Thermodynamic Properties of EuCl₂ and the NaCl-EuCl₂ System

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The temperature and enthalpy of the phase transition and fusion of EuCl₂ were determined and found to be 1014 K, 11.5 kJ mol⁻¹ and 1125 K, 18.7 kJ mol⁻¹, respectively. Additionally, the heat capacity of solid EuCl₂ was measured by Differential Scanning Calorimetry in the temperature range 306 - 1085 K. The results were fitted to the linear equation Cₚ,m = (68.27 + 0.0255 T/K) J mol⁻¹ K⁻¹ in the temperature range 306 - 900 K. Due to discrepancies in the literature on the temperature of fusion of EuCl₂, the determination of the NaCl-EuCl₂ phase diagram was repeated. It consists of a simple eutectic equilibrium at Tₑut = 847 K with x(EuCl₂) = 0.49.

Key words: Europium Dichloride; Sodium Chloride; Phase Diagram; Enthalpy of Transition; Heat Capacity.

Introduction

Lanthanide elements possess high melting points, high densities, high thermal and electrical conductivities, etc. Therefore they play a significant role both in everyday life (TV, light bulbs, computers...) and in more sophisticated industrial applications (optical fibres, high performance alloys, magnets). Such rare earth metals (or rare-earth based alloys) are produced from the corresponding halides either by metathesis or by molten salt electrolysis. Many processes are under development at the international level dealing with reprocessing of nuclear wastes and recycling of spent fuel [1 - 6]. The aim is to remove the actinides and lanthanides from spent fuel. Lanthanides are extracted by molten salt electrolysis of the prepared Eu₂O₃ (Johnson Matthey, 99.9%). Thionyl chloride (Johnson Matthey, 99%) was used as a chlorinating agent. The SOCl₂ vapour was carried by argon through solid Eu₂O₃ at 823 K during 6 hours. EuCl₂ was obtained in this first step of the synthesis. Reduction to EuCl₃ was performed by Zn. Europium trichloride, and zinc in a twofold excess with respect to stoichiometry, were put into a quartz ampoule inside a quartz vessel, which was evacuated to a pressure of about 1 Pa. The temperature was gradually increased up to 773 K and maintained for 3 h under static vacuum. Then the temperature was increased up to 1093 K and kept during 5 h, still under static vacuum. Finally, dynamic vacuum was established in order to purify the EuCl₃ compound, obtained in this way, from Zn by distillation at 1193 K. Chemical analysis of the prepared EuCl₂ was performed by use of mercurimetry (chloride) and complexometry (EDTA in presence of xylene orange - europium). Results of the analysis are presented in Table 1.

As all lanthanide halides, EuCl₂ is very moisture sensitive and was therefore stored in sealed glass ampoules. All further handling of europium dichloride...
Table 1. Chemical analysis of EuCl$_2$.

<table>
<thead>
<tr>
<th>Cl$_{exp}$/mass%</th>
<th>Cl$_{theor}$/mass%</th>
<th>Eu$_{exp}$/mass%</th>
<th>Eu$_{theor}$/mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.76</td>
<td>31.81</td>
<td>68.23</td>
<td>68.19</td>
</tr>
</tbody>
</table>

Table 2. Temperature and enthalpy of phase transition and fusion of EuCl$_2$.

<table>
<thead>
<tr>
<th>$T_{tr}$/K</th>
<th>$\Delta_{tr}H_m$/kJ mol$^{-1}$</th>
<th>$T_{ fus}$/K</th>
<th>$\Delta_{fus}H_m$/kJ mol$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1014</td>
<td>11.5</td>
<td>1125</td>
<td>18.7</td>
<td>This work</td>
</tr>
<tr>
<td>1020</td>
<td>20.5</td>
<td>1127</td>
<td>23.0</td>
<td>[10 - 12]</td>
</tr>
<tr>
<td>1015</td>
<td>-</td>
<td>1126</td>
<td>-</td>
<td>[13]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1004</td>
<td>-</td>
<td>[14]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1011</td>
<td>-</td>
<td>[15 - 16]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1030</td>
<td>-</td>
<td>[17]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>1123</td>
<td>-</td>
<td>[18]</td>
</tr>
</tbody>
</table>

* In the original paper another temperature (1124 K) was improperly attributed to a "liquid phase transition".

and filling of experimental cells were performed in a controlled argon atmosphere glove-box (water content < 1 ppm).

Sodium chloride was purchased from Merck (99.9% min.). It was dehydrated by continuous and progressive heating just above the melting point, under gaseous HCl atmosphere. Excess HCl was then removed by bubbling argon through the melt. The salt was handled in the glove box and stored in sealed glass ampoules, as explained above.

Experimental Procedure

A Differential Scanning Calorimeter (DSC) was used for the determination of the temperature and enthalpy of the phase transitions. The experimental procedure was described in [7]. The samples were contained in sealed quartz ampoules (5 mm diameter, 15 mm high). The side walls were ground in order to fit the cells snugly into the heat flow detector. This consists of two thermopiles, connected in electrical opposition, accommodating both the previous experimental cell with the sample and another empty and identical cell, which acts as a reference. This experimental DSC set up shows both a high sensitivity and an excellent integration of the thermal heat flow, since the sensing thermocouples in each thermopile are evenly distributed all over the cell surface. The determination of the temperature and enthalpy of fusion of EuCl$_2$ was performed separately with a high temperature Calvet microcalorimeter because of the temperature limit of the DSC.

The DSC was also employed for the determination of the heat capacity by the "step method" [8]. In this method, small heating steps are followed by isothermal delays, which allow the sample to return to thermal equilibrium before the next heating step. The heating and cooling rate was 1.5 K per minute, and each temperature step was $\Delta T = 5$ K with 400 s isothermal delays.

Because of the inconsistency in the literature on the melting temperature of EuCl$_2$ (Table 2), the investigation of the NaCl-EuCl$_2$ phase diagram was repeated in order to check the reliability of a recent work which included that inconsistency [9]. Twenty-three mixtures of different composition were investigated by DSC. Heating and cooling runs showed undercooling upon crystallisation. Equilibrium temperatures were thus taken from heating thermograms.

Results and Discussion

Pure EuCl$_2$

According to Laptev and Kulagin [10 - 12], EuCl$_2$ is orthorhombic at room temperature ($a = 0.8861 \pm 0.0017$ nm, $b = 0.7462 \pm 0.0015$ nm, $c = 0.4430 \pm 0.0013$ nm) and undergoes a phase transition to a cubic structure ($a = 0.7150 \pm 0.0001$ nm) at higher temperature. About the temperature of the phase transition and fusion very contradictory data were reported, especially for the melting temperature (Table 2). The corresponding enthalpies also scatter much from author to author.

The temperature and enthalpy of the solid-solid and solid-liquid phase transitions were therefore determined in the present work. Our earlier investigation [19], which yielded preliminary values for the temperature and enthalpy of fusion, 1120 K and 10.7 kJ mol$^{-1}$, respectively, had to be confirmed because of the uncertainty caused by the slow kinetics of the fusion. The corresponding thermograms were quite different from those generally observed with well-defined fusion peaks. The enthalpy determined from the thermograms has thus been obtained with quite a large experimental uncertainty. Careful determinations were therefore repeated with another technique. The Calvet microcalorimeter used for these new sets of measurements had a higher experimental temperature range and moreover could be run at a very low heating rate (20 K h$^{-1}$). It was found that the fusion occurs at higher temperature, 1125 K, with a larger enthalpy, 18.7 kJ mol$^{-1}$.
These results on the temperature agree well with some literature data. However, for those authors who reported far lower temperatures, it seems that the fusion temperature had been confused with the transition temperature [14 - 17]. Similarly, in a very recent work, Koyama et al. [9] have reported that fusion occurs at 1017 K, although an effect was detected at 1124 K but supposedly attributed to a transition in the liquid phase. This assumption was supported by the authors from their interpretation of Raman spectra. There is much evidence that this conclusion is in error. The X-Ray investigations performed by Laptev et al. [10 - 12] and by Fink and Seifert [13] did show that a solid-solid phase transition occurs before melting. Simple visual observations, that we performed separately in the course of the present work, undoubtedly indicate that EuCl₂ is solid at temperatures below 1125 K. However, it should be mentioned that an unusual behaviour of EuCl₂ after a solid-solid phase transition was also observed in recent and preliminary investigations (neutron diffraction [20], Raman spectroscopy [21]), which can explain the above misleading conclusion of Koyama et al. [9].

Our enthalpy of transition compares quite well with that measured by Koyama et al., but is two times lower than that proposed by Laptev et al. [10 - 12]. When the enthalpies of fusion are compared, our experimental result (18.7 kJ mol⁻¹) is in better agreement with the value given by Laptev et al. [10 - 12] (23.0 kJ mol⁻¹) than with that of Koyama et al. [9] (11.1 kJ mol⁻¹). The discrepancy between the three sets of results cannot be explained only in terms of the difference in the experimental methods. It is likely that the purity of the samples used by Koyama et al. [9] is questionable: indeed, the shape of the experimental thermogram reported in that paper (strong deviation of the base line after the phase transition) suggests that the sample under investigation was not pure EuCl₂ but probably a EuCl₂-EuCl₃ mixture [12, 22, 23]. This is the reason why their enthalpy of fusion is significantly lower and even semiquantitative data of Laptev are in better agreement with our value.

The heat capacity \( C_p \) of solid EuCl₂ was measured by DSC using the “step method” as described above. Figure 1 shows its temperature dependence in the whole range (306 - 1085 K). In addition, the range between the solid-solid phase transition (1014 K) and fusion (1125 K) was investigated in more detail in separate experiments with smaller temperature increment steps of \( \Delta T = 2 \) K (Fig. 2).

No experimental data were reported in the literature for the whole temperature range. The only available data were those reported by Tolmach et al. [24] for the low temperature range 6.58 - 310 K, by adiabatic calorimetry, and those of Laptev [25] for higher temperatures, between 550 and 630 K. In the small range where Tolmach’s data are comparable with ours, the agreement is very good. It has to be stressed that this agreement occurs even though the techniques used are completely different: at low temperature, adiabatic calorimetry was used. The \( C_p \) values proposed by Laptev are by about 4% larger than ours. As they were deduced from e.m.f. measurements in the temperature range 550 - 630 K, the agreement with our direct determination can be judged as very good. Our experimental heat capacity values were fitted to the linear equation

\[
C_{p,m}^0 = (68.27 + 0.0255 \frac{T}{K}) \text{ J mol}^{-1}\text{K}^{-1}
\]

in the temperature range 306 - 900 K, with a deviation less than 4%.

After the transition, the decrease of \( C_p \), already observed in the global temperature range (Fig. 1) was confirmed by the detailed run performed in the range 1014 - 1085 K (Fig. 2). Although the experimental scattering is larger, probably because of slower return to equilibrium after a temperature increase, the heat capacity decreases up to the melting temperature. No theoretical explanation can be offered so far to explain this behaviour. Only for the purpose of data implementation in a data base, these data were fitted to the equation (\( T \) in Kelvins)

\[
C_{p,m}^0 = (6748.2 - 12.26 T + 5.6621*10^{-3}T^2) \text{ J mol}^{-1}\text{K}^{-1}
\]

with a standard deviation ± 5 J mol⁻¹K⁻¹.

Figure 1 also reports the \( C_p \) values calculated using the Neumann-Kopp additive law assuming that \( C_p \) of a compound can be estimated from the weighted \( C_p \) contributions of the reagents forming this compound. We considered the reaction of formation of EuCl₂ from Eu and EuCl₃:

\[
C_{p,m}^0(\text{EuCl}_2) = \frac{1}{3}C_{p,m}^0(\text{Eu}) + \frac{2}{3}C_{p,m}^0(\text{EuCl}_3).\]

The data used for this calculation are from the SGTE data bank [26]. These \( C_p \) values, calculated by the addition rule, are approximately 6% larger than our experimental data. However, we performed quite recently thermodynamic investigations on the EuCl₃ compound. Indeed, the high temperature \( C_p \) data,
Fig. 1. Molar heat capacity of EuCl$_2$ against temperature. White circles: experimental results, black circles: Tolmach results, ---: linear fitting, $\times\times\times$: Laptev results, ---: values calculated from the Neumann-Kopp equation.

Fig. 2. Molar heat capacity of EuCl$_2$ after solid-solid phase transition against temperature. Open circles: experimental results, dashed line: polynomial fitting.

Fig. 3. Tamman diagram of NaCl-EuCl$_2$ system.

Fig. 4. NaCl-EuCl$_2$ phase diagram. ---: this work, ---: Koyama et al. [9].
reported in thermodynamic tables and used in the above calculation were not experimental data: they have been estimated from the low temperature heat capacities obtained by Sommers and Westrum by adiabatic calorimetry [27]. Our direct determinations [28] indicate lower $C_p$ values for EuCl$_3$. Accordingly, from these values, a better agreement was observed between the experimental heat capacity of EuCl$_2$ and that obtained from a new Neumann-Kopp calculation.

**NaCl-EuCl$_2$ Phase Diagram**

The discrepancies in the melting temperature of EuCl$_2$ observed above led us to repeat the investigation of the NaCl-EuCl$_2$ phase diagram already performed by Koyama et al. [9]. The NaCl-EuCl$_2$ phase diagram is of the simple eutectic type. The DSC investigation performed on samples with 23 compositions yielded both the temperature and the fusion enthalpy of the concerned mixtures. The eutectic contribution to the enthalpy was then deduced and plotted against the composition in Figure 3. This so-called Tamman construction makes it possible to evaluate accurately the eutectic composition from the intercept of the two linear parts in Fig. 3, described by the equations $\Delta_{\text{fus}}H_m^0 = 46.68 \times (\text{EuCl}_2) \text{kJ-mol}^{-1}$ and $\Delta_{\text{fus}}H_m^0 = 44.78 \times (1 - x(\text{EuCl}_2)) \text{kJ-mol}^{-1}$, respectively.

We obtained $x(\text{EuCl}_2) = 0.49$ for the eutectic composition while the eutectic temperature, observed in all thermograms, is $T = 847$ K. The enthalpy of fusion for the eutectic composition is $\Delta_{\text{fus}}H_m^0 = 22.86 \text{kJ-mol}^{-1}$. In the construction of the Tamman diagram it was considered that there was no solubility in the solid state. Thus straight lines intercept the composition axis at $x(\text{EuCl}_2) = 0$ and $x(\text{EuCl}_2) = 1$.

The phase diagram obtained is given in Figure 4. Substantial differences of these with the previous investigations by Koyama et al. [9] can be noted. As already explained, since the temperature of fusion of EuCl$_2$ was confused with that of the transition, the phase diagram was incomplete in the high temperature range. Also, even though the eutectic temperature was similar to ours (848 K), the eutectic composition as well as the overall diagram were different from ours. Fink and Seifert [13] also reported a simple eutectic phase diagram, but only the eutectic composition ($x(\text{EuCl}_2) = 0.50$) and the temperature (747 K) were given. This composition is in good agreement with our result. It turned out that the eutectic temperature should read 847 K, instead of 747 K, thus in excellent agreement with our results.

**Conclusion**

In this work, several thermodynamic data concerning pure EuCl$_2$, and the NaCl-EuCl$_2$ system were determined. Direct measurements of the heat capacity were conducted at high temperature on EuCl$_2$. They agree quite well with the low temperature results obtained previously by adiabatic calorimetry and also with the values derived from e.m.f. measurements in a more restricted high temperature range. Enthalpy of fusion and transition data were obtained and literature contradictions assessed.

Finally, from a new determination of the NaCl-EuCl$_2$ phase diagram it was concluded that the only reference available in literature is not correct, while other previously determined eutectic coordinates are.


