(Ga-Al)}}$  - T - n graph for U/Me couples in fused Me(Ga-Al)/3LiCl-2KCl system.

Low values of the activity coefficients show strong interaction between lanthanides and the liquid alloy. It was found that the activity coefficients decreased with increasing the atomic number of the element from La to Nd in the Periodic Table. Rising temperature shifted the system towards more ideal behavior, in agreement with the literature [9].

The separation factor values for Ln/U systems showed that uranium will be concentrated in the alloy phase, while lanthanides will stay in the molten salt phase. The results of the calculations indicated that high values of SF of actinides and lanthanides can be achieved. For the more effective separation of the actinides from the lanthanides lower temperatures and Ga–Al alloy should be preferred. Separation factor values decreased with increasing temperature (due to the entropy factor) and increasing lanthanide's atomic number from La to Nd. All the results are listed in Tables 1 and 2, and shown in Figs. 1–4.

**Table 1**

Calculated values of the apparent standard potentials of the alloys, activity coefficients of La, Pr, Nd, U and separation factor of La/U, Pr/U and Nd/U in “(La, Pr, Nd, U)Ga–In/3LiCl–2KCl” systems at 723 K

Metal	$E^{**}/V$	$\log \gamma$	$\gamma$	$\log \theta$	$\theta$
U	-2.223	-7.23	$5.87 \cdot 10^{-8}$	-	-
Nd	-2.476	-13.37	$4.28 \cdot 10^{-14}$	5.08	$1.19 \cdot 10^5$
Pr	-2.490	-13.55	$2.83 \cdot 10^{-14}$	5.39	$2.45 \cdot 10^5$
La	-2.495	-14.86	$1.38 \cdot 10^{-15}$	5.46	$2.88 \cdot 10^5$

**Table 2**

Calculated values of the apparent standard potentials of alloys, activity coefficients of La, Pr, Nd, U and separation factor of La/U, Pr/U and Nd/U in “(La, Pr, Nd, U)Ga–Al/3LiCl–2KCl” systems at 723 K

Metal	$E^{**}/V$	$\log \gamma$	$\gamma$	$\log \theta$	$\theta$
U	-2.346	-4.87	$1.35 \cdot 10^{-5}$	-	-
Nd	-2.613	-10.49	$3.23 \cdot 10^{-11}$	5.59	$3.87 \cdot 10^5$
Pr	-2.629	-10.65	$2.25 \cdot 10^{-11}$	5.92	$8.87 \cdot 10^5$
La	-2.647	-11.66	$2.17 \cdot 10^{-12}$	6.29	$1.95 \cdot 10^6$

#### 4. Conclusions

The basic thermodynamic properties of lanthanum, praseodymium, neodymium and uranium were determined in liquid Ga–In and Ga–Al alloys between 723 and 823 K. Low values of the activity coefficients showed strong interaction between lanthanides and the liquid alloys. The values of uranium and lanthanides separation factors showed that the alloys investigated here have considerable advantage compare to liquid cadmium. Analysis of the data obtained

showed that Ga–In and Ga–Al alloys are the prospective media for application in partitioning technologies of spent nuclear fuels and nuclear wastes treatment.

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