Heat Capacity of the Rb_3LnCl_6 Compounds with Ln = La, Ce, Pr, Nd

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The heat capacities of the solid and liquid Rb_3LnCl_6 compounds, where Ln = La, Ce, Pr, Nd, have been determined by differential scanning calorimetry (DSC) in the temperature range 300 - 1100 K. The heat capacity shows a small decrease with increasing temperature from the temperature of phase transition up to 150 - 200 K above this transition for the Rb_3CeCl_6, Rb_3PrCl_6 and Rb_3NdCl_6 compounds. The measured heat capacities were used to calculate the formation enthalpy of the liquid phase. The results obtained compare satisfactorily with the known experimental data.

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

Introduction

The lanthanide halides and their mixtures with alkali metal halides have been extensively investigated recently. Several multiinstrumental techniques were used complementarily to characterise the macroscopic and microscopic behaviour of these mixtures [1 - 8].

The present paper reports heat capacity (C_p) measurements performed on Rb_3LnCl_6 compounds and is a continuation of our investigations on K_3LnCl_6 compounds [9]. These Rb_3LnCl_6 (Ln = La, Ce, Pr, Nd) compounds form in all the (Rb, $Ln_{1/3}$)Cl systems [10 - 13], but they do not exist at room temperature, as they form from RbCl and Rb_2LnCl_5 at higher temperatures and then melt congruently. Earlier work suggested a limited temperature range of existence of these compounds [10 - 13]. However our recent differential scanning calorimetry (DSC) or differential thermal analysis (DTA) investigations did not confirm the temperatures of their formation [1h]. Other effects at different temperatures were detected instead, which may be qualitatively related to formation / decomposition processes. The compounds investigated exhibit some specific features, rather unusual in stoichiometric binary halide compounds, i. e. a limited temperature range of existence and a tendency to the formation of metastable phases below the decomposition temperature [14, 15]. These facts, together with the occurrence of solid-solid phase transitions, give rise to rather complicated C_p vs. T curves with noticeable features related to the effects of compound formation and of phase transition, resulting in marked non-linearity. The polynomial

$$C_p = a + bT + cT^2 \qquad (1)$$

was used to represent the experimental heat capacity as a function of temperature.

Experimental

The method used for the synthesis of lanthanide chlorides, the sample preparation and the the procedure of C_p measurements with a differential scanning calorimeter have been described in [1h, 9, 16]. Samples with masses of 300 - 500 mg were sealed under low pressure of argon in quartz cells (15 mm long and 7 mm diameter). The cells were placed into the calorimeter and the measurements were carried out by the step method, each heating step (1.5 K/min) of 5 K being followed by a 400 s isothermal delay. The apparatus was calibrated by the Joule effect, and a secondary calibration was performed from time to time with NIST 720 α-alumina.

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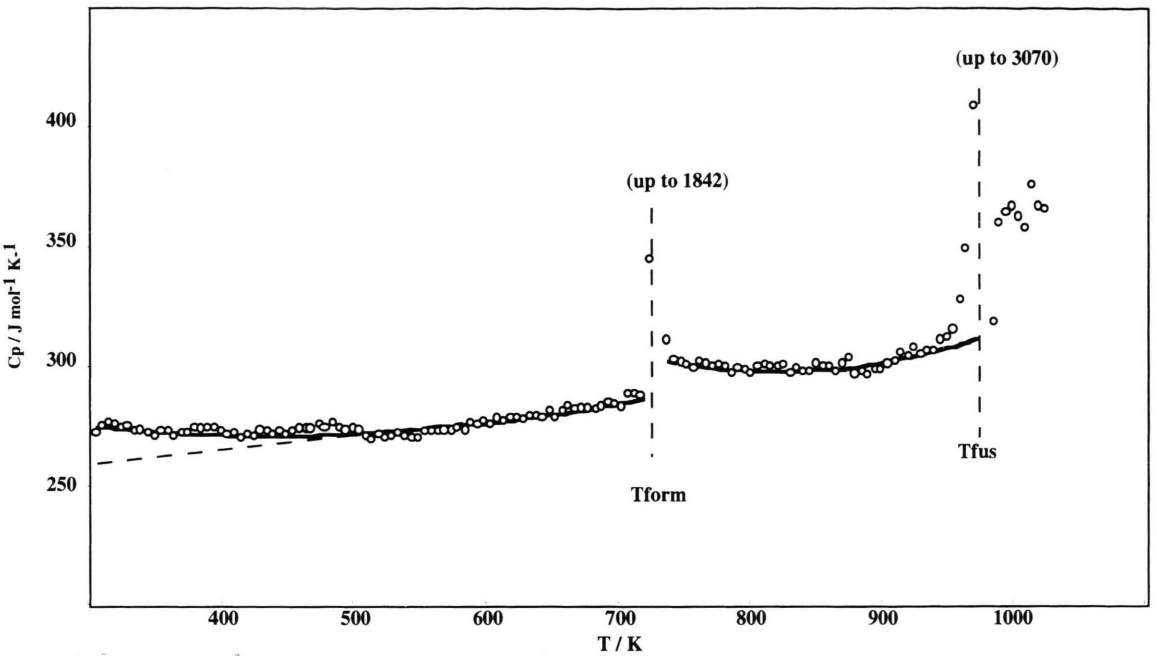

Fig. 1. Molar heat capacity of Rb_3LaCl_6 against temperature; circles: experimental values, solid line: values calculated from (1), dashed line: literature values [17].

Results

Rb_3LaCl_6

Rb_3LaCl_6 forms at 725 K from RbCl and Rb_2LaCl_5, as reported in [10], while the decomposition temperature, determined from cooling curves, was 685 K [1h]. A similar effect of supercooling to a metastable phase was observed by Seifert et al. [10] and ascribed to a retarded rearrangement of ions. The formation enthalpy of Rb_3LaCl_6 from RbCl and Rb_2LaCl_5 and the enthalpy of fusion were previously determined as $\Delta_{form}H_m$ = 48.4 kJ mol^{-1} and $\Delta_{fus}H_m$ = 50.2 kJ mol^{-1}, respectively [1h].

Experimental heat capacity data are plotted against temperature in Figure 1. The C_p values were slightly larger than reported in [17] at lower temperatures, but were nearly identical above 500 K. After compound formation, the heat capacity vs. temperature curve exhibited a very flat minimum at 860 K. Equation (1) was used for Rb_3LaCl_6 (and the stoichiometric mixture of RbCl and Rb_2LaCl_5), and very good agreement between the experimental and calculated C_p values was obtained. The parameters in (1) for the two solid phases and for the liquid are presented in Table 1. A constant heat capacity C_p = 365.4 J mol^{-1} K^{-1} was determined for the liquid compound.

Table 1. Regression coefficients and standard error of estimation of C_p (J mol^{-1} K^{-1}) = $a + bT + cT^2$ for Rb_3LnCl_6 compounds.

Compound		Temp. range K	a Jmol^{-1} K^{-1}	b Jmol^{-1} K^{-2}	$c*10^4$ Jmol^{-1} K^{-3}	S.E. Jmol^{-1} K^{-1}
Rb_3LaCl_6	(s)	300 - 717	308.09	–0.16741	1.92	2.71
	(s)	735 - 955	712.62	–1.0079	6.13	3.63
	(l)	990 - 1025	365.38			2.43
Rb_3CeCl_6	(s)	300 - 390	274.83	0.01348		2.54
	(s)	420 - 643	486.85	–0.74019	6.26	5.21
	(s)	662 - 980	693.29	–0.99720	6.13	3.67
	(l)	1016 - 1074	345.73			3.15
Rb_3PrCl_6	(s)	300 - 400	621.75	–2.12574	33.96	2.99
	(s)	405 - 654	472.63	–0.75499	7.43	1.93
	(s)	664 - 1000	794.60	–1.22287	7.23	3.15
	(l)	1037 - 1097	329.89			2.48
Rb_3NdCl_6	(s)	300 - 380	360.46	-0.54373	8.77	1.51
	(s)	400 - 660	391.21	–0.52122	5.53	1.40
	(s)	675 - 1050	636.70	–0.79808	4.26	3.82
	(l)	1060 - 1093	325.77			3.05

Rb_3CeCl_6

Rb_3CeCl_6 has been found to form from RbCl and Rb_2CeCl_5 at 651 K [11] as confirmed by the endothermic effect at 650 K with a related enthalpy change of 8.5 kJ mol^{-1} observed in [1h]. However an additional

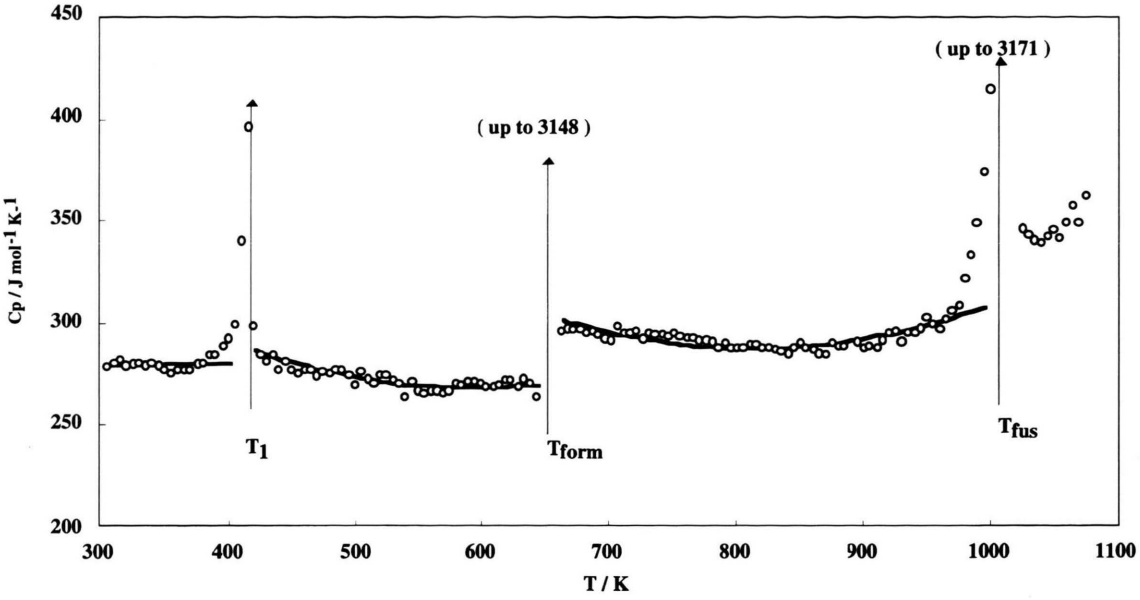

Fig. 2. Molar heat capacity of Rb_3CeCl_6 against temperature; circles: experimental values, solid line: values calculated from (1).

effect at 411 K with an enthalpy of about 1.2 kJ mol^{-1} was also reported [1h] together with congruent melting at 1016 K with $\Delta_{fus}H_m$ = 52.4 kJ mol^{-1}.

The parameters of (1) for the three temperature ranges are presented in Table 1 and the C_p vs. T curve is given in Figure 2.

Over the existence range of Rb_3CeCl_6 (from 650 K up to fusion), the heat capacity slowly decreases up to 860 K. A constant heat capacity C_p = 345.7 J mol^{-1} K^{-1} was determined for liquid Rb_3CeCl_6 in the temperature range 1016 - 1090 K.

Rb_3PrCl_6

Rb_3PrCl_6 is the first Rb_3LnCl_6 compound to undergo a phase transition [12]. This compound was reported to form at 598 K from RbCl and Rb_2PrCl_5, while a solid-solid transition and fusion occurred at 659 K and 1040 K, respectively. We confirmed the transition and fusion temperatures and also determined the related enthalpy changes. The phase transition and fusion were observed at T_{trs} = 658 K and T_{fus} = 1037 K with the corresponding enthalpies $\Delta_{trs}H_m$ = 6.6 kJ mol^{-1} and $\Delta_{fus}H_m$ = 54.0 kJ mol^{-1}, respectively [1h]. However we did not observe any compound formation at 598 K. An additional effect was observed instead at 396 K with an enthalpy of 1.0 kJ mol^{-1}.

The experimental heat capacity data are presented in Figure 3. (T_1 denotes the temperature of a small endothermic effect of unknown origin). The heat capacity dependence on temperature was approximated by (1) for the three temperature ranges (300 K - T_1), (T_1 - T_{trs}) and (T_{trs} - T_{fus}). The calculated values were compared with the experimental heat capacities in Fig. 3, the parameters of (1) being listed in Table 1. A constant heat capacity C_p = 329.9 J mol^{-1} K^{-1} was found for the liquid phase.

Rb_3NdCl_6

In [13] Rb_3NdCl_6 was found to form from RbCl and Rb_2NdCl_5 at 547 K, to show a solid phase transition at 667 K and congruent melting at 1060 K. Later [1h] we determined the corresponding enthalpies of phase transition $\Delta_{trs}H_m$ = 6.7 kJ mol^{-1} and of fusion $\Delta_{fus}H_m$ = 58.8 kJ mol^{-1} and also found an excellent agreement with the higher two temperatures (T_{trs} = 667 K and T_{fus} = 1060 K). Our observations did not support, however, the temperature reported for Rb_3NdCl_6 formation. Our DSC experiments [1h] showed reproducibly that no thermal effect took place at 547 K either on heating or on cooling. Actually, in [13] that temperature was extrapolated from e.m.f. vs. T measurements, while the same authors postulated a metastable phase as they did not observe any thermal

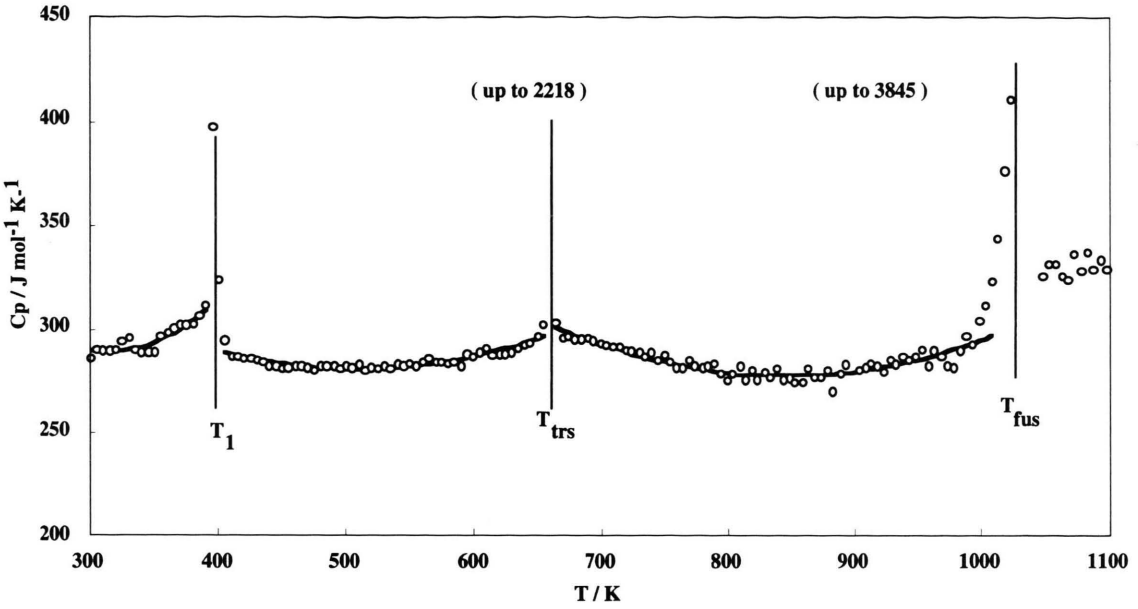

Fig. 3. Molar heat capacity of Rb_3PrCl_6 against temperature; circles: experimental values, solid line: values calculated from (1).

evidence for formation / decomposition of Rb_3NdCl_6, unless the mixture had been annealed with some water.

We did observe an endothermic effect in Rb_3NdCl_6 at a lower temperature, obtained consistently on heating as 382 K by DSC in [1h] and by heat capacity measurements in the present work. The reverse exothermic effect also occurred at the same temperature on cooling.

The only structural information available so far on solid Rb_3NdCl_6 was obtained from X-ray powder diffraction experiments. Two, low- and high-temperature modifications were reported, monoclinic and cubic, respectively [13]. It seems unclear, however, whether the low temperature modification was observed below or above 382 K, the temperature at which we observed a thermal phenomenon. New structural investigations by neutron diffraction are in progress [7] in order to determine whether this can be related to a phase transition in solid Rb_3NdCl_6.

Heat capacity measurements were performed on the solid and liquid compound. The experimental heat capacity data are presented in Figure 4. (T_1 denotes the temperature of a small endothermic effect of unknown origin). The heat capacity dependence on temperature was again described by (1) for the three temperature ranges : (300 K - T_1), (T_1 - T_{trs}) and (T_{trs} - T_{fus}). The calculated values are compared with the experimental heat capacities in Fig. 4, the parameters of (1) being listed in Table 1. A constant heat capacity C_p = 325.8 J mol^{-1} K^{-1} was found for the liquid phase.

Table 2. Literature values of the enthalpy of formation of Rb_2LnCl_5's and Rb_3NdCl_6 at 298 K.

Compound	$\Delta_{form}H_m$(s, 298)/kJ·mol^{-1}
Rb_2LaCl_5	–33.3 [10]
Rb_2CeCl_5	–37.4 [11]
Rb_3NdCl_6	–21.9 [13]

Discussion

No heat capacity data were available in literature on the Rb_3LnCl_6 compounds excepted for solid Rb_3LaCl_6 in the range 200 - 250 K [17]. These results are in fairly good agreement with ours with a maximum deviation less than 4 percent.

In order to assess the consistency of these original C_p data with other thermodynamic data on solid and liquid compounds, they were used in the calculation of the enthalpy of formation $\Delta_{form}H_m$ (Rb_3LnCl_6,l,T) of the liquid Rb_3LnCl_6 and compared with the experimental enthalpy measured previously by direct calorimetry for the $(Rb,Ln_{1/3})Cl$ melts [1c, 18, 19].

This calculation included the enthalpy of formation at 298 K, ($\Delta_{form}H_m$ (Rb_2LnCl_5,s,298), where Ln = La

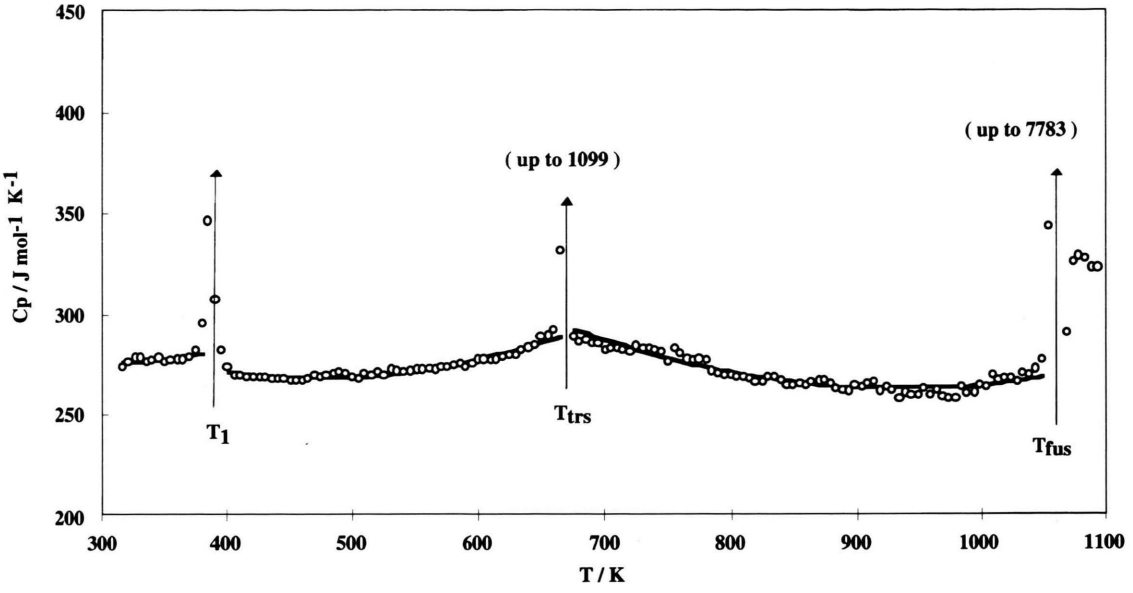

Fig. 4. Molar heat capacity of Rb_3NdCl_6 against temperature; circles: experimental values, solid line: values calculated from (1).

and Ce, and $\Delta_{form}H_m$ (Rb_3NdCl_6,s,298) (Table 2), and the enthalpies relative to the solid-solid and solid-liquid phase transitions occurring in the temperature range 298 K - T:

$$\Delta_{form}H_m(Rb_3LnCl_6, l, T) = \Delta_{form}H_m(Rb_3LnCl_6, s, 298) + [\Delta H_m(Rb_3LnCl_6, s, (T_{trs} - 298)) + \Delta_{trs}H_m(Rb_3LnCl_6, s, T_{trs}) + \Delta H_m(Rb_3LnCl_6, s, (T_{fus} - T_{trs})) + \Delta_{fus}H_m(Rb_3LnCl_6, T_{fus}) + \Delta H_m(Rb_3LnCl_6, l, (T - T_{fus}))] - [\Delta H_m(LnCl_3, s, (T_{fus} - 298)) + \Delta_{fus}H_m(LnCl_3, T_{fus}) + \Delta H_m(LnCl_3, l, (T - T_{fus}))] - 3\cdot[\Delta H_m(RbCl, s, (T_{fus} - 298)) + \Delta_{fus}H_m(RbCl, T_{fus}) + \Delta H_m(RbCl, l, (T - T_{fus}))] \quad (2)$$

Since Rb_3LaCl_6 and Rb_3CeCl_6 form from RbCl and Rb_2LaCl_5 or Rb_2CeCl_5 at T_{form}, this extra contribution was accordingly incorporated on the right-hand side of (2):

$$\Delta_{form}H_m(Rb_3LnCl_6, l, T) = \Delta_{form}H_m(Rb_2LnCl_5, s, 298) + [\Delta H_m(Rb_2LnCl_5{+}RbCl, s, (T_{form} - 298)) + \Delta_{form}H_m(Rb_3LnCl_6, s, T_{form}) + \Delta H_m(Rb_3LnCl_6, s, (T_{fus} - T_{form})) + \Delta_{fus}H_m(Rb_3LnCl_6, T_{fus}) + \Delta H_m(Rb_3LnCl_6, l, (T - T_{fus}))] - [\Delta H_m(LnCl_3, s, (T_{fus} - 298)) + \Delta_{fus}H_m(LnCl_3, T_{fus}) + \Delta H_m(LnCl_3, l, (T - T_{fus}))] - 3\cdot[\Delta H_m(RbCl, s, (T_{fus} - 298)) + \Delta_{fus}H_m(RbCl, T_{fus}) + \Delta H_m(RbCl, l, (T - T_{fus}))]. \quad (3)$$

The enthalpies of formation $\Delta_{form}H_m$ (Rb_3LnCl_6, s, T_{form}) and phase transitions $\Delta_{trs}H_m(Rb_3LnCl_6, s, T_{trs})$ of Rb_3LnCl_6 were determined in [1h]. The thermodynamic quantities relative to RbCl were taken from [20]. The data relative to the lanthanide chlorides were also previously determined.

$LaCl_3$

The heat capacity of solid $LaCl_3$ is given by

$C_{p,s} = 82.51 + 3.816\cdot10^{-2}T$, (300 - 1100 K) [16].

The heat capacity of the liquid is reported contradictorily by Dworkin and Bredig [21] (158 J $mol^{-1}K^{-1}$) and Savin [22] (350 J $mol^{-1}K^{-1}$). It seems that the latter value is not very reliable as it was obtained by a discutable extrapolation method. Therefore heat capacity of [21] was used in the calculations. Different values of the melting enthalpy were reported: 39.1 kJ mol^{-1} [22] and 54.3 kJ mol^{-1} [21]. Our own experimental determinations [1i] were carried out on heating and on cooling. Though the value (55.7 kJ mol^{-1}) obtained on heating seems to confirm the value of [21], a reproducible and substantially larger value was obtained upon cooling (64.2 k J mol^{-1}). This difference of about 15%, which does not exist for the other lanthanide chlorides, obtained reproducibly on several heating / cooling cycles is beyond the experimental accuracy. It has already been addressed [1i] and, from the "post-fusion" effect reported by Savin [22], it was concluded that the value of the crystallisation enthalpy had to be preferred in the calculation.

$CeCl_3$

The heat capacity of solid $CeCl_3$ is given by

$$C_{p,s} = 89.05 + 1.790 \cdot 10^{-2} T,$$
$$(300 - 1040\ K)\ [16].$$

The heat capacity of the liquid is reported by Walden [23] as (160 J mol^{-1} K^{-1}). Different values of melting enthalpy were reported: 33.5 kJ mol^{-1} [24] and 53.5 kJ mol^{-1} [25]. Our own experimental determinations [1i] were carried out on heating and on cooling. The value obtained (55.5 kJ mol^{-1}), which is in accordance with that in [25], was used in the calculation.

$NdCl_3$

The heat capacity of solid $NdCl_3$ is given by

$$C_{p,s} = 102.27 + 2.170 \cdot 10^{-2} T,$$
$$(300 - 980\ K)\ [16].$$

Our experimental determination [16] (149.5 J mol^{-1} K^{-1}) used in the following calculation was in agreement with the heat capacity of the liquid (146 J $mol^{-1}K^{-1}$) reported by Dworkin and Breding [21]. Different values of melting enthalpy were reported: 33.5 kJ mol^{-1} [24] and 50.2 kJ mol^{-1} [21]. Our own experimental determinations [1i] were carried out on heating and on cooling. The value obtained (48.1 kJ mol^{-1}) confirms that in [21] and was used here.

Table 3. Experimental and calculated values of formation enthalpy of Rb_3LnCl_6's in the liquid state.

Compound	T/K	$\Delta_{form}H_m(Rb_3LnCl_6, l, T)$ / kJ·mol^{-1} (experimental)	(calculated)
Rb_3LaCl_6	1173	–65.3 [18]	–42.2
Rb_3CeCl_6	1118	–68.2 [19]	–70.8
Rb_3NdCl_6	1122	–68.8 [1c]	–69.5

Table 3 shows the excellent agreement between calculated and experimental enthalpies of formation of liquid Rb_3NdCl_6 and Rb_3CeCl_6. The value calculated for Rb_3LaCl_6 deviates more from the calorimetric result.

Conclusions

No heat capacity data have been previously reported on the 3:1 stoichiometric compounds Rb_3LnCl_6 formed by RbCl and $LnCl_3$ lanthanide chlorides (Ln = La, Ce, Pr, Nd), excepted Seifert's [17] on solid Rb_3LaCl_6, which are in quite good agreement with the results obtained in the present work. The other heat capacity values reported here were obtained for the first time. They were fitted by an equation that provided a satisfactory representation up to the temperature of C_p discontinuity. These heat capacity data were checked for thermodynamic consistency by calculating the enthalpy of Rb_3LaCl_6, Rb_3CeCl_6, and Rb_3NdCl_6 formation in the liquid phase, which had been previously measured. An excellent agreement between calculated and experimental values was found for Rb_3CeCl_6 and Rb_3NdCl_6 while a small discrepancy was observed for Rb_3LaCl_6.

The heat capacity dependence on temperature of the Rb_3LnCl_6 compounds is rather unusual. After compound formation or a solid phase transition, the heat capacity decreases with temperature over about 150 - 200 K, and then increases up to the melting temperature. Structure investigations are planned to explain this phenomenon in more detail and also to identify the lower temperature effect which occurs in Rb_3CeCl_6, Rb_3PrCl_6, and Rb_3NdCl_6. Though the structure of these compounds, investigated by X-ray, has been determined as monoclinic and cubic before and after the phase transition, when it occurs (Pr, Nd), or cubic only when it does not occur (La, Ce), a more detailed characterisation of the structure by neutron diffraction of powder, at several temperatures before and after the characteristic temperature reported in this work is in progress.

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