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Thermodynamic Characterization of the Congruently Melting Cs_3CeCl_6 Compound

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The thermodynamic properties of the congruently melting Cs_3CeCl_6 compound, which is known to exist in the $CeCl_3-CsCl$ system, were studied by differential scanning calorimetry and Knudsen effusion mass spectrometry. The heat capacity of solid and liquid Cs_3CeCl_6 was measured as a function of temperature in the range (300 to 1100) K. The thermodynamic activities of CsCl and $CeCl_3$ were determined in the two-phase field $\{Cs_3CeCl_6(s) + \text{liquid}\}$. These data were used to calculate the whole set of thermodynamic functions for the solid and liquid compound as well as the temperature variation of the Gibbs free energy and enthalpy of compound formation according to the reaction $CeCl_{3(s,l)} + 3CsCl_{(s,l)} = Cs_3CeCl_{6(s,l)}$.

1. Introduction

Several compounds may exist in LnX_3-MX mixtures (Ln = lanthanide, X = halide, M = alkali metal). These systems have relatively simple phase diagrams when they include the lighter alkali metal halides (LiX and NaX), while those with KX, RbX, and CsX exhibit generally several compounds of stoichiometry, M_3LnX_6, M_2LnX_5, and MLn_2X_7. The stability of these compounds depends on the nature of both cations (lanthanide Ln, alkali M) and anions X.[1−3] We have paid much attention to the M_3LnX_6 stoichiometric compounds that exist in most LnX_3-MX systems[4−11] and have a more extended stability range than those of other stoichiometry. These congruently melting compounds were found[12] to exist also in the $CeCl_3-MCl$ systems (M = K, Rb, and Cs).

The present work reports on the thermodynamic properties of the Cs_3CeCl_6 compound. It has been established earlier that this compound is metastable at ambient temperature.[12,13] It undergoes a solid−solid state transition at 676 K and melts congruently at 1078 K with the respective enthalpies (7.8 ± 0.4 and 67.4 ± 0.8) $kJ \cdot mol^{-1}$.[2,3,14] Its formation enthalpy from the system components—CsCl and $CeCl_3$—was determined as $-26.0\ kJ \cdot mol^{-1}$ at 298.15 K[12] by solution calorimetry.

Our purposes were to measure the (i) heat capacity of Cs_3CeCl_6 over a broad temperature range for calculating its thermodynamic functions, (ii) variation of the Gibbs free energy and enthalpy of the compound formation reaction with temperature, (iii) thermodynamic activities of CsCl and $CeCl_3$ in the two-phase field $\{Cs_3CeCl_6(s) + \text{liquid}\}$, and (iv) the absolute entropy of the Cs_3CeCl_6 compound at 298.15 K.

2. Experimental

*2.1. **Chemicals.*** Cerium(III) chloride was synthesized from cerium(III) carbonate hydrate (Aldrich 99.9 %). $Ce_2(CO_3)_3 \cdot xH_2O$ was dissolved in hot concentrated HCl acid. The solution was evaporated, and $CeCl_3 \cdot xH_2O$ was crystallized. Ammonium chloride was then added, and this wet mixture of hydrated $CeCl_3$ and NH_4Cl was first slowly heated up to 450 K and then up to 570 K to remove the water. The resulting mixture was subsequently heated up to 650 K for sublimation of NH_4Cl. Finally the salt was melted at 1150 K. Crude $CeCl_3$ was purified by distillation under reduced pressure (~0.1 Pa) in a quartz ampule at 1150 K. $CeCl_3$ prepared in this way was of a high purity, min. 99.9 %. Chemical analysis was performed by the mercurimetric (chlorine) and complexometric (cerium) methods. The results were as follows: Ce, (56.83 ± 0.04) % (56.85 % theoretical); Cl, (43.17 ± 0.03) % (43.15 % theoretical).

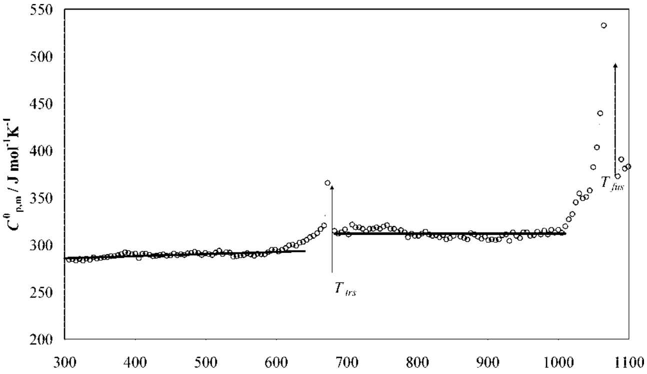

Figure 1. Molar heat capacity $C°_{p,m}$ of Cs_3CeCl_6: open circles, mean values from experimental results; broken line, global heat capacity; solid lines, polynomial fitting of experimental results.

Cesium chloride was a Merck Suprapur reagent (min. 99.9 %). Prior to use, it was progressively heated up to fusion under a gaseous HCl atmosphere. HCl in excess was then removed from the melt by argon bubbling.

The Cs_3CeCl_6 stoichiometric compound and the mixture of compositions $x(CsCl) = 0.70$ were prepared from the cerium and cesium chlorides, which were weighed in a proper molar ratio. All mixtures were prepared in a glovebox filled with purified and water-free argon. Although only a small amount of sample was used for the differential scanning calorimetry

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Table 1. Values of *A*, *B*, *C*, *D*, and *E* Parameters in Equations 1, 2, 3, and 4

	T range	*A*	$B\cdot10^2$	*C*	*D*	*E*
compound	K	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-2}$	$J\cdot mol^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$
$Cs_3CeCl_{6(s)}$	300 to 676	278.04 ± 1.33	2.525 ± 0.283	−84020 ± 520	−1095.69 ± 8.42	−1373.73 ± 9.74
$Cs_3CeCl_{6(s)}$	676 to 1078	311.94 ± 11.26	-	−93370 ± 6358	−1287.98 ± 71.21	−1599.93 ± 82.45
$Cs_3CeCl_{6(l)}$	1078 to 1100	381.93 ± 7.41	-	−101420 ± 2430	−1714.19 ± 44.33	−2096.12 ± 51.72

Table 2. Thermodynamic Functions of Cs_3CeCl_6 at Selected Temperatures from (298.15 to 1100) K

	$C^o_{p,m}(T)$	$S^o_m(T)$	$-(G^o_m(T) - H^o_m(298.15\ K))/T$	$H^o_m(T) - H^o_m(298.15\ K)$	$\Delta_r H^o_m(T)$	$\Delta_r G^o_m(T)$
T/K	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$J\cdot mol^{-1}\cdot K^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$
298.150	285.57	496.00	496.00	0.00	−26.00	−38.46
300	285.62	497.76	496.00	0.53	−25.94	−38.54
400	288.14	580.28	507.24	29.22	−22.85	−43.21
500	290.67	644.84	528.53	58.16	−20.06	−48.63
600	293.19	698.06	552.48	87.35	−17.43	−54.60
676	295.11	733.14	570.86	109.70	−15.53	−59.42
676	311.94	744.68	570.86	117.50	−7.73	−59.42
700	311.94	755.56	577.01	124.99	−6.75	−61.27
743	311.94	774.16	587.89	138.40	−5.04	−64.67
743	311.94	774.16	587.89	138.40	−16.44	−64.67
800	311.94	797.22	601.99	156.18	−14.71	−68.43
900	311.94	833.96	625.76	187.38	−13.57	−75.24
918	311.94	840.14	629.91	192.99	−13.62	−76.48
918	311.94	840.14	629.91	192.99	−74.52	−76.48
1000	311.94	866.83	648.26	218.57	−76.13	−76.59
1078	311.94	890.25	664.93	242.90	−78.10	−76.56
1078	381.93	952.77	664.93	310.30	−78.10	−76.56
1086	381.93	955.60	667.06	313.36	−78.33	−77.05
1086	381.93	955.60	667.06	313.36	−78.33	−77.05
1100	381.93	960.49	670.76	318.70	−78.73	−77.20

(DSC) and mass spectrometric experiments [(300 to 500) mg and (30 to 50) mg, respectively], batches of several grams were synthesized to avoid deviation from stoichiometry. Stoichiometric mixtures of chlorides were melted in vacuum-sealed quartz ampoules in an electric furnace. Melts were homogenized by shaking and solidified. These samples were ground in an agate mortar in a glovebox. All chemicals were handled in an argon glovebox with a measured volume fraction of water of about $2\cdot10^{-6}$ and continuous gas purification by forced recirculation through external molecular sieves.

2.2. Measurements. Heat capacity was measured by differential scanning calorimetry with a Setaram DSC 121 operated in a stepwise mode. This so-called "step method" has been described[2,3] previously. The heat capacity of the sample was determined over an extended temperature range from two experimental runs in an identical stepwise mode. The first one was registered with two empty cells (containers) of identical mass and the second with one of these cells loaded with the sample. For each heating step, the difference of heat flux between the two series is proportional to the amount of heat (Q_i) necessary to increase the sample temperature by a small temperature increment ΔT_i. Therefore, in the absence of any phase transition, the heat capacity of the sample is equal to $C_{p,m} = (Q_i\cdot M_s)/(\Delta T_i\cdot m_s)$, where m_s is the mass of the sample and M_s is the molar mass of the sample. The same operating conditions (i.e., initial and final temperatures, temperature increment, isothermal delay, and heating rate) were used in the two experimental series. Experimental monitoring, data acquisition, and processing were performed with the Setaram Setsys software. The apparatus was calibrated by the Joule effect. Additionally, some test measurements with NIST 720 α-Al_2O_3 Standard Reference material have been carried out separately prior to investigation. According to this test, which gave C_p values consistent with standard data for Al_2O_3 (difference of less than 1.5 %), the step method may be considered as suitable for C_p measurements. The main advantage of this method when compared with a continuous method is achievement of thermal equilibrium of the sample under investigation during isothermal delay following each heating step. In the present heat capacity experiments, each 5 K heating step was followed by a 400 s isothermal delay. The heating rate was 1.5 $K\cdot min^{-1}$. All experiments were performed in the (300 to 1100) K temperature range. The mass difference of the quartz cells in any individual experiment did not exceed 1 mg (cell mass: (400 to 500) mg).

To establish the repeatability and uncertainty of the results, three different samples of compound (from different batches) were used in the measurements. All these results were used in calculation of coefficients in the equation describing the temperature dependence of heat capacity as well as the standard deviation on $C^\circ_{p,m}$. The maximal deviations of individual series from mean values did not exceed ± 3%.

The measurements of thermodynamic activity in the two-phase field $\{Cs_3CeCl_6(s) + \text{liquid}\}$ were carried out with the $CeCl_3-CsCl$ mixture of composition $x(CsCl) = 0.70$ by Knudsen effusion mass spectrometry. The technique of thermionic emission current ratio was used[15] for this purpose.

The thermal emission of ions was measured using a single focusing magnetic-sector-field mass spectrometer, MI 1201 (200 mm radius of curvature, 90°). The furnace assembly consisted of a molybdenum effusion cell (0.7 mm effusion orifice diameter and about 500 evaporation-to-effusion area ratio), a molybdenum resistance heater, tantalum radiation shielding, and a tungsten/tungsten−rhenium thermocouple, which was inserted into the hole drilled in the bottom of the effusion cell. Heating was controlled to provide temperatures to be constant within ± 1 K. The ions thermally emitted inside the cell were extracted by a weak electric field (field strength at most $5\cdot10^4\ V\cdot m^{-1}$) applied between the effusion cell and the extracting electrode. To measure the emission of charged particles of both signs, the same positive or negative electric potential with respect to earth was applied to all parts of the furnace assembly. A detailed scheme of the evaporation assembly and ion source is given elsewhere.[16] After passing the

Table 3. Thermodynamic Parameters for the Reaction 5 and the Absolute Entropy $S°(\mathrm{Cs_3CeCl_6}, 298.15)$ of the $\mathrm{Cs_3CeCl_6}$ Compound

	T				$\Delta_r G°(T)$	$\Delta_r H°(T)$	$\Delta_r S°(T)$	$\Delta_r S°(298.15)$	$S°(\mathrm{Cs_3CeCl_6}$, cr, 298.15)
run	K	a[CsCl]	$a[\mathrm{CeCl_3}]$	ln K_p	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{kJ \cdot mol^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
1	1007	0.116± 0.007	0.101 ± 0.016	8.76	−73.3	−83.7	−10.3	42.3	496.8
2	1007	0.118 ± 0.008	0.119 ± 0.018	8.54	−71.5	−83.7	−12.1	40.5	495.0
ref 20	950	0.092 ± 0.016	0.054 ± 0.022	10.08	−79.6	−81.6	−2.1	48.3	502.8

extracting electrode, the ions were accelerated in an electrostatic field to an energy of 3 keV, mass analyzed in a variable magnetic field, and collected on the first plate of an electron multiplier. The output from the multiplier was amplified by an electrometer utilizing a 10^2 to 10^4 MΩ resistor.

3. Results and Discussion

3.1. Heat Capacity. Experimental heat capacity data (mean values from measurements performed on three different samples) are plotted against temperature in Figure 1. Heat capacity measurements performed on $\mathrm{Cs_3CeCl_6}$ evidenced two anomalies, at temperatures which corresponded well to the solid−solid phase transition (676 K) and melting (1078 K) as determined from DSC curves. Accordingly, experimental heat capacity data $C^{\circ}_{p,\mathrm{m}}$ of solid $\mathrm{Cs_3CeCl_6}$ were fitted to a linear dependence on temperature

$$C^{\mathrm{o}}_{p,\mathrm{m}}/\mathrm{J \cdot mol^{-1} \cdot K^{-1}} = A + B \cdot (T/\mathrm{K}) \qquad (1)$$

in the two temperature ranges: (300 to 676) K and (676 to 1078) K. The corresponding coefficients A and B in eq 1 are collected in Table 1, together with standard deviations. The standard deviation of heat capacity calculated from eq 1 was (2.28 and 11.26) $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, in the temperature ranges (300 to 676) K and (676 to 1078) K, respectively.

A constant heat capacity value, $C°_{p,\mathrm{m}}$ = (381.93 ± 7.41) $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, was found for liquid $\mathrm{Cs_3CeCl_6}$.

3.2. Thermodynamic Functions. The thermodynamic functions, namely, enthalpy increments $[H°_\mathrm{m}(T) - H°_\mathrm{m}(298.15)]$ in $\mathrm{J \cdot mol^{-1}}$, entropy $S°_\mathrm{m}(T)$, and Gibbs energy functions $-[(G°_\mathrm{m}(T) - H°_\mathrm{m}(298.15))/T]$ in $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$, were calculated by using the heat capacity dependence on temperature ($C°_{p,\mathrm{m}} = f(T)$).

$$H^{\mathrm{o}}_{\mathrm{m}}(T) - H^{\mathrm{o}}_{\mathrm{m}}(298.15) = A \cdot T + 1/2 \cdot B \cdot T^2 + C \qquad (2)$$

$$S^{\mathrm{o}}_{\mathrm{m}}(T) = A \cdot \ln T + B \cdot T + D \qquad (3)$$

$$-(G^{\mathrm{o}}_{\mathrm{m}}(\mathrm{T}) - H^{\mathrm{o}}_{\mathrm{m}}(298.15))/T = A \cdot \ln T + 1/2 \cdot B \cdot T - C \cdot T^1 + E \qquad (4)$$

The parameters C, D, and E in the above equations were calculated by setting T = 298.15 K into eqs 2, 3, and 4. They are also presented in Table 1. Our experimental transition and fusion temperatures and enthalpies[2,3,14] together with heat capacity data were used in this calculation. The heat capacity value $C°_{p,\mathrm{m}}$(s, 298.15 K) was extrapolated from experimental results to 298.15 K (Table 2). The value of standard entropy at 298.15 K also necessary in these calculations was calculated by a novel approach (see section 3.4). The calculated thermodynamic functions are presented in Table 2 at selected temperatures.

From the thermodynamic data in Table 2, the enthalpy and Gibbs free energy of $\mathrm{Cs_3CeCl_6}$ formation ($\Delta_f H^0_\mathrm{m}$ and $\Delta_f G^0_\mathrm{m}$) via reaction 5 were calculated as a function of temperature.

The formation of $\mathrm{Cs_3CeCl_6}$ from cerium and cesium chlorides can be described by the reaction

$$\mathrm{CeCl_{3(s,l)}} + 3\mathrm{CsCl_{(s,l)}} = \mathrm{Cs_3CeCl_{6(s,l)}} \qquad (5)$$

and the related thermodynamic functions of formation depend on the thermodynamic functions of cerium and cesium chlorides. The latter were calculated using literature data for $C°_{p,\mathrm{m}}$ and $S°_\mathrm{m}$(298.15 K)[2,3,17] (heat capacity of solid $\mathrm{CeCl_3}$ was taken from our previous work,[2,3] other data from Kubaschewski et al.[17]). The enthalpy of reaction 5 at 298.15 K, $\Delta_r H^{\circ}_\mathrm{m}(\mathrm{Cs_3CeCl_6}$, s, 298.15 K) = $-26.0\ \mathrm{kJ \cdot mol^{-1}}$, also required in this calculation, was taken from Seifert et al.[12]

Five phase changes occur in the system described by reaction 5: solid−solid phase transition of $\mathrm{Cs_3CeCl_6}$ at 676 K with enthalpy of 7.8 $\mathrm{kJ \cdot mol^{-1}}$, melting of $\mathrm{Cs_3CeCl_6}$ at 1078 K with enthalpy of 67.4 $\mathrm{kJ \cdot mol^{-1}}$, melting of $\mathrm{CeCl_3}$ at 1086 K with enthalpy of 55.5 $\mathrm{kJ \cdot mol^{-1}}$, and solid−solid transition of CsCl at 743 K and its fusion at 918 K with related enthalpies of (3.8 and 20.3) $\mathrm{kJ \cdot mol^{-1}}$, respectively. Accordingly, the enthalpy $\Delta_r H°_\mathrm{m}$ ($\mathrm{kJ \cdot mol^{-1}}$) and the Gibbs energy of formation $\Delta_f G^0_\mathrm{m}$ ($\mathrm{kJ \cdot mol^{-1}}$) of $\mathrm{Cs_3CeCl_6}$ via reaction 5 are described by the equations given below.

$\mathrm{Cs_3CeCl_6}$ solid, 298.15 K < T < 676 K:

$$\Delta_r H^{\mathrm{o}}_{\mathrm{m}} = 27.79 \cdot 10^{-3} T - 3.40 \cdot 10^{-6} T^2 - 6.51 \cdot 10^2 T^{-1} - 31.80$$

$$\Delta_r G^{\mathrm{o}}_{\mathrm{m}} = 138.652 \cdot 10^{-3} T + 3.41 \cdot 10^{-6} T^2 - 3.255 \cdot 10^2 T^1 - 27.792 \cdot 10^{-3} T \ln T - 31.80.15$$

$\mathrm{Cs_3CeCl_6}$ solid, 676 K < T < 743 K:

$$\Delta_r H^{\mathrm{o}}_{\mathrm{m}} = 61.69 \cdot 10^{-3} T - 16.025 \cdot 10^{-6} T^2 - 6.51 \cdot 10^2 T^{-1} - 41.15$$

$$\Delta_r G^{\mathrm{o}}_{\mathrm{m}} = 364.842 \cdot 10^{-3} T + 16.025 \cdot 10^{-6} T^2 - 3.255 \cdot 10^2 T^{-1} - 61.69 \cdot 10^{-3} T \ln T - 41.15$$

$\mathrm{Cs_3CeCl_6}$ solid, 743 K < T < 918 K:

$$\Delta_r H^{\mathrm{o}}_{\mathrm{m}} = 211.69 \cdot 10^{-3} T - 118.76 \cdot 10^{-6} T^2 - 11.55 \cdot 10^2 T^{-1} - 106.61$$

$$\Delta_r G^{\mathrm{o}}_{\mathrm{m}} = 1368.672 \cdot 10^{-3} T + 118.76 \cdot 10^{-6} T^2 - 5.775 \cdot 10^2 T^{-1} - 211.69 \cdot 10^{-3} T \ln T - 106.61$$

$\mathrm{Cs_3CeCl_6}$ solid, 918 K < T < 1078 K:

$$\Delta_r H^{\mathrm{o}}_{\mathrm{m}} = 47.77 \cdot 10^{-3} T - 35.165 \cdot 10^{-6} T^2 - 0.24 \cdot 10^2 T^{-1} - 88.71$$

$$\Delta_r G^{\mathrm{o}}_{\mathrm{m}} = 306.942 \cdot 10^{-3} T + 35.165 \cdot 10^{-6} T^2 - 0.12 \cdot 10^2 T^{-1} - 47.772 \cdot 10^{-3} T \ln T - 88.69$$

$\mathrm{Cs_3CeCl_6}$ liquid, 1078 K < T < 1086 K:

$$\Delta_r H^{\mathrm{o}}_{\mathrm{m}} = 117.76 \cdot 10^{-3} T - 35.165 \cdot 10^{-6} T^2 - 0.24 \cdot 10^2 T^{-1} - 96.76$$

$$\Delta_r G^{\mathrm{o}}_{\mathrm{m}} = 803.14 \cdot 10^{-3} T + 35.165 \cdot 10^{-6} T^2 - 0.12 \cdot 10^2 T^{-1} - 117.76 \cdot 10^{-3} T \ln T - 96.74$$

$\mathrm{Cs_3CeCl_6}$ liquid, 1086 K < T < 1100 K:

$$\Delta_r H^o_m = 62.78 \cdot 10^{-3} T - 26.865 \cdot 10^{-6} T^2 - 102.36$$

$$\Delta_r G^o_m = 432.96 \cdot 10^{-3} T + 26.865 \cdot 10^{-6} T^2 - 62.78 \cdot 10^{-3} T \ln T - 102.34$$

The calculated values of Cs_3CeCl_6 thermodynamic functions of formation are presented in Table 2 at selected temperatures.

3.3. Thermodynamic Activities. In the mass spectra of thermal ion emission corresponding to the $CsCl-CeCl_3$ mixture, $x(CsCl) = 0.70$, the following positive Cs^+, Cs_2Cl^+, $Cs_3Cl_2^+$, $Cs_2CeCl_4^+$, $Cs_3CeCl_5^+$, $Cs_4CeCl_6^+$, and negative Cl^-, $CeCl_4^-$, $Ce_2Cl_7^-$, $CsCeCl_5^-$, $CsCe_2Cl_8^-$ ions were detected at the temperatures corresponding to the existence of the two-phase field $\{Cs_3CeCl_6(s) + \text{liquid}\}$.[12] This fact enables the thermodynamic activities of CsCl and $CeCl_3$ to be determined by the ion current ratio method according to the equations:

$$a_{CsCl} = \frac{I^s(Cs_3Cl_2^+)/I^s(Cs_2Cl^+)}{I^o(Cs_3Cl_2^+)/I^o(Cs_2Cl^+)} \tag{6}$$

and

$$a_{CeCl_3} = \frac{I^s(Ce_2Cl_7^-)/I^s(CeCl_4^-)}{I^o(Ce_2Cl_7^-)/I^o(CeCl_4^-)} \tag{7}$$

Here I^s and I^o are the ion currents measured at $T = \text{const}$ for the system and the pure component ($T = \text{const}$), respectively. The current ratios $I°(Cs_3Cl_2^+)/I°(Cs_2Cl^+)$ and $I°(Ce_2Cl_7^-)/I°(CeCl_4^-)$ were taken from refs 18 and 19, respectively. The activities measured in two runs were averaged and are presented in Table 3. Our activity values are compared with those obtained in ref 20 for the same phase field using the dimer-to-monomer ratio technique, the reliability of which is strongly dependent on interpretation correctness of the electron-ionization mass spectra. One can see in Table 3 that the activity data obtained in both works are in good agreement.

3.4. Entropy S°(298.15) of Cs_3CeCl_6. To calculate the absolute entropy of the Cs_3CeCl_6 compound at 298.15 K, the following approach is proposed.

The equilibrium constant of reaction 5 for the two-phase field $\{Cs_3CeCl_6(s) + \text{liquid}\}$ equals

$$K_p = \frac{1}{a^3_{CsCl} a_{CeCl_3}} \tag{8}$$

The Gibbs free energies for this reaction

$$\Delta_r G^o(T)^o = \Delta_r H^o(T) - T\Delta_r S^o(T) = -RT \ln K_p \tag{9}$$

at the experimental temperatures are given in Table 3. Using this value along with the thermodynamic functions presented in Table 2 and enthalpy $\Delta_r H°(298.15)$ of reaction 5[12] the entropy $\Delta_r S°(298.15)$ of reaction 5 can be derived as

$$\begin{aligned}\Delta_r S^o(298.15) &= \Delta_r S^o(T) - \Delta_r[S^o(T) - S^o(298.15)] \\ &= [\Delta_r H^o(T) - \Delta_r G^o(T)]/T - \Delta_r[S^o(T) - S^o(298.15)] \\ &= \{\Delta_r H^o(298.15) + \Delta_r[H^o(T) - H^o(298.15)] - \\ &\qquad \Delta_r G^o(T)\}/T - \Delta_r[S^o(T) - S^o(298.15)]\end{aligned} \tag{10}$$

Eventually the absolute entropy value can be calculated as

$$S^o(Cs_3CeCl_6, s, 298.15) = \Delta_r S^o(298.15) + 3S^o(CsCl, s, 298.15) + S^o(CeCl_3, s, 298.15) \tag{11}$$

The results of calculations are presented in Table 3. For further usage, we recommend the value $S°(Cs_3CeCl_6, s, 298.15) = 496$ $J \cdot mol^{-1} \cdot K^{-1}$.

4. Summary

A new approach coupling differential scanning calorimetry and the thermionic emission technique of Knudsen effusion mass spectrometry was developed for the thermodynamic characterization of the M_3LnX_6 stoichiometric compounds that exist in most LnX_3-MX systems. In the present study, this approach was successfully applied to the Cs_3CeCl_6 case.

The heat capacity of solid and liquid Cs_3CeCl_6 was measured as a function of temperature. The thermodynamic activities of CsCl and $CeCl_3$ were determined in the two-phase field $\{Cs_3CeCl_6(s) + \text{liquid}\}$. These data enabled experimental derivation of the absolute entropy of Cs_3CeCl_6 at 298.15 K and were used to calculate the whole set of thermodynamic functions for solid and liquid compounds together with the Gibbs free energy and the enthalpy variation with temperature of the compound formation reaction $CeCl_{3(s,l)} + 3CsCl_{(s,l)} = Cs_3CeCl_{6(s,l)}$.

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