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Thermodynamics and Separation Factor of Uranium from Fission Products in "Liquid Metal-Molten Salt" System

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Alexander Bychkov, Vladimir Volkovich,
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Additional information is available at the end of the chapter

Abstract

The present chapter contains the results of studying electrochemical and thermodynamic properties of La, Nd, and U in "liquid metal-molten salt" systems, where liquid metals were binary Ga-Al and Ga-In alloys of various compositions. The apparent standard potentials of ternary U-Ga-In, U-Ga-Al, La-Ga-In, La-Ga-Al, Nd-Ga-In, and Nd-Ga-Al alloys at various temperatures were determined, and the temperature dependencies were obtained. Primary thermodynamic properties (activity coefficients, partial excess Gibbs free energy change, partial enthalpy change of mixing, and excess entropy change) were calculated. The influence of the bimetallic alloy composition and the nature of lanthanide on thermodynamic properties of compounds are discussed. The values of U/Nd separation factors on gallium-aluminum and U/La on gallium-indium alloys were calculated. The value of the separation factors strongly depends on the alloy composition. Uranium in this case is accumulating in the metallic phase and lanthanides in the salt melt. Analysis of the data obtained showed the perspective use of the active cathodes (Ga-Al and Ga-In instead of single Cd) in future innovative methods for reprocessing spent nuclear fuels (SNF) and high-active nuclear wastes in the future of closed nuclear fuel cycle.

Keywords: uranium, lanthanum, neodymium, gallium-aluminum alloys, gallium-indium alloys, molten salts, liquid metals, thermodynamic properties, separation factor

1. Introduction

Pyrochemical technologies of reprocessing spent nuclear fuels (SNF) attract growing interest due to the necessity to ensure safety and efficiency of the nuclear fuel cycle. These technologies

have a number of significant advantages compared to the existing hydrometallurgical technology, which include a drastic decrease of radioactive wastes, engineering support of nonproliferation principle of using the fissile materials, and lowering cost of SNF reprocessing. Development of nonaqueous SNF reprocessing technologies allows closing nuclear fuel cycle on the basis of the expanded construction of fast reactors with inherent safety. Currently, several variants of pyrochemical technologies are under study: electrochemical technology in molten salts, fluoride volatility process, extraction of technology in molten metals, and some others. The results obtained provide evidence for both the complexity of technological processes and equipment and their potential possibilities [1, 2].

Electrochemical reprocessing of SNF in chloride melts is one of the most developed and promising processes. It is going to be used in the experimental industrial complex of a fast neutron reactor with the solid fuel reprocessing. The major steps of the pyrochemical technology include electrorefining or reductive extraction in molten chloride/liquid metal systems for recovering actinides, including the minor actinides, from the spent metallic or nitride nuclear fuels and high-level radioactive wastes [3, 4]. Actinides recycling by separation and transmutation are considered worldwide as one of the most promising strategies for a more efficient use of the nuclear fuel as well as for nuclear waste minimization. The goal of one of the main strategies (partitioning and transmutation) is achieving the highest possible reduction of the nuclear waste radiotoxicity in the back end of the fuel cycle. High radiation resistance of molten chlorides and the absence of neutron moderators allow reprocessing spent nuclear fuels with high fissile materials content after a short cooling time. Selectivity of high-temperature separation process taking place at the molten salt-liquid metal interface depends on different characteristics of both phases. Knowing thermodynamics of the main fission products in working media is essential for determining applicability of a particular system for practical application [5].

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 [5]. Cadmium is currently considered as the low-melting metal electrode for separating actinides and fission products in the pyrochemical spent nuclear fuel 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. 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, for example, aluminum or indium, can be employed instead of pure Ga. Ga-In and Ga-Al alloys are very prospective for reprocessing SNF [6–11].

The goal of this work was to investigate the effect of Al and In concentration on the thermodynamic properties of La, Nd, and U in ternary Ga-In and Ga-Al-based alloys and the separation factor of Ln/Ac couple in a "molten salt-liquid metal" system.

2. Experiment

The experiments were carried out at 723–823 K with the step 20–25 K under dry argon atmosphere in a three-electrode silica cell. All operations were performed in a SPEKS GB 02 M glovebox (< 1 ppm oxygen and <1 ppm moisture content). The electrochemical measurements were performed employing an Autolab 302 N potentiostat-galvanostat controlled by NOVA 1.11 software. Salts and metal mixtures of the required compositions were prepared from the individual components, LiCl (Sigma-Aldrich, 99.99%), KCl (Reachim, 99.9%), LaCl$_3$ (Sigma-Aldrich, 99.99%), PrCl$_3$ (Sigma-Aldrich, 99.99%), NdCl$_3$ (Sigma-Aldrich, 99.99%), Ga (GA-000, 99.99%), and In (IN-000, 99.98%). Ga-Al and Ga-In alloys of the specified composition were prepared from batches of the individual metals in the inert atmosphere in glovebox. The Ga-Al and Ga-In alloys prepared were metallic, silvery liquids free from any visible oxide films. Uranium (III) ions were introduced to electrolyte by electrolysis (anodic dissolution of U metal). The amount of lanthanum or uranium in the alloys was less than 0.40 wt.%. Liquid gallium-aluminum (gallium-indium) mixture was used as cathode and placed in a beryllium oxide crucible. The dilute solutions of prepared alloys were used directly in the experiments during the electromotive force (EMF) measurements vs. the Cl$^-$/Cl$_2$ reference electrode. The standard construction of it was described earlier in detail [12]. The following galvanic cell was used for measuring the electrode potentials of the alloys $E^{**}_{Me(Ga-In)}$:

$$(-)\,Me(alloy)\,|\,3LiCl-2KCl, Me(III)\,\|\,3LiCl-2KCl\,|\,C_{(s)}, Cl_{2(g)}\,(+) \qquad (1)$$

The experimental procedure was the following. After preparation of the ternary alloy of a required composition, the potential-time dependence was recorded using potentiometric method at zero current at different temperatures in the experiment. The potential value of the horizontal part of the curve corresponded to the equilibrium potential of the alloy.

The lanthanide (uranium) concentrations in the chloride salts were determined by taking samples from the melts that were then dissolved in nitric acid solutions. Ln (U)-containing alloys were washed with water and then dried by ethanol. All solutions were analyzed by ICP-MS.

3. Results and discussion

3.1. Nd(U)-(Ga-Al)/3LiCl-2KCl system

Potentiometry method at zero current was used for determination of the apparent standard potentials of the alloys. The potential-time dependences were recorded at various temperatures and of the horizontal part of the curve corresponded to the equilibrium potential of the alloy [13–15]. In molten salts the activity coefficients of the solute species Me^{n+} are constant at concentrations below $(3-5) \times 10^{-2}$ mole fraction [12]. For the dilute solutions of Me in the alloys, the activity coefficients are also constant [5]. To characterize the electrochemical behavior of the alloy, an apparent standard potential of the alloy, $E^{**}_{Me(Ga-Al)}$, was used [5]:

$$E_{Me(Ga-Al)} = E^{**}_{Me(Ga-Al)} + \frac{RT}{nF} \ln \frac{C_{Me(III)}}{x_{Me(Ga-Al)}}, \tag{2}$$

where Me = Nd or U, $E_{Me(Ga-Al)}$ is the equilibrium potential of the alloy (V), $E^{**}_{Me(Ga-Al)}$ is the apparent standard potential of the alloy (V), n is the number of electrons exchanged, $C_{Me(III)}$ is the concentration of the metal ions in the solvent (mole fraction), and $x_{Me(Ga-Al)}$ is the concentration of the metal in the alloy (atomic fraction).

The apparent standard potentials of the alloys Me(Ga-Al) as a function of temperature were fitted to the following equations using OriginPro version 7.5 Software, Eqs. (3)–(8):

$$E^{**}_{Nd(Ga-Al)} = -(2.987 \pm 0.007) + (5.2 \pm 0.5) \cdot 10^{-4} \cdot T \pm 0.005 \ V \quad 1.5 \ wt.\%Al \tag{3}$$

$$E^{**}_{Nd(Ga-Al)} = -(3.068 \pm 0.004) + (6.0 \pm 0.2) \cdot 10^{-4} \cdot T \pm 0.003 \ V \quad 5.0 \ wt.\%Al \tag{4}$$

$$E^{**}_{Nd(Ga-Al)} = -(3.143 \pm 0.006) + (6.8 \pm 0.2) \cdot 10^{-4} \cdot T \pm 0.004 \ V \quad 20.0 \ wt.\%Al \tag{5}$$

$$E^{**}_{U(Ga-Al)} = -(2.715 \pm 0.006) + (5.1 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.003 \ V \quad 1.5 \ wt.\%Al \tag{6}$$

$$E^{**}_{U(Ga-Al)} = -(2.758 \pm 0.004) + (5.3 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.002 \ V \quad 5.0 \ wt.\%Al \tag{7}$$

$$E^{**}_{U(Ga-Al)} = -(2.791 \pm 0.005) + (5.5 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.003 \ V \quad 20.0 \ wt.\%Al \tag{8}$$

Newton interpolation polynomial expressions were obtained to construct three-dimensional $E^{**}_{Me(Ga-Al)} - C_{(Ga-Al)} - T$ graphs on the basis of the functional dependencies of the apparent standard electrode potentials of the alloys, Ga-Al mixture compositions, and temperature. Universal mathematical Maple 11 software was used for this purpose. Three-dimensional $E^{**}_{Me(Ga-Al)} - C_{(Ga-Al)} - T$ plots for Nd-(Ga-Al) and U-(Ga-Al) alloys and 3LiCl-2KCl eutectic-based melts are presented in **Figures 1** and **2**, respectively. The following expressions describe the three-dimensional graphs:

$$E^{**}_{Nd(Ga-Al)} = \left(4.8 \cdot 10^{-4} + 2.9 \cdot 10^{-5} \cdot C - 9.5 \cdot 10^{-7} \cdot C^2\right) \cdot T - 2.9 - 0.03 \cdot C + 9.8 \cdot 10^{-4} \cdot C^2 \ V \tag{9}$$

$$E^{**}_{U(Ga-Al)} = \left(5 \cdot 10^{-4} + 7.2 \cdot 10^{-6} \cdot C - 2.4 \cdot 10^{-7} \cdot C^2\right) \cdot T - 2.7 - 0.02 \cdot C + 5.4 \cdot 10^{-4} \cdot C^2 \ V \tag{10}$$

where C is the concentration of Al in Ga-Al alloy (wt. %).

The activity coefficients of Nd and U in liquid Ga-Al metallic alloys were determined from the following expression [5]:

$$\log \gamma_{Me(Ga-Al)} = \frac{3F}{2.303} \left(E^*_{Me(III)/Me} - E^{**}_{Me(Ga-Al)}\right) \tag{11}$$
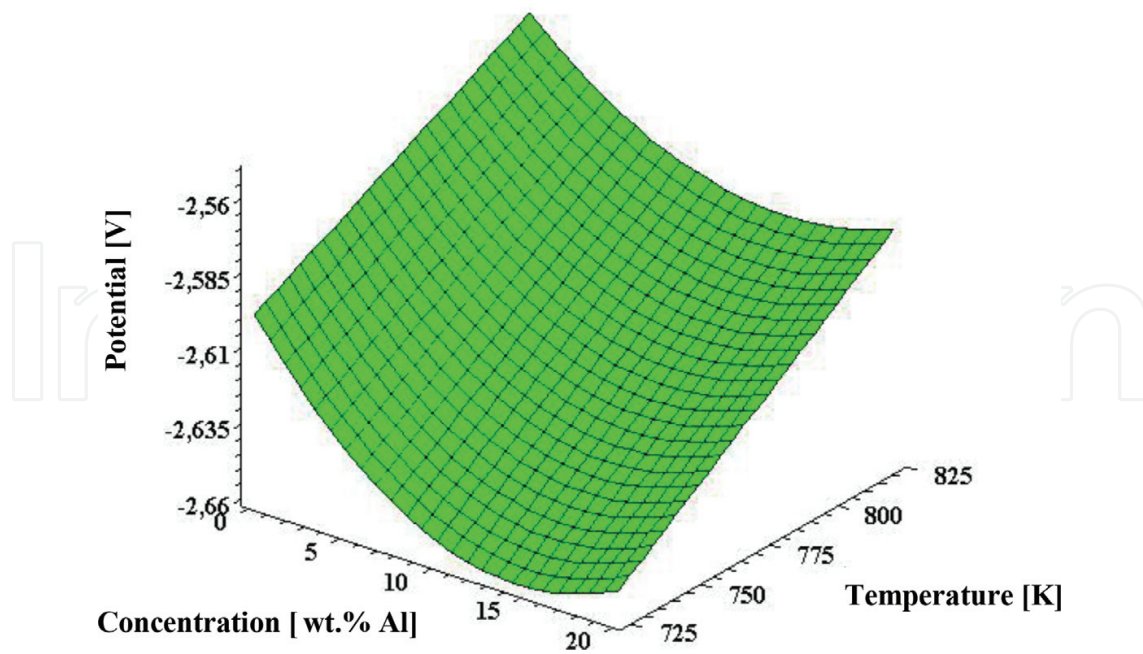
Figure 1. Apparent standard electrode potentials of Nd-Ga-Al alloys in fused Nd(Ga-Al)/3LiCl-2KCl system as a function of temperature and composition of Ga-Al alloy (3D diagram). Reference electrode: Cl^-/Cl_2.
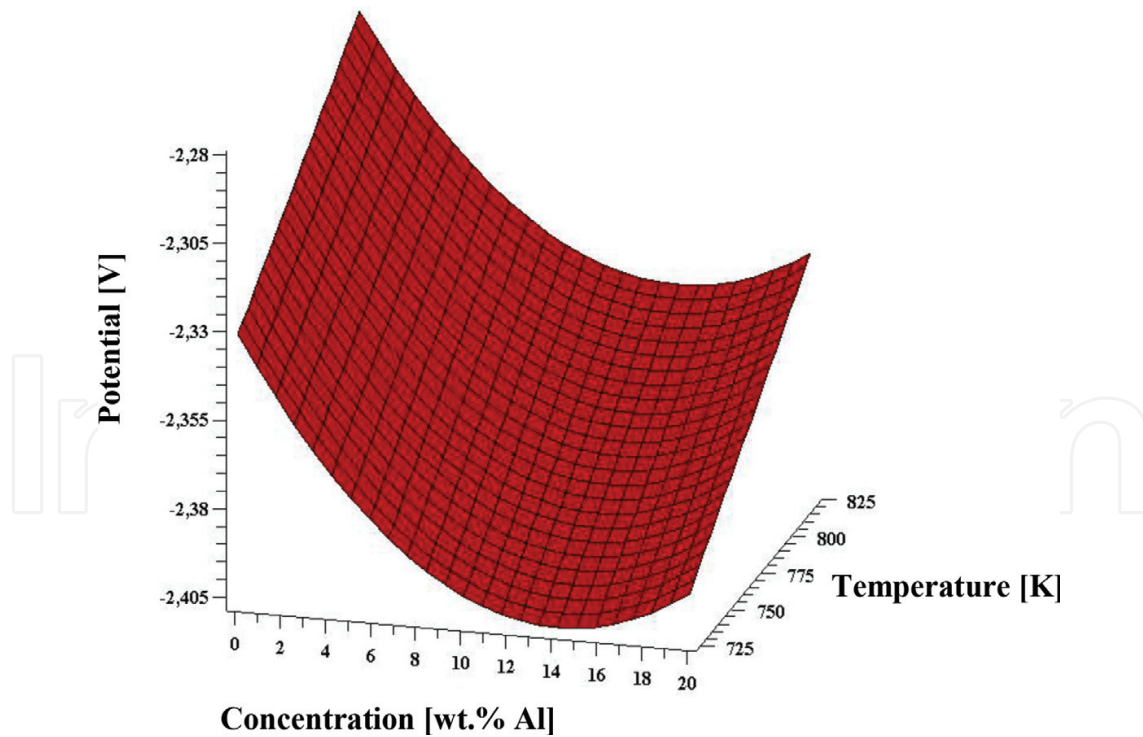

Figure 2. Apparent standard electrode potentials of U-Ga-Al alloy in the fused U(Ga-Al)/3LiCl-2KCl system as a function of temperature and composition of Ga-Al alloy (3D diagram). Reference electrode: Cl^-/Cl_2.

The data on Nd^{3+}/Nd and U^{3+}/U apparent standard electrode potentials in 3LiCl-2KCl eutectic were taken from the literature [7]. Temperature dependencies of Nd and U activity coefficients in liquid Ga-Al alloys were fitted to the Eqs. (12)–(17):

$$\log \gamma_{\mathrm{Nd(Ga-Al)}} = 5.12 - \frac{11260}{T} \pm 0.06 \quad 1.5 \text{ wt.\%Al} \tag{12}$$

$$\log \gamma_{\mathrm{Nd(Ga-Al)}} = 5.07 - \frac{11006}{T} \pm 0.04 \quad 5.0 \text{ wt.\%Al} \tag{13}$$

$$\log \gamma_{\mathrm{Nd(Ga-Al)}} = 4.94 - \frac{10713}{T} \pm 0.05 \quad 20.0 \text{ wt.\%Al} \tag{14}$$

$$\log \gamma_{\mathrm{U(Ga-Al)}} = 1.21 - \frac{4393}{T} \pm 0.05 \quad 1.5 \text{ wt.\% Al} \tag{15}$$

$$\log \gamma_{\mathrm{U(Ga-Al)}} = 1.17 - \frac{3935}{T} \pm 0.05 \quad 5.0 \text{ wt.\%Al} \tag{16}$$

$$\log \gamma_{\mathrm{U(Ga-Al)}} = 1.11 - \frac{3619}{T} \pm 0.06 \quad 20.0 \text{ wt.\%Al} \tag{17}$$

Three-dimensional $\log \gamma_{\mathrm{Nd(Ga-Al)}} - C_{\mathrm{(Ga-Al)}} - T$ and $\log \gamma_{\mathrm{U(Ga-Al)}} - C_{\mathrm{(Ga-Al)}} - T$ plots for fused Nd-(Ga-Al)/3LiCl-2KCl and U-(Ga-Al)/3LiCl-2KCl systems were presented in **Figures 3** and **4**, respectively. The following expressions describe these three-dimensional graphs:

$$\log \gamma_{\mathrm{Nd(Ga-Al)}} = \left(-11390 + 91.2 \cdot C - 2.8 \cdot C^2\right)/T + 5.14 - 0.016 \cdot C + 3 \cdot 10^{-4} \cdot C^2 \tag{18}$$

$$\log \gamma_{\mathrm{U(Ga-Al)}} = \left(-4638 + 169.4 \cdot C - 5.9 \cdot C^2\right)/T + 1.23 - 0.014 \cdot C + 4 \cdot 10^{-4} \cdot C^2 \tag{19}$$

where C is the concentration of Al in Ga-Al alloy (wt. %).

Low values of the activity coefficients show strong interaction between Ln (An) and the liquid alloy. Increasing temperature shifts the system toward more ideal behavior, in agreement with the literature.

Partial excess Gibbs free energy change of Nd and U in liquid Ga-Al-based alloys was calculated using Eq. (21) and previously obtained in expressions (12)–(17):

$$\Delta G^{ex.}_{Me(Ga-Al)} = \Delta H_{Me(Ga-Al)} - T \Delta S^{ex.}_{Me(Ga-Al)} \tag{20}$$

$$\Delta G^{ex.}_{Me(Ga-Al)} = 2.303 RT \log \gamma_{Me(Ga-Al)} \tag{21}$$

$$\Delta G^{ex}_{Nd(Ga-Al)} = -229.1 + 115.0 \cdot 10^{-3} T \pm 3.7 \text{ kJ/mol} \quad 1.5 \text{ wt.\%Al} \tag{22}$$

$$\Delta G^{ex}_{Nd(Ga-Al)} = -211.7 + 100.1 \cdot 10^{-3} T \pm 3.6 \text{ kJ/mol} \quad 5.0 \text{ wt.\%Al} \tag{23}$$

$$\Delta G^{ex}_{Nd(Ga-Al)} = -175.8 + 57.9 \cdot 10^{-3} T \pm 3.4 \text{ kJ/mol} \quad 20.0 \text{ wt.\%Al} \tag{24}$$

$$\Delta G^{ex}_{U(Ga-Al)} = -83.9 + 23.2 \cdot 10^{-3} T \pm 3.6 \text{ kJ/mol} \quad 1.5 \text{ wt.\%Al} \tag{25}$$

$$\Delta G_{U(Ga-Al)}^{ex} = -78.9 + 27.1 \cdot 10^{-3} T \pm 3.2 \ \text{kJ/mol} \quad 5.0 \ \text{wt.\%Al} \tag{26}$$

$$\Delta G_{U(Ga-Al)}^{ex} = -70.7 + 23.2 \cdot 10^{-3} T \pm 3.5 \ \text{kJ/mol} \quad 20.0 \ \text{wt.\%Al} \tag{27}$$
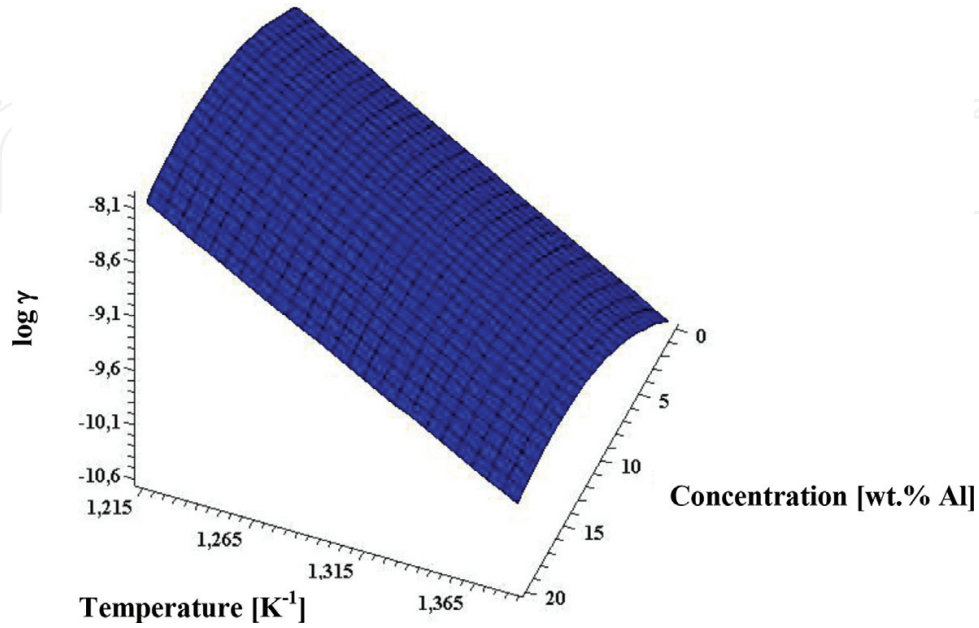

Figure 3. The activity coefficients of Nd in Ga-Al alloys as a function of temperature and composition of Ga-Al alloy (3D diagram).
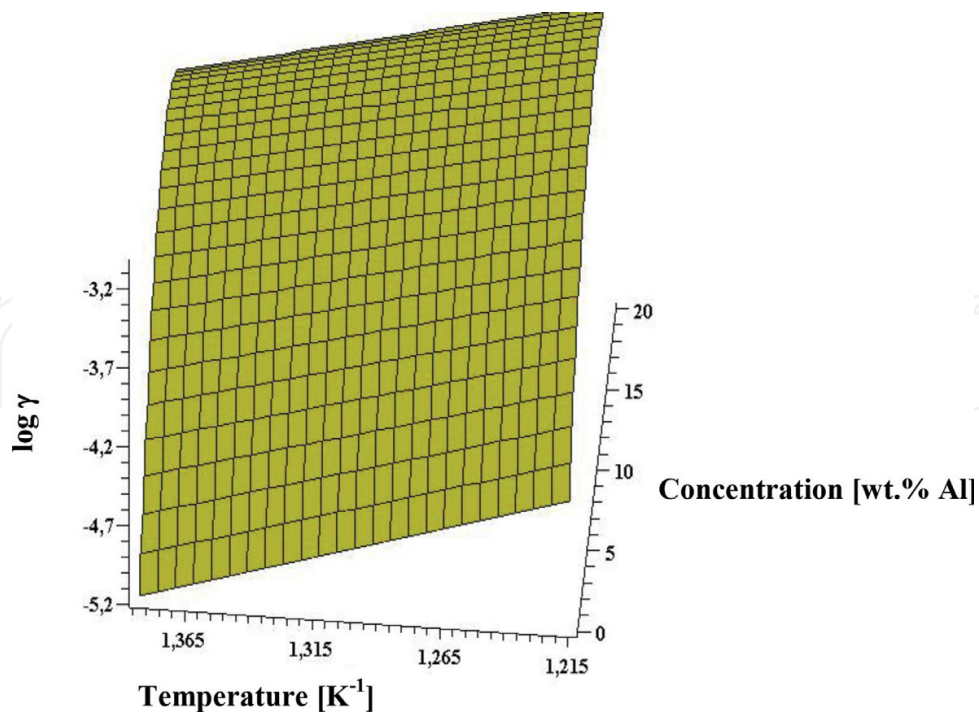

Figure 4. The activity coefficients of U in Ga-Al alloys as a function of temperature and composition of Ga-Al alloy (3D diagram).

where $\Delta G^{ex.}$ is the partial excess Gibbs free energy change (kJ/mol), ΔH is the partial enthalpy change of mixing (kJ/mol), $\Delta S^{ex.}$ is the partial excess entropy change (J/mol·K), and γ is the activity coefficient.

The general alloy formation reaction can be written in the following way:

$$[MeCl_6]^{3-} + 3\bar{e} + n(Ga - Al) = Me(Ga - In)_n + 6Cl^- \tag{28}$$

The efficiency of the electrochemical separation of metals in molten salts during their deposition is characterized by the value of the separation factor:

$$\Theta = \frac{C_2 x_1}{C_1 x_2} \tag{29}$$

where C_1 and C_2 are the concentrations of separated metals M_1 and M_2 in electrolyte in mole fraction and x_1 and x_2 are the quantity of separated metals M_1 and M_2 in alloy in atomic fraction.

The expression for calculation of the separation factor (SF) of uranium and neodymium in gallium-aluminum alloys can be written as follows [5]:

$$\log \Theta = \frac{3F}{2.303RT} \left(E^{**}_{U(Ga-Al)} - E^{**}_{Nd(Ga-Al)} \right) \tag{30}$$

where $E^{**}_{U(Ga-Al)}$ is the apparent standard potential of U-Ga-Al alloy (V) and $E^{**}_{Nd(Ga-Al)}$ is the apparent standard potential of Nd-Ga-Al alloy (V).

The following expressions for separation factor of uranium and neodymium were obtained in Eqs. (31)–(33):

$$\log \Theta_{U/Nd} = 1.18 + \frac{3088}{T} \pm 0.03 \quad 1.5 \text{ wt.\%Al} \tag{31}$$

$$\log \Theta_{U/Nd} = 1.05 + \frac{3003}{T} \pm 0.02 \quad 5.0 \text{ wt.\%Al} \tag{32}$$

$$\log \Theta_{U/Nd} = 1.01 + \frac{3004}{T} \pm 0.02 \quad 20.0 \text{ wt.\%Al} \tag{33}$$

A three-dimensional $\log \Theta_{Me(Ga-Al)} - C_{(Ga-Al)} - T$ graph showing the relationship between Nd/U separation factor, Al concentration in the Ga-Al solvent alloy, and temperature, for molten Me-(Ga-Al)/3LiCl-2KCl system, is presented in **Figure 5** and is described by the following equation:

$$\log \Theta_{U/Nd} = \left(3134.3 - 32.84 \cdot C + 1.32 \cdot C^2\right)/T + 1.25 - 0.05 \cdot C + 0.0019 \cdot C^2 \tag{34}$$

The separation of neodymium from uranium in molten chloride salts shows that uranium will be concentrated in the alloy phase, while neodymium will stay in the salt phase. The calculations of
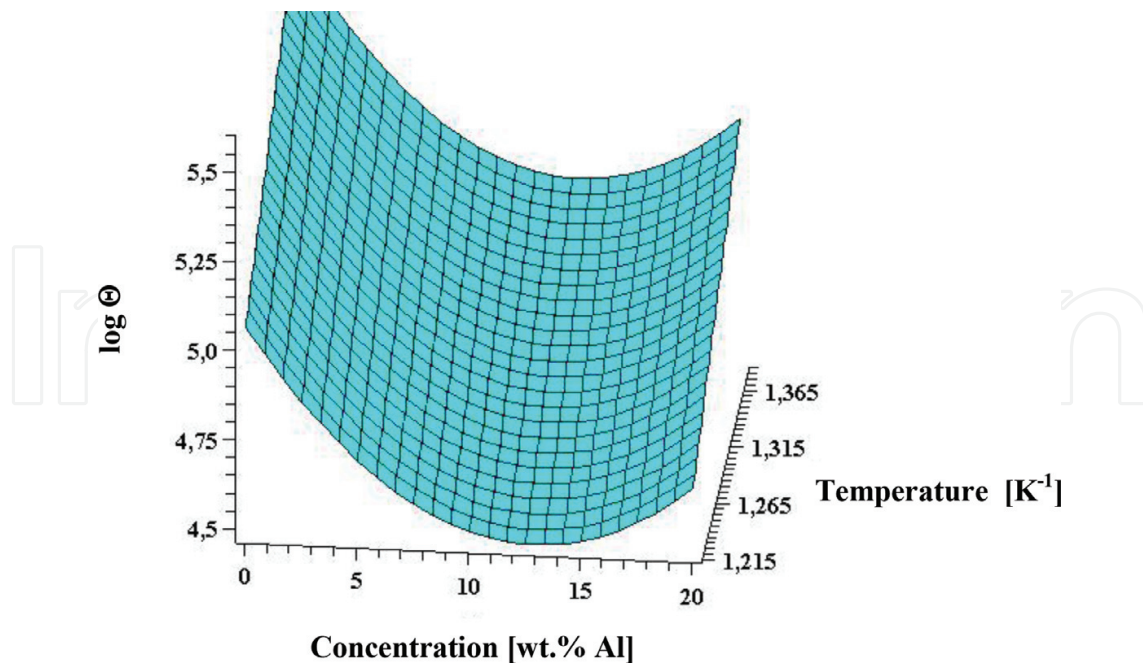
Figure 5. The separation factor of U/Nd couple as a function of temperature and composition of Ga-Al alloy (3D diagram).

SF for fused Nd/U(Ga-Al)/3LiCl-2KCl system show the high values of partitioning. For this technique the effect of lower temperatures should be preferred. Separation factor of Nd/U decreases by increasing the temperature due to the entropy factor.

3.2. La(U)-(Ga-In)/3LiCl-2KCl system

Potentiometry method at zero current was used for determination of the apparent standard potentials of the alloys. The dependencies of the apparent standard potential of Me(Ga-Al) alloys versus the temperature were fitted by the following equations using OriginPro version 7.5 Software:

$$E^{**}_{La(Ga)} = -2.851 + 5.18 \cdot 10^{-4} \cdot T \ V \quad [5] \tag{35}$$

$$E^{**}_{La(Ga-20wt.\%In)} = -(2.906 \pm 0.003) + (5.7 \pm 0.6) \cdot 10^{-4} \cdot T \pm 0.002 \ V \tag{36}$$

$$E^{**}_{La(Ga-40wt.\%In)} = -(3.357 \pm 0.005) + (10.9 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.002 \ V \tag{37}$$

$$E^{**}_{La(Ga-70wt.\%In)} = -(3.401 \pm 0.004) + (10.8 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.004 \ V \tag{38}$$

$$E^{**}_{La(In)} = -3.081 + 6.25 \cdot 10^{-4} \cdot T \ V \quad [5] \tag{39}$$

$$E^{**}_{U(Ga)} = -2.723 + 6.72 \cdot 10^{-4} \cdot T \ V \quad [5] \tag{40}$$

$$E^{**}_{U(Ga-20wt.\%In)} = -(2.508 \pm 0.006) + (3.8 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.003 \ V \tag{41}$$

$$E^{**}_{U(Ga-40wt.\%In)} = -(2.934 \pm 0.006) + (8.3 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.005 \ V \tag{42}$$

$$E^{**}_{U(Ga-70wt.\%In)} = -(2.950 \pm 0.008) + (7.3 \pm 0.1) \cdot 10^{-4} \cdot T \pm 0.006 \ V \tag{43}$$

$$E^{**}_{U(In)} = -2.921 + 6.12 \cdot 10^{-4} \cdot T \ V \quad [5] \tag{44}$$

Newton interpolation polynomial expressions were obtained to develop three-dimensional $\gamma_{Me(Ga-In)} - C_{(Ga-In)} - 1/T$ graphs on the basis of the functional dependencies of the apparent standard electrode potentials of the alloys, Ga-In mixture composition, and temperature (**Figures 6** and **7**).
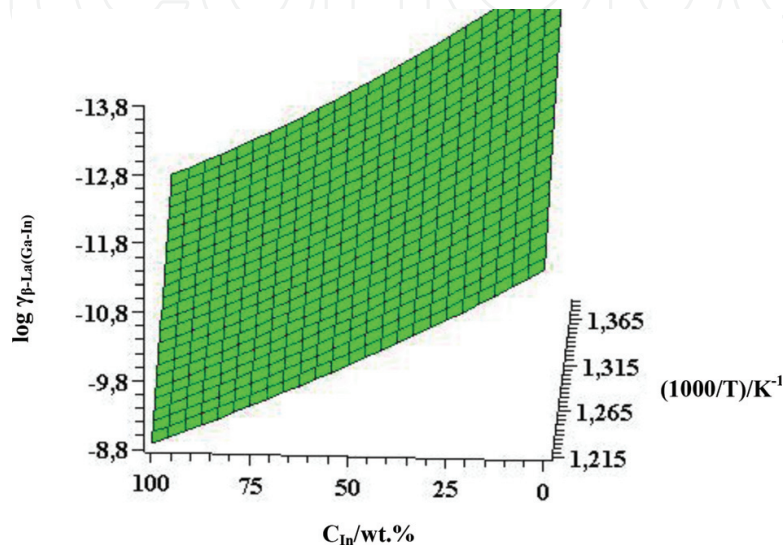

Figure 6. The activity coefficients of La in Ga-In alloys as a function of temperature and composition of Ga-In alloy (3D diagram).
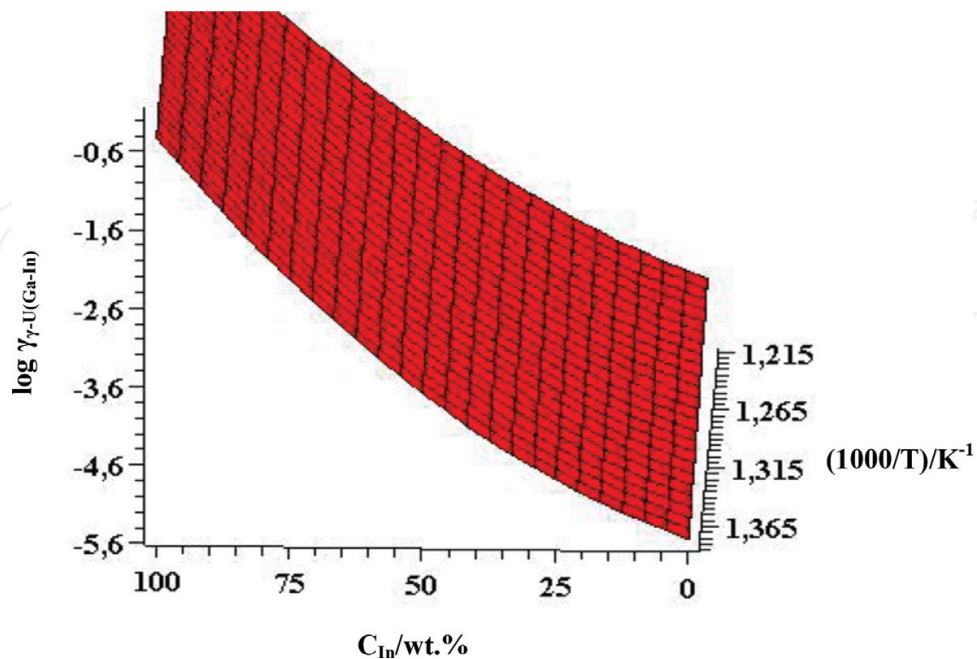

Figure 7. The activity coefficients of U in Ga-In alloys as a function of temperature and composition of Ga-In alloy (3D diagram).

The following expressions describe these three-dimensional graphs:

$$\log\gamma_{\beta-La(Ga-In)} = \left(-13333 + 59 \cdot C - 0.24 \cdot C^2\right)/T + 4.72 - 0.04 \cdot C + 0,0025 \cdot C^2 \tag{45}$$

$$\log\gamma_{\gamma-U(Ga-In)} = \left(-4977 - 10 \cdot C + 0.4 \cdot C^2\right)/T + 1.38 + 0.037 \cdot C - 0.0003 \cdot C^2 \tag{46}$$

where C is the concentration of In in Ga-In alloy (wt.%). The small values of activity coefficients show strong interaction of lanthanide and actinide with the liquid alloy. Increasing temperature shifts the system toward more ideal behavior.

Partial excess Gibbs free energy change of La and U in liquid Ga-In alloys was calculated:

$$\Delta G^{ex}_{La(Ga)} = -254.8 + 90.2 \cdot 10^{-3}T \ \text{kJ/mol} \tag{47}$$

$$\Delta G^{ex}_{La(Ga-20wt.\%In)} = -233.6 + 68.6 \cdot 10^{-3}T \pm 3.2 \ \text{kJ/mol} \tag{48}$$

$$\Delta G^{ex}_{La(Ga-40wt.\%In)} = -217.1 + 66.5 \cdot 10^{-3}T \pm 2.9 \ \text{kJ/mol} \tag{49}$$

$$\Delta G^{ex}_{La(Ga-70wt.\%)} = -201.2 + 55.0 \cdot 10^{-3}T \pm 3.2 \ \text{kJ/mol} \tag{50}$$

$$\Delta G^{ex}_{La(In)} = -188.1 + 59.3 \cdot 10^{-3}T \ \text{kJ/mol} \tag{51}$$

$$\Delta G^{ex}_{U(Ga)} = -95.1 + 26.4 \cdot 10^{-3}T \ \text{kJ/mol} \tag{52}$$

$$\Delta G^{ex}_{U(Ga-20wt.\%In)} = -143.3 + 56.8 \cdot 10^{-3}T \pm 3.9 \ \text{kJ/mol} \tag{53}$$

$$\Delta G^{ex}_{U(Ga-40wt.\%In)} = -90.9 + 46.3 \cdot 10^{-3}T \pm 3.8 \ \text{kJ/mol} \tag{54}$$

$$\Delta G^{ex}_{U(Ga-70wt.\%In)} = -73.8 + 40.5 \cdot 10^{-3}T \pm 3.8 \ \text{kJ/mol} \tag{55}$$

$$\Delta G^{ex}_{U(In)} = -38.9 + 44.7 \cdot 10^{-3}T \ \text{kJ/mol} \tag{56}$$

Using the temperature dependencies of the apparent standard potentials of lanthanum (35)–(39) and uranium (40)–(44) alloys, the following expressions for separation factor of uranium and lanthanum were obtained:

$$\log\theta_{La-U(Ga)} = 2.33 + \frac{1935}{T} \tag{57}$$

$$\log\theta_{La-U(Ga-20wt.\%In)} = -2.85 + \frac{6006}{T} \pm 0.02 \tag{58}$$

$$\log\theta_{La-U(Ga-40wt.\%In)} = -3.97 + \frac{6421}{T} \pm 0.02 \tag{59}$$

$$\log\theta_{La-U(Ga-70wt.\%In)} = -5.25 + \frac{6818}{T} \pm 0.02 \tag{60}$$

$$\log\theta_{La-U(In)} = -0.20 + \frac{2419}{T} \tag{61}$$

The results obtained show the shift of the partial enthalpy change of mixing toward more positive values with increasing concentration of indium in the binary alloys. A three-dimensional $\log\Theta_{La/U} - C_{(Ga-In)} - 1/T$ graph showing the relationship between La/U separation factor, In concentration in Ga-In solvent alloy, and temperature for molten Me-(Ga-In)/3LiCl-2KCl system is presented in **Figure 8** and is described by the following equation:

$$\log\Theta_{U/La} = \left(1935 + 184 \cdot C - 2 \cdot C^2\right)/T + 2.33 - 0.246 \cdot C + 0.002 \cdot C^2 \tag{62}$$

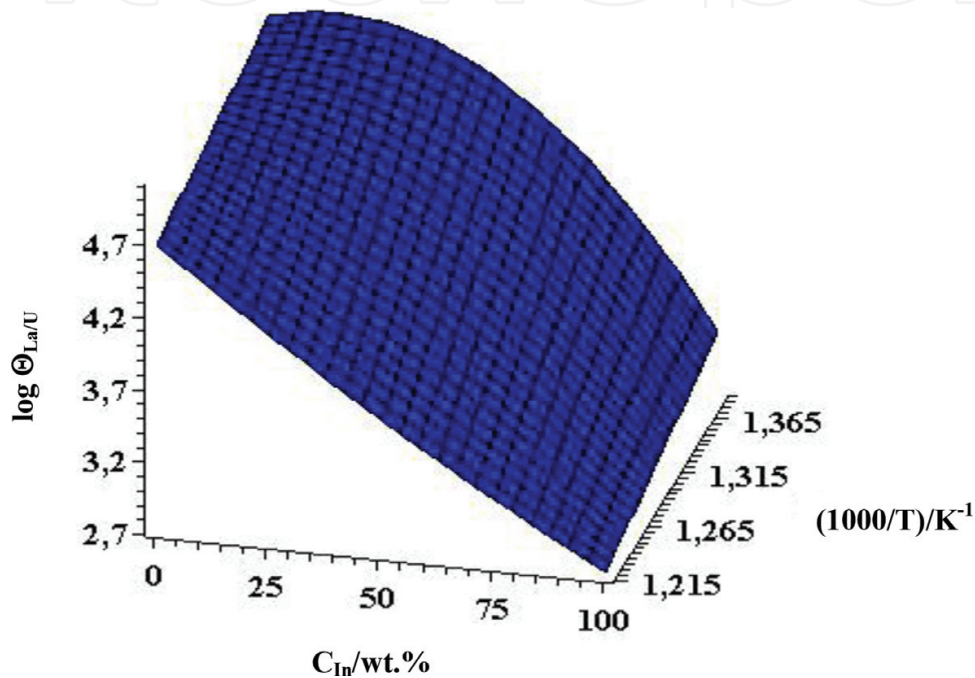where C is the concentration of In in Ga-In alloy (wt.%).

Figure 8. Three-dimensional $\log\Theta_{U/La} - C_{(Ga-In)} - 1/T$ graph for U/La couple.

4. Conclusions

The basic thermodynamic properties of lanthanum, neodymium, and uranium in liquid Ga-In and Ga-Al alloys between 723 and 823 K were determined. Low values of the activity coefficients showed strong interaction between lanthanides and the liquid alloys. The values of uranium and lanthanide separation factors showed that the alloys investigated here have considerable advantage compared 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 waste treatment.

Acknowledgements

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