Electrochemical Cocrystallization Experiments with Gd$_2$Cl$_3$

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Cluster, Electrochemical Reduction, Cocrystallization

Gd$_2$Cl$_3$ is electrocrystallized from molten GdCl$_3$ at 900 K with a current efficiency of 70% referring to the reaction $2$GdCl$_3$ + 3 e$^-$ = Gd$_2$Cl$_3$ + 3 Cl$^-$. 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$_2$Cl$_3$ [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$_2$Cl$_3$ [6, 7].

Here we report on electro-cocrystallization of some trivalent and divalent elements in tracer amounts with Gd$_2$Cl$_3$.

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$_4$Cl 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$_2$Cl$_3$. 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$_2$Cl$_3$ 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 CH₃COOH which was quickly decanted from small amounts of GdOCl and Gd to be dissolved in 4 N HNO₃. 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 NH₄SCN, 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/GdCl₃/GdCl₅ were characterized by the modified Guinier technique [10]. Only GdCl₃ and Gd₂Cl₅ could be detected in the reaction products. After extraction with ethanol the residue showed the slightly diffuse diagram of pure Gd₂Cl₅.

Results and Discussion

The thermal reaction of the Gd rod and the melt of GdCl₃ 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 2GdCl₃+3e⁻→Gd₂Cl₅+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 Gd₂Cl₅ [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 Gd₂Cl₅ and the melt. The small deviations of the analysed compositions from the value Cl/Gd = 1.5 may be due to the presence of GdClHₓ formed with traces of H₂O [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 GdCl₃, equation (1) derived for this system [13] can be used to calculate the cocrystallization coefficient.

\[
\ln \frac{a}{a-x} = 2 \lambda \cdot \ln \frac{2b}{2b-y}
\]

\[
\ln \frac{a}{a-x} = \lambda \cdot \ln \frac{a_{Gd}}{a_{Gd-x_{Gd}}}
\]

where \( a, b \) 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. \( \lambda \) is the cocrystallization coefficient of the microcomponent with Gd₂Cl₅, \( AE_{M}^{°} \) is the difference of standard oxidation potentials of the pairs M⁵⁺/M²⁺ for macro-(M) and micro-(μ) components, and \( k \) is the Gd³⁺/Gd²⁺ ratio. In this equation \( k \) is unknown. Since for cocrystallization of Y and Cm with Gd₂Cl₅, \( AE_{Gd-Y}^{°} \) and \( AE_{Gd-Cm}^{°} \) are close to 0, equation (1) may be approximated by equation (2),

\[
\ln \frac{a}{a-x} = \lambda \cdot \ln \frac{2b}{2b-y}
\]

If we calculate the cocrystallization coefficient for the microelement compared to that for ¹⁵⁵Gd we get

\[
\ln \frac{a}{a-x} = \lambda_{Gd} \cdot \ln \frac{a_{Gd}}{a_{Gd-x_{Gd}}}
\]

which is the Derner-Hoskins equation.

From the data listed in Table 1 it follows that those normally trivalent elements which in their divalent state are characterized by the presence of valence electrons in the d orbitals (Y²⁺ = [Kr]4d¹ and Cm²⁺ = [Rn]5f⁶d¹) do cocrystallize with Gd₂Cl₅. Ions with empty d states like Nd²⁺ = [Xe]4f⁶d⁰ 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 Gd₂Cl₅ 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-co-crystallization.
Table I. Distribution of isotopes between the GdCl₃ melt and solid Gd₂Cl₃ and resulting $\frac{\Delta E}{Gd}$ values in eq. (3).

<table>
<thead>
<tr>
<th>Quantity in cluster [%]</th>
<th>$\frac{\Delta E}{Gd}$</th>
<th>Gd:Cl in Gd₂Cl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu Yb Nd Sr Cm Y Gd</td>
<td>1.15  -    -    -</td>
<td>53  43</td>
</tr>
<tr>
<td></td>
<td>0.03  -    -    -</td>
<td>1.34  1:1.47</td>
</tr>
<tr>
<td></td>
<td>0.04  -    0.07 -</td>
<td>2.02  1.84  1:1.44</td>
</tr>
<tr>
<td></td>
<td>0.01  -    0.02 -</td>
<td>1.34  1:1.38</td>
</tr>
</tbody>
</table>

The value of the oxidation potential, which is reached in the cathode space during synthesis of Gd₂Cl₃, 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 Gd₂Cl₃ 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 $\lambda$, $\Delta E_{M-\mu}$ 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 Gd₂Cl₃, one can determine $k$ and use it for determining the oxidation potential of the system. The value $\Delta E_{M-\mu}$ has to differ significantly from zero, because otherwise equation (2) holds which does not contain $k$. A rather high value of $\Delta E_{M-\mu} = 0.26$ V is observed during cocrystallization of Gd₂Cl₃ 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 GdCl₃, which are necessary 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 Gd₂Cl₃ occurs due to dissolution of metallic gadolinium in GdCl₃ without applying a voltage. Thus, when the electrochemical technique is used, the synthesis occurs under the condition 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 Gd³⁺/Gd²⁺ ratio in the system during electrochemical formation of Gd₂Cl₃, determined in terms of eq. (1) for distribution of Pu.

<table>
<thead>
<tr>
<th>Voltage during electrolysis, V</th>
<th>a x b y</th>
<th>k = $\frac{Gd^{3+}}{Gd^{2+}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4</td>
<td>100 43.5 100 71.7</td>
<td>12</td>
</tr>
<tr>
<td>0.6</td>
<td>100 6   100 11.2</td>
<td>9</td>
</tr>
</tbody>
</table>