Thermochimica Acta, 237 (1994) 219–228
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01661-L

The heat capacities of ternary lanthanum chlorides A_nLaCl_{3+n} from 200 to 770 K and the ΔC_p values for their formation from nACl + $LaCl_3$

G. Reuter and H.-J. Seifert *

Inorganic Chemistry FB 19, University Gh Kassel, Heinrich-Plett-Str. 40, 34109 Kassel, Germany

(Received 29 November 1993; accepted 7 December 1993)

Abstract

The heat capacities of the eight existing ternary lanthanum chlorides A_nLaCl_{3+n} (A is K, Rb, Cs) and the four binary chlorides ACl and $LaCl_3$ were determined from 200 to 770 K with a power-compensated differential scanning calorimeter. The results are expressed in polynomials $C_p = a + bT + cT^2$. The measured C_p values were used to form the differences $\Delta C_p = C_p(A_nLaCl_{3+n}) - [nC_p(ACl) + C_p(LaCl_3)]$ by either taking the heat capacities for the single compounds or by direct measurements of samples of the ternary chlorides compared with samples of the binary chlorides with the same composition. All the ΔC_p values proved to be zero and thus confirmed findings from e.m.f. measurements in the temperature range 600–850 K, which yielded temperature-independent enthalpies and entropies for the formation of the ternary chlorides from (nACl + $LaCl_3$).

INTRODUCTION

Our investigations of solid electrolytes using galvanic cells concerning the thermodynamic conditions for the formation of ternary chlorides, especially the chloro-lanthanides [1], according to the general equation

$$n\mathrm{ACl} + \mathrm{LnCl_3} = \mathrm{A}_n\mathrm{LnCl}_{3+n}$$

have revealed that in the temperature range 600–850 K, the formation enthalpies $\Delta_f H^\ominus$ and entropies $\Delta_f S^\ominus$ are temperature independent. The condition for this is $\Delta C_p = 0$, where

$$\Delta C_p = C_p(\mathrm{A}_n\mathrm{LnCl}_{3+n}) - [nC_p(\mathrm{ACl}) + C_p(\mathrm{LnCl_3})]$$

However, in general, the entropies $\Delta_f S^\ominus(A_nLnCl_{3+n})$ themselves are not zero; that is, they must be generated at lower temperatures. Therefore, it is of interest to measure C_p values at low temperatures at which, in a certain range ($T_1 - T_2$), the difference in the C_p's values must become different from zero, so that

---

* Corresponding author.

$$\Delta_f S^\ominus = \int_{T_1}^{T_2} \Delta C_p \, \mathrm{d} \ln T$$

Experience has shown that such measurements from 0 to 200 K should be made with adiabatic calorimeters. At higher temperatures, the more convenient DSC method can be used.

In this paper, measurements with a Perkin-Elmer DSC7 on ternary chlorides of lanthanum, A_nLaCl_{3+n} (A is K, Rb and Cs) are described. From these and the similarly measured values for ACl and $LaCl_3$, the ΔC_p values could be calculated. In addition, experiments were performed for a direct determination of ΔC_p, replacing the reference sample with a mixture of $(n\mathrm{ACl} + \mathrm{LaCl_3})$ of the same mass and composition as A_nLaCl_{3+n}. These experiments were made in order to minimize the succession of errors that result from a calculation of the difference of three independently measured C_p values.

THE SYSTEMS $ACl/LaCl_3$ (A is K, Rb, Cs)

We investigated the $LaCl_3$ systems in 1985 [2]. All experimental descriptions can be taken from this earlier paper. For the present compounds, the following thermodynamic functions for their formation from ACl and $LaCl_3$, given as Gibbs–Helmholtz relations $\Delta_f G^\ominus = \Delta_f H^\ominus - T\Delta_f S^\ominus$, were found. In addition, the formation enthalpies measured by solution calorimetry at 298 K are given. (Corrections made during the present investigation are marked with an asterisk.)

$KCl/LaCl_3$ system

$K_{0.6}LaCl_{3.6}$: melts incongruently at 885 K. Stable >297 K.

$\Delta_f G^\ominus/\mathrm{kJ\,mol^{-1}} = -5.3 - 0.0094T/\mathrm{K}$;

$\Delta_f H^\ominus(\mathrm{calor.}) = -6.8\ \mathrm{kJ\,mol^{-1}}$.

K_2LaCl_5: melts congruently at 913 K. Stable at all temperatures.

$\Delta_f G^\ominus/\mathrm{kJ\,mol^{-1}} = -22.5 - 0.0151T/\mathrm{K}$;

$\Delta_f H^\ominus(\mathrm{calor.}) = -24.5\ \mathrm{kJ\,mol^{-1}}$.

$RbCl/LaCl_3$ system

$Rb_{0.5}LaCl_{3.5}$: melts incongruently at 902 K. Phase transition at 703 K. Stable >595 K.

(*) $\Delta_f G^\ominus/\mathrm{kJ\,mol^{-1}} = -2.2 - 0.0127T/\mathrm{K}$;

$\Delta_f H^\ominus(\mathrm{calor.}) = -1.5\ \mathrm{kJ\,mol^{-1}}$.

Rb_2LaCl_5: melts incongruently at 806 K. Stable at all temperatures.

$\Delta_f G^\ominus/\mathrm{kJ\,mol^{-1}} = -31.4 - 0.0127T/\mathrm{K}$;

$\Delta_f H^\ominus(\mathrm{calor.}) = -33.3\ \mathrm{kJ\,mol^{-1}}$.

Rb_3LaCl_6: melts congruently at 989 K. Stable >717 K.

(*) $\Delta_f G^\ominus/\mathrm{kJ\,mol^{-1}} = 13.5 - 0.0790T/\mathrm{K}$.

CsCl/LaCl₃ system

$Cs_{0.5}LaCl_{3.5}$: melts incongruently at 975 K.

(*) $\Delta_f H^\ominus(\mathrm{calor.}) = -6.7\ \mathrm{kJ\,mol^{-1}}$.

Cs_2LaCl_5: decomposition at 790 K.

$\Delta_f H^\ominus(\mathrm{calor.}) = -33.3\ \mathrm{kJ\,mol^{-1}}$.

Cs_3LaCl_6: melts congruently at 1053 K. Phase transition at 674 K.

$\Delta_f H^\ominus(\mathrm{calor.}) = -14.8\ \mathrm{kJ\,mol^{-1}}$.

For the reaction: $CsCl + Cs_2LaCl_5 = \text{D-}Cs_3LaCl_6$ [3]:

$\Delta_r G^\ominus/\mathrm{kJ\,mol^{-1}} = 24.8 - 0.0537T/\mathrm{K}$; D-$Cs_3LaCl_6$ is stable >462 K;.

For H-Cs_3LaCl_6: $\Delta_r G^\ominus/\mathrm{kJ\,mol^{-1}} = 34.9 - 0.0691T/\mathrm{K}$.

The transition enthalpy is 10.1 kJ mol^{-1}, the entropy 15.4 J K^{-1} mol^{-1}.
An enthalpy of 7.84(6) kJ mol^{-1} was determined by DSC measurements [4].

EXPERIMENTAL

The heat capacity measurements were made with a Perkin-Elmer DSC7 differential scanning calorimeter. The investigated compounds, eight ternary chlorides, three alkali metal chlorides and $LaCl_3$, of mass between 60 and 150 mg, were each pressed in Al pans with approx. 60 kN. (It has been shown that the use of pressed discs yields better values than measurements with powders, because of a more homogeneous heat transfer in the sample.) To avoid a pan correction, about one hundred pans with lids with a maximum weight difference of 0.08 mg were chosen. At least five samples were prepared for each compound. The measuring cell was purged with dried nitrogen flowing at a rate of 14 ml min^{-1}.

Measurements below 320 K were performed with a low-temperature measuring cell, which was cooled with liquid nitrogen via a cryostat. To avoid the condensation of moisture below 298 K, a dry box was mounted on the DSC7, which was purged with dried nitrogen (water content, approx. 10 ppm).

For the determination of the heat capacity and its dependence on temperature, sapphire discs were used as the calibration material, according to the NBS certificate, standard reference material 720 [5].

RESULTS OF THE C_p MEASUREMENTS

For the measurements the 'scanning method' [6] was used, which allows determination of specific heats at individual temperatures in a heating region of ≈150 K. Three scans, empty, standard, and specimen, are required to determine the heat capacity. The empty scan is subtracted from both the standard and the specimen scan, giving the net displacements D. The specific heat capacity is then

$$C_{\text{samp}} = (m_{\text{std}}/m_{\text{samp}})(D_{\text{samp}}/D_{\text{std}})C_{\text{std}}$$

The temperature range from 140 to 770 K was divided into six overlapping sections, so that six series of measurements were made: Series 1, 140–290 K; Series 2, 220–370 K; Series 3, 320–470 K; Series 4, 420–570 K; Series 5, 520–670 K; Series 6, 620–770 K. All measurements were performed using the same temperature programming: 3 min isothermal start, followed by heating at a rate of 10 K min^{-1} to the final temperature; then 3 min isothermal heating terminates the scan. At least 7 independent measurements were made for each compound, accompanied by two measurements of the baseline (empty pans with lids) and 2 calibration measurements with sapphire as standard.

According to Poessnecker [7], it is important for the quality of C_p measurements with the scanning method that for the subtraction procedure one uses only baselines that show sufficiently small deviations in their end isotherms compared with the sample scan. This was ensured by processing the results of all the measurements of a series with the table-calculation program Microsoft Exel 4.0 [8]. Rejecting all combinations with deviations of more than 7% of the sample signal, at least five measurements remained for each compound. The average values of these data sets for all the series were fitted with polynomials $C_p = a + bT + cT^2$ by the method of least-squares using the program Mathematica [9]. They are listed in Table 1 together with the standard deviations of the coefficients, in parentheses.

To estimate the reliability of the results, the averages of the standard deviations of the measurements for one compound in each temperature range were calculated. They are given as the relative standard deviation of the measured heat capacity for each compound in Table 2. The reliability range of 0.9–2.3% is in good agreement with those found by other authors using DSC measurements. Figure 1 shows the polynomials and averages of the measured heat capacities for RbCl, $LaCl_3$ and Rb_2LaCl_5.

TABLE 1

Coefficients of the polynomials $C_p = a + bT + cT^2$

Compound	a/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	b/ ($\mathrm{J\,mol^{-1}\,K^{-2}}$)	$c \times 10^{-4}$/ ($\mathrm{J\,mol^{-1}\,K^{-3}}$)	Temperature range in K
KCl	47.29 (2)	0.01420 (5)		200–770
RbCl	48.59 (2)	0.01333 (3)		200–770
CsCl	47.22 (1)	0.01684 (3)		200–660
$LaCl_3$	83.9 (1)	0.0538 (5)	−0.279 (5)	200–770
K_2LaCl_5	174.7 (1)	0.1052 (6)	−0.527 (7)	200–770
$K_3La_5Cl_{18}$	531.7 (4)	0.472 (2)	−3.22 (2)	200–770
Rb_3LaCl_6	230.3 (3)	0.097 (2)	−0.46 (2)	200–530
Rb_2LaCl_5	176.4 (1)	0.0891 (6)	−0.313 (6)	200–770
$RbLa_2Cl_7$	208.3 (3)	0.168 (2)	−1.24 (2)	200–710
Cs_3LaCl_6	214.8 (4)	0.161 (2)	−0.82 (3)	200–600
Cs_2LaCl_5	171.7 (2)	0.128 (1)	−0.76 (1)	200–750
$CsLa_2Cl_7$	216.4 (2)	0.112 (1)	−0.40 (1)	200–670

Comparing the polynomials for the specific heat capacities of the binary compounds with values measured by adiabatic calorimeters at low temperatures [10–12], a difference occurs at 200 K which becomes more marked at lower temperatures. Therefore, the lower limit of the temperature range valid for the polynomials has to be set at 200 K. The difference between the polynomial and the values measured by Sommers and Westrum [10] for $LaCl_3$ is the greatest; this is depicted in Fig. 2 together with the estimated polynomial of Barin and Knacke [13].

The differences $\Delta C_p = C_p(A_n LnCl_{3+n}) - [nC_p(ACl) + C_p(LnCl_3)]$ were determined from both the polynomials and from the single C_p values. They

TABLE 2

Relative standard deviations of the specific heat capacities in the different temperature ranges

Compound	Series 1	Series 2	Series 3	Series 4	Series 5	Series 6
KCl	1.52%	1.34%	0.83%	1.25%	1.34%	1.51%
RbCl	1.51%	1.35%	0.91%	1.27%	1.36%	1.82%
CsCl	1.52%	1.33%	0.89%	1.23%	1.34%	–
$LaCl_3$	1.69%	1.47%	1.08%	1.42%	1.48%	2.14%
K_2LaCl_5	1.61%	1.39%	1.05%	1.35%	1.42%	1.74%
$K_3La_5Cl_{18}$	1.58%	1.38%	0.98%	1.32%	1.38%	1.99%
Rb_3LaCl_6	1.64%	1.39%	1.01%	1.33%	–	–
Rb_2LaCl_5	1.62%	1.41%	1.04%	1.36%	1.41%	1.65%
$RbLa_2Cl_7$	1.59%	1.45%	1.04%	1.34%	1.51%	2.30%
Cs_3LaCl_6	1.60%	1.39%	0.99%	1.31%	1.38%	–
Cs_2LaCl_5	1.63%	1.41%	1.02%	1.45%	1.42%	1.74%
$CsLa_2Cl_7$	1.58%	1.40%	1.01%	1.36%	1.39%	1.86%

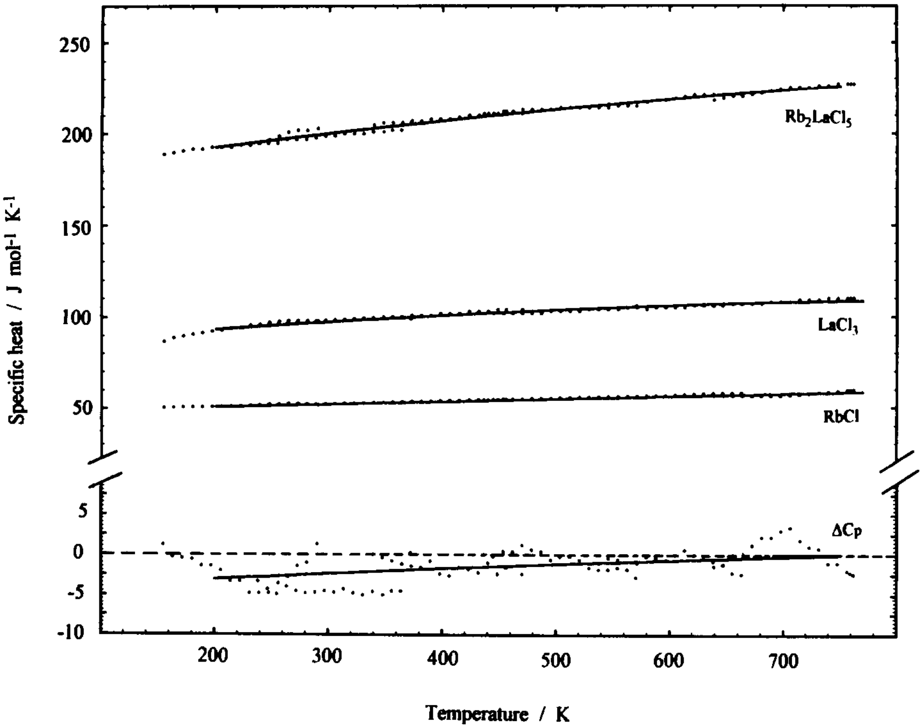

Fig. 1. Experimental values and polynomials for C_p of RbCl, Rb_2LaCl_7 and $LaCl_3$, and the calculated ΔC_p values.

are given for the example mentioned above in the lower part of Fig. 1. It can be seen that ΔC_p differs from zero by not more than 5 J mol^{-1} K^{-1}. The experimental deviation in each case is less than 2.5% of the specific heat capacity of the ternary compound. As a criterion for the greatest possible deviation from zero, the additive errors for the calculation of ΔC_p from the heat capacities of the two binary compounds and the ternary compounds were taken. This is a maximum of 2.8% of the specific heat capacity of Rb_2LaCl_5 in the temperature range (Series 1). With this criterion, i.e. $\Delta C_p <$ additive errors, ΔC_p is zero over the whole temperature range.

Table 3 lists the calculated additive errors for all eight ternary chlorides. It can be seen that under the conditions applied, their ΔC_p values are also zero.

DIRECT MEASUREMENTS OF ΔC_p VALUES

To avoid the additive errors described above, it was attempted to measure ΔC_p directly. For this purpose, the twin construction of the measuring cell was utilized; the sample pan was charged with the ternary compound, and the reference cell with discs of the binary compounds with the same mass and composition. For $\Delta C_p = 0$, the measured curves should

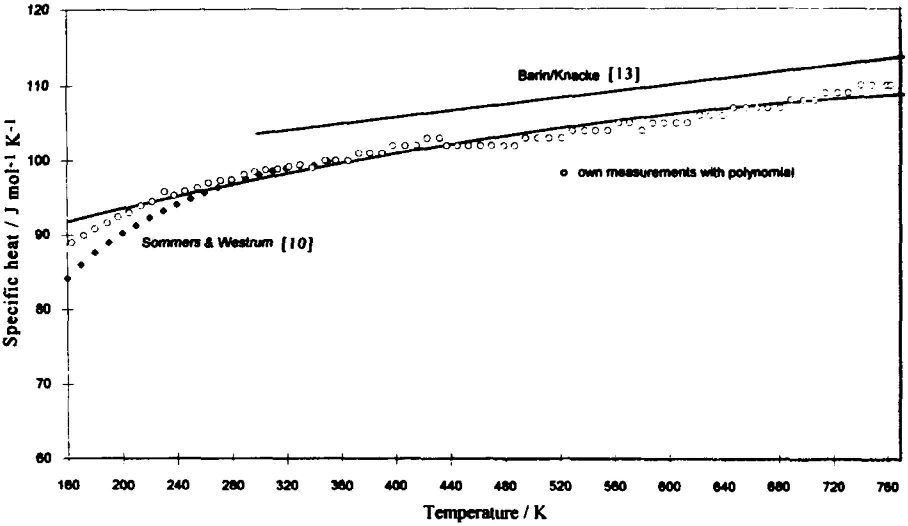

Fig. 2. Specific heat capacities of $LaCl_3$ measured in this work compared with those in the literature [10, 13].

not deviate from a baseline measured under the same conditions. The criterion for the accuracy of ΔC_p is given by the reliability of the baselines.

Our own investigations have shown that mixtures of alkali metal chlorides and $LaCl_3$ react with one another when being compressed, especially when they were heated afterwards. Therefore, it was necessary to separate the binary compounds. This was achieved by the preparation of two independent sample discs in individual pans, which were stacked in the measuring cell. To compensate for the additional heat transfer from one pan to the other and to maintain the equivalence of the masses, an empty crucible was placed on the disc of the ternary compound. The baselines were measured with two empty crucibles in each measuring cell stacked in the same way.

TABLE 3

Additive error for the calculation of ΔC_p

Compounds	Series 1	Series 2	Series 3	Series 4	Series 5	Series 6
K_2LaCl_5 vs. $KCl/LaCl_3$	2.79%	2.42%	1.72%	2.32%	2.50%	3.14%
$K_3La_5Cl_{18}$ vs. $KCl/LaCl_3$	2.78%	2.42%	1.68%	2.32%	2.42%	3.29%
Rb_3LaCl_6 vs. $RbCl/LaCl_3$	2.79%	2.42%	1.74%	2.32%	–	–
Rb_2LaCl_5 vs. $RbCl/LaCl_3$	2.79%	2.43%	1.75%	2.34%	2.45%	3.26%
$RbLa_2Cl_7$ vs. $RbCl/LaCl_3$	2.78%	2.42%	1.75%	2.33%	2.51%	3.36%
Cs_3LaCl_6 vs. $CsCl/LaCl_3$	2.79%	2.42%	1.70%	2.29%	2.42%	–
Cs_2LaCl_5 vs. $CsCl/LaCl_3$	2.79%	2.42%	1.72%	2.37%	2.45%	–
$CsLa_2Cl_7$ vs. $CsCl/LaCl_3$	2.78%	2.42%	1.72%	2.32%	2.43%	–

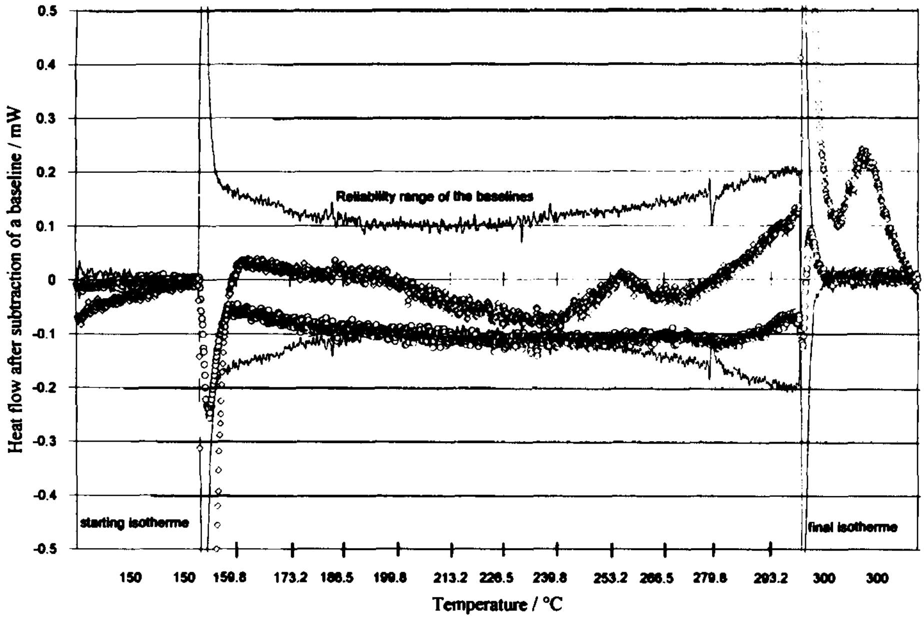

Fig. 3. Directly measured ΔC_p values of Cs_3LaCl_6 from 150 to 300°C.

It is most important to ensure that the masses and stoichiometry of both specimens correlate as closely as possible. This was accomplished by the following preparation technique. Again, pairs of pans + lids were selected that had weight differences smaller than 0.8 mg between each pair. The calculated masses of the single compounds were weighed within the error range of the semi-micro balance used (0.05 mg). The crucibles were prepared as described above. Thus the masses of the pairs (ACl/$LaCl_3$ and A_nLaCl_{3+n}/empty) were controlled. Only pairs with differences below 0.1 mg were used for the measurements.

The ΔC_p measurements were performed in the same temperature ranges and with the same heating program as for the C_p measurements. A baseline scan with four empty crucibles (one pair in the sample cell and the other pair in the reference cell) was followed by a simple scan. A second sample scan was performed after replacing sample and reference. This was done for each ternary chloride. Thus 8 baselines and two ΔC_p scans were available for analysis.

The reliability of the baselines was determined by subtracting the two baselines with the greatest deviation in the final isotherms from each other. A further evaluation of the measured curves was made as described above. Figure 3 shows the result of this procedure in temperature range 2 for the example Cs_3LaCl_6 vs. CsCl and $LaCl_3$. All measurements yielded ΔC_p values that are smaller than the reliability margin of the baselines. Thus, the ΔC_p values are again zero.

To estimate the error margin in comparison with the additive errors described in the previous section, the ordinate signal (heat flow rate) of an ordinary C_p measurement was used. This is about 10 mW when measuring samples with masses above 100 mg. The error margin of ≈ 0.1 mW is approx. 1% of the heat capacity of a ternary compound. With this assumption the errors in the individual temperature ranges can be defined as follows: Series 1, 4%; Series 2, 1%; Series 3, 1.5%; Series 4, 1.7%; and Series 5, 6%. In Series 2–4, the error range is smaller than that from the additive errors of single measurements: for these series the determination of ΔC_p is improved. In the other temperature ranges, the error is greater than the additive errors. This may be because the asymmetry between the sample and measuring cell becomes more marked; thus, an additional heat transfer results. The results of these temperature ranges were rejected.

DISCUSSION

The result of the described investigations is that in the temperature range from 200 to 770 K, ΔC_p is zero for all known chloro-lanthanides. This has two consequences:

(i) The temperature dependances of $\Delta_f H^\ominus$ and $\Delta_f S^\ominus$, found by e.m.f. measurements in the temperature range ≈ 550–850 K, is present down to 200 K.

(ii) The generation of entropy combined with the formation reaction from nACl + $LaCl_3$ must occur at temperatures below 200 K.

These conclusions are valid in the limits given by the accuracy of the ΔC_p measurements. Taking the most unfavourable situation, arising from the error ranges valid in the individual series, we can estimate the maximum possible gain in entropy with the formula

$$\Delta_f S^\ominus = \int_{T_1}^{T_2} \Delta C_p \,\mathrm{d}\ln T$$

The range of possible reaction entropies calculated in this way lies between 4.5 and 6.5 J mol^{-1} K^{-1}, for the measurements of individual specific heats, and between 3.0 and 4.5 entropy units using the directly measured ΔC_p values from Series 2–4. The maximal temperature range for these estimations lies between 200 and 660 K. From e.m.f. measurements for Cs_3LaCl_6 and Rb_3LaCl_6, $\Delta_f S^\ominus$ values of 53.7 and 83.0 J mol^{-1} K^{-1} were found, compared with 10–15 J mol^{-1} K^{-1} for the other compounds.

Thus, the 3:1 compounds are most suitable for C_p measurements from 0 to 200 K with adiabatic calorimeters. Both types of compounds are metastable at ambient or lower temperatures. Cs_3LaCl_6 is formed above 462 K but does not decompose when cooled, for kinetic reasons; it is not possible to decompose the compound by quenching at lower temperatures. In contrast, Rb_3LaCl_6 is formed at 717 K and can be kept metastable at ambient temperatures by quenching. When heated, the exothermic decomposition occurs at ≈530 K. Thus, a special kind of ΔC_p determination was applied, derived from an idea of Harmelin and Jiang [14]. Two pans with the same mass of Rb_3LaCl_6 were measured against each other from 330 to 500 K to obtain a baseline. The compound in one of the pans was decomposed by annealing at ≈650 K. A further measurement thus yielded ΔC_p. Under the conditions of the error ranges described above, ΔC_p was zero once again. Finally, a measurement of the reaction enthalpy of formation from the neighbouring compounds Rb_2LaCl_5 and RbCl was made. Calibration was performed according to the GEFTA proposals [15]. The results at 725 K were $\Delta_r H^\ominus = 47.5(5)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_r S^\ominus = 65.5(6)\ \mathrm{J\ mol^{-1}\ K^{-1}}$. These values agree very well with the results of e.m.f. measurements with an RbCl cell versus 30 mol% $LaCl_3$ (the mean of four measurements performed recently): $\Delta_r H^\ominus_{717} = 47.5(6)\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_r S^\ominus_{717} = 66.3(8)\ \mathrm{J\ mol^{-1}\ K^{-1}}$.

It must be pointed out that the reaction temperature measured by dynamic methods is a ‘kinetic temperature’ and in heating experiments falls above the equilibrium temperature found from e.m.f. measurements [16].

ACKNOWLEDGEMENTS

G.R. is grateful for a grant from the Otto Braun Stiftung. Support from the Deutsche Forschungsgemeinschaft (DFG) and the Fonds der Chemischen Industrie is gratefully acknowledged.

REFERENCES

1 H.-J. Seifert, J. Sandrock and G. Thiel, Z. Anorg. Allg. Chem., 598/599 (1991) 307.
2 H.-J. Seifert, H. Fink and G. Thiel, J. Less-Common Met., 110 (1985) 139.
3 H.-J. Seifert, H. Fink and B. Baumgartner, J. Solid State Chem., 106 (1993) 19.
4 G. Friedrich, H. Fink and H.-J. Seifert, Thermochim. Acta, 234 (1994) 287.
5 NATIONAL BUREAU of STANDARDS, Certificate: Standard Reference Material 720, Synthetic Sapphire, Washington, 1982.
6 J.E. Callanan and S. A. Sullivan, Rev. Sci. Instrum., 57 (1986) 2584.
7 W. Poessnecker, J. Therm. Anal., 36 (1990) 1123.
8 MICROSOFT EXCEL 4.0®, (Tabellenkalkulation) Microsoft Geschäftsstelle Deutschland, Munich, 1992.
9 S. Wolfram, MATHEMATICA PC Vers. 2.2.1®, 1993.
10 J.A. Sommers and E.F. Westrum, J. Chem. Thermodyn., 8 (1976) 1115.
11 A.R. Taylor, T.E. Gardner and D.F. Smith, Bull. U.S. Bur. Mines (1963) RI 6157.
12 W.T. Berg and J.A. Morrison, Proc. R. Soc. London Ser. A, 242 (1957) 467.
13 I. Barin and O. Knacke, Thermodynamical Properties of Inorganic Compounds, Springer-Verlag, Berlin, 2 (1973) XXXIII.
14 M. Harmelin and J. Jiang, Thermochim. Acta, 162 (1990) 453.
15 H.K. Cammenga, W. Eysel, E. Gmelin, W. Hemminger, G.W.H. Höhne and S. Sarge, Thermochim. Acta, 219 (1993) 333.
16 H.-J. Seifert, J. Therm. Anal., 35 (1989) 1879.