Thermodynamics of EuCl$_3$: Experimental Enthalpy of Fusion and Heat Capacity and Estimation of Thermodynamic Functions up to 1300 K

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The heat capacity of solid EuCl$_3$ was measured by differential scanning calorimetry from 300 K up to the melting temperature, and beyond. These results were compared with literature data and fitted by a polynomial temperature dependence. The enthalpy of EuCl$_3$ fusion was measured. Furthermore, by combination of these results with literature data on the entropy at 298.15 K, S_m^0(EuCl$_3$, s, 298.15 K) and the standard molar enthalpy of formation of $\Delta_{form}H_m^0$(EuCl$_3$, s, 298.15 K), the thermodynamic functions have been calculated up to 1300 K.

Key words: Europium Chloride; Heat Capacity; Differential Scanning Calorimetry.

Introduction

There exist some published experimental investigations on the lanthanide chlorides (LnCl$_3$) and their mixtures with alkali chlorides (MCl). The enthalpy variation and heat capacity of these solid and liquid chlorides [1, 2] and several stoichiometric M$_x$LnCl$_{3+x}$ compounds [3 - 6] that exist in most LnCl$_3$-MCl mixtures were measured over a wide temperature range . Enthalpies of mixing were also determined [7 - 11].

The present work focuses on EuCl$_3$. Indeed, on solid EuCl$_3$ the only available experimental thermodynamic information is the low temperature heat capacity C_p [12], the molar formation enthalpy at 298.15 K [13], and the temperature and enthalpy of fusion [14]. To the best of our knowledge no data on the solid above 350 K or on the liquid are reported.

However, from this single information on C_p (temperature range 5 - 350 K), two estimations of all thermodynamic functions were made not only for an extended temperature range of the solid, but also beyond the melting temperature [15, 16].

A calorimetric investigation was conducted on EuCl$_3$ in order to investigate the enthalpy changes, including the fusion enthalpy, that take place in the maximum temperature range compatible with the thermal stability of the sample. The heat capacities of the solid and liquid were also measured in the same temperature range.

All these new data were used to estimate the whole set of thermodynamic functions.

Experimental

Sample Preparation

As described earlier [6], lanthanide chlorides can be prepared by chlorinating the corresponding lanthanide oxides with NH$_4$Cl. This synthesis includes several steps with a final double distillation ensuring that no residual oxychloride contaminates the lanthanide chloride obtained in this way. However, this method should not be used for the synthesis of EuCl$_3$ because of the decomposition tendency of this compound. Thus EuCl$_3$ was prepared by chlorinating the oxide (Merck, 99.9%) under a stream of high purity argon (water and oxygen content less than 2 and 0.5 ppmV, respectively) saturated with SOCl$_2$ vapour in a quartz reactor at 793 - 813 K for 24 hours. This procedure was developed empirically. No attempt was made to reduce the duration of the chlorinating cycle, although this may be possible.

The chemical analysis of the synthesised EuCl$_3$ was performed by titration methods for chlorides

Table 1. Chemical analysis of europium trichloride.

Compound	Cl$_{observed}$ mass %	Cl$_{theoretical}$ mass %	Eu$_{observed}$ mass %	Eu$_{theoretical}$ mass %
EuCl$_3$	41.18	41.17	58.82	58.83

(mercurimetric) and lanthanides (complexometric). These results are presented in Table 1.

All handling of chloride was performed in an argon glove box (water content less than 2 ppmV). Continuous argon purification was achieved by forced recirculation through external molecular sieves.

Differential Scanning Calorimeter (DSC)

The enthalpy of fusion and heat capacities were measured with a SETARAM DSC 121 differential scanning calorimeter. The apparatus and the measurement procedure were described in [2].

The so-called "step-method", used for C_p measurements, was already described [1, 2, 4]. In this method, small heating steps are followed by isothermal delays, when thermal equilibrium of the sample is achieved. Two correlated experiments should be carried out to determine the heat capacity of the sample. The first one with two empty cells (containers) of identical mass, and the second with one of these cells loaded with the sample. The heat flux is recorded as a function of time and temperature in both runs. The difference of heat flux in the two runs is proportional to the amount of heat (Q_i) necessary to increase the temperature of the sample by a small temperature increment ΔT_i. Therefore the heat capacity (C_p) of the sample is

$$C_{p,m}^0 = (Q_i \cdot M_s)/(\Delta T_i \cdot m_s),$$

where m_s is the mass and M_s the molar mass of the sample.

The same operating conditions (e. g. initial and final temperatures, temperature increment, isothermal delay and heating rate) are required for the two experimental runs. The original SETARAM program performs all necessary calculations.

The apparatus was calibrated by the Joule effect. Additionally, some test measurements with NIST 720 α-Al$_2$O$_3$ Standard Reference material have been carried out separately before investigating the lanthanide chlorides [2]. According to this test, which gave C_p values consistent with standard data for Al$_2$O$_3$, the

step method may be considered as suitable for C_p measurements.

Measurements

Quartz cells (7 mm diameter and 15 mm long) were filled with europium chloride in a glove-box, sealed under vacuum and then placed into the DSC 121 calorimeter.

Fusion enthalpy measurements were carried out with heating and cooling rates between 1 and 5 K min^{-1}.

Heat capacity measurements were performed by the "step-method" – each heating step of 5 K was followed by 400 s isothermal delay. The heating rate was 1.5 K min^{-1}. All experiments were started at 300 K and were performed only up to 980 K, since a high pressure of chlorine gas inside the ampoule (resulting from partial decomposition of EuCl$_3$) could result in explosion of the ampoule. The difference between the mass of the quartz cells in a particular experiment did not exceed 1 mg (mass of the cells: 400 - 500 mg). The mass of the samples was 200 - 500 mg.

Results and Discussion

Enthalpy of Phase Transition

Analysis of several DSC curves of EuCl$_3$ showed an interesting phenomenon presented in Figure 1. Upon primary heating, the thermograms show one endothermic effect at $T_{ons} = 894$ K (melting of EuCl$_3$) (Fig. 1a), while an additional effect appears at $T_{ons} = 796$ K upon cooling (Fig. 1b). A further heating-cooling cycle was run. The corresponding thermogram evidenced that also two effects take place now on heating at 804 K and 887 K, respectively (Fig. 1c). Chemical analysis of the EuCl$_3$ samples after primary heating showed a reduced chlorine content with respect to the stoichiometric composition (EuCl$_{2.97}$ instead of EuCl$_3$). Also visual observations confirmed chlorine loss above molten samples.

This thermal decomposition of EuCl$_3$ is likely to occur at temperatures very close to melting. When EuCl$_3$ decomposition takes place, EuCl$_2$ is formed and the sample under investigation turns into an EuCl$_3$-EuCl$_2$ mixture. On subsequent heating, on the thermogram two thermal effects appear. They can be related to the eutectic temperature $T = 804$ K and the
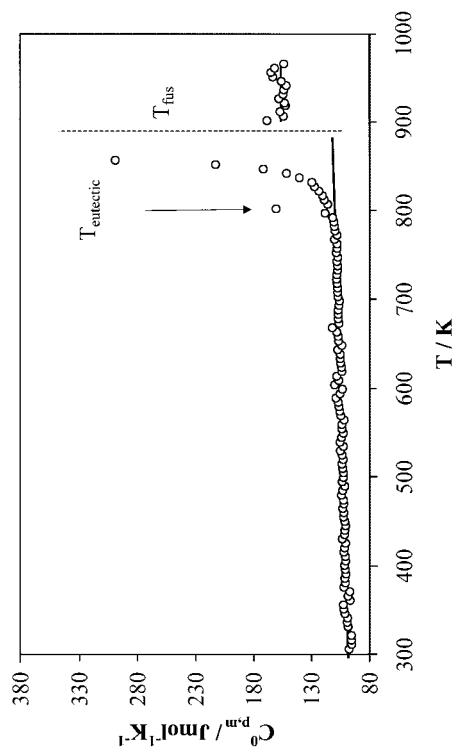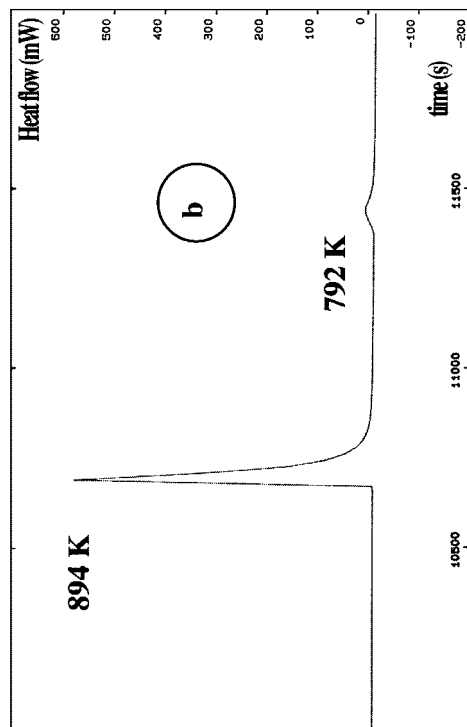
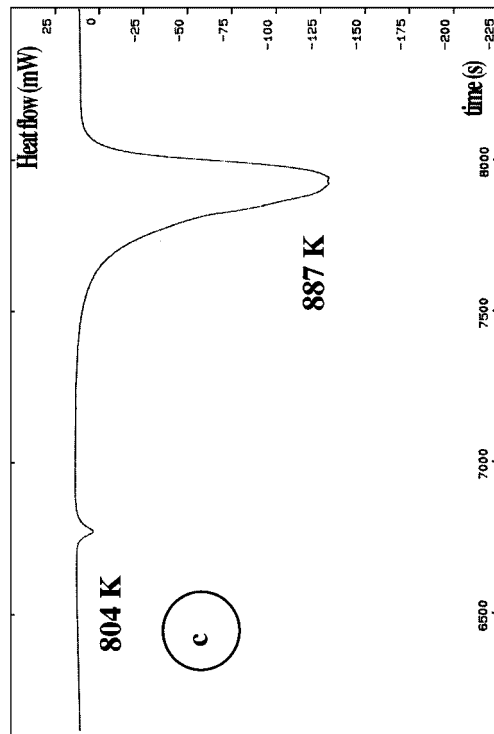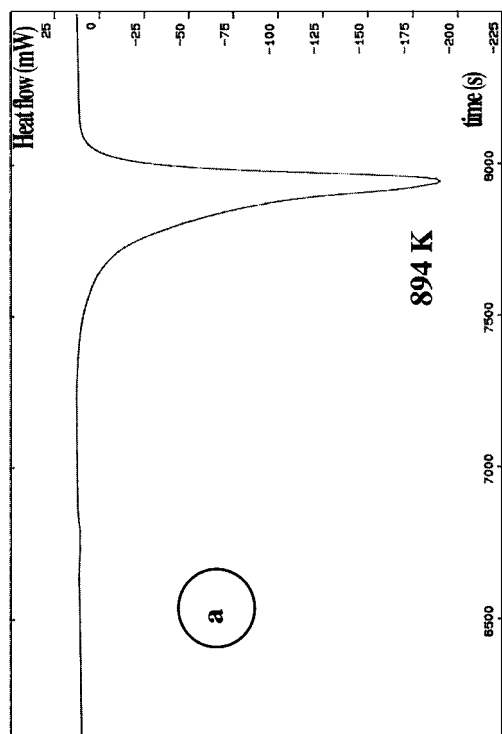Fig. 1. DTA curves of EuCl$_3$. a: first heating, b: first cooling, c: second heating.

Fig. 2. Molar heat capacity of EuCl$_3$. Open circles: experimental values, solid line: polynomial fitting of experimental values.

liquidus temperature $T = 887$ K of this EuCl$_3$-EuCl$_2$ system.

The eutectic temperature agrees well with that reported by Laptiev *et al.* [17]. These authors also observed thermal decomposition of EuCl$_3$ upon melting [14].

Therefore the single peak observed upon primary heating corresponds to real melting of EuCl$_3$, since it was obtained from a decomposition-free initial sample. This melting temperature of EuCl$_3$ determined from our experiments (894 K) agrees well with the data of Kulagin and Laptev [14] and Moriatry [18] (897 and 896 K, respectively). Another literature source [19] gives 901 K as the melting temperature of EuCl$_3$, but this was obtained by a questionable extrapolation of experimental results from a partially dissociated compound.

Also the fusion enthalpy of EuCl$_3$, $\Delta_{\mathrm{fus}}H_{\mathrm{m}}^0 = 45.0$ kJ mol^{-1}, was obtained during primary heating. This value is by about 10% smaller than the previous semi-quantitative fusion enthalpy obtained by DTA [14].

Heat Capacity

Our experimental determinations were conducted on samples that had not been premelted. These $C_{\mathrm{p,m}}^0$ data are plotted against temperature in Figure 2. In the temperature range where the heat capacity of EuCl$_3$ varies smoothly with temperature (300 - 800 K), the $C_{\mathrm{p,m}}^0$ data were fitted to the classical equation

$$C_{\mathrm{p,m}}^0 = a + b \cdot 10^{-3}T + c \cdot 10^5 T^{-2}. \qquad (1)$$

As already indicated, the only other experimental heat capacity data have been obtained by adiabatic calorimetry [12] but, where the comparison is possible (300-350 K), they differ substantially (by about 8%) from ours. It should be stressed that the thermodynamic evaluation performed by Pankratz [15] is based on these data, while a more recent estimation [16], taking into account the global behaviour of all lanthanide chloride series, gives a lower heat capacity at 298.15 K (98.29 J K^{-1}mol^{-1}) , i. e. very similar to the experimental result obtained in the present work. As a consequence, the heat capacities estimated by Pankratz [15] for the high temperature solid are also globally larger than ours (by 8% at 300 K and 11% at 790 K), the former agreeing with the most recent evaluation [16].

Table 2. Thermodynamic functions of EuCl$_3$ at selected temperatures from 298.15 to 1300 K.

T	$C_{\mathrm{p,m}}$	S_{m}^0	$-(G-H_{298.15}^0)$ /T	H_T^0 $-H_{298.15}^0$	Δ_{form} H_{m}^0	Δ_{form} G_{m}^0
K	— J K^{-1}mol^{-1} —			— kJ mol^{-1} —		
298.15	98.52	144.10	144.10	0.00	–935.4	–855.4
300	98.57	144.71	144.10	0.18	–935.4	–854.9
400	100.86	173.38	148.00	10.15	–933.4	–828.4
500	103.10	196.13	155.42	20.35	–931.4	–802.4
600	105.32	215.12	163.83	30.77	–929.4	–776.8
700	107.54	231.53	172.36	41.42	–927.3	–751.5
765	108.97	241.14	177.80	48.45	–925.9	–735.3
765	108.97	241.14	177.80	48.45	–926.1	–735.3
800	109.74	246.03	180.68	52.28	–925.3	–726.6
894	111.81	258.33	188.20	62.69	–923.3	–703.4
894	155.96	308.63	188.21	107.69	–878.3	–703.4
900	155.96	309.68	189.01	108.63	–877.9	–702.2
1000	155.96	326.11	201.92	124.23	–871.5	–683.0
1096	155.96	340.40	213.43	139.20	–865.7	–665.2
1096	155.96	340.40	213.43	139.20	–874.9	–665.2
1100	155.96	340.97	213.90	139.82	–874.6	–664.4
1200	155.96	354.54	225.06	155.42	–868.4	–645.6
1300	155.96	367.03	235.51	171.01	–862.1	–627.2

For liquid EuCl$_3$ a constant heat capacity $C_{\mathrm{p,m}}^0 = 155.96$ J K^{-1}mol^{-1} was found, that is by about 10% larger than literature estimations [15, 16].

Thermodynamic functions of europium trichloride were calculated up to 1300 K using our experimental melting temperature and enthalpy together with heat capacity data. We determined $C_{\mathrm{p,m}}^0$(298.15 K) by extrapolation of our results at 298.15 K.

The standard entropy S_{m}^0(EuCl$_3$, s, 298.15 K) = 144.10 J K^{-1}mol^{-1} was taken from literature [20].

Equation (1) was then used to calculate the molar heat capacity $C_{\mathrm{p,m}}^0(T)$ in J K^{-1}mol^{-1}, the enthalpy increments $H_{\mathrm{m}}^0(T) - H_{\mathrm{m}}^0$(298.15 K) in kJ mol^{-1}, and the entropy S_{m}^0 and Gibbs energy functions $(G_{\mathrm{m}}^0(T) - H_{\mathrm{m}}^0(298.15))/T$ in J K^{-1}mol^{-1}, both for solid as well as liquid EuCl$_3$. The corresponding equations are given below. The results for selected temperatures are presented in Table 2.

Solid EuCl$_3$, 298.15 K < T < 894 K:

$$C_{\mathrm{p,m}}^0 = 92.199 + 21.967 \cdot 10^{-3}T - 0.20 \cdot 10^5 T^{-2},$$

$$H_{\mathrm{m}}^0(T) - H_{\mathrm{m}}^0(298.15) = 92.199 \cdot 10^{-3}T$$
$$+ 10.983 \cdot 10^{-6}T^2 + 0.20 \cdot 10^2 T^{-1} - 28.53,$$

$$S_{\mathrm{m}}^0(T) = 92.199 \ln T + 21.967 \cdot 10^{-3}T$$
$$+ 0.10 \cdot 10^5 T^{-2} - 387.87,$$

$$-(G_{\mathrm{m}}^0(T) - H_{\mathrm{m}}^0(298.15))/T =$$
$$91.199 \ln T + 10.983 \cdot 10^{-3}T$$
$$- 0.10 \cdot 10^5 T^{-2} + 28533 T^{-1} - 480.07.$$

While the $C_{p,m}^0$ given above was used up to 894 K, the coefficients were obtained by least-squares fitting up to temperature 802 K, where the sharp heat capacity jump indicates that decomposition takes place.

Liquid EuCl$_3$, 894 K < T < 1300 K:

$C_{p,m}^0 = 155.96$,

$H_m^0(T) - H_m^0(298.15) = 155.96 \cdot 10^{-3}T - 31.73$,

$S_m^0(T) = 155.96 \ln T - 751.22$,

$-(G_m^0(T) - H_m^0(298.15))/T = 155.96 \ln T$
$\qquad + 31735\,T^{-1} - 907.15.$

From these thermodynamic functions for EuCl$_3$ one can calculate the thermodynamic functions of formation as a function of temperature. Formation of EuCl$_3$ from the elements can be described by the reaction

$$\text{Eu(s)} + 1.5\,\text{Cl}_2(\text{g}) = \text{EuCl}_3(\text{s,l}), \qquad (2)$$

The thermodynamic functions of metallic Eu and gaseous Cl$_2$ ($C_{p,m}^0$ and S_m^0 at 298.15 K), necessary for the calculation, were taken from [16]. The also required enthalpy of EuCl$_3$ formation at 298.15 K, $\Delta_{\text{form}}H_m^0(\text{EuCl}_3, \text{s}, 298.15\text{ K}) = -935.4$ kJ mol^{-1}, was taken from Cordfunke and Konings [13].

There are some phase changes which occur in the system (2): first EuCl$_3$ melting at 984 K, second solid-solid phase transition of Eu at 765 K with the related molar enthalpy 0.2 kJ mol^{-1}, and third its fusion at 1096 K with an enthalpy of 9.2 kJ mol^{-1} [16]. Accordingly, the formation enthalpy $\Delta_{\text{form}}H_m^0$ (kJ mol^{-1}) and Gibbs energy of formation $\Delta_{\text{form}}G_m^0$ (kJ mol^{-1}) of EuCl$_3$ are described by the following equations:

Solid EuCl$_3$ solid, 298.15 K < T < 765 K:

$\Delta_{\text{form}}H_m^0 = 3.035 \cdot 10^{-3}T + 20.460 \cdot 10^{-6}T^2$
$\qquad - 6.288 \cdot 10^2 T^{-1} - 7.950 \cdot 10^{-9}T^3 - 935.8,$

$\Delta_{\text{form}}G_m^0 = 296.141 \cdot 10^{-3}T - 20.460 \cdot 10^{-6}T^2$
$\qquad - 3.144 \cdot 10^2 T^{-1} + 3.975 \cdot 10^{-9}T^3$
$\qquad - 3.035 \cdot 10^{-3}T \ln T - 935.8.$

Solid EuCl$_3$ solid, 765 K < T < 894 K:

$\Delta_{\text{form}}H_m^0 = 3.035 \cdot 10^{-3}T + 20.460 \cdot 10^{-6}T^2$
$\qquad - 6.288 \cdot 10^2 T^{-1} - 7.950 \cdot 10^{-9}T^3 - 936.0,$

$\Delta_{\text{form}}G_m^0 = 296.141 \cdot 10^{-3}T - 20.460 \cdot 10^{-6}T^2$
$\qquad - 3.144 \cdot 10^2 T^{-1} + 3.975 \cdot 10^{-9}T^3$
$\qquad - 3.035 \cdot 10^{-3}T \ln T - 935.8.$

Liquid EuCl$_3$ solid, 894 K < T < 1096 K:

$\Delta_{\text{form}}H_m^0 = 66.796 \cdot 10^{-3}T + 9.477 \cdot 10^{-6}T^2$
$\qquad - 6.488 \cdot 10^2 T^{-1} - 7.950 \cdot 10^{-9}T^3 - 939.2,$

$\Delta_{\text{form}}G_m^0 = 723.514 \cdot 10^{-3}T - 9.477 \cdot 10^{-6}T^2$
$\qquad - 3.244 \cdot 10^2 T^{-1} + 3.975 \cdot 10^{-9}T^3$
$\qquad - 66.796 \cdot 10^{-3}T \ln T - 939.3.$

Liquid EuCl$_3$ solid, 1096 K < T < 1300 K:

$\Delta_{\text{form}}H_m^0 = 62.536 \cdot 10^{-3}T - 0.188 \cdot 10^{-6}T^2$
$\qquad - 4.268 \cdot 10^2 T^{-1} - 942.8,$

$\Delta_{\text{form}}G_m^0 = 691.061 \cdot 10^{-3}T + 0.188 \cdot 10^{-6}T^2$
$\qquad - 2.134 \cdot 10^2 T^{-1} - 62.536 \cdot 10^{-3}T \ln T - 942.9.$

These results are also tabulated at selected temperatures in Table 2.

The heat capacity measurements confirmed the decomposition of EuCl$_3$ at higher temperatures. The sudden increase of $C_{p,m}^0$ at 802 K up to 160 J K^{-1}mol^{-1} (T_{eutectic} in Fig. 2) corresponds well to the temperature of an additional thermal effect at 804 K observed on the DTA curves during a secondary heating of EuCl$_3$ (Fig. 1c).

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