Vapour-Liquid Equilibria in the System TlI–NdI₃

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Total vapour pressures above liquid TlI–NdI₃ mixtures have been determined using the boiling point method. The vapour phase composition has been determined in the temperature range 950–1150 K by a condensation technique. It is confirmed that the complex TlNd₄(g) is formed in the vapour phase. From the experimental data the logarithm of the equilibrium constant for the reaction

\[ TlI(g) + NdI₃(g) = TlNd₄(g) \]

is calculated to be \( \ln K = -17.32 + 24270 (T/K)^{-1} \). The liquid shows negative deviations from ideal Raoultian mixtures, and the volatility enhancement factor for NdI₃ at \( x_{NdI₃} = 0.5 \) in the liquid mixture at 1000 K is 22.

The increasing interest in liquid-vapour equilibria of lanthanide iodide (LnI₃) based mixtures is due to the use of such salts in multi-vapour lamps. The light quality of such lamps is determined by the content of ionic species in the discharge region, which is again determined by equilibria between the gas phase and condensed liquids on the inner lamp wall.

Some lanthanide-alkali-iodide mixtures [CsI–LaI₃, CsI–NdI₃, MI–CeI₃, MI–SmI₃ and MI–ScI₃ (MI = alkali iodide)] have been investigated by Liu et al.¹,² by mass spectrometry, absorption spectroscopy and vapour pressure measurements. They found that the dominant lanthanide-containing vapour species was MLnI₄ (Ln = lanthanide). The total vapour pressure of lanthanide-containing species increased by a factor of 45 at 1000 K relative to the pure LnI₃.

Foosnæs,³ and Foosnæs and Øye³ investigated the vapour phase above LiI–NdI₃, CsI–NdI₃ and TlI–NdI₃ mixtures by absorption spectroscopy. Once again, the dominant species in the vapour phase was MNdI₄.

The volatility enhancement at 1100 K is 7.5 in the LiI–NdI₃, and 8.9 in the CsI–NdI₃ system.³

The standard enthalpy and entropy change for the complex formation reaction

\[ MI(g) + NdI₃(g) = MNdI₄(g) \]  

have been determined by Foosnæs³ for the Li, Cs and Tl systems: \( \Delta H_{Li}^0 = -210 \) kJ mol⁻¹, \( \Delta H_{Cs}^0 = -205 \) kJ mol⁻¹ and \( \Delta H_{Tl}^0 = -113 \) kJ mol⁻¹, \( \Delta S_{Li}^0 = -115 \) J mol⁻¹K⁻¹, \( \Delta S_{Cs}^0 = -93 \) J mol⁻¹K⁻¹ and \( \Delta S_{Tl}^0 = -60 \) J mol⁻¹K⁻¹. For the TlI–NdI₃ system, the changes in enthalpy and entropy for reaction (1) are based on equilibrium constants determined from molar absorption data for a shoulder in the absorption spectrum, calculated over a limited temperature range (=70°C). We therefore decided to reinvestigate this system using vapour pressure measurements to obtain more accurate thermodynamic data for the TlI–NdI₃ system.

Principles

An improved variation of the boiling point method of Ruff and Bergdahl,⁴ described by Motzfeldt, Kvande and Wahlbeck,⁵ was used in the present study to obtain total vapour pressures above TlI–NdI₃ melts. A combination of total vapour pressures and data on the gas phase com-

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position, obtained by condensation of the equilibrium vapour as described by Knapstad, Linga and Øye, provides a method for calculating partial pressures above the melt.

In the present system it is assumed that the vapour phase consists of the gaseous species TI1, NdI3, TiNdI4 and Ti2I3. Relationships between the partial pressures are given by equilibria (2)–(5):

\[ \text{TI1 (mix, l) = TI1(g)} \]
\[ K_2 = \frac{P_{\text{TI1}}}{a_{\text{TI1}}} \]  
(2)

\[ 2 \text{TI1(g) = Ti2I3(g)} \]
\[ K_3 = \frac{P_{\text{Ti2I3}}}{P_{\text{TI1}}^2} \]  
(3)

\[ \text{NdI3 (mix, l) = NdI3(g)} \]
\[ K_4 = \frac{P_{\text{NdI3}}}{a_{\text{NdI3}}} \]  
(4)

and

\[ \text{TI1(g) + NdI3(g) = TiNdI4(g)} \]
\[ K_5 = \frac{P_{\text{TiNdI4}}}{P_{\text{TI1}} \cdot P_{\text{NdI3}}} \]  
(5)

For low pressures (<1 atm) activities may be defined as

\[ a_i = \frac{P_i}{P_i^c} \]  
(6)

where \( P_i \) is the partial pressure of component \( i \) and \( P_i^c \) is the vapour pressure above pure liquid \( i \). \( K_5 \) may then be written as

\[ K_5 = \frac{P_{\text{TiNdI4}}}{a_{\text{TiNdI4}} \cdot P_{\text{NdI3}} \cdot a_{\text{TI1}} \cdot P_{\text{TI1}}} \]  
(7)

The activity of TI1, \( a_{\text{TI1}} \), in the liquid mixture at a given composition and temperature may be calculated in the following manner:

1. \( P_{\text{TI1}} \) is first set approximately equal to the total pressure \( P_{\text{tot}} \).
2. \( P_{\text{NdI3}} \) is calculated from the equilibrium constant [eqn. (3)] obtained from data in the literature

\[ \log K_3 = -8.69 + 4780 \ (T/K)^{-1} \]  
+ 1.006 log (T/K).  
(8)

3. \( P_{\text{TiNdI4}} \) is then used to calculate the new vapour pressure of TI1 by approximating \( P_{\text{TI1}} \) by \( P_{\text{tot}} - P_{\text{NdI3}} \), i.e. assuming that \( P_{\text{TI1}} > P_{\text{NdI3}} \). The activity of TI1 in the liquid is then calculated using eqn. (6), and the NdI3 activity is obtained by a Gibbs-Duhem integration.
4. The equilibrium constant \( K_5 \) may now be obtained. The calculated activities of TI1 and NdI3, together with the vapour pressures of pure TI1 and NdI3, where

\[ \log(P_{\text{NdI3/atm}}) = 31.838 - 7.047 \log (T/K) \]  
- 15490(T/K)^{-1} \]  
(9)

are used in combination with eqn. (5) and the mole fraction of Nd in the gas phase defined by eqn. (10)

\[ x_{\text{Nd}} = \frac{P_{\text{NdI3}} + P_{\text{NdI3}}}{2 P_{\text{TiNdI4}} + P_{\text{NdI3}} + P_{\text{TI1}} + 2 K_3 P_{\text{TI1}}^c} \]  
(10)

By solving eqn. (10) with respect to the pressure of TiNdI4 and introducing this expression into eqn. (7), we obtain

\[ K_5 = \frac{[x_{\text{Nd}}(g) - 1](P_{\text{TI1}}^c a_{\text{TI1}})^{-1} + x_{\text{Nd}}(g)(P_{\text{NdI3}} a_{\text{NdI3}})^{-1}}{1 - 2 x_{\text{Nd}}(g)} \]  
(11)

5. Having obtained a value for the equilibrium constant \( K_5 \) using this procedure, the above calculation may be repeated to obtain a refined value for \( K_5 \).

**Experimental**

The methods used in the present work are described in detail elsewhere. Only a few comments specific to the present investigation will be given.

**Chemicals.** NdI3 was prepared by reacting Nd(s) (p.a. grade, E. Merck AG) with doubly sublimed I3(s) (E. Merck AG) at 990 K in sealed, evacuated silica ampoules. The NdI3 product was sublimed once at 990 K (sublimation time ~1 month) before use (see also Ref. 3). TI1 (p.a., E. Merck AG) was recrystallized from the liquid state (cooling rate 3 K min⁻¹). Handling of salts was performed in a glove box with a moisture content of less than 5 ppm.

**Vapour pressures.** During a vapour pressure measurement, weight changes of the experimental cell are recorded. Since TI1(g) is the main vapour phase species in the present case, a change in composition of the liquid mixture occurs during a run. The new mole fraction of TI1 in the melt, \( x_{\text{TI1}} \), may be calculated from
\[ x'_{\text{Th}} = (n^0_{\text{Th}} - \Delta n_{\text{Th}}) \cdot \left( \frac{n^0_{\text{Th}} + n_{\text{NdI}_3} - \Delta n_{\text{NdI}_3} - \Delta n_{\text{Th}}}{n^0_{\text{Th}} + n_{\text{NdI}_3} - \Delta n_{\text{NdI}_3} - \Delta n_{\text{Th}}} \right)^{-1} \]  

(12)

where \( n^0 \) is the number of moles of salt \( i \) and \( \Delta n \) is the loss of moles of salt \( i \) by evaporation. To calculate \( \Delta n \), the vapour phase composition is determined from condensation experiments and the mass loss is obtained from the recorded cell weight. By plotting the total pressure versus melt composition at constant temperature for temperature intervals of 40 K in the range 916 K–1116 K, the change in pressure due to composition changes is calculated according to

\[ P_{\text{tot}}^\text{corr} = P_{\text{tot}}^\text{obs} + \tan \alpha \left( x^0_{\text{Th}} - x'_{\text{Th}} \right). \]  

(13)

In this eqn., \( x^0_{\text{Th}} \) is the initial liquid mole fraction of \( \text{Th} \) and \( \tan \alpha \) is the slope of the line drawn between the points \([P(x^0_{\text{Th}}), x^0_{\text{Th}}], [P(x'_{\text{Th}}), x'_{\text{Th}}]\) on the \( P_{\text{tot}} \) versus \( x_{\text{Th}} \) (1) curve.\(^*\)

Composition of equilibrium vapour. The condensate of the equilibrium vapour was dissolved in 4 M HNO\(_3\) and the solution extracted with CHCl\(_3\). NdI\(_3\) dissolves in H\(_2\)O while ThI\(_3\) dissolves via the reaction

\[ \text{ThI}_3(s) + 2 \text{HNO}_3(aq) = \text{I}_2 + \frac{1}{2} \text{H}_2\text{O} + \text{Th(NO}_3)_2(aq) + \frac{1}{2} \text{N}_2\text{O}_4(g). \]  

(14)

The CHCl\(_3\) was used to extract the I\(_2\) produced. The concentrations of Nd\(^{3+}\) and Th\(^{4+}\) in the aqueous phase were determined by Mikroanalytisches Labor Pascher, Buschstr. 54, D-5300 Bonn (FRG).

Results and discussion

In Fig. 1, total vapour pressures above \( \text{ThI}_3 \)–NdI\(_3\) melts are plotted versus \((T/K)^{-1}\) for different liquid mole fractions of ThI\(_3\). For pure ThI\(_3\), reasonable agreement (1–2 % deviation between observed and literature values\(^{89}\)) is seen.

Results obtained by condensation of the equilibrium vapour at three different temperatures are given in Table 1. The weight of condensed salt was determined either by weighing the cell before and after dissolution of the sample or by chemical analysis. The former method was difficult, since the total cell weight was 350 g and the cell length 50 cm. Nevertheless, fair agreement (± 2 %) between the two methods is observed. Chemical analysis for Nd in control samples revealed an accuracy of ±5 mol %.

The corrected vapour pressures are fitted to an equation of the form

\[ \log(P/\text{atm}) = a + b(T/K)^{-1}. \]  

(15)

The constants in this equation are given in Table 2.

Using the total gas pressures together with the equilibrium vapour compositions, as described earlier above, the activities of ThI\(_3\) and NdI\(_3\) in the liquid mixtures and the equilibrium constant \( K_3 \)

\[ \text{Fig. 1. Total vapour pressures above} \]  

\[ \text{ThI}_3 \text{–NdI}_3 \text{ liquid mixtures vs. } (T/K)^{-1} \text{ and melt composition } (x_{\text{Th}} = 0.2, 0.42, 0.5, 0.8 \text{ and } 1.0). \ldots; x_{\text{Th}} = 1.9; \ldots; x_{\text{Th}} = 1.8 ; \]  

observed values, ○: corrected values [eqn. (13)].

\[ \ast \text{ Complete data sets which are the basis for the correction procedure are available upon request.} \]

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Table 1. Mol % NdI₃ in equilibrium vapour determined from condensation experiments.

<table>
<thead>
<tr>
<th>Liquid composition T/K</th>
<th>Mole fraction of Nd in vapour [eqn. (10)]</th>
<th>Weight of condensed salt by weighing cell, A/g · g⁻¹</th>
<th>A/B · 100/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TII–NdI₃/mol %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20–80</td>
<td>1145</td>
<td>0.0271</td>
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<tr>
<td>40–60</td>
<td>1051</td>
<td>0.0101</td>
<td>0.1573</td>
</tr>
<tr>
<td>60–40</td>
<td>947</td>
<td>0.00233</td>
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<td></td>
<td></td>
<td>0.5176</td>
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<td></td>
<td></td>
<td>0.5283</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Synthetic sample of TII–NdI₃/mol %</th>
<th>Weight, A/g · g⁻¹</th>
<th>Chemical analysis of TII–NdI₃/mol %</th>
<th>Weight from analysis, B/g · g⁻¹</th>
<th>A/B · 100/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>93.53–6.47</td>
<td>1.047</td>
<td>93.23–6.77</td>
<td>1.051</td>
<td>–0.4</td>
</tr>
</tbody>
</table>

Table 2. Constants in eqn. (15), log (P/atm) = a + b (T/K)⁻¹, where P is the total equilibrium pressure above TII–NdI₃ melts.

<table>
<thead>
<tr>
<th>Composition TII–NdI₃/mol %</th>
<th>T/K</th>
<th>a (SD)</th>
<th>b (SD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100–0</td>
<td>830–870</td>
<td>5.42 (0.07)</td>
<td>–5910 (60)</td>
</tr>
<tr>
<td>80–20</td>
<td>870–1000</td>
<td>5.10 (0.04)</td>
<td>–5760 (40)</td>
</tr>
<tr>
<td>60–40</td>
<td>910–1050</td>
<td>4.98 (0.03)</td>
<td>–5970 (30)</td>
</tr>
<tr>
<td>50–50</td>
<td>950–1080</td>
<td>4.95 (0.08)</td>
<td>–6160 (80)</td>
</tr>
<tr>
<td>42–58</td>
<td>950–1080</td>
<td>4.77 (0.04)</td>
<td>–6170 (50)</td>
</tr>
<tr>
<td>20–80</td>
<td>990–1120</td>
<td>4.23 (0.02)</td>
<td>–6100 (20)</td>
</tr>
</tbody>
</table>

Table 3. Raoultian activities and activity coefficients of TII and NdI₃ in TII–NdI₃ liquid mixtures at 1000 K.

<table>
<thead>
<tr>
<th>Melt composition Xₘ₃</th>
<th>aₘ₃</th>
<th>aₙ₃</th>
<th>a₄₃</th>
<th>a₅₃</th>
<th>a₆₃</th>
<th>a₇₃</th>
<th>a₈₃</th>
<th>a₉₃</th>
<th>a₁₀₃</th>
<th>a₁₁₃</th>
<th>a₁₂₃</th>
<th>a₁₃₃</th>
<th>a₁₄₃</th>
<th>a₁₅₃</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.15</td>
<td>0.70</td>
<td>0.54</td>
<td>0.30</td>
<td>0.22</td>
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<tr>
<td>0.2</td>
<td>0.03</td>
<td>0.15</td>
<td>0.70</td>
<td>0.88</td>
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<tr>
<td>0.4</td>
<td>0.18</td>
<td>0.46</td>
<td>0.32</td>
<td>0.54</td>
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<tr>
<td>0.6</td>
<td>0.50</td>
<td>0.84</td>
<td>0.12</td>
<td>0.30</td>
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<tr>
<td>0.8</td>
<td>0.78</td>
<td>0.98</td>
<td>0.044</td>
<td>0.22</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
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</table>

of eqn. (5) are calculated. The activities are calculated for a temperature of 1000 K.

The calculated activities are given in Table 3, and the equilibrium constant is plotted versus temperature in Fig. 2. It is assumed in the calculation of $K_3$ that the activities of TII and NdI₃ are independent of temperature. This assumption is not strictly correct. However, the error in $K_3$ is
Table 4. Enthalpy and entropy changes and equilibrium constants for the reaction NdI₃(g) + Ml(g) = MnNdI₄(g).

<table>
<thead>
<tr>
<th>Complex</th>
<th>ΔH°/kJ mol⁻¹</th>
<th>ΔS°/J mol⁻¹ K⁻¹</th>
<th>K(1000K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNdI₄(g)⁴</td>
<td>-210.3</td>
<td>-115.5</td>
<td>8.9·10⁴</td>
</tr>
<tr>
<td>CsNdI₄(g)⁵</td>
<td>-238</td>
<td>-105</td>
<td>8.9·10⁶</td>
</tr>
<tr>
<td>CsI₈(g)⁶</td>
<td>-205.2</td>
<td>-93.3</td>
<td>7·10⁵</td>
</tr>
<tr>
<td></td>
<td>-226.0</td>
<td>-105.0</td>
<td>2·10⁶</td>
</tr>
<tr>
<td>TiNdI₄(g)⁷</td>
<td>-113³</td>
<td>-60</td>
<td>580</td>
</tr>
<tr>
<td>TiNdI₄(g)²</td>
<td>-200</td>
<td>-140</td>
<td>1040</td>
</tr>
</tbody>
</table>

⁴Ref. 3. ⁵Ref. 1. ⁶Calculated by different methods. ³Quotation from Foosnæs. ³"The enthalpy and entropy which are calculated for the reaction are probably uncertain due to the reaction between NdI₃ and quartz." ²This work.

Fig. 2. The equilibrium constant for the equilibrium [eqn. (5)] TiI(g) + NdI₃(g) = TiNdI₄(g), plotted as ln K vs. (T/K)⁻¹.

ln K₂ vs. 10³(1/T(K))⁻¹

1200 1150 1100 1050 1000 950

T/K

Fig. 3. Calculated partial pressures, Pₐ = aP₂, above TiI–NdI₃ liquid mixtures at 1000 K.

of the same order of magnitude as that introduced in Kₛ due to the ±5% uncertainty in the values of xNdI₃(g) determined from chemical analysis of the condensed equilibrium vapour. The total uncertainty in the values of Kₛ can be estimated to be less than 10%.

The temperature variation of the equilibrium constant for the reaction

\[ \text{TiI(g) + NdI}_3(g) = \text{TiNdI}_4(g) \]  \hspace{1cm} (5)

may obtained from linear regression of the evaluated values of Kₛ shown in Fig. 2.

\[ \ln K_s = -17.32 + 24270 \ (T/K)^{-1}. \]  \hspace{1cm} (16)

From this eqn. we obtain ΔH°₂ = -200 kJ mol⁻¹ and ΔS°₂ = -140 J mol⁻¹ K⁻¹. These values are in accordance with the previous results¹ for the LiI–NdI₃ and CsI–NdI₃ systems (see Table 4).

In Fig. 3, the partial pressures of the components in the vapour above the TiI–NdI₃ liquid mixture at 1000 K are plotted versus composition. The volatility enhancement factor for NdI₃ is 22 at 1000 K, and xNdI₃(l) = 0.5.

References


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