Mechanism of the Electrochemical Reduction of Dysprosium(III) Ions on Inert and Active Electrodes in Molten Cesium Chloride

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Abstract—The cathodic reduction of Dy(III) ions to the metal in molten cesium chloride in the temperature range from 963 to 1063 K at inert molybdenum and active gallium electrodes in an inert gas atmosphere was studied by cyclic and square-wave voltammetry and open-circuit potentiometry. All procedures on assembling an experimental cell were carried out in a dry box excluding oxygen and moisture impurities in the reagents used. The cyclic voltammograms of the $CsCl-DyCl_3$ molten mixture recorded at the inert molybdenum electrode at different scan rates and at 987 K were characterized by one reduction current peak and the corresponding oxidation current peak. This fact indicates that the cathodic reduction of Dy(III) ions to the metal proceeds in one step possibly involving three electrons. The square-wave voltammogram exhibits an asymmetric cathodic curve of the Gaussian shape with one distinct current peak. The number of electrons involved in the electrochemical reduction and calculated from the width of the half-peak of the cathodic curve was close to three ($n = 2.89 \pm 0.05$). The mechanism of the cathodic deposition of metallic dysprosium at the inert Mo electrode was determined. The electrode reaction is shown to proceed irreversibly in one step and is controlled by the charge transfer rate. The diffusion coefficients of complex ions $[DyCl_6]^{3-}$ were calculated at different temperatures, and the activation energy of diffusion was determined. The temperature dependence of the diffusion coefficients of dysprosium(III) ions obeys the Arrhenius law and is described by the equation $\log D = -3.15 - 2010/T \pm 0.02$. The diffusion activation energy is calculated to be -38.7 kJ/mol. An experimental temperature dependence of the apparent standard potential of the Dy(III)/Dy couple is found. It is described by the linear equation $E^*_{Dy(III)/Dy} = -(3.921 \pm 0.007) + (6.8 \pm 0.1) \times 10^{-4} T \pm 0.005$ V. The main thermodynamic characteristics of dysprosium trichloride were calculated. The electrochemical deposition of dysprosium at the active gallium electrode was found to be related to alloy formation and occurs with depolarization. The equilibrium potentials of the Dy–Ga alloy are measured. The temperature dependence of the apparent standard potential of the alloy was determined and described by the equation $E^{**}_{Dy(Ga)} = -(3.069 \pm 0.005) + (3.2 \pm 0.2) \times 10^{-4} T \pm 0.006$ V. A scheme was proposed for the formation of Dy–Ga intermetallic compounds. The activity coefficients and the partial excess Gibbs free energy change for dysprosium in liquid gallium are calculated.

Keywords: electrochemistry, thermodynamics, dysprosium trichloride, molten salts, cathodic processes, diffusion coefficients, alloy formation

DOI: 10.1134/S0036029522080249

INTRODUCTION

High-purity rare earth metals (REMs) are applied in diverse industrial areas: radioelectronics, instrument-making and machine-building, metallurgy, chemical and ceramic industries, and so on. In nature, REMs are divided into two subgroups: the cerium subgroup including light lanthanides from lanthanum to gadolinium and the yttrium subgroup consisting of yttrium and other lanthanides. Pure metals or their alloys cannot be obtained from aqueous solutions because of a high reactivity of lanthanide compounds and, therefore, they are prepared by the metallothermy and electrolysis of molten salt media. For the development and improvement of technological procedures of the electrolytic synthesis and refining of REMs, comprehensive data on the physicochemical characteristics of molten salts containing rare earth elements are needed; in particular, one has to know the electrochemical and thermodynamic properties [1–3].

Molten alkaline metal chlorides are good reaction media for the selective dissolution or deposition of

REMs. They are ionic liquids with the long-range Coulomb interaction of particles. The dissolution of multicharge cations in the molten chloride media is accompanied by the formation of complex ions of various configuration, for example, tetrahedral or octahedral ions [4, 5].

The literature data on the electrochemical properties of the dysprosium compounds in the molten salt mixtures are contradictory. The electronic absorption spectra of such rare earth metal ions as Sm(III), Dy(III), Ho(III), and Er(III) were studied in the row from LiCl to CsCl [6]. It was shown that the complex $[LnCl]_6^{3-}$ ions were formed in the melts. The electrochemical behavior of Dy(III) ions in the halide electrolytes at the inert and active electrodes was studied. The cathodic reactions at the active electrodes were found to occur with depolarization to form intermetallic compounds of diverse composition [7−13]. The electroreduction of Dy(III) ions in the 3LiCl−2KCl melt at the inert tungsten and active aluminum electrodes was studied [14]. For instance, at the inert electrode the process proceeds in two consecutive steps: Dy(III) + ē → Dy(II) and Dy(II) + 2ē → Dy, whereas at the active electrode one step with depolarization occurs. The electrochemical behavior and efficiency of dysprosium extraction from 3LiCl−2KCl solutions containing $DyCl_3$ and $GdCl_3$ were studied by stationary and nonstationary electrochemical methods. It was found that at the W electrode Dy(III) ions were reduced to the metallic state in two consecutive steps [15]. The mechanisms of the reduction of Sm(III) and Dy(III) ions at the tungsten and binary Bi−Pb electrodes were studied [16]. The reduction of Dy(III) and Sm(III) at the inert electrode was found to proceed in one step for dysprosium and in two steps for samarium. As proved later [17−19], the cathodic reduction of Dy(III) ions to the metal at the inert electrodes proceeded irreversibly in one step involving three electrons.

The purpose of this work was to determine the mechanisms of the cathodic reduction of Dy(III) ions to the metal on inert Mo and active Ga electrodes and to calculate the thermodynamic characteristics of the dysprosium compounds in molten CsCl.

EXPERIMENTAL

Cesium chloride (reagent grade, 99.9%, Nevskii khimik, Russia), metallic gallium (99.9999%, Pikalevskii glinozemnyi zavod), and all other reagents were used as received. All procedures on assembling the cell and reagent loading were carried out in SPEKS GB02 glove box (oxygen content was <1 ppm, moisture content was <1 ppm).

Experiments were carried out in a three-electrode quartz cell placed in a glassy carbon crucible in a dry argon atmosphere in the temperature range from 963 to 1063 K. A glassy carbon rod with a diameter of 3 mm served as the counter electrode. A molybdenum wire with a diameter of 1 mm and a quartz microcrucible with liquid gallium were used as the working electrodes. The surface area of the solid electrode was calculated from the immersion depth, and that of the liquid electrode was calculated from the microcrucible diameter. The measurements were carried out versus standard chloride reference electrode.

The electrochemical behavior of Dy(III) ions in molten cesium chloride was studied by cyclic and square-wave voltammetries and open-circuit potentiometry. The measurements were carried out on an AUTOLAB PGSTAT302N potentiostat/galvanostat equipped with the NOVA 1.11 software.

Samples of dysprosium-containing solutions were analyzed by the ICP-MS method on an OPTIMA 4300 DV (Perkin Elmer) inductively coupled plasma optical emission spectrometer.

RESULTS AND DISCUSSION

The first part of the work is associated with studying the mechanism of the cathodic reduction of Dy(III) ions to the metal. These studies are necessary to search for optimum conditions of the electrolytic preparation of high-purity metallic dysprosium in molten salts. The stable oxidation states of the dysprosium compounds were determined by different electrochemical methods. The cyclic voltammograms of the molten CsCl−$DyCl_3$ mixture obtained at the inert molybdenum electrode at different scan rates at 987 K were shown in Fig. 1. They are characterized by one cathodic reduction peak and one anodic oxidation peak. This indicates that the cathodic reduction of Dy(III) ions to the metal proceeds in one step possibly involving three electrons. An increase of the scan rate resulted in the shift of the potential of the cathodic current peak to the negative side. At the same time, the cathodic current peaks were directly proportional to the square root of the scan rate.

Square-wave voltammetry was used to determine the number of electrons of the electrode reaction. The asymmetric cathodic curve of the Gaussian shape was obtained in the CsCl−$DyCl_3$ solution at 695 K (Fig. 2). Inset in Fig. 2 shows an interrelation between the cathodic current peak and square root of the frequency. This dependence is linear and passes through the origin, which makes it possible to use Eq. (1) to calculate the number of electrons in the electrode reaction in the frequency range from 10 to 18 Hz

$$W_{1/2} = 3.52 \frac{RT}{nF}, \qquad (1)$$

where $W_{1/2}$ is the half-peak width (V), R is the universal gas constant (J mol^{-1} K^{-1}), T is the absolute temperature (K), n is the number of the exchange electrones, and F is Faraday's constant (C/mol).
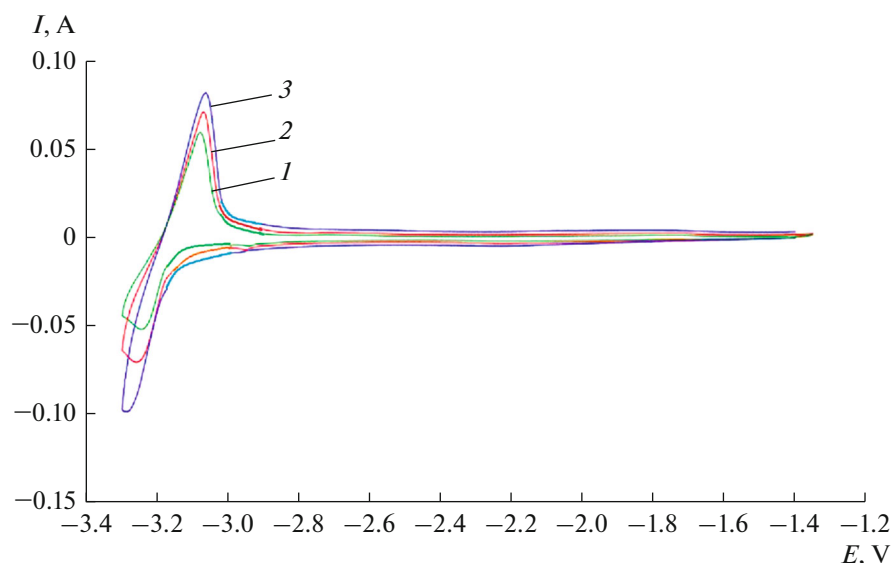
Fig. 1. Cyclic voltammograms of the CsCl–DyCl$_3$ melt recorded on a Mo electrode (S = 0.15 cm^2) at scan rates of (*1*) 0.1, (*2*) 0.2, and (*3*) 0.3 V/s; m(DyCl$_3$) = 2.64 wt %, T = 987 K.
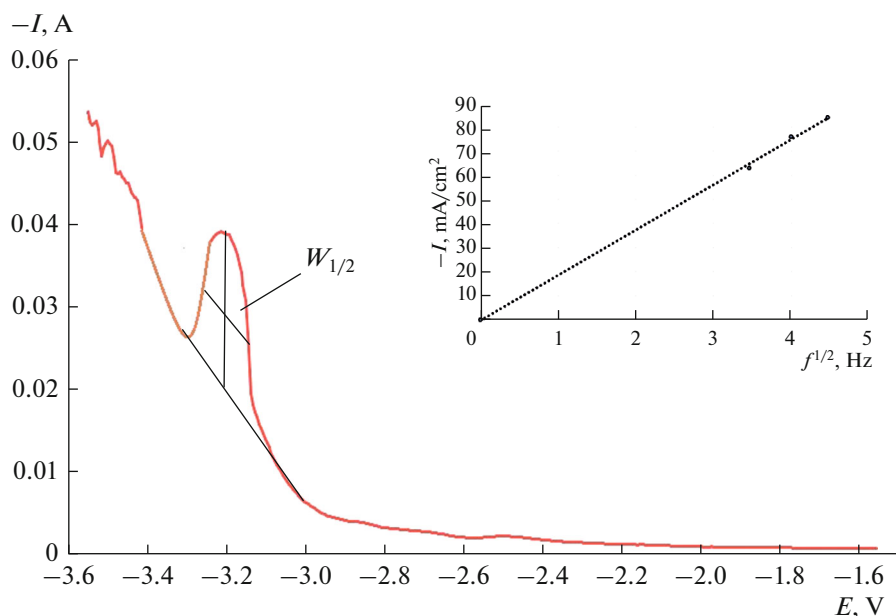
Fig. 2. Square-wave voltammogram for the CsCl–DyCl$_3$ melt at a frequency of 14 Hz, a pulse height of 25 mV, and a potential increment of 1 mV; m(DyCl$_3$) = 2.93 wt %, T = 1023 K. (inset) Ratio of the current peak to the square root of frequency.

The calculated number of the exchange electrones of the cathodic reaction was close to three (n = 2.89 ± 0.05).

Based on an analysis of the obtained results and according to the theory of cyclic voltammetry, we can conclude that the cathodic reduction of Dy(III) ions to the metal at the inert electrode is irreversible, proceeds in one step, is controlled by the charge-transfer rate [20], and in dilute solutions is described by the equation

$$\text{Dy(III)} + 3\bar{e} \rightarrow \text{Dy}. \tag{2}$$

The diffusion coefficients of the [DyCl$_6$]$^{3-}$ complex ions in the molten salt were determined using cyclic voltammetry by Eq. (3) [20], which is valid for the irreversible system at the scan rates used.

$$I_\mathrm{p} = 0.496 n F S C_0 \left(\frac{\alpha n F D v}{RT} \right), \tag{3}$$

where I_p is the peak current (A), S is the surface area of the working electrode (cm^2), C_0 is the concentration of dysprosium ions (mol/cm^3), D is the diffusion coefficient (cm^2/s), and v is the scan rate (V/s).

Table 1. Diffusion coefficients and activation energy of $[DyCl_6]^{3-}$ ions in molten CsCl at various temperatures

T, K	$D \times 10^5$, cm^2/s	E_A, kJ/mol
963	0.60 ± 0.03	
995	0.68 ± 0.03	
1023	0.77 ± 0.03	-38.7
1063	0.94 ± 0.03	

The temperature dependence of the diffusion coefficient obeys the Arrhenius law and was described by the following equation:

$$\log D = -3.15 - \frac{2010}{T} \pm 0.02. \qquad (4)$$

The determined diffusion coefficients were used to calculate the activation energy of the diffusion.

$$D = D_0 \exp\left(-\frac{E_A}{RT}\right) \pm \Delta, \qquad (5)$$

where ΔE_A is the activation energy of the diffusion (kJ/mol), D_0 is the preexponential term (cm^2/s), and Δ is the experimental error.

The diffusion coefficients and activation energy of dysprosium(III) ions in molten cesium chloride at different temperatures are given in Table 1.

The equilibrium electrode potential of the Dy(III)/Dy couple was determined at different tem-peratures by open-circuit potentiometry. For this purpose, the inert molybdenum electrode was polarized with a current of 25−75 mA for 20−35 s and then the potential−time dependence was recorded. The typical chronopotentiogram of the CsCl−DyCl$_3$ melt is shown in Fig. 3. The Nernst equation was applied to calculate the apparent standard potential

$$E_{Dy(III)/Dy} = E^*_{Dy(III)/Dy} + \frac{RT}{nF} \ln C_{DyCl_3}, \qquad (6)$$

where

$$E^*_{Dy(III)/Dy} = E^o_{Dy(III)/Dy} + \frac{RT}{nF} \ln\gamma_{DyCl_3}. \qquad (7)$$

The experimental dependence obtained using the Origin Pro software (version 7.5) in the temperature range from 963 to 1063 K was described by the linear equation
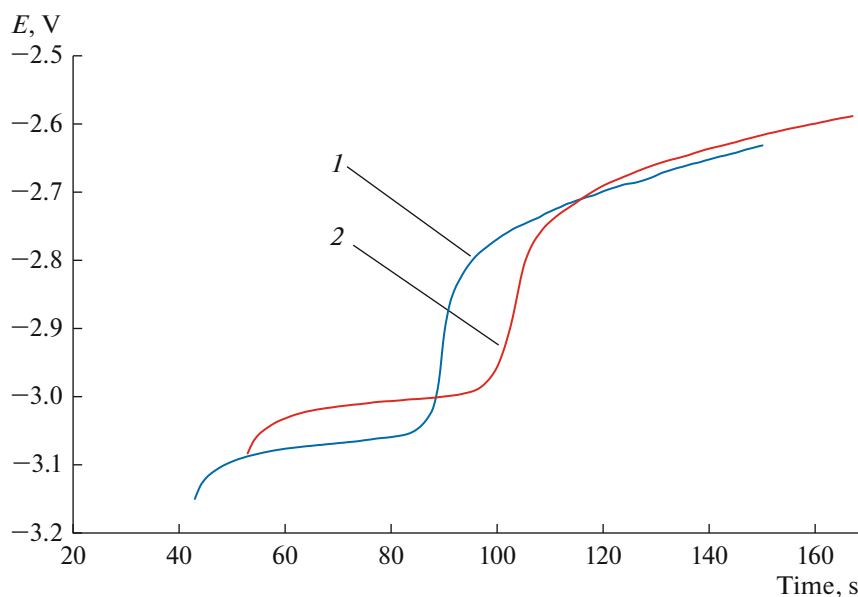
$$E^*_{Dy(III)/Dy} = -(3.921 \pm 0.007) \\ + (6.8 \pm 0.1) \times 10^{-4} T \pm 0.005 \text{ V}. \qquad (8)$$

The partial excess Gibbs free energy change upon the formation of dysprosium trichloride from the elements was calculated by Eq. (9). The resulting dependence is described by Eq. (10).

$$\Delta G^*_{DyCl_3} = nFE^*_{Dy(III)/Dy}, \qquad (9)$$

$$\Delta G^*_{DyCl_3} = -1135.1 + 0.197T \pm 1.1 \text{ kJ/mol}. \qquad (10)$$

The results are summarized in Table 2.

Fig. 3. Potential−time dependences recorded after the cathodic polarization of an inert Mo electrode in the CsCl−DyCl$_3$ melt at $I = 25-75$ mA, $\tau = 20-35$ s, and $m(DyCl_3) = 2.72$ wt % and the equilibrium potential of the Dy(III)/Dy couple at (1) $T = 1007$ K and (2) $T = 965$ K.

Table 2. Apparent standard potentials of the Dy(III)/Dy couple and the formal standard Gibbs free energy change of formation of dysprosium trichloride in molten CsCl at various temperatures

T, K	$E^*_{Dy(III)/Dy}$, V	$\Delta G^*_{DyCl_3}$, kJ/mol	$\Delta H^*_{DyCl_3}$, kJ/mol	$\Delta S^*_{DyCl_3}$, J/mol
963	-3.255 ± 0.005	-945.6 ± 1.1		
995	-3.244 ± 0.005	-939.2 ± 1.1	-1135.1	197.0
1023	-3.225 ± 0.005	-933.7 ± 1.1		
1063	-3.187 ± 0.005	-925.9 ± 1.1		

The chronopotentiograms of the CsCl−DyCl₃ melt recorded at the molybdenum and gallium electrodes at 965 K are shown in Fig. 4. The potential−time dependence after the short polarization of the Ga electrode is shown by line *1* in Fig. 4. The plateau at a potential of −2.58 V corresponds to the equilibrium potential of the cathodic product, i.e., Dy−Ga alloy. In the case of the cathodic polarization of the inert Mo electrode, the chronopotentiogram exhibits the distinct plateau corresponding to the equilibrium potential of the Dy(III)/Dy couple (Fig. 4, line *2*). The studies showed that the depolarization during the discharge of dysprosium ions at the gallium electrode ranged from 0.50 to 0.55 V. This is related to the alloy formation when the active cathodes are used in the electrolysis of the melt.

The equilibrium standard potential of the alloy was determined by open-circuit potentiometry (Fig. 4, line *1*). The Nernst equation was applied to calculate the apparent standard potential

$$E_{Me(alloy)} = E^{**}_{Me(alloy)} + \frac{RT}{3F} \ln \frac{c_{Me^{3+}}}{x_{Me(alloy)}}, \quad (11)$$

where $E_{Me(alloy)}$ is the equilibrium potential of the alloy (V), $E^{**}_{Me(alloy)}$ is the apparent standard potential of the alloy (V), n is the number of exchange electrones, $C_{Me(III)}$ is the concentration of metal ions in the solvent (molar fractions), and $x_{Me(alloy)}$ is the concentration of metal atoms in the alloy (molar fractions).

The change in the apparent standard potentials of the alloys at different temperatures was determined using the Origin Pro 7.5 software. The obtained dependence was approximated by the linear equation

$$E^{**}_{Dy(Ga)} = -(3.069 \pm 0.005) \\ + (3.2 \pm 0.2) \times 10^{-4} T \pm 0.006 \text{ V}. \quad (12)$$

The activity coefficients of dysprosium in the liquid gallium alloy were calculated by Eq. (13) [21]. The temperature dependence of the activity coefficient was described by the following equation [14]:

$$\log\gamma_{Dy(Ga)} = \frac{nF}{2.303RT}\left(E^*_{Dy(III)/Dy} - E^{**}_{Dy-Ga}\right), \quad (13)$$

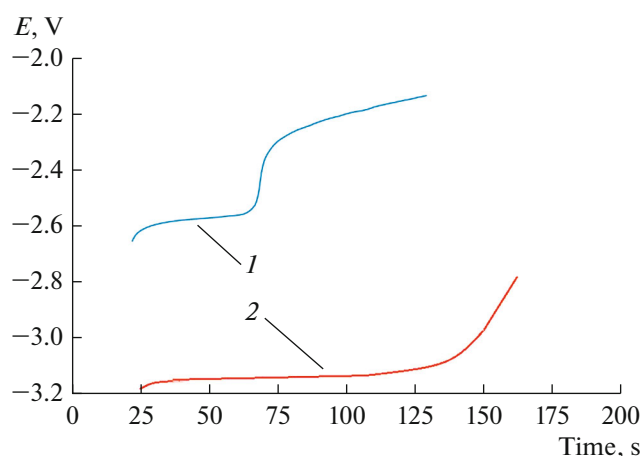$$\log\gamma_{Dy(Ga)} = 5.45 - \frac{12905}{T} \pm 0.14. \quad (14)$$

The low activity coefficients indicate a strong interaction between dysprosium and liquid gallium. An increase of the temperature resulted in system ordering [22].

The excess partial Gibbs energy for dysprosium in liquid gallium was calculated by Eq. (16) [21]

$$\Delta G^{ex}_{Dy(Ga)} = \Delta H_{Dy(Ga)} - T\Delta S^{ex}_{Dy(Ga)}, \quad (15)$$

$$\Delta G^{ex}_{Dy(Ga)} = 2.303RT \log \gamma_{Dy(Ga)}, \quad (16)$$

$$\Delta G^{ex}_{Dy(Ga)} = -383.4 + 0.241T \pm 2.5 \text{ kJ/mol}. \quad (17)$$

Fig. 4. Potential−time dependences recorded after the short cathodic polarization of (*1*) Ga and (*2*) Mo working electrodes in the CsCl−DyCl₃ melt at $m(DyCl_3) = 2.57$ wt %, $T = 961$ K, $I = 25-75$ mA, and $\tau = 20-35$ s. The equilibrium potentials of (*1*) Dy−Ga alloy and (*2*) Dy(III)/Dy couple.

Table 3. Apparent standard potentials of the Dy−Ga alloy and the activity coefficients and thermodynamic characteristics of dysprosium in liquid gallium in molten CsCl at various temperatures

T, K	$E^{**}_{\text{Dy−Ga}}$, V	$\log \gamma_{\text{Dy−Ga}}$	$\Delta G^{\text{ex}}_{\text{Dy(Ga)}}$, kJ/mol	$\Delta H_{\text{Dy(Ga)}}$, kJ/mol	$\Delta S^{\text{ex}}_{\text{Dy(Ga)}}$, J/mol
963	-2.761 ± 0.006	-7.95	-151.9 ± 2.5		
995	-2.750 ± 0.006	-7.52	-143.7 ± 2.5	-383.4	240.6
1023	-2.741 ± 0.006	-7.16	-136.9 ± 2.5		
1063	-2.729 ± 0.006	-6.69	-127.8 ± 2.5		

A scheme for the formation of the Dy−Ga intermetallic compounds can be represented as follows [23]:

$$xDy + 3x\bar{e} + yGa = Dy_xGa_y. \qquad (18)$$

The thermodynamic characteristics of the liquid Dy−Ga alloy are given in Table 3.

CONCLUSIONS

The cathodic reduction of Dy(III) ions to the metal in molten CsCl in the temperature range from 963 to 1063 K on molybdenum and gallium electrodes was studied by cyclic and square-wave voltammetry and open-circuit potentiometry. The mechanism of the cathodic deposition of metallic dysprosium at the inert Mo electrode was determined. The electrode reaction was shown to proceed irreversibly in one step and be controlled by the charge-transfer rate. The temperature dependence of the diffusion coefficients of dysprosium(III) ions was determined to obey the Arrhenius law. The activation energy of the diffusion process was calculated. The temperature dependence of the apparent standard potential for the Dy(III)/Dy couple was determined. The main thermodynamic characteristics of dysprosium trichloride were calculated.

The electrochemical deposition of dysprosium at the active Ga electrode was found to be related to the alloy formation and to occur with depolarization. The equilibrium potentials of the Dy−Ga alloy were measured, and the temperature dependence of the apparent standard potential of the alloy was determined. A scheme was proposed for the formation of Dy−Ga intermetallic compounds. The activity coefficients and the partial excess Gibbs free energy change for dysprosium in liquid gallium were calculated.

FUNDING

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Translated by E. Yablonskaya