

Heat capacity of LaCl_3 , CeCl_3 , PrCl_3 , NdCl_3 , GdCl_3 , DyCl_3

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Received 14 July 1995; in final form 11 September 1995

Abstract

Heat capacities of LaCl_3 , CeCl_3 , PrCl_3 , NdCl_3 , GdCl_3 , DyCl_3 have been measured by differential scanning calorimetry in the temperature range from 300 K to melting temperatures of the compounds. Heat capacities of liquid PrCl_3 , NdCl_3 , GdCl_3 , DyCl_3 have also been registered. These results have been compared with literature data and fitted by a linear temperature dependence. The temperature coefficients have been given.

Keywords: Lanthanide chlorides; Heat capacity; Differential scanning calorimetry

1. Introduction

Lanthanide chlorides may be used as substrates in lanthanide metal production [1,2]. The physicochemical properties of these substances are the subject of our interest from the viewpoint of technological equilibria calculations as well as from the viewpoint of systematising the original thermochemical information. Related literature data are often contradictory. For instance, the melting enthalpy of NdCl_3 has been reported as 50.2 [3] or 33.5 [4] kJ mol^{-1} and the melting enthalpy of CeCl_3 as 53.6 [5] and 33.5 [4] kJ mol^{-1} . The same is true for the heat capacity. The heat capacity of the liquid LaCl_3 is given in the literature as 349.8 $\text{kJ mol}^{-1} \text{K}^{-1}$ [6] or as 158 $\text{kJ mol}^{-1} \text{K}^{-1}$ [7].

A general research program of the thermodynamic and transport properties of lanthanide halides and their melts with alkali metal halides is the subject of collaboration between the Technical University of Wrocław and the University of Provence (IUSTI) [8–11]. The present work continues this program. It presents results of specific heat capacity measurements of the pure lanthanide chlorides LaCl_3 , CeCl_3 , PrCl_3 , NdCl_3 , GdCl_3 and DyCl_3 performed with a SETARAM DSC 121 differential scanning microcalorimeter. The results are compared with original

data [12–14] and some literature estimations [7,15,16]. Sometimes, like in the case of popular JANAF Thermochemical Tables [17], these original data are not given.

2. Experimental

2.1. Sample preparation

The lanthanide chlorides studied have been prepared from oxides of 99.9% purity supplied by 'Hydro-Met' Kowary, Poland (La_2O_3 , CeO_2 , Pr_4O_{11}), by the Chemistry Department of the Lublin University, Poland (Nd_2O_3) and by Merck (Gd_2O_3 , Dy_2O_3). The synthesis included the following steps:

- dissolution of the oxide in hot concentrated hydrochloric acid;
- crystallisation of the hydrate $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$;
- partial dehydration of the $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ to $\text{LnCl}_3 \cdot \text{H}_2\text{O}$;
- final dehydration and distillation to form pure LnCl_3 .

Owing to the resistance of CeO_2 to acids a different first synthesis step for this compound was adopted. It involved gradual heating of the mixture of CeO_2 and concentrated sulphuric acid to the solid residue. The residue was the cerium sulphate $\text{Ce}_2(\text{SO}_4)_3$. This was dissolved in cold water, then $\text{Ce}(\text{OH})_3$ was precipi-

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tated with NH_4OH . The precipitate was filtered and washed with water to remove sulphate ions. $\text{Ce}(\text{OH})_3$ was dissolved in concentrated hydrochloric acid, then the next steps of the synthesis procedure were performed.

Before the final dehydration $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ had been mixed with NH_4Cl (10 wt.%) and heated up to 450 K over 12 h under reduced (300 Pa) pressure. The product (a mixture of $\text{LnCl}_3 \cdot \text{H}_2\text{O}$ and NH_4Cl) was put into an alumina crucible placed inside a quartz tube and heated under gaseous HCl up to 100 K above the melting temperature of the pure anhydrous salt. The excess HCl was removed by argon. As this product was contaminated by oxychloride, LnOCl , the dehydration was followed by double distillation of the crude LnCl_3 from the less volatile residue (mainly LnOCl). Details of the distillation procedure have been described elsewhere [10]. All handling of the prepared LnCl_3 was performed in a dry-box under argon. This method of LnCl_3 preparation leads to products of the same 99.9% quality as initial oxides.

2.2. Differential scanning calorimeter (DSC)

Heat capacity measurements were carried out with a SETARAM DSC (DSC 121). As more precise information on the applied method for C_p measurements is often necessary for better evaluation of the quality of results, some basic features are presented below in the form provided by the SETARAM documentation.

The measuring part of the apparatus contains two Inconel tubes, a reference tube and an operating tube surrounded by the thermal fluxmeters, located inside a silver block. Linear increase or decrease of the temperature of the Inconel tubes is computer controlled by the equipment. Fluxmeters are connected in opposition, enabling measurement of the thermal imbalance between the tubes. Two correlated runs of the heat capacity measurements in the same conditions should be performed—one with the investigated sample in its container and the second with the container only (the reference should be the same). The difference between these two runs gives the ‘pure’ heat capacity of the investigated sample.

Usually the ‘scanning method’ is used for the heat capacity measurements performed by DSC [18]. Three runs of the heat flux are recorded during heating. The first is made with the empty container, the second with the container and the sample, and the third with the container and the standard substance (e.g. sapphire), all of them against the same reference. The difference between the heat flows of the second and the first runs is compared with the difference between the heat flows of the third and the first runs and simple

recalculation gives the heat capacity of the investigated sample:

$$\frac{C_{p_{\text{sample}}}}{C_{p_{\text{standard}}}} = \frac{m_{\text{standard}}}{m_{\text{sample}}} \frac{D_{\text{sample}}}{D_{\text{standard}}} \quad (1)$$

where $C_{p_{\text{sample}}}$, $C_{p_{\text{standard}}}$ are the heat capacities of the sample and the standard, D_{sample} , D_{standard} are the differences between the heat flows obtained for the sample and for the standard and m_{sample} , m_{standard} are the masses of the sample and the standard.

In the case of the ‘scanning method’, the investigated sample is not in thermal equilibrium.

SETARAM [19] has developed another method—the ‘step method’. In this method the small heating steps are followed by isothermal delays. During these delays a thermal equilibrium of the sample is achieved. Two correlated experiments should be carried out with this method to determine the heat capacity of the sample. The first one with two empty cells (containers) of the same masses and the second with the same cells but one of them (operating) should contain the sample. The heat flux as a function of time and temperature is recorded for the both runs (Fig. 1). The surface between curve 1 (empty cells) and curve 2 (one cell with the sample and second cell as reference) is proportional to the amount of heat necessary to increase the temperature of the sample by ΔT_i . Therefore, the value of the heat capacity of the sample is equal to

$$C_p = \frac{Q_i}{\Delta T_i} \quad (2)$$

The same conditions for both experiments (i.e. starting temperature, temperature increment and isothermal delay) are required. All necessary calculations, especially calculations of the heat capacities, are performed by the original SETARAM program. The apparatus is calibrated by the Joule effect.

Some test measurements with NBS Standard Refer-

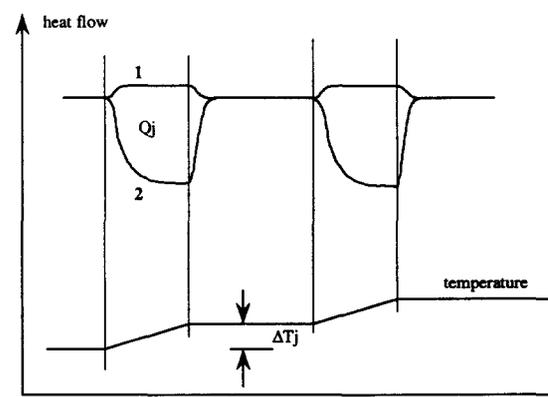


Fig. 1. The heat flux as a function of time for the ‘step method’ (see text).

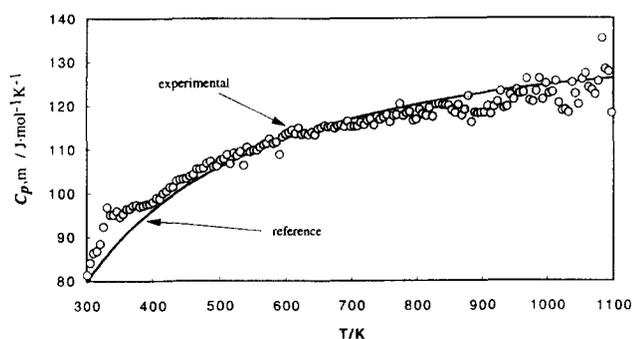


Fig. 2. Comparison of the values of the heat capacities of $\alpha\text{-Al}_2\text{O}_3$, recorded with SETARAM DSC 121 with original reference data [20].

ence Material 720 $\alpha\text{-Al}_2\text{O}_3$ had been carried out before the investigations of the lanthanide chlorides were started. Results of the heat capacity measurement of the Al_2O_3 standard and a comparison with the reference values [20] are presented in Fig. 2. According to this test the method may be considered as suitable. There are only two rather significant deviations from a good fitting of the C_p curve to the reference. The first one is a decrease of the single measurement precision at the highest temperatures (but the mean value may be acceptable). The second effect appears at temperatures from ambient to 370–380 K. This latter irregularity should be ascribed to vaporisation processes from the surface of the cells (especially quartz cells). Its character depends on the cell preparation, and sometimes it is very difficult to avoid these effects.

2.3. Measurements

Quartz cells of 7 mm diameter and 15 mm length were filled with the lanthanide chlorides in a dry-box under an argon atmosphere (the H_2O content in the atmosphere of the box was less than 1.5 vppm). The cells were sealed under vacuum and then placed into the DSC 121 calorimeter. Measurements were performed by the 'step method'—each heating step of 5 K was followed by an isothermal delay of 400 s. The heating rate was 1.5 K min^{-1} . All experiments were started at 300 K and were performed up to 1100 K. Differences between masses of the quartz cells in a particular experiment did not exceed 1 mg (masses of the cells varying from 400 to 500 mg).

3. Results

We presented very recently [21] some preliminary results of the heat capacity measurements of the

LaCl_3 , CeCl_3 , PrCl_3 and NdCl_3 . We have repeated these measurements and the final data, together with the data for the GdCl_3 and DyCl_3 compounds are presented in this paper.

3.1. LaCl_3

Our experimental results are presented in Fig. 3, together with existing literature data [12,14] and estimations [7,15,16] in the form of the molar heat capacity dependence on temperature. They can be well fitted by a simple linear temperature dependence. The corresponding coefficients are given in Table 1 together with the standard error of estimation. Our C_p values are somewhat lower than those estimated by Pankratz [7] and Knacke et al., [16] (both give the same values of the heat capacity) and exhibit different slope for temperature dependence in comparison with the estimation of Barin and Knacke [15]. For temperatures higher than 400 K our data are in a good agreement with the experimental results of Reuter and Seifert [14] (also obtained by DSC for the temperature range 200–770 K), although the data obtained from adiabatic calorimetry measurements of Sommers and Westrum [12] are slightly higher (about $4 \text{ J mol}^{-1} \text{ K}^{-1}$) in the temperature range from 300–350 K. The heat capacities measured by Sommers and Westrum [12] are in a very good agreement with the results of Reuter and Seifert [14]. The heat capacity of the liquid LaCl_3 is equal to $125.7 \text{ J mol}^{-1} \text{ K}^{-1}$ according to Barin and Knacke [15] and $158 \text{ J mol}^{-1} \text{ K}^{-1}$ according to the original measurements of Dworkin and Bredig [3] as well as Knacke et al. [16]. The highest value of the heat capacity of liquid LaCl_3 is given by Savin et al. [6], $349.8 \text{ J mol}^{-1} \text{ K}^{-1}$, in the temperature range 1135–1180 K. Unfortunately, we could not do measurements for liquid LaCl_3 because of limitations of the apparatus.

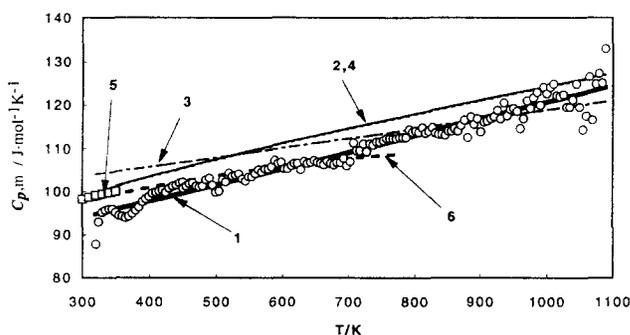


Fig. 3. Molar heat capacity of the LaCl_3 , \circ , experimental values; (1) linear fitting of the experimental values (Table 1); (2) estimation of Pankratz [7]; (3) estimation of Barin and Knacke [15]; (4) estimation of Knacke et al. [16]; (5) data of Sommers and Westrum [12]; (6) data of Reuter and Seifert [14].

Table 1

Coefficients of the linear fitting of the experimental data for LnCl_3 compounds according to equation $C_{p,m} (\text{J mol}^{-1} \text{K}^{-1}) = a + bT$: SE, standard error of estimation; (s) solid; (l) liquid

Compound	Temperature range (K)	<i>a</i>	<i>b</i>	SE
LaCl_3 (s)	300–1100	82.51	3.816×10^{-2}	2.01
CeCl_3 (s)	300–1040	89.05	1.790×10^{-2}	1.10
PrCl_3 (s)	300–1000	91.32	3.459×10^{-2}	1.11
PrCl_3 (l)	1068–1090	155.28	—	1.24
NdCl_3 (s)	300–980	102.27	2.170×10^{-2}	1.71
NdCl_3 (l)	1035–1090	149.53	—	2.39
GdCl_3 (s)	300–770	95.29	1.584×10^{-2}	1.51
GdCl_3 (l)	880–970	139.89	—	1.14
DyCl_3 (s)	300–610; 635–860	98.65	1.102×10^{-2}	3.6
DyCl_3 (l)	935–960	159.43	—	1.35

3.2. CeCl_3

The dependence of the heat capacity of CeCl_3 on temperature calculated from the equation given by Pankratz [7] (whose estimations were based on the drop calorimetry measurements of Walden and Smith [5]) is rather unusual and differs significantly from our results (Fig. 4). Surprisingly, the values of Pankratz [7] are reproduced by the estimation of Knacke et al. [16] even if the earlier compilation of Barin and Knacke [15] gives a more reliable dependence (curve 3 in Fig. 4). The difference between our experimental results and the values of Barin and Knacke [15] does not exceed 4% in the entire temperature range of the measurements. The heat capacity of the liquid CeCl_3 is reported in the literature as $160 \text{ J mol}^{-1} \text{ K}^{-1}$ [5,7,16,22]. We could not measure the heat capacity of the liquid phase of this compound either.

3.3. PrCl_3

The heat capacity of PrCl_3 was measured by Sommers and Westrum [12] with an adiabatic calorimeter in the temperature range from 5 to 350 K. Dworkin and Bredig [3] reported values of the heat capacities of

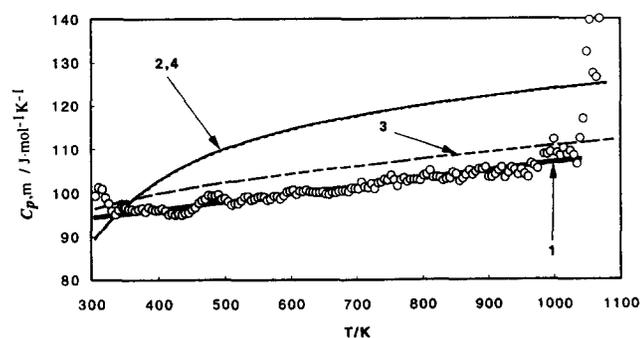


Fig. 4. Molar heat capacity of the CeCl_3 . \circ , experimental values; (1) linear fitting of the experimental values (Table 1); (2) estimation of Pankratz [7]; (3) estimation of Barin and Knacke [15]; (4) estimation of Knacke et al. [16].

solid ($135 \text{ J mol}^{-1} \text{ K}^{-1}$) and liquid ($134 \text{ J mol}^{-1} \text{ K}^{-1}$) PrCl_3 at the melting temperature of 1059 K obtained on the basis of enthalpy measurements. Using these data Pankratz [7] estimated heat capacities of the solid PrCl_3 in the temperature range from 298 to 1059 K. Exactly the same estimation was given by Knacke et al. [16], and almost the same by Barin and Knacke [15]. Fig. 5 presents our experimental results, these estimations and the literature data of Sommers and Westrum [12]. All of them are in a very good agreement at low temperatures. At temperatures close to 1000 K our results are about 6% lower than the literature estimations. We have also measured the heat capacity of the liquid PrCl_3 in a small temperature range from 1068 to 1090 K and evaluated its value as $155 \text{ J mol}^{-1} \text{ K}^{-1}$. According to Savin [6] the specific heat capacity of liquid PrCl_3 is equal to $180.2 \text{ J mol}^{-1} \text{ K}^{-1}$, and according to the above estimations [7,15,16] equals $134 \text{ J mol}^{-1} \text{ K}^{-1}$ (the value of Dworkin and Bredig [3]).

3.4. NdCl_3

Similarly to PrCl_3 , the heat capacity of the NdCl_3 was measured by Sommers and Westrum [12] with an adiabatic calorimeter in the same temperature range

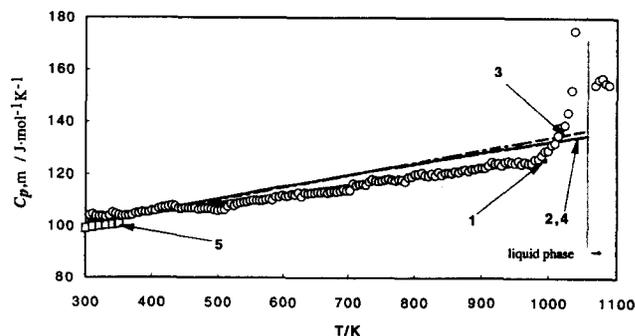


Fig. 5. Molar heat capacity of the PrCl_3 . \circ , experimental values; (1) linear fitting of the experimental values (Table 1); (2) estimation of Pankratz [7]; (3) estimation of Barin and Knacke [15]; (4) estimation of Knacke et al. [16]; (5) data of Sommers and Westrum [12].

of 5–350 K and by Dworkin and Bredig [3]. The values of Dworkin and Bredig are: $132 \text{ J mol}^{-1} \text{ K}^{-1}$ for the solid and $146 \text{ J mol}^{-1} \text{ K}^{-1}$ for the liquid phase of NdCl_3 at the melting temperature of 1032 K. Our experimental results are presented in Fig. 6, together with the data of Sommers and Westrum [12] and the literature estimations. There are estimations of Pankratz [7] for the temperature range 300–1032 K (based on the Dworkin and Bredig [3] data), Barin and Knacke [15] and Knacke et al. [16]. Our values of the heat capacity are slightly higher than those given by Sommers and Westrum [12]. The data of Barin and Knacke [15] differ from our data as well as from data of Pankratz [7] and Knacke et al. [16] with respect to the slope of the temperature dependence of the heat capacity, so that their values are the highest at high temperatures. For the liquid phase we determined that the heat capacity equals $150 \text{ J mol}^{-1} \text{ K}^{-1}$. This value is in a good agreement with data of Dworkin and Bredig [3] (they gave a value of $146 \text{ J mol}^{-1} \text{ K}^{-1}$). According to Savin and Mikhailova [22] heat capacity of the liquid NdCl_3 is equal to $161.6 \text{ J mol}^{-1} \text{ K}^{-1}$.

3.5. GdCl_3

Our experimental values of the heat capacity of GdCl_3 are given in Fig. 7 together with the literature estimation of Pankratz [7], which was based on results of Sommers and Westrum [13] for low temperatures and on the results of Dworkin and Bredig [23] for the higher temperatures (drop calorimetry). Also included in Fig. 7 are estimations of Barin and Knacke [15] and Knacke et al. [16] and the original results of Sommers and Westrum [13]. Our results are again in very good agreement with the above estimations and the original data of Sommers and Westrum [13] at lower temperatures; at higher temperatures our values are lower by 5%. For the liquid phase our value of the heat capacity is equal to $140 \text{ J mol}^{-1} \text{ K}^{-1}$ and literature

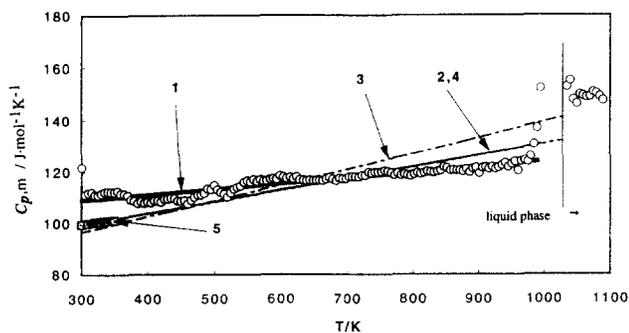


Fig. 6. Molar heat capacity of the NdCl_3 . \circ , experimental values; (1) linear fitting of the experimental values (Table 1); (2) estimation of Pankratz [7]; (3) estimation of Barin and Knacke [15]; (4) estimation of Knacke et al. [16]; (5) data of Sommers and Westrum [12].

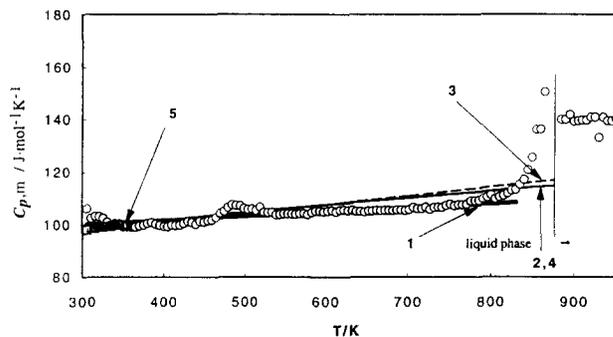


Fig. 7. Molar heat capacity of the GdCl_3 . \circ , experimental values; (1) linear fitting of the experimental values (Table 1); (2) estimation of Pankratz [7]; (3) estimation of Barin and Knacke [15]; (4) estimation of Knacke et al. [16]; (5) data of Sommers and Westrum [13].

estimations [7,15,16] (based on the Dworkin and Bredig [23] data) are equal to $139 \text{ J mol}^{-1} \text{ K}^{-1}$.

3.6. DyCl_3

Pankratz's [7] heat capacity estimations, based on the drop calorimetry investigation results of Dworkin and Bredig [23], as well as estimations of Barin and Knacke [15] and Knacke et al. [16] are presented in Fig. 8 and compared with our experimental results. They are in very good agreement in almost the whole temperature range, with a small exception for the range 300–400 K. The effect at temperatures 610–635 K is the phase transition of DyCl_3 [8]; this transition temperature is equal to 611 K and the enthalpy change $\Delta_{\text{trs}} H_m^0$ equals 1.4 kJ mol^{-1} . Generally, this effect, as well as other irregularities of the $C_{p,m}$ curve suggest that the structure of the compound should be carefully investigated in the temperature range from 450 to 750 K. For the liquid phase of DyCl_3 we measured a heat capacity value of $159 \text{ J mol}^{-1} \text{ K}^{-1}$, which differs significantly from the literature estimations [7,15,16] (based on the data of Dworkin and Bredig [23]) which give the value of $145 \text{ J mol}^{-1} \text{ K}^{-1}$.

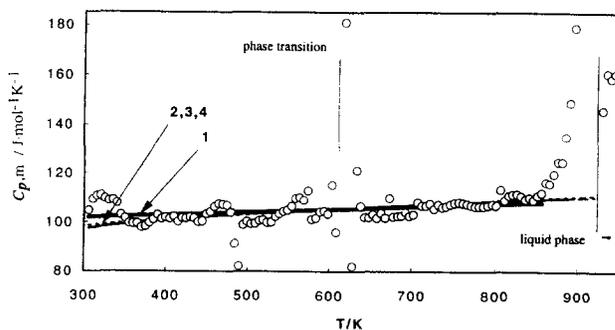


Fig. 8. Molar heat capacity of the DyCl_3 . \circ , experimental values; (1) linear fitting of the experimental values (Table 1); (2) estimation of Pankratz [7]; (3) estimation of Barin and Knacke [15]; (4) estimation of Knacke et al. [16].

4. Summary

The results presented here may be summarised as follows.

- The only original data we have found in the literature on the experimental heat capacity values for the solid lanthanide chlorides was given by Dworkin and Bredig [3, 24], Sommers and Westrum Jr. [12, 13] and Reuter and Siefert [14].
- Estimations given by Pankratz [7] and Knacke et al. [16] are almost identical. Estimations of Barin and Knacke [15] are in a good agreement with data of Pankratz [7] and Knacke et al. [16] for PrCl_3 , GdCl_3 and DyCl_3 , but are different for NdCl_3 , LaCl_3 and especially for CeCl_3 . Our results are 5% lower than heat capacities estimated by Pankratz [7] and Knacke et al. [16] for LaCl_3 and 4% lower than those estimated by Barin and Knacke [15] for CeCl_3 . Generally, the slope of temperature dependence of our heat capacity results for PrCl_3 , NdCl_3 and GdCl_3 is smaller than given by the above estimations so our heat capacity values are lower at high temperatures; we registered the greatest difference of 6% for PrCl_3 .
- For DyCl_3 our experimental data are almost identical with the above literature estimations in the temperature range from 400 to 860 K. Note that there is a phase transition at 611 K which was not observed by Dworkin and Bredig [23].
- There is a serious difference between our results of the heat capacity measurements and the heat capacity given by Pankratz [7] and Knacke et al. [16] for CeCl_3 . The curve plotted according to these estimations exhibits a rather unusual shape (in comparison with the other investigated lanthanide chlorides), so these data are probably incorrect.
- There is a very good agreement between our results and the most recent results of Reuter and Seifert [14] for LaCl_3 .
- Data given by Sommers and Westrum [12] for PrCl_3 and GdCl_3 are in a good agreement with our results, although this comparison can only be made in a narrow temperature range. For LaCl_3 our results are 4% lower and for NdCl_3 10% higher than values given by Sommers and Westrum [12].

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