Physicochemical analysis of inorganic systems

HERMOCHEMISTRY AND FLUORINATING ABILITY OF CERIUM TETRAFLUORIDE

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Experimental data on the thermal stability and fluorinating ability of cerium(IV) fluoride are critically reviewed. From experiments on the joint fluorination of CeF3k and platinum, the value ΔfHo(CeF4, k, 298 K) = -1939.9±7.6 kJ/mol was determined. The most reliable value of the enthalpy of sublimation of cerium tetrafluoride ΔsHo(CeF4, 298 K) = 270.2±1.7 was selected and ΔfHo(CeF4, g, 298 K) = -1669.6±7.8 kJ/mol was calculated. A comparison of CeF4(k) with other solid-phase fluorinating agents was carried out.

Keywords: cerium fluorides, thermal stability, standard enthalpy of formation, heterogeneous equilibria

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INTRODUCTION

Cerium fluorides are convenient starting semi-finished products used in various technological processes, such as the production of solid electrolytes, special optical glasses and laser materials, composites for hydrogen storage and the production of cerium by metallothermy [1–3]. In particular, cerium tetrafluoride is used as a fluorinating agent in the synthesis of inorganic and organic fluorides [4]. Due to the lack of experimental data, only rough and unreliable estimates of the thermodynamic characteristics of cerium(I) and cerium(II) fluorides are given in the literature. Therefore, only experimental studies [5–16], in which cerium(III) and cerium(IV) fluorides were studied, and reference data from studies [17–19] will be considered below.

SELECTION OF THERMODYNAMIC CHARACTERISTICS OF CERIUM FLUORIDES

All thermodynamic characteristics of the substances considered in this work (standard Gibbs energy, enthalpy of formation and sublimation, entropy, reduced

thermodynamic potential, and saturated vapor pressure) were taken from the literature or calculated based on them and are presented in Table 1. All data from the cited works were critically analyzed and, in some cases, recalculated, with some of the obtained values differing from the recommendations of the measurement authors. The uncertainties of the values are given with the accuracy indicated in the cited work, and in cases where a value was calculated, the calculated expanded uncertainty is provided in accordance with GOST 34100.3-2017. To assess the reliability of published experimental values, the experimental conditions, absence of side reactions or, conversely, their accounting, data reproducibility, and consistency of values calculated by different methods were considered.

The difference between the values of the standard enthalpy of formation determined by different methods for both crystalline cerium trifluoride [5-7] and crystalline cerium tetrafluoride [12, 13, 17] significantly exceeds the measurement uncertainties. In this work, the value of $\Delta_f H^\circ(CeF_3, c, 298\ K) = -1735.6 \pm 5.5$ kJ/mol is adopted, based on measurements [6], taking into account thermodynamic functions selected from the most recent sources [17]. The small discrepancy with the data [17] is apparently related to the modified set of necessary thermodynamic functions. Their recommended values are taken for CeF_3(g) from [18], for CeF_3(c) from [8]. The values of the enthalpy of formation of crystalline cerium tetrafluoride, determined by the calorimetry of dissolution method in [12] or obtained by combining the enthalpies of several reactions involving gaseous CeF_3 and CeF_4 in [13], appear quite unreliable due to a number of factors, discussed in detail below. On the other hand, the value recommended in [17] is based on data from earlier works (1976), the shortcomings of which have already been analyzed in [15, 16].

The enthalpy of sublimation $\Delta_s H^\circ(CeF_3, 298\ K)$ was determined in works [7-10], and the recommended value of $\Delta_s H^\circ(CeF_3, 298\ K) = 439.6 \pm 2.0$ kJ/mol, obtained based on the analysis of literature data in work [8], was adopted.

The thermodynamic functions of gaseous cerium tetrafluoride were calculated by us using the rigid rotator-harmonic oscillator approximation with the structure, molecular constants, and vibrational frequencies taken from work [20]. The obtained values of the reduced thermodynamic potential ($\Phi'(T) = -\frac{G^\circ(T) - H^\circ(0)}{T}$), standard entropy at temperature T ($S^\circ(T)$) and the enthalpy change of the substance when the temperature changes from 298 K to T ($H^\circ(T) - H^\circ(298\ K)$) are presented in

Table 2. The enthalpy change of CeF_4(g) when the temperature changes from 0 to 298 K was $H°(298) - H°(0) = 24.738$ kJ/mol.

Experimental data for calculating the thermodynamic functions of crystalline cerium tetrafluoride or their estimates are not available in the literature, except for work [17]. The original article [21] from 1976 does not contain information about the origin of the value $S°_f$, 298.15(CeF_4, cr), but contains arithmetic errors. Therefore, the thermodynamic functions of CeF_4(cr) are taken to be the same as for CrF_4(cr) [18], taking into account the Latimer contribution (15 J/(mol K) was added to the entropy value), and $H°(T) - H°(298\ K)$ is the same as for CrF_4(cr). The difference between the entropy values we selected from the data on chromium tetrafluoride and from work [17] is approximately 44 J/(mol K). The correctness of our choice is confirmed by better agreement of the standard enthalpy of sublimation of CeF_4, calculated in accordance with the second and third laws of thermodynamics using data from [16].

Phase diagram of the CeF_3-CeF_4 system, studied using XRD, visual and thermal analysis, represents a simple eutectic with a composition in the range of $CeF_{3.66}$ – $CeF_{3.71}$ (accepted as $CeF_{3.68}$) at a temperature of 808 °C [22] (Fig. 1). The existence of solid solutions was not detected. The authors of [22] could not investigate the system at temperatures above 1200°C, since at these temperatures the liquid becomes unstable and forms solid cerium trifluoride, gaseous fluorine, and cerium fluorides. In the absence of precisely controlled pressure, it was not possible to determine the temperature at which instability begins, so the authors drew a wide hatched band in the figure.

ANALYSIS OF LITERATURE EXPERIMENTAL DATA

For a long time, since its synthesis in 1934, the vaporization process of cerium(IV) fluoride was described contradictorily. Thus, the range of thermal stability of CeF_4(s) varied from 400 °C followed by decomposition into fluorine and trifluoride [23] to congruent melting at 841 °C, occurring with practically no decomposition [24]. Accordingly, the composition of the gas phase was described differently: from F_2 [23] to CeF_4, the partial pressure of which was not measured [24].

Chemically quite active CeF_4 even at moderately high temperatures can interact with the apparatus material, which should not release gas, and possible impurities in the preparation, forming volatile products. The main and difficult-to-remove impurity is adsorbed water, which leads to thermohydrolysis with the formation of hydrogen fluoride. The contribution of the partial pressure of CeF_4 to the total may turn out to be extremely small. Therefore, studies, including those cited in [17], which measured total pressure, are not considered. This is discussed in more detail in [15, 16]. In these works, unlike earlier ones, as well as in [13], the evaporation of cerium tetrafluoride was investigated using the Knudsen method with mass spectrometric analysis (electron impact ionization) of the vapor composition, and the most reliable and accurate results were obtained, explaining the discrepancy in the gas phase composition.

The synthesized in [16] CeF_4(s) preparation was characterized by the authors using XRD and elemental analysis. The authors took all possible measures to avoid errors. All manipulations with the preparation were carried out in an inert atmosphere of a dry box (the absence of water was confirmed by DSC method), and thermal effects associated with the presence of water in the samples were not detected. Platinum or fluorine-passivated nickel effusion chambers were used. The constancy of CeF_4 pressure during isothermal evaporation was monitored by the ion current I (CeF_3^+/CeF_4), as the fraction of the molecular ion in the mass spectrum was extremely small. The completeness of evaporation was determined by its sharp decrease to the background level. CeF_3 (s) formed during evaporation was determined gravimetrically, and the mass of evaporated cerium(IV) fluoride was calculated by the difference in the mass of the chamber with the sample before and after the experiment. The vaporization process, reactions, and their mechanisms are described in detail in works [15, 16].

The results obtained in [16] on the saturated vapor pressure and the enthalpies $\Delta_s H^\circ$(298 K) calculated by us from these data according to the III law are given in Table 3. Multiple studies of the temperature dependence of the ion current CeF_3^+ with increasing and decreasing temperature in the range of 723-923 K allowed the authors [16] to determine, according to the II law, the enthalpy of sublimation $\Delta_s H^\circ$(840 K) with good reproducibility.

With the thermodynamic functions of CeF_4(s) adopted in this work, there is a good agreement between the calculation results of $\Delta_s H^\circ(CeF_4, 298\ K)$ according to

the II and III laws. Using $\Phi'(CeF_4(s), T)$ from [17] leads to an unjustifiably large discrepancy. It should be noted that in [16], for calculation according to the III law, the values of $\Delta_s\Phi'(CeF_4, T)$ for ZrF_4 and UF_4 were used, which give values of $\Delta_s H^\circ(CeF_4, 298\ K) = 269$ and 267 kJ/mol, almost coinciding with the value obtained in this work.

It should be noted that during the mass spectral experiment at maximum temperature, the ion currents obtained by ionization of platinum fluorides formed during interaction with the chamber material were immeasurably small. For comparison, Table 3 shows the vapor pressure values of CeF_4, obtained in work [13], recalculated by us using the thermodynamic functions adopted in that work, and related to the saturated vapor pressure from [16].

It can be seen that the activity of CeF_4, calculated using the formula $a = P$ [13]/ P°, either has an absurd value or is clearly less than unity and does not correlate with temperature in any way. The reason for this is the imperfection of the CeF_4 synthesis methodology and the method of processing experimental data used in [13], as well as the use of unreliable values from the literature. In [13], for the synthesis of CeF_4, they used fluorination of crystalline CeF_3 in a platinum effusion chamber equipped with a molecular fluorine injection system, installed near the ion-optical system of a mass spectrometer with electron impact ionization, equipped with a molecular fluorine injection system. The use of such an aggressive reagent can lead to very significant changes in the sensitivity coefficient of the instrument during measurements.

The aim of the work was to determine the equilibrium constants of reaction (1).

$$CeF_4(g) = CeF_3(g) + F(g). \qquad (1)$$

The vapor composition was determined by mass spectrometry with electron impact ionization. The CeF_3^+ ions observed during fluorine injection were attributed to dissociative ionization of the CeF_4 molecule rather than direct ionization of CeF_3, since the vapor pressure of CeF_3 at the experimental temperatures is immeasurably small [13]. The mass spectrum of platinum-containing ions was decoded using individual mass spectra of PtF_2 and PtF_4 molecules [25, 26], with the presence of PtF_3 molecules in the vapor being excluded. The pressure of atomic

fluorine was calculated from the ratios of total ion currents $\sum I(PtF_n)$ from PtF_4 and PtF_2 molecules and the constant $K^\circ(T)$ of reaction (2):

$$PtF_2(g) + 2F(g) = PtF_4(g). \qquad (2)$$

The instrument sensitivity coefficient $_4$ was calculated using k required for determining the vapor pressure of CeF $K^\circ(T)$ of reaction (3):

$$Pt(s) + PtF_4(g) = 2PtF_2(g), \qquad (3)$$

$$K^\circ((3), T) = k\,T \sum I(PtF_2)\,[\sum I(PtF_2)/\sum I(PtF_4)]\,[\sigma(PtF_4)/\sigma(PtF_2)^2], \qquad (4)$$

where $K^\circ((3), T)$ is the constant of reaction (3), k is the instrument sensitivity coefficient, T is the temperature, $I(i)$ is the total ion current generated by ionization of the i-th component, $\sigma(i)$ is the total ionization cross-section of the i-th component of the gas phase.

It should be noted that in [13], apart from the temperatures and mass spectrum of CeF_4, the primary experimental data in the form of ion currents are not provided. This does not allow for calculations of the final values. The necessity for this arises from the use in [13] of literature data on the enthalpies of formation of gaseous PtF_2 and PtF_4 and equilibrium constants of some reactions involving them [25, 26]. In a later work [27], these values were significantly changed. For example, in [13] the value of $\Delta(\Delta_f H^\circ(PtF_4) - \Delta_f H^\circ(PtF_2)) = -384.4$ kJ/mol (298 K) was accepted, while in [27] – the value of –335.5 kJ/mol (0 K). In [27], instead of reaction (1), reaction (5) was used for calculations assuming unit activities of CeF_3 and CeF_4:

$$2CeF_4(g) + PtF_2(g) = 2CeF_3(g) + PtF_4(g). \qquad (5)$$

Table 4 compares the results of processing what appear to be the same experimental data obtained in [13] and corrected in [27]. These results differ significantly and lead to completely different final values of $\Delta_f H^\circ(CeF_4, g)$ (–1651.9 kJ/mol (298 K) and –1609 kJ/mol (0 K)), which is mainly due to the discrepancy in the values of the enthalpies of formation of platinum fluorides.

Given this, the following most reliable information should be used in further calculations:

1) in the CeF_3–CeF_4 system (Fig. 1) up to the eutectic temperature of 1081 K, the activities $a(CeF_3) = a(CeF_4) = 1$ [22];

2) the values selected above for the sublimation enthalpy of CeF_4 and CeF_3 $\Delta_s H^\circ(CeF_4, 298\ K) = 270.2 \pm 1.7$ kJ/mol; $\Delta_s H^\circ(CeF_3, 298\ K) = 439.6 \pm 2.0$ kJ/mol and the formation enthalpy of CeF_3(s) $\Delta_f H^\circ(CeF_3, s, 298\ K) = -1735.6 \pm 5.5$ kJ/mol;

3) the ratio of total ion currents from PtF_4 and PtF_2 molecules in [13, 27] is calculated with acceptable error that has little effect on the results;

4) the most reliable formation enthalpies of platinum fluorides are given in papers [28–30];

5) at temperatures above the eutectic, the activity of CeF_4 is estimated from the phase diagram of the CeF_3–CeF_4 system [22] (Fig. 1) and is assumed to be equal to its mole fraction based on the ideal solution model.

Based on the proposed recommendations, one can write the equation of reaction (6), the equilibrium constant of which is described by equation (7). The calculation results are presented in Table 5 and Fig. 2.

$$2CeF_4(s) + PtF_2(g) = 2CeF_3(s) + PtF_4(g), \quad (6)$$

$$K^\circ((6), T\ K) = [\sigma(PtF_2)/\sigma(PtF_4)] \sum I(PtF_4)/\sum I(PtF_2)]/ a(CeF_3)/ a(CeF_4)]^2, \quad (7)$$

where $K^\circ((6), T)$ is the constant of reaction (6), $\sigma(i)$ is the total ionization cross-section of the i-th component of the gas phase, $I(i)$ is the total ion current formed during the ionization of the i-th component, $a(i)$ is the activity of the i-th component.

RESULTS AND DISCUSSION

The recommended value of $\Delta_s H^\circ(CeF_3, 298\ K) = 439.6$ kJ/mol and the details of the selection are presented in paper [8], from which $\Delta_f H^\circ(CeF_3, g, 298\ K) = -1735.6 + 439.6 = -1296.0 \pm 5.9$ kJ/mol.

The advantages of papers [15, 16] mentioned above for determining the vapor pressure of cerium(IV) fluoride are the result of overcoming the shortcomings of earlier works [23, 24]. In the present work, the standard enthalpy of sublimation of cerium tetrafluoride determined by the third law is accepted as $\Delta_s H^\circ(CeF_4, 298\ K) = 270.2 \pm 1.7$ kJ/mol.

The enthalpies of reactions (2) and especially (1), which involve gaseous CeF_4, require unjustifiably cumbersome calculations. However, the main disadvantage

of using them is the lack of experimental verification that these reactions reach equilibrium, especially at temperatures of ~1000 K and below. It is in this range that significant changes in the composition of the vapor occur, i.e., the partial pressure of platinum di-, tri-, and tetrafluorides [28]. It is possible that this lack of equilibrium allowed the measurement of the temperature dependence of the saturated vapor pressure of CeF_4 in [16] up to a temperature of 923 K without interaction with platinum. With a sufficiently large temperature range, the determination of the enthalpies of reactions (1) and (2) becomes incorrect, at least according to the second law. Despite the fact that these shortcomings for reactions (1) and (5) are not completely eliminated, when excluding the three lowest temperature points and with a low correlation coefficient R (Fig. 2) for reaction (6), the agreement of the calculation data according to the second and third laws of the enthalpy of reaction (6) (albeit not very satisfactory) is observed within the error limits.

The combination of the reaction enthalpy $\Delta_r H^\circ((6), 298\ K) = -3.8 \pm 5.3$ kJ/mol and standard enthalpies of formation of $PtF_4(g)$ and $PtF_2(g)$, equal at 298 K to 518.2 ± 6.2 [29] and -105.9 ± 6.7 [30] kJ/mol respectively, allowed to calculate the enthalpy of formation $\Delta_f H^\circ(CeF_4, s, 298\ K) = -1939.9 \pm 7.6$ kJ/mol. Taking into account the accepted value of sublimation enthalpy, the enthalpy of formation of gaseous cerium tetrafluoride is $\Delta_f H^\circ(CeF_4, g, 298\ K) = -1669.6 \pm 7.8$ kJ/mol.

Using the values of standard enthalpies of formation of crystalline platinum fluorides PtF_4 and Pt_2F_6, equal to –679.5 [29] and –1051.2 kJ/mol [30] respectively, two additional estimates for $CeF_4(s)$ can be made by considering reactions (8) and (10).

$$CeF_3(s) + 1/4PtF_4(s) = CeF_4(s) + 1/4Pt(s), \quad (8)$$

$$K^\circ(8) = a(CeF_4)/a(CeF_3)]\, a(Pt)/a(PtF_4)]^{1/4}, \quad (9)$$

$$CeF_3(s) + 1/6Pt_2F_6(s) = CeF_4(s) + 1/3Pt(s), \quad (10)$$

$$K^\circ(10) = a(CeF_4)/a(CeF_3)]\, a(Pt)^2/a(Pt_2F_6)]^{1/6}. \quad (11)$$

Under experimental conditions in [13], the fluorine pressure in the effusion chamber at the initial stage is set by its injection from an external reservoir. After accumulation of cerium tetrafluoride and platinum fluorides in the condensed phase and fluorine pumping out, the pressure depends only on temperature and activity ratios of either cerium fluorides or metallic platinum and its fluorides. Assuming the

latter case, it was accepted that the activities of platinum fluorides in expressions K°(8) and K°(10) in the temperature range of 975-1057 K are less than unity. This is evident even without calculations. It is known that the vapor pressure of PtF_4 at 650 K is already 10^{-3} atm [28], and Pt_2F_6(s) actively disproportionates into gaseous tetrafluoride and metallic platinum up to 700 K [30]. Due to interaction with CeF_4 entering from the gas phase onto the platinum surface, it becomes covered with a layer of CeF_3. Microphotographs show that this layer is not continuous and consists of crystals up to 20 μm in size [16]. This allows considering platinum activity close to unity. As mentioned above, the activity of cerium tri- and tetrafluoride equals unity [22]. Substituting these values into the equilibrium constant expressions (8), (10), we get $K^\circ(8) > 1$ and $K^\circ(10) > 1$. Table 6 presents mutually consistent estimates of the enthalpy of reactions (8) and (10). Although the accuracy of calculating the enthalpy of formation of crystalline CeF_4 using equations (8) and (10) is practically the same, the more accurate estimation is the calculation by the latter reaction: $\Delta_f H^\circ(CeF_4, s, 298\ K) < -1735.6-1051.2/6-5.9 \le -1916.7$ kJ/mol, which confirms the recommended value of the enthalpy of formation of crystalline CeF_4.

With the limited scope of the article and the impossibility of further expanding the range of substances considered, this work does not analyze equilibria of reactions with simultaneous participation of fluorides and chlorides of REEs, studied by solution calorimetry. Nevertheless, the difference in enthalpies of formation of crystalline cerium(III) fluorides from this work and cerium(IV) from [12] (–1729.7...–1939.9) = 210.2 kJ/mol agrees well with the value of 207 kJ/mol found in this work.

Transition metal tetrafluorides are generally not used as fluorinating agents due to their hygroscopicity, complexity of synthesis, thermal instability, etc. It is much more convenient to use available trifluorides. Therefore, CeF_4(s), like TbF_4(s), is rather an exception. For trifluorides, a characteristic for comparing their effectiveness may be the bond dissociation energy $D^\circ_0(MF_{n-1} - F)$ for a molecule in the gas phase or the equilibrium pressure of atomic fluorine, determined by the difference in enthalpies of formation of two crystalline fluorides $\Delta_f H^\circ_0(MF_{n-1}) - \Delta_f H^\circ(MF_n)$ and their activities in the condensed phase. For cerium(IV) fluoride, no analogs with known characteristics were found. Therefore, the criterion for comparison may be the equilibrium fluorine pressure in the tri-, tetrafluoride system with unit activities. Table 7 provides several examples.

It is evident that cerium tetrafluoride is a stronger fluorinating agent than manganese and cobalt trifluorides. Its advantage, compared to the latter, lies in the possibility of application at higher temperatures. Thus, at 900 K $P^{\circ}(CeF_4) = 5.5 \times 10^{-6}$ atm, and the pressure of atomic fluorine is 1.5×10^{-5} atm. This is explained by the relatively large enthalpy of sublimation of CeF_3 and very low partial pressure $P^{\circ}(CeF_3)$. It is also important that during the decomposition of CeF_4(s) the activities of CeF_4 and CeF_3 remain equal to unity, and the pressure of atomic fluorine does not change over time. Therefore, CeF_4(s) is the best known reagent for the synthesis of gaseous FeF_4 [32].

CONCLUSION

In the authors' opinion, the thermodynamic characteristics of cerium fluorides recommended in this work are reliable values and can be used in scientific and technical calculations, as well as in the compilation of reference publications.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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Table 1. Experimental and reference works on thermodynamic properties of cerium fluorides

Year, cited work	Research method	Value and error	Year, cited work	Research method	Value and error
CeF_3			CeF_4		
$\Delta_f H^\circ(CeF_3, s, 298\ K)$, kJ/mol			$\Delta_f H^\circ(CeF_4, s, 298\ K)$, kJ/mol		
1969 [5]	Solution calorimetry	–1682 ± 6	1981 [12]	Solution calorimetry	–1935.2 ± 4.1
1976 [6, 17]	EMF	–1732.594 ± 4.184	1982 [13]	Calculation	–1945.6 ± 17.5
2003 [7, 8, 19]	Fluorine calorimetry	–1689.2 ± 5.0	1978 [17]	Reference value	–1769.413 ± 8.368
$\Delta_s H^\circ(CeF_3, 298\ K)$, kJ/mol			$\Delta_s H^\circ(CeF_4, 298\ K)$, kJ/mol		
1968 [9]	MS	414.2 ± 12.6	1982 [13]	Effusion from Pt	278.4 ± 12.4
1977 [10]	Calculation in rigid rotator ─ harmonic oscillator approximation	430.1 ± 11.7	1988 [14]	Effusion from LaF_3	209.4
1978 [17]	Reference value	414.132 ± 0.836	2013 [15]	Effusion from Pt	252 ± 5
2003 [7]	Calculation from previously published data	438.3 ± 2.0	2015 [16]	DSC, MS	268 ± 14 (II law)
2007 [8]	Calculation from previously published data	439.6		Recalculation to 298 K from ZrF_4 and $UF_{4\ data}$	274 ± 12 (III law)
$\Delta_f H^\circ(CeF_3, g, 298\ K)$, kJ/mol			$\Delta_f H^\circ(CeF_4, g, 298\ K)$, kJ/mol		
1978 [17]	Calculated value	1316.462 ± 4.184	1982 [13]	MS	–1651.1 ± 12.4
2003 [7]	Calculated value	─ 1262.4 ± 5.4			
$C_p(CeF_3, 298\ K)$ J/(mol K)			$C_p(CeF_4, 298\ K)$ J/(mol K)		
1961 [11, 17]	Adiabatic calorimeter	93.470 ± 0.292	No data		
2007 [8]	Calculation	92.15			
S°(CeF_3, s, 298 K), J/(mol K)			S°(CeF_4, s, 298 K), J/(mol K)		
1961 [11, 17]	Adiabatic calorimeter	115.227 ± 0.418	1978 [17]	Reference value	138.072 ± 12.552
2007 [8, 18]	Reference value	119.42			

Table 2. Thermodynamic functions of gaseous cerium(IV) fluoride

T, K	$\Phi'(T)$, J/(mol K)	$S^\circ(T)$, J/(mol K)	$H^\circ(T) - H^\circ(298\ \mathrm{K})$, kJ/mol
298	354.119	354.120	0.000
700	373.561	423.829	35.188
800	380.914	433.859	42.356
900	388.097	442.534	48.994
1000	395.020	450.199	55.179
1100	401.651	457.089	60.982

Table 3. Vapor pressure P° and standard sublimation enthalpy $\Delta_s H^\circ(298\ \mathrm{K})$ CeF_4

$P^\circ \times 10^{-6}$ atm (873 K), [16]	$\Delta_s H^\circ(298\ \mathrm{K})$ (Third law), kJ/mol	$\Delta_s H^\circ(840\ \mathrm{K})$ (Second law), kJ/mol [16]	T, K [13]	$P \times 10^{-4}$, atm [13]	$P^\circ \times 10^{-4}$, atm [16]	a (CeF_4)
3.33	268.8	255.9	975	2.85	0.933	3.06
2.93	269.8	263.9	1007	4.47	2.52	1.78
2.63	270.6	248.5	1013	2.54	3.02	0.84
3.03	269.5	252.3	1037	1.49	6.04	0.25
2.12	272.1	254.1	1057	7.98	10.5	0.76
		259.9	1088		23.7	–
		256.9	1130	6.88	66.1	0.10
		266.1	1023*	1.31	4.04	0.33

*Here and in other tables, measurement in the CeF_3–CeF_4–Pt system without fluorine injection.

$\Delta_s H^\circ(CeF_4, 298\ \mathrm{K}) = 270.2 \pm 1.7$ kJ/mol (Third law); 275.9 ± 5.9 kJ/mol (Second law).

Table 4. Partial pressure of cerium tetrafluoride P (CeF_4), enthalpy $\Delta_r H^\circ$ and Gibbs energy $\Delta_r G^\circ$ of reaction (1), equilibrium constant and enthalpy $\Delta_r H^\circ$ of reaction (5)

T, K	P (CeF_4) × 10^4, atm [13]	$\Delta_r G^\circ$(1), kJ/mol [13]	$\Delta_r H^\circ$((1), 298 K), kJ/mol [13]	P (CeF_4) × 10^4, atm [27]	–ln K°(5) [27]	$\Delta_r H^\circ$((5), 298 K), kJ/mol [27]
975	2.85	303.1	452.3	0.85	37.43	324
1007	4.47	293.4	446.8	1.3	35.22	318
1013	2.54	292.9	447.7	0.94	35.08	319
1037	1.49	280.6	439.3			
1048				7.0	31.69	301
1057	7.98	271.2	432.6			
1073				4.0	29.05	286
1088	0.121*	262.7	428.8	0.79	30.02	300
1130	6.88	266.3	439.7	2.6	29.15	305
1023	1.31	288.4	444.8	4.5	33.83	312

* Apparently, a typo.

Table 5. Equilibrium constant and standard enthalpy of reaction (6), kJ/mol

T, K [13]	$\sum I$ (PtF_4)/ $\sum I$ (PtF_2)	K°(6), T K × 100*	–$\Delta_r H^\circ$(6), 298 K*
975	3.3	*2.63*	*22.0*
1007	1.57	*1.25*	*16.9*
1013	0.92	*0.733*	*12.6*
1037	0.52	0.414	8.19
1057	0.24	0.191	1.78
1088 **	0.12	0.210	3.03
1130 **	0.1	0.200	3.21
1023	0.29	0.231	2.96
Mean value			-3.8 ± 5.3 kJ/mol

*Values highlighted in italics in the table and marked with **x** in Fig. 2 were not used in further calculations.

** a (CeF_4) = 0.7 at 1088 K and 0.6 at 1130 K (according to Fig. 1 from [22]).

Table 6. Estimation of standard enthalpies of reactions (8), (10) at $K_\circ((6), T) > 1$, determined by the Third Law

T, K	$<\Delta_r H_\circ((8), 298\ K)$, kJ/mol	$<\Delta_r H_\circ((10), 298\ K)$, kJ/mol
976	-0.6	-5.4
1006	-0.8	-5.7
1013	-0.8	-5.8
1048	-1.0	-6.2
1073	-1.2	-6.4
1023	-0.9	-5.9
Mean value	$<-0.9 \pm 0.2$	$< -5.9 \pm 0.4$

Table 7. Comparative characteristics of trifluorides of some d -elements and cerium(IV) fluoride

MF_n	$\Delta_f H_{\circ 0}((MF_{n-1} - MF_n)s)$, kJ/mol	$D_{\circ 0}(MF_{n1} - F)$, kJ/mol	P (F), atm (750 K)	Reference
MnF_3	1046 – 852 = 194	303	1.2×10^{-12}	Calculation data taken from [31]
FeF_3	990 – 712 = 288	359	1.2×10^{-18}	
CoF_3	861 – 672 = 189	357	2.3×10^{-12}	
CeF_4	1939.9 – 1732.9 = 207.0	482	4.2×10^{-8}	Present work

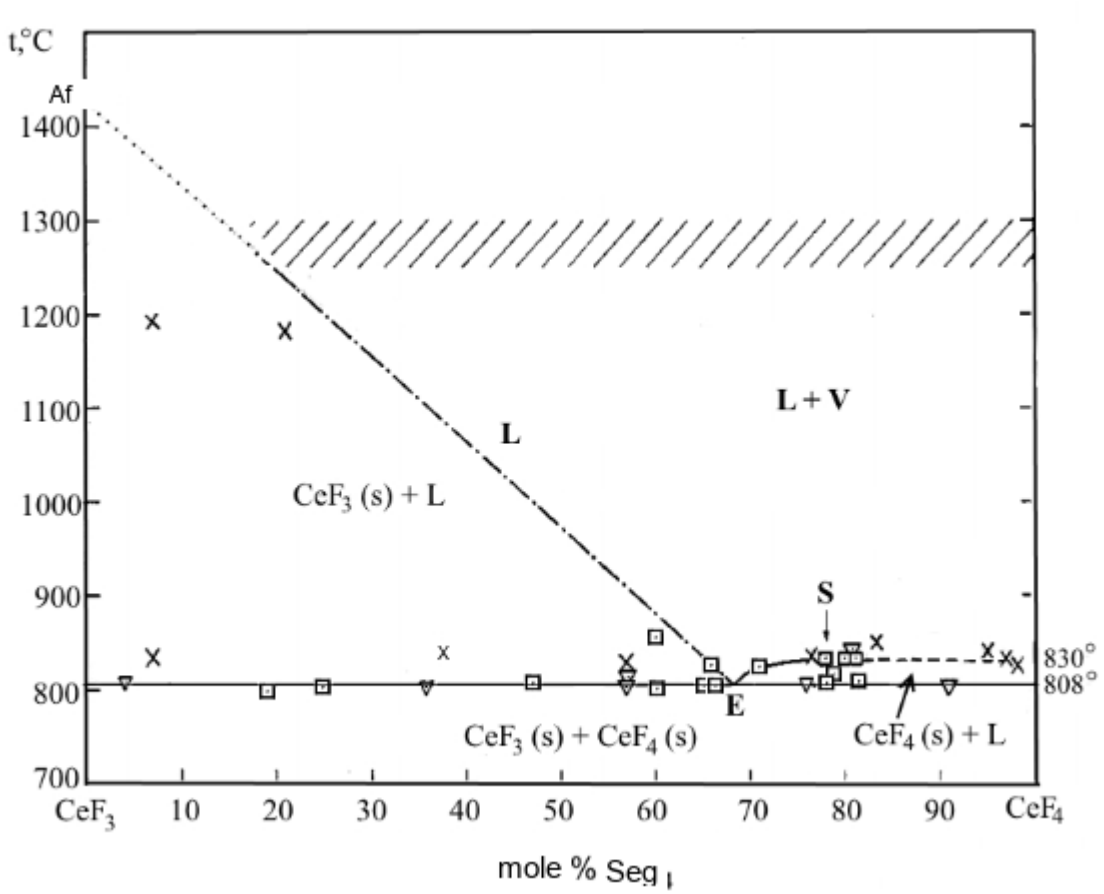

Fig. 1. Adapted approximate phase diagram of CeF_4–CeF_3 [22], where □ – points obtained from thermal analysis; ▽ – points obtained by differential thermal analysis; x – quenched compositions; //// – region where it is impossible to describe system behavior depending on temperature. t italic; CeF_4, mol. %; (s) replace with (s) and place next to formula w/o space

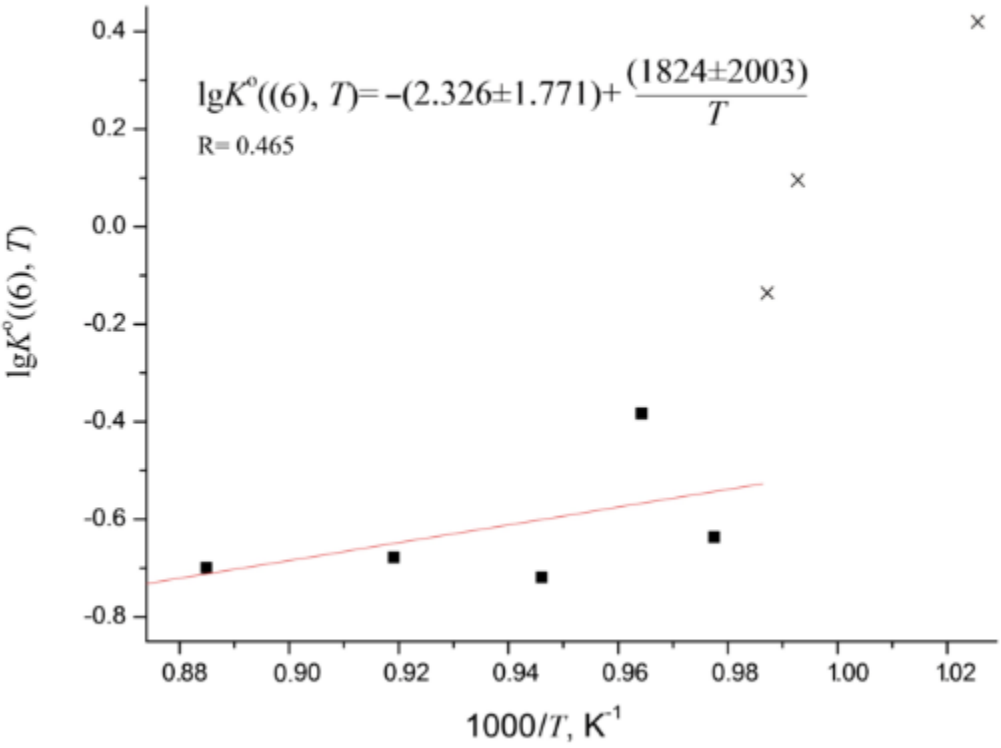

Fig. 2. Dependence of the equilibrium constant of reaction (6) on inverse temperature. Points marked with **X** were not used in calculations.