

# Heat Capacity of $K_3LnCl_6$ Compounds with $Ln = La, Ce, Pr, Nd$

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The heat capacities of the solid and liquid  $K_3LnCl_6$  compounds ( $Ln = La, Ce, Pr, Nd$ ) have been determined by differential scanning calorimetry (DSC) in the temperature range 300 - 1100 K. Their temperature dependence is discussed in terms of the phase transitions of these compounds as reported in literature. The heat capacity increases and decreases strongly in the vicinity of a phase transition but else varies smoothly. The  $C_p$  data were fitted by an equation which provides a satisfactory representation up to the temperatures of  $C_p$  discontinuity. The measured heat capacities were checked for consistency by calculating the enthalpy of formation of the liquid phase, which had been previously measured. The results obtained compare satisfactorily with these experimental data.

**Key words:** Lanthanum Chloride; Cerium Chloride; Praseodymium Chloride; Neodymium Chloride; Alkali Metals Chlorides; Heat Capacity; Differential Scanning Calorimetry.

## Introduction

The present paper reports the results of heat capacity ( $C_p$ ) measurements. It is a continuation of our previous investigations of some physicochemical properties of the following halide compounds and systems:

- pure  $LnCl_3$ , where  $Ln = La, Ce, Pr, Nd, Gd, Dy, Er, Tm$  [1];
- compounds  $M_3LnCl_6$ , where  $M = K, Rb, Cs$  and  $Ln = La, Ce, Pr, Nd$  [2], and  $K_2LaCl_5$  [2];
- $(M, Ln_{1/3})Cl$  liquid mixtures, where  $M = Li, Na, K, Rb, Cs$  and  $Ln = Pr, Nd, Dy$  [3 - 6];
- $(Ca_{1/2}, Ln_{1/3})Cl$  liquid mixtures, where  $Ln = Pr, Nd$  [7];
- $(Dy_{1/3}, Pr_{1/3})Cl$  liquid mixtures [5];
- $(M, Ln_{1/3})Br$  liquid mixtures, where  $M = Li, Na, K, Rb, Cs$  and  $Ln = La, Nd$  [8 - 9].

Different techniques, such as isothermal calorimetry, differential scanning calorimetry (DSC) [1 - 11], electrical conductivity measurements [12], density measurements [13], X-Ray and neutron diffraction

have been used [14 - 17]. Molecular dynamics calculations have also been performed [6, 18].

The  $M_3LnCl_6$  compounds ( $M = K, Rb, Cs$ ) are formed at higher temperatures and melt congruently [19 - 22]. Their temperature range of existence strongly depends on the alkali metal cation.

The  $K_3LnCl_6$  compounds do not form in all the  $(K, Ln_{1/3})Cl$  systems. There is no compound of this type in the  $(K, La_{1/3})Cl$  system [19] and  $K_2LaCl_5$  is the only congruently melting compound. Starting with  $Ce$  in the lanthanide series, the  $K_3LnCl_6$  compounds melt congruently [20 - 22] even if they only exist over a limited temperature range.

There are also other types of compounds in the  $(K, Ln_{1/3})Cl$  systems, corresponding to the  $K_2LnCl_5$ ,  $KLn_2Cl_7$  and  $K_3Ln_5Cl_{18}$ . Generally, the  $K_2LnCl_5$  compounds exist from room temperature up to the congruent melting temperature ( $K_2LaCl_5$  [19],  $K_2CeCl_5$  [20]) or incongruent melting temperature ( $K_2PrCl_5$  [21],  $K_2NdCl_5$  [22]).  $KLn_2Cl_7$  and  $K_3Ln_5Cl_{18}$  type compounds exist only in the  $(K, Nd_{1/3})Cl$  and  $(K, Ce_{1/3})Cl$  systems, respectively [20, 22].

Our research focused on the  $M_3LnCl_6$  compounds because of the important role of the  $LnCl_6^{3-}$  complexes in the thermodynamic modelling of melts and, more generally, in the physical description of the

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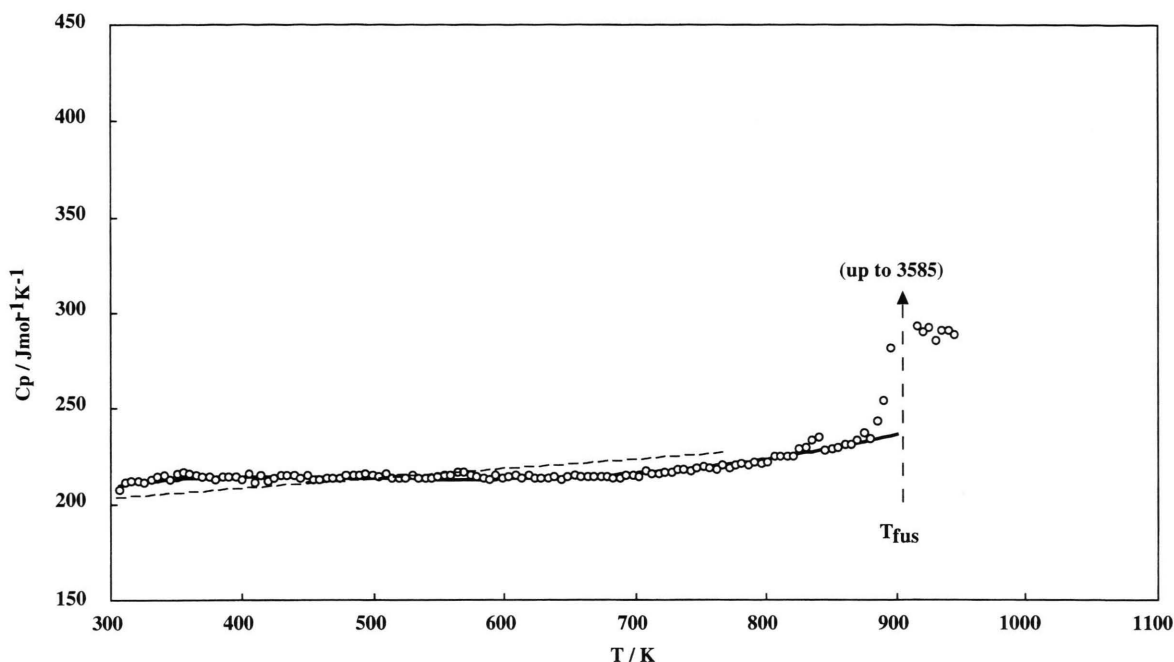


Fig. 1. Molar heat capacity of  $K_2LaCl_5$  against temperature; circles: experimental values, solid line: values calculated with (1), dashed line: literature values [25].

liquid state. But other possible combinations of ions corresponding to the stoichiometry of compounds existing in the solid phase should also be kept in mind.

### Experimental

The experimental procedure for  $C_p$  measurements with a differential scanning calorimeter SETARAM DSC 121, the method of lanthanide chloride synthesis and the preparation of samples have been described in [1, 2]. Samples with masses of 300 - 500 mg were sealed under a low pressure of argon in quartz cells (15 mm long and 7 mm diameter). These cells were placed in the DSC 121 calorimeter and measurements were carried out by the step method – each heating step of 5 K being followed by a 400 s isothermal delay. The apparatus was calibrated by the Joule effect, and some test experiments were carried out with NIST 720  $\alpha$ -alumina for secondary calibration, to monitor the  $C_p$  measurements.

### Results and Discussion

The compounds investigated exhibited some features which are not very common for binary stoi-

chiometric compounds of halides. These are, firstly, a limited temperature range of existence and, secondly, a tendency to form metastable phases at temperatures below the decomposition [23 - 24]. These factors, together with the occurrence of solid-solid phase transitions, give rather complicated  $C_p$  vs. temperature curves. The classical heat capacity polynomial equation

$$C_p = a + bT + cT^2 + \frac{d}{T} \quad (1)$$

was used to fit the experimental results.

The potassium compounds were the first group in the series of alkali metal-lanthanide chloride systems that we investigated. Though the  $K_3LnCl_6$  compounds exist for almost all the lanthanides, an exception is to be noted for lanthanum, since the only known chloride compound with potassium is  $K_2LaCl_5$ .

#### $K_2LaCl_5$

This compound exists at room temperature [19] and melts congruently at 906 K [2]. No phase transition has been reported in the literature, and we also found no evidence for one in the heat capacity  $C_p$

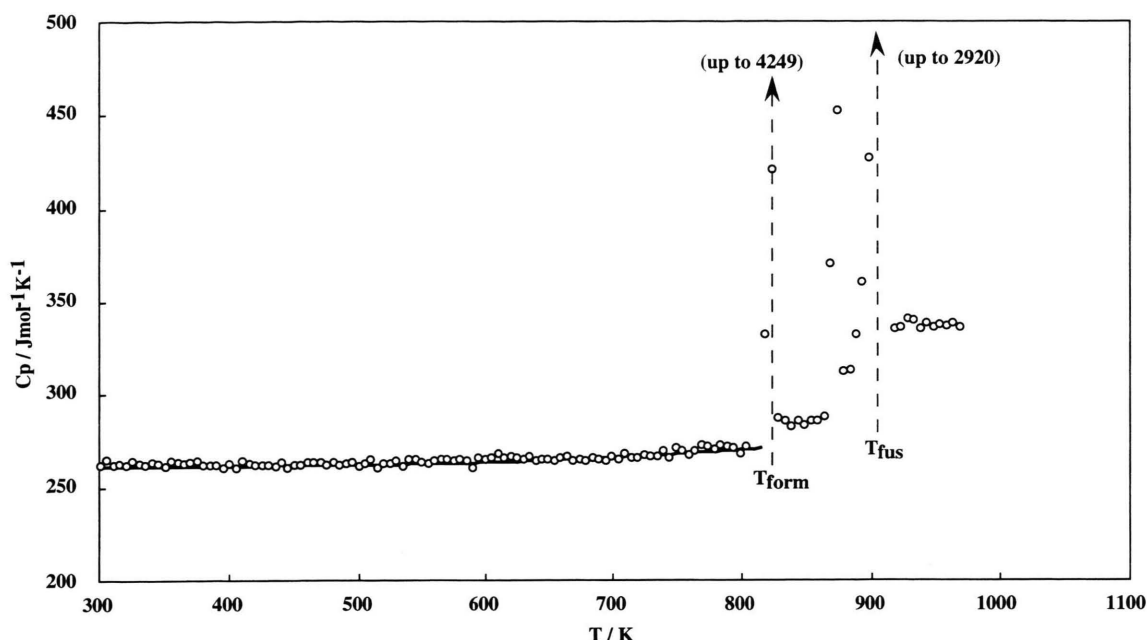


Fig. 2. Molar heat capacity of  $K_3CeCl_6$  against temperature; circles: experimental values, solid line: values calculated with (1).

Table 1.  $K_2LaCl_5$  and  $K_3LnCl_6$  compounds: Regression coefficients and standard error of estimation of  $C_p$  ( $J mol^{-1} K^{-1}$ ) =  $a + bT + cT^2 + d/T$ .

Compound	Temp. range K	$a$ $Jmol^{-1}$ $K^{-1}$	$b \cdot 10^{-2}$ $Jmol^{-1}$ $K^{-2}$	$c \cdot 10^{-4}$ $Jmol^{-1}$ $K^{-3}$	$d \cdot 10^4$ $Jmol^{-1}$ $K^{-1}$	S.E. $Jmol^{-1}$ $K^{-1}$
$K_2LaCl_5$ (s)	300 - 866	453.33	-49.824	3.37	-3.7506	1.63
(l)	915 - 945	290.0				2.52
$K_3CeCl_6$ (s)	300 - 805	306.52	-11.105	0.95	-0.5995	1.60
(s)	815 - 865	284.60				1.75
(l)	915 - 970	337.40				2.41
$K_3PrCl_6$ (s)	380 - 760	612.49	-66.488	4.36	-5.8489	1.03
(s)	780 - 930	262.19	3.998			2.43
(l)	950 - 1100	278.30	5.8030			4.26
$K_3NdCl_6$ (s)	300 - 715	363.84	-20.699	1.63	-2.1254	1.58
(s)	740 - 940	1346.61	-261.78	15.98		2.70
(l)	985 - 1020	321.90				3.89

vs. temperature  $T$  curve – in agreement with our previous DTA experiments [2] on the same compound. The experimental heat capacity data determined for  $K_2LaCl_5$  are presented in Figure 1. The experimental values for the solid (in  $J \cdot mol^{-1} K^{-1}$ ) are very well fitted by (1) in the temperature range 300 - 866 K. The parameters of this equation are given in Table 1.

In this solid range, the non-significant deviation from a very smooth curvature in Fig. 1 at temper-

atures close to 850 K results from the small non-stoichiometry of the sample (effect of the eutectic between  $K_2LaCl_5$  and  $KCl$ ).

The heat capacity of the liquid  $K_2LaCl_5$  compound was also determined in a narrow temperature range from 915 to 945 K. A constant value  $C_p = 290.0 J mol^{-1} K^{-1}$  was found.

The melting enthalpy of the  $K_2LaCl_5$  has been reported in our previous paper [2] and is  $\Delta_{fus}H_m = 78.1 kJ \cdot mol^{-1}$ .

### $K_3CeCl_6$

Among the  $M_3LnCl_6$  compounds under investigation,  $K_3CeCl_6$  corresponds to the smallest atomic numbers of both the alkali metal and the lanthanide. It showed a very limited temperature range of existence: the compound forms at 811 K [2] and melts congruently at 908 K [2]. The endothermic effect of compound formation resulted in a sharp jump in the  $C_p$  curve, see Figure 2. The discontinuity at 870 K resulted from the small deviation from stoichiometry of the sample. Only a few heat capacity values were measured for  $K_3CeCl_6$  in the temperature range from 815 K up to the eutectic temperature (865 K), so it was difficult to determine accurately the temperature

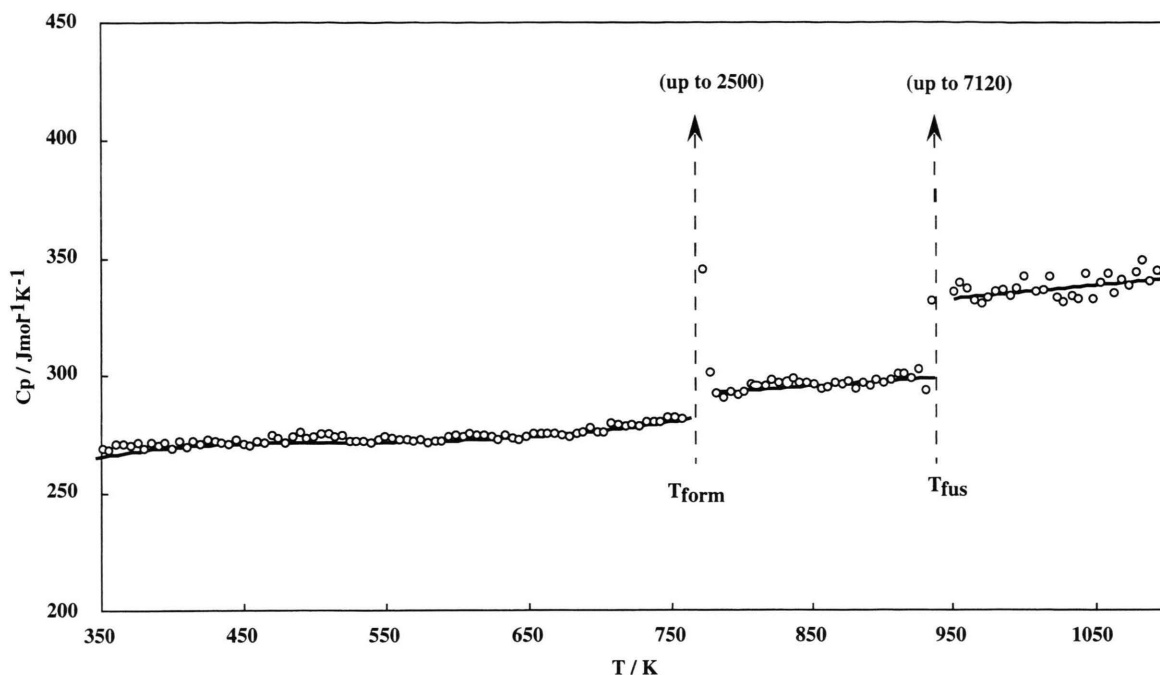


Fig. 3. Molar heat capacity of  $K_3PrCl_6$  against temperature; circles: experimental values, solid line: values calculated with (1).

Table 2. Enthalpies of formation of the  $(K_2LnCl_5 + KCl)$  mixtures at 298 K [28].

$\Delta_{\text{form}}H_m((K_2LnCl_5 + KCl), s, 298)/\text{kJ}\cdot\text{mol}^{-1}$	
$K_2CeCl_5 + KCl$	-27.9
$K_2PrCl_5 + KCl$	-32.7
$K_2NdCl_5 + KCl$	-22.1

dependence, and the heat capacity was assumed to be constant:  $C_p = 284.6 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ . The heat capacity of liquid  $K_3CeCl_6$  was found to be constant over the temperature range 915 - 970 K and  $C_p = 337.4 \text{ J}\cdot\text{mol}^{-1}\text{K}^{-1}$ . All the parameters of the heat capacity dependence on temperature are given in Table 2.

In a previous paper [2] we reported the formation enthalpy  $\Delta_{\text{form}}H_m = 55.4 \text{ kJ}\cdot\text{mol}^{-1}$  and the melting enthalpy  $\Delta_{\text{fus}}H_m = 39.1 \text{ kJ}\cdot\text{mol}^{-1}$ .

### $K_3PrCl_6$

The stability of the  $K_3LnCl_6$  compounds increased with the atomic number of the lanthanide, and  $K_3PrCl_6$  existed over a broader temperature range from 768 to 944 K [2]. The corresponding enthalpies of formation,  $\Delta_{\text{form}}H_m$ , and of melting,  $\Delta_{\text{fus}}H_m$ , are 52.6 and 48.9  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively.

The experimental heat capacity results are presented in Fig. 3, and the parameters of (1) are given in Table 1. After formation of the compound, the heat capacity dependence on temperature changed and  $C_p$  decreased up to about 860 K. Due to the wide existence range of the compound it has been possible to use (1) to represent this variation with temperature.

The heat capacity of liquid  $K_3PrCl_6$  gradually increased with temperature and varied linearly in the range 950 - 1100 K.

### $K_3NdCl_6$

$K_3NdCl_6$  is the last compound investigated in the potassium series. It had the largest existence range, as it formed at 724 K and melted congruently at 973 K [2]. The corresponding enthalpies of formation and of fusion are:  $\Delta_{\text{form}}H_m = 46.3 \text{ kJ}\cdot\text{mol}^{-1}$  and  $\Delta_{\text{fus}}H_m = 48.0 \text{ kJ}\cdot\text{mol}^{-1}$  [2], respectively.

The experimental heat capacity results (Fig. 4) are well fitted by (1) up to the formation temperature of  $K_3NdCl_6$  (Figure 4). But  $K_3NdCl_6$  was the first to show a marked decrease of  $C_p$  immediately after the formation of the compound. Equation (1) fitted all

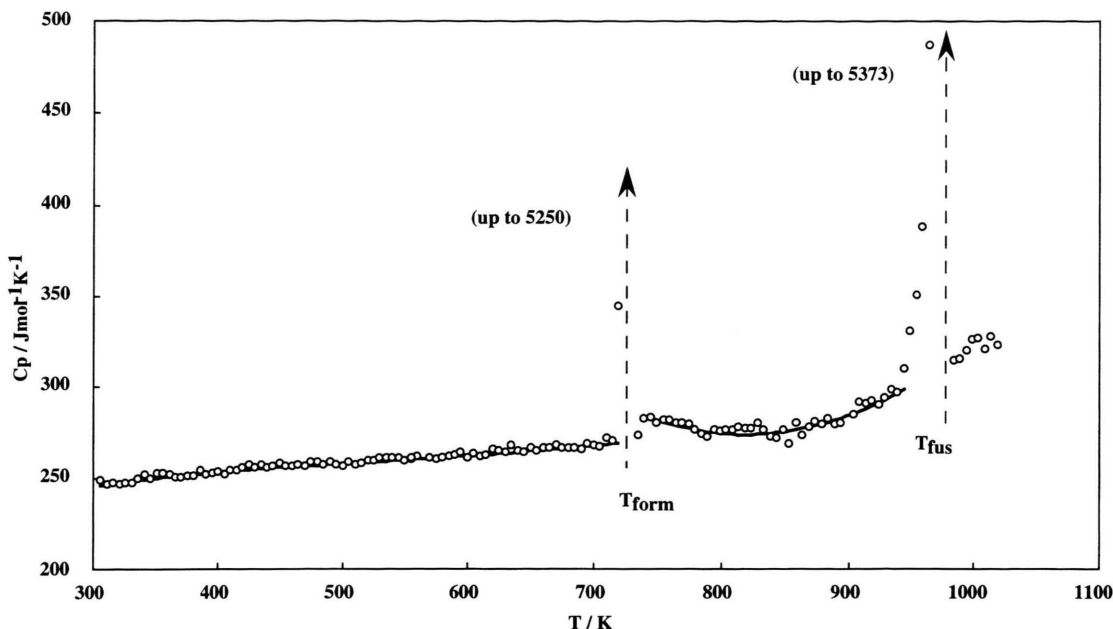


Fig. 4. Molar heat capacity of  $K_3NdCl_6$  against temperature; circles: experimental values, solid line: values calculated with (1).

the experimental points very well and gave a small minimum at 850 K (Figure 4).

For the liquid phase obtained after fusion of  $K_3NdCl_6$  only a few experimental data have been obtained, and the heat capacity dependence on temperature was not determined for this melt. But assuming that the heat capacity of this phase is constant we obtained  $C_p = 321.9 \text{ J mol}^{-1} \text{ K}^{-1}$  in the temperature range 985 - 1020 K.

No heat capacity data are available so far in the literature on the lanthanide compounds with the exception of  $K_2LnCl_5$  in the temperature range 200 - 770 K [25]. These values were smaller than ours in the range 300 - 400 K, then nearly identical between 400 and 550 K and finally larger in the range 550 - 770 K (see Figure 1). Due to the lack of literature data for the other  $K_3LnCl_6$  compounds, it was not possible to compare and to assess our heat capacity values. Therefore we decided to use for this purpose the available enthalpies of formation at 298 K and to calculate, using the experimental heat capacities, the corresponding enthalpies of formation in the liquid state and to compare these calculated values with the experimental enthalpies of formation determined previously [2, 4, 26].

These heat capacity values were used in the calculation of the formation enthalpies of some compounds in the liquid state. The enthalpies of formation at 298 K of the  $(K_2LnCl_5 + KCl)$  mixtures are presented in Table 2. They were taken from Blachnik [27 - 28] who assumed that the  $K_3LnCl_6$  compounds were stable at room temperature. Even if this assumption was not correct, his data can be used in our calculations, since the compounds would then decompose into mixtures of  $K_2LnCl_5$  and  $KCl$  and Blachnik's data correspond to the enthalpy of formation of those mixtures at 298 K.

The enthalpies of formation of the  $K_3LnCl_6$  liquid compounds  $\Delta_{\text{form}} H_m(K_3LnCl_6, l, T)$  at the temperature  $T$  can be calculated from the enthalpies of formation of  $(K_2LnCl_5 + KCl)$  at 298 K ( $\Delta_{\text{form}} H_m(K_2LnCl_5 + KCl, s, 298)$  [27 - 28]), from the heat capacity data and from our previous values of enthalpies of formation and of fusion.

It is possible to calculate for  $K_3LnCl_6$  ( $Ln = Ce, Pr, Nd$ ):

$$\begin{aligned} \Delta_{\text{form}} H_m(K_3LnCl_6, l, T) = & \\ & \Delta_{\text{form}} H_m(K_2LnCl_5 + KCl, s, 298) \\ & + [\Delta H_m(K_2LnCl_5 + KCl, s, (T_{\text{form}} - 298))] \end{aligned}$$



Table 3. Enthalpies of formation (from  $K_2LnCl_5 + KCl$  mixtures) and enthalpies of fusion ( $\Delta_{form}H_m$  and  $\Delta_{fus}H_m$  in  $kJ \cdot mol^{-1}$ ) of the  $M_3LnCl_6$  compounds [2]. (Corresponding temperature in parenthesis).

	Ce	Pr	Nd
$\Delta_{form}H_m / kJ \cdot mol^{-1}$	55.4 (811 K)	52.6 (768 K)	46.3 (724 K)
$\Delta_{fus}H_m / kJ \cdot mol^{-1}$	39.3 (908 K)	48.9 (944 K)	48.0 (973 K)

$$\begin{aligned}
 &+ \Delta_{form}H_m(K_3LnCl_6, s, T_{form}) \\
 &+ \Delta H_m(K_3LnCl_6, s, (T_{fus} - T_{form})) \\
 &+ \Delta_{fus}H_m(K_3LnCl_6, T_{fus}) \\
 &+ \Delta H_m(K_3LnCl_6, l, (T - T_{fus})) \\
 &- [\Delta H_m(LnCl_3, s, (T_{fus} - 298)) \\
 &+ \Delta_{fus}H_m(LnCl_3, T_{fus}) \\
 &+ \Delta H_m(LnCl_3, l, (T - T_{fus}))] \\
 &- 3[\Delta H_m(KCl, s, (T_{fus} - 298)) \\
 &+ \Delta_{fus}H_m(KCl, T_{fus}) \\
 &+ \Delta H_m(KCl, l, (T - T_{fus}))].
 \end{aligned}$$

The enthalpies of formation  $\Delta_{form}H_m(K_3LnCl_6, s, T_{form})$  of the solid  $K_3LnCl_6$  at  $T_{form}$  and the enthalpies of fusion  $\Delta_{fus}H_m(M_3LnCl_6, T_{fus})$ , determined previously [2], are shown in Table 3.

The heat capacity data used in these calculations, relative to the  $M_3LnCl_6$ , were given above, and those relative to the pure lanthanide halides and to KCl were taken from [29] and [30], respectively.

The values calculated in this way for the enthalpies of formation of the  $K_3LnCl_6$  compounds were compared with the experimental data reported in Table 4.

Table 4.  $M_3LnCl_6$  compounds: experimental and calculated enthalpies of formation  $\Delta_{form}H_m$  in the liquid state.

	$T/K$	$\Delta_{form}H_m / kJ \cdot mol^{-1}$ (experimental)	$\Delta_{form}H_m / kJ \cdot mol^{-1}$ (calculated)
$K_3CeCl_6$	1118	-55.7 [15]	-56.9
$K_3PrCl_6$	1122	-55.9 [2]	-63.3
$K_3NdCl_6$	1065	-55.2 [4]	-62.2

A quite good agreement was found, which argues for the reliability of the experimental heat capacity values obtained.

## Conclusion

The only literature data on the heat capacity of the  $K_2LnCl_5$  compounds were given by Seifert [25] for the solid phase of  $K_2LaCl_5$ . They are in a quite good agreement with the results obtained in this work. The other heat capacities were obtained for the first time. They were fitted by an equation which provides a satisfactory representation up to the temperature of the  $C_p$  discontinuity. The measured heat capacities were checked for consistency by calculating the enthalpy of  $K_3CeCl_6$ ,  $K_3PrCl_6$  and  $K_3NdCl_6$  formation in the liquid phase, which had been previously measured. An excellent agreement between calculated and experimental values of this formation enthalpy for  $K_3CeCl_6$  and a quite good one for  $K_3PrCl_6$  and  $K_3NdCl_6$  melts was found. It shows the reliability of the experimental heat capacities obtained by differential scanning calorimetry.

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