# 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 TlNdI₄(g) is formed in the vapour phase. From the experimental data the logarithm of the equilibrium constant for the reaction

$$TlI(g) + NdI_3(g) = TlNdI_4(g)$$
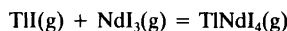
is calculated to be $\ln K = -17.32 + 24270 \, (T/K)^{-1}$. The liquid shows negative deviations from ideal Raoultian mixtures, and the volatility enhancement factor for NdI₃ at $x_{NdI_3} = 0.5$ in the liquid mixture at 1000 K is 22.

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−SmI₂ 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 LnI_n. Foosnæs[3] and Foosnæs and Øye[4] 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]

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The standard enthalpy and entropy change for the complex formation reaction

$$MI(g) + NdI_3(g) = MNdI_4(g) \qquad (1)$$

have been determined by Foosnæs[3] for the Li, Cs and Tl systems: $\Delta H^\circ_{Li} = -210$ kJ mol⁻¹, $\Delta H^\circ_{Cs} = -205$ kJ mol⁻¹ and $\Delta H^\circ_{Tl} = -113$ kJ mol⁻¹; $\Delta S^\circ_{Li} = -115$ J mol⁻¹K⁻¹, $\Delta S^\circ_{Cs} = -93$ J mol⁻¹K⁻¹ and $\Delta S^\circ_{Tl} = -60$ 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.
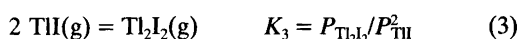
Principles

An improved variation of the boiling point method of Ruff and Bergdahl,[5] described by Motzfeldt, Kvande and Wahlbeck,[6] 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-
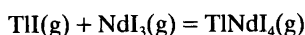
position, obtained by condensation of the equilibrium vapour as described by Knapstad, Linga and Øye,[7] provides a method for calculating partial pressures above the melt.

In the present system it is assumed that the vapour phase consists of the gaseous species TlI, NdI₃, TlNdI₄ and Tl₂I₂. Relationships between the partial pressures are given by equilibria (2)–(5):

$$\text{TlI (mix, l)} = \text{TlI(g)} \qquad K_2 = P_{\text{TlI}}/a_{\text{TlI}}(\text{l}) \qquad (2)$$

$$2\,\text{TlI(g)} = \text{Tl}_2\text{I}_2(\text{g}) \qquad K_3 = P_{\text{Tl}_2\text{I}_2}/P_{\text{TlI}}^2 \qquad (3)$$

$$\text{NdI}_3(\text{mix, l}) = \text{NdI}_3(\text{g}) \quad K_4 = P_{\text{NdI}_3}/a_{\text{NdI}_3}(\text{l}) \qquad (4)$$

and

$$\text{TlI(g)} + \text{NdI}_3(\text{g}) = \text{TlNdI}_4(\text{g})$$

$$K_5 = P_{\text{TlNdI}_4}/P_{\text{TlI}} \cdot P_{\text{NdI}_3} \qquad (5)$$

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

$$a_i = P_i/P_i^{\circ} \qquad (6)$$

where P_i is the partial pressure of component i and P_i° is the vapour pressure above pure liquid i. K_5 may then be written as

$$K_5 = P_{\text{TlNdI}_4}/a_{\text{NdI}_3} \cdot P_{\text{NdI}_3}^{\circ} \cdot a_{TlI} \cdot P_{\text{TlI}}^{\circ}. \qquad (7)$$

The activity of TlI, a_{TlI}, in the liquid mixture at a given composition and temperature may be calculated in the following manner:

1. P_{TlI} is first set approximately equal to the total pressure P_{tot}.
2. $P_{\text{Tl}_2\text{I}_2}$ is calculated from the equilibrium constant [eqn. (3)] obtained from data in the literature[8]

$$\log K_3 = -8.69 + 4780\,(T/K)^{-1}$$

$$+ 1.006 \log (T/K). \qquad (8)$$

3. $P_{\text{Tl}_2\text{I}_2}$ is then used to calculate the new vapour pressure of TlI by approximating P_{TlI} by $P_{\text{tot}} - P_{\text{Tl}_2\text{I}_2}$, i.e. assuming that $P_{\text{TlI}} > P_{\text{NdI}_3} + P_{\text{TlNdI}_4}$. The activity of TlI 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 ob-

tained. The calculated activities of TlI and NdI₃, together with the vapour pressures of pure TlI[8,9] and NdI₃,[10,11] where

$$\log(P_{\text{NdI}_3}^{\circ}/\text{atm}) = 31.838 - 7.047 \log\,(T/K)$$

$$- 15490(T/K)^{-1} \qquad (9)$$

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

$$x_{\text{Nd}}(g) = \frac{P_{\text{TlNdI}_4} + P_{\text{NdI}_3}}{2\,P_{\text{TlNdI}_4} + P_{\text{NdI}_3} + P_{\text{TlI}} + 2\,K_3 P_{\text{TlI}}^2} \qquad (10)$$

By solving eqn. (10) with respect to the pressure of TlNdI₄ and introducing this expression into eqn. (7), we obtain

$$K_5 \approx \frac{[x_{\text{Nd}}(g) - 1](P_{\text{TlI}}^{\circ} a_{\text{TlI}})^{-1} + x_{\text{Nd}}(g)(P_{\text{NdI}_3}^{\circ} a_{\text{NdI}_3})^{-1}}{1 - 2\,x_{\text{Nd}}(g)}. \qquad (11)$$

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.[6,7] 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 I₂(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). TlI (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 TlI(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 TlI in the melt, x'_{TlI}, may be calculated from

$$x'_{TlI} = (n^\circ_{TlI} - \Delta n_{TlI}) \cdot$$

$$(n^\circ_{TlI} + n^\circ_{NdI_3} - \Delta n_{NdI_3} - \Delta n_{TlI})^{-1} \qquad (12)$$

where n°_i is the number of moles of salt i and Δn_i is the loss of moles of salt i by evaporation. To calculate Δn_i, 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

$$P^{corr}_{tot} = P^{abs}_{tot} + \tan \alpha \, (x^\circ_{TlI} - x'_{TlI}). \qquad (13)$$

In this eqn., x°_{TlI} is the initial liquid mole fraction of TlI and $\tan \alpha$ is the slope of the line drawn between the points $[P(x^\circ_{TlI}), \ x^\circ_{TlI}]$, $[P(x'_{TlI}), \ x'_{TlI}]$ on the P_{tot} versus $x_{TlI}(l)$ 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_2O while TlI dissolves via the reaction

$$TlI(s) + 2 HNO_3(aq) =$$

$$\tfrac{1}{2} \, I_2 + H_2O + TlNO_3(aq) + \tfrac{1}{2} \, N_2O_4(g). \qquad (14)$$
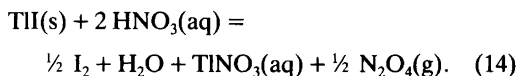
The $CHCl_3$ was used to extract the I_2 produced. The concentrations of Nd^{3+} and Tl^+ in the aqueous phase were determined by *Mikroanalytisches Labor Pascher,* Buschstr. 54, D-5300 Bonn (FRG).

Results and discussion

In Fig. 1, total vapour pressures above $TlI-NdI_3$ melts are plotted versus $(T/K)^{-1}$ for different liquid mole fractions of TlI. For pure TlI(l), reasonable agreement (1–2 % deviation between observed and literature values[8,9]) 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

$$\log (P/atm) = a + b(T/K)^{-1}. \qquad (15)$$

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 TlI and NdI_3 in the liquid mixtures and the equilibrium constant K_5

Fig. 1. Total vapour pressures above $TlI-NdI_3$ liquid mixtures vs. $(T/K)^{-1}$ and melt composition (x_{TlI} = 0.2, 0.42, 0.5, 0.8 and 1.0). ·····: x_{TlI} = 1,[9] ----: x_{TlI} = 1,[8] +: observed values, O: corrected values [eqn. (13)].

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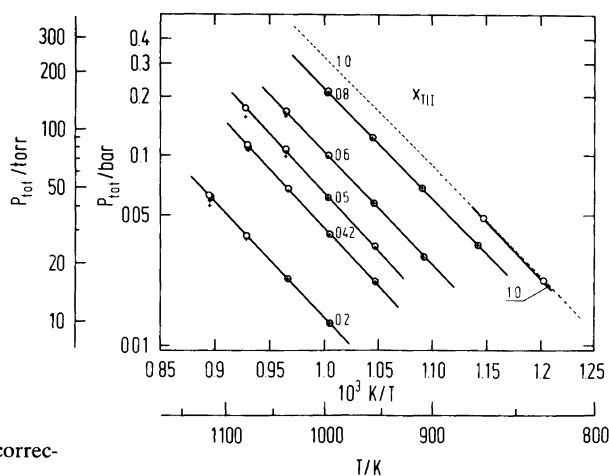
* Complete data sets which are the basis for the correction procedure are available upon request.

Table 1. Mol % NdI$_3$ in equilibrium vapour determined from condensation experiments.

Liquid composition TlI–NdI$_3$/mol %	T/K	Mole fraction of Nd in vapour [eqn. (10)]	Weight of condensed salt by weighing cell, A/g·g^{-1}	Weight of condensed salt by analysis, B/g·g^{-1}	$\dfrac{A-B}{A} \cdot 100/\%$
20–80	1145	0.0271	0.1573	–	–
40–60	1051	0.0101	0.5639	0.5542	+1.7
60–40	947	0.00233	0.5176	0.5283	–2.0

Synthetic sample of TlI–NdI$_3$/mol %	Weight, A/g·g^{-1}	Chemical analysis of TlI–NdI$_3$/mol %	Weight from analysis, B/g·g^{-1}	$\dfrac{A-B}{A} \cdot 100/\%$
93.53–6.47	1.047	93.23–6.77	1.051	–0.4

Table 2. Constants in eqn. (15), log $(P/\text{atm}) = a + b\,(T/\text{K})^{-1}$, where P is the total equilibrium pressure above TlI–NdI$_3$ melts.

Composition TlI–NdI$_3$/mol %	T/K	a (SD)	b (SD)
100–0	830–870	5.42 (0.07)	–5910 (60)
80–20	870–1000	5.10 (0.04)	–5760 (40)
60–40	910–1050	4.98 (0.03)	–5970 (30)
50–50	950–1080	4.95 (0.08)	–6160 (80)
42–58	950–1080	4.77 (0.04)	–6170 (50)
20–80	990–1120	4.23 (0.02)	–6100 (20)

Table 3. Raoultian activities and activity coefficients of TlI and NdI$_3$ in TlI–NdI$_3$ liquid mixtures at 1000 K.

Melt composition x_{NdI_3}	a_{NdI_3}	γ_{NdI_3}	a_{TlI}	γ_{TlI}
0	0		1	1
0.2	0.03	0.15	0.70	0.88
0.4	0.18	0.46	0.32	0.54
0.6	0.50	0.84	0.12	0.30
0.8	0.78	0.98	0.044	0.22
1	1	1	0	

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_5 that the activities of TlI and NdI$_3$ are independent of temperature. This assumption is not strictly correct. However, the error in K_5 is

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Table 4. Enthalpy and entropy changes and equilibrium constants for the reaction $NdI_3(g) + MI(g) = MNdI_4(g)$.

Complex	$\Delta H^\circ/kJ\ mol^{-1}$	$\Delta S^\circ/J\ mol^{-1}K^{-1}$	$K(1000K)$
$LiNdI_4(g)^a$	−210.3	−115.5	$8.9 \cdot 10^4$
$CsNdI_4(g)^b$	−238	−105	$8.9 \cdot 10^6$
$CsNdI_4(g)^a$	−205.2	− 93.3	$7 \cdot 10^5$
	$−226.0^c$	−105.0	$2 \cdot 10^6$
$TlNdI_4(g)^a$	$−113^d$	− 60	580
$TlNdI_4(g)^e$	−200	−140	1040

^{a}Ref. 3. ^{b}Ref. 1. ^{c}Calculated by different methods. ^{d}Quotation from Foosnæs:^{3} "The enthalpy and entropy which are calculated for the reaction are probably uncertain due to the reaction between NdI_3 and quartz." ^{e}This work.
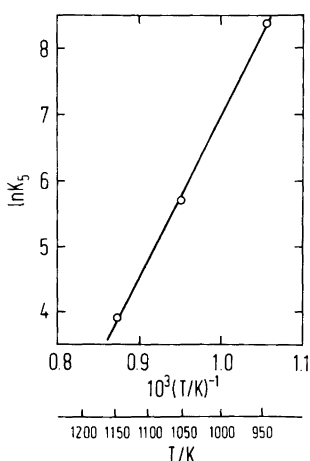

Fig. 2. The equilibrium constant for the equilibrium [eqn. (5)] $TlI(g) + NdI_3(g) = TlNdI_4(g)$, plotted as ln K vs. $(T/K)^{-1}$.
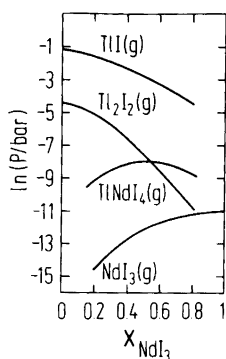

Fig. 3. Calculated partial pressures, $P_i = a_i P_i^\circ$, above $TlI-NdI_3$ liquid mixtures at 1000 K.

of the same order of magnitude as that introduced in K_5 due to the ±5 % uncertainty in the values of $x_{Nd}(g)$ determined from chemical analysis of the condensed equilibrium vapour. The total uncertainty in the values of K_5 can be estimated to be less than 10 %.

The temperature variation of the equilibrium constant for the reaction

$$TlI(g) + NdI_3(g) = TlNdI_4(g) \qquad (5)$$

may obtained from linear regression of the evaluated values of K_5 shown in Fig. 2.

$$\ln K_5 = -17.32 + 24270\ (T/K)^{-1}. \qquad (16)$$

From this eqn. we obtain $\Delta H_5^\circ = -200$ kJ mol^{-1} and $\Delta S_5^\circ = -140$ J mol^{-1}K^{-1}. These values are in accordance with the previous results[1,3] for the $LiI-NdI_3$ and $CsI-NdI_3$ systems (see Table 4).

In Fig. 3, the partial pressures of the components in the vapour above the $TlI-NdI_3$ liquid mixture at 1000 K are plotted versus composition. The volatility enhancement factor for NdI_3 is 22 at 1000 K, and $x_{NdI_3}(l) = 0.5$.

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