Electrochemical Cocrystallization Experiments with Gd_2Cl_3

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Gd_2Cl_3 is electrocrystallized from molten $GdCl_3$ at 900 K with a current efficiency of 70% referring to the reaction $2GdCl_3+3e^-=Gd_2Cl_3+3Cl^-$. The reaction is used to determine cocrystallization coefficients for trivalent rare earths and actinoids (Y, Nd, Cm, Pu), divalent lanthanoids (Eu, Yb), and Sr. The oxidation potential for the above reaction is determined as $2.65 \leq E^\circ \leq 2.68$ V.

Introduction

Among compounds of metals in anomalously low oxidation states those of the rare earth elements containing discrete or condensed clusters are of particular interest [1]. The first discovered compound, Gd_2Cl_3 [2–4], with an oxidation state below +2 can be prepared in a slow thermal reaction from Gd and $GdCl_3$ at 870–930 K. The reaction can be enhanced by starting from "activated" Gd obtained from its hydride, yet it becomes only quantitative after several weeks of continuous heating. An acceleration of the reaction is possible electrochemically as shown earlier [5]. Such electrocrystallization can be successfully applied in cocrystallization experiments involving Gd_2Cl_3 [6, 7].

Here we report on electro-cocrystallization of some trivalent and divalent elements in tracer amounts with Gd_2Cl_3.

Experimental

Anhydrous $GdCl_3$ was prepared as described elsewhere [8, 9] and purified by vacuum sublimation to remove any GdOCl impurity. All handling was done in a dry box under Argon. The isotopes ^{152}Eu, ^{169}Yb, ^{85}Sr, ^{153}Gd, ^{88}Y, ^{147}Nd, ^{239}Pu, and ^{244}Cm were introduced into the system as their chlorides. These were prepared in tracer amounts from an HCl solution to which approx. 10 mg $GdCl_3$ and 100 mg NH_4Cl had been added. Evaporation to dryness was followed by a gradual increase of temperature to 670 K.

Electrolysis was carried out at 900 K in a quartz glass vessel similar to that described in [5] in a stream of Ar which was purified by passing it through Ti chips at approx. 1100 K. About 4 g of $GdCl_3$ with the isotopes introduced was placed into a Ta crucible (diameter and height 15 mm) which served as a cathode. A Ta anode was used in the first stage of the experiments. However, it did not remain inert, and after the experiment finely dispersed Ta powder (20–400 mg) was found in the reaction product together with $GdCl_3$ and Gd_2Cl_3. Therefore, a Gd anode (rod with 5 mm diameter and 9 mm length) was used, made from 99.8% pure metal which was connected to the current source *via* a Ta junction and stainless steel wire (Fig. 1). A quartz glass plate fixed to the top

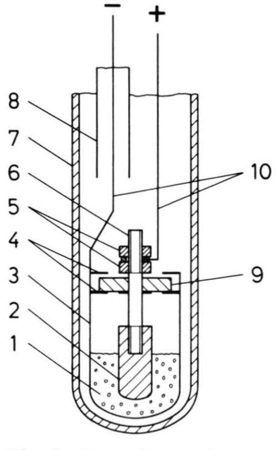

Fig. 1. Experimental setup for the electrolytic formation of Gd_2Cl_3 from molten $GdCl_3$.
1 $GdCl_3$ melt, 2 gadolinium anode, 3 tantalum crucible, cathode, 4 Ta wires, 5 stainless steel nuts, 6 tantalum rod, 7 quartz glass vessel, 8 quartz glass tube, 9 quartz glass plate, 10 stainless steel wires.

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of the crucible by welded-on Ta wires kept the anode in the center of the crucible and approx. 2 mm away from the bottom of the crucible. At the end of the reaction this distance had increased by 1−2 mm due to the dissolution of the anode.

The content of the crucible was melted for 30 min at 900 K, before electrolysis was started at a voltage of 0.2−0.4 V (70−120 mA). After electrolysis the cooled product was treated with 8−9 portions (6 ml each) of dried and deoxygenated ethanol or a 3:1 mixture of ethanol and THF. THF had been distilled in Ar immediately before use. The crystalline black residue was dissolved in 10 ml 0.5 N CH_3COOH which was quickly decanted from small amounts of GdOCl and Gd to be dissolved in 4 N HNO_3. The relative amount of Gd in the latter fraction was less than 2%.

Analysis for Gd and Cl was performed by back titration with EDTA and NH_4SCN, respectively, and the distribution of isotopes between the ethanol-THF, acetic and nitric acid solutions was determined using γ-spectroscopy. The phases in the pure macrocomponent system $Gd/Gd_2Cl_3/GdCl_3$ were characterized by the modified Guinier technique [10]. Only $GdCl_3$ and Gd_2Cl_3 could be detected in the reaction products. After extraction with ethanol the residue showed the slightly diffuse diagram of pure Gd_2Cl_3.

Results and Discussion

The thermal reaction of the Gd rod and the melt of $GdCl_3$ at 900 K was negligible, as experiment showed. The reaction rate was dramatically enhanced by making the rod the anode in an electrolytic cell. However, after 4 to 4.5 h of electrolysis, as with most experiments, the current efficiency for the reaction $2GdCl_3+3e^-=Gd_2Cl_3+3Cl^-$ reached only approximately 40%. An explanation is provided by the observation that the current stayed constant (~ 100 mA) after cooling the melt under the working voltage. Obviously, a shortcut between the electrodes had formed by the semiconducting Gd_2Cl_3 [11]. Decreasing the time of electrolysis to 1 to 1.5 h increased the current efficiency up to 70%.

Table 1 presents the data on the distribution of isotopes between the solid phase Gd_2Cl_3 and the melt. The small deviations of the analysed compositions from the value Cl/Gd = 1.5 may be due to the presence of $GdClH_x$ formed with traces of H_2O [12] or due to a partial dissolution of metallic Gd in acetic acid.

Since the mechanism of cocrystallization during the electrochemical synthesis is the same as that of the thermal reaction between Gd and $GdCl_3$, equation (1) derived for this system [13] can be used to calculate the cocrystallization coefficient.

$$\ln\frac{a}{a-x} = 2\lambda\,\frac{(1+k)\cdot\exp\left[\dfrac{\Delta E^\circ_{M-\mu}}{RT/F}\right]}{1+k\cdot\exp\left[\dfrac{\Delta E^\circ_{M-\mu}}{RT/F}\right]}\cdot\ln\frac{2b}{2b-y} \qquad (1)$$

a, b are the initial quantities of micro- and macroelements in the melt, and x, y are the final amounts of micro- and macrocomponent in the solid phase. λ is the cocrystallization coefficient of the microcomponent with Gd_2Cl_3, $\Delta E^\circ_{M-\mu}$ is the difference of standard oxidation potentials of the pairs M^{3+}/M^{2+} for macro-(M) and micro-(μ) components, and k is the Gd^{3+}/Gd^{2+} ratio. In this equation k is unknown. Since for cocrystallization of Y and Cm with Gd_2Cl_3, ΔE°_{Gd-Y} and ΔE°_{Gd-Cm} are close to 0, equation (1) may be approximated by equation (2),

$$\ln\frac{a}{a-x} = 2\lambda\cdot\ln\frac{2b}{2b-y} \qquad (2)$$

If we calculate the cocrystallization coefficient for the microelement compared to that for ^{153}Gd we get

$$\ln\frac{a}{a-x} = \frac{\lambda_\mu}{\lambda_{Gd}}\cdot\ln\frac{a_{Gd}}{a_{Gd}-x_{Gd}} \qquad (3)$$

which is the Derner-Hoskins equation.

From the data listed in Table I it follows that those normally trivalent elements which in their divalent state are characterized by the presence of valence electrons in the d orbitals (Y^{2+} = $[Kr]4d^1$ and Cm^{2+} = $[Rn]5f^76d^1$) do cocrystallize with Gd_2Cl_3. Ions with empty d states like Nd^{2+} = $[Xe]4f^4d^0$ practically remain in the melt, and $\lambda \ll 1$ holds. The same behaviour, of course, is found for the normally divalent elements Eu, Yb and Sr. The result is not unexpected, if the essential role of metal-metal bonding for the stability of Gd_2Cl_3 is considered, and it corroborates conclusions drawn earlier [6, 7]. There is also good agreement between cocrystallization coefficients determined from thermal reactions [6] and from electro-cocrystallization.

Table I. Distribution of isotopes between the $GdCl_3$ melt and solid Gd_2Cl_3 and resulting λ_μ/λ_{Gd} values in eq. (3).

	Quantity in cluster [%]							λ_μ/λ_{Gd}						Gd : Cl in Gd_2Cl_3
	Eu	Yb	Nd	Sr	Cm	Y	Gd	Eu	Yb	Nd	Sr	Cm	Y	
1.	1.5	–	–	–	–	53	43	0.03	–	–	–	–	1.34	1 : 1.47
2.	–	0.8	–	–	47	44	27	–	0.03	–	–	2.02	1.84	1 : 1.44
3.	1.3	–	2.3	–	–	–	30	0.04	–	0.07	–	–	–	1 : 1.41
4.	0.4	–	–	0.8	–	–	40	0.01	–	–	0.02	–	–	1 : 1.38

The value of the oxidation potential, which is reached in the cathode space during synthesis of Gd_2Cl_3, is still not clear. The difficulty of this problem consists in the fact that one does not know where the compound deposits. This might occur in the melt near the cathode, directly on the cathode or on the vertex of the growing Gd_2Cl_3 crystal, receiving electrons from the cathode due to electroconductivity of the compound. Nevertheless, the problem may be solved using equation (1).

Obviously, such parameters as λ, $\Delta E^\circ_{M-\mu}$ do not depend on the change of the oxidation potential of the system. Based on the distribution of the components under the specific conditions of the electrolytic formation of Gd_2Cl_3, one can determine k and use it for determining the oxidation potential of the system. The value $\Delta E^\circ_{M-\mu}$ has to differ significantly from zero, because otherwise equation (2) holds which does not contain k. A rather high value of $\Delta E^\circ_{M-\mu} = 0.26$ V is observed during cocrystallization of Gd_2Cl_3 with Pu. For this system $\lambda = 2.03$ has been determined [7]. Table II contains the data on the distribution of plutonium and gadolinium in the system during electrochemical reduction of $GdCl_3$, which are neccessary to calculate k. As is clear from Table II, k lies in the range of 9 to 12. For comparison, k is equal to 16, when the synthesis of Gd_2Cl_3 occurs due to dissolution of metallic gadolinium in $GdCl_3$ without applying a voltage. Thus, when the electrochemical technique is used, the synthesis occurs under the conditions of a higher concentration of divalent Gd. Using the k values obtained, and Nernst's equation, we calculate the oxidation potential of this system to be $-2.65 \leq E^\circ \leq -2.68$ V.

Table II. The Gd^{3+}/Gd^{2+} ratio in the system during electrochemical formation of Gd_2Cl_3, determined in terms of eq. (1) for distribution of Pu.

Voltage during electrolysis, V	a	x	b	y	$k = \frac{Gd^{3+}}{Gd^{2+}}$
0.4	100	43.5	100	71.7	12
0.6	100	6	100	11.2	9

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