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Thermodynamic Properties Determination in LiF-CaF₂ Using Electrochemistry in High Temperature Fused Salts: Application to CeF₃

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Combining thermodynamic database and electrochemical measurements, CeF₃ thermodynamics properties were determined between 1113 K and 1233 K in LiF-CaF₂ solution. First, standard potentials of CeF₃/Ce were calculated in different reference states: liquid and solid, and infinite dilution. Then activity coefficients of CeF₃ were estimated in the different reference states and for different composition scales: molarity, molality and molar fraction. Finally, constants which interconnected the infinite dilution reference state and the solid and liquid reference states were evaluated.

Hydrometallurgical process (PUREX) is currently used for nuclear spent fuel reprocessing. In novel generation reactors, this process is no more available for lanthanides-actinides extraction (low solubility in aqueous medium). An alternative route is the use of pyrochemistry in molten salts and particularly molten fluorides, which exhibit several advantages: a non-sensitivity to radiolytic degradation, a good fuel dissolution properties and a large electrochemical window to extract the radioactive compounds in a metallic form. Pyrochemical route is then a promising option in an innovative closed fuel cycle.¹

The major step of spent fuel reprocessing is the actinides-lanthanides separation performed by electrochemical processes. In this partitioning strategy, the most radiotoxic elements (actinides) are separated from the lowest ones (lanthanides) to decrease the volume of high activity nuclear waste disposal. The knowledge of thermodynamic properties of actinides and lanthanides in solution is then crucial to predict their behavior in a complex multi-element system.

In this article, thermodynamic calculations have been done on cerium fluoride in the LiF-CaF₂ eutectics from 1113 to 1233 K. From electrochemical measurements, the main thermodynamic properties needed for the electrochemical separation evaluation were determined: standard potentials and activity coefficients in different reference states (liquid or solid reference state, and infinite dilution reference state) and for different composition scales (molarity, molality, or molar fraction), and also standard enthalpy and standard entropy of formation in the 1113–1233 K temperature range.

Experimental

- The cell consisted of a vitreous carbon crucible placed in a cylindrical vessel made of refractory steel and closed by a stainless steel lid cooled by circulating water. The inner part of the walls was protected against fluoride vapors by a graphite liner. The experiments were performed under an inert argon atmosphere (U-grade: less than 5 ppm O₂), previously dehydrated and deoxygenated using a purification cartridge (Air Liquide). The cell was heated using a programmable furnace and the temperature was measured using a Chromel-Alumel thermocouple.
- The electrolytic bath consisted of the eutectic LiF/CaF₂ (SDS Carlo-Erba 99.99%) mixture (79/21 molar ratio). Before use, it was dehydrated by heating under vacuum (3.10⁻² bar) from ambient temperature up to its melting point (762°C) for 72 h. Ions were introduced into the bath in the form of powder: CeF₃ (99.99%).
- Electrodes: Tungsten wire (1 mm diameter) was used as working electrode. The surface area of the working electrode was determined by measuring the immersion depth in the bath. The

auxiliary electrode was a vitreous carbon rod (3 mm diameter) with a large surface area. A platinum wire (0.5 mm diameter) immersed in the molten electrolyte acted as a quasi-reference electrode Pt/PtO_x/O²⁻.²

- Electrochemical equipment: all electrochemical studies and electrolyses were performed with an Autolab PG-STAT 30 potentiostat/galvanostat controlled by a computer using the research software NOVA 2.0.

Results and Discussion

Preliminary discussion.—Fluoroacidity.—To investigate the Ln/An separation process, their electrochemical behavior in the solution has to be known (electrochemical and thermodynamical properties are interconnected). Up to now, almost every lanthanides and actinides have been studied electrochemically,³⁻⁷ but only few thermodynamic properties in solution are available.

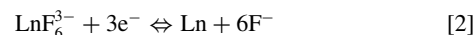
Acquisition of thermodynamic data in molten salts, especially in fluoride salts, is quite complex as each solvent has specific properties related to its fluoroacidity.⁸⁻⁹

Acidity definition consists in considering that anion donors from the ionic dissociation of a solvent molecule are “bases” although the anion acceptors are “acids”. For instance in water (Equation 1), bases are OH⁻ donors and acids are OH⁻ acceptors.



This definition is in agreement with the Bronsted acidity, valid for aprotic solvent such as fluoride salts. For instance, LiF solvent dissociation releases one anion (F⁻) and one cation (Li⁺), meaning that bases are F⁻ donors and acids F⁻ acceptors.

Several authors demonstrated that lanthanide fluorides are dissolved in the salt as LnF₆³⁻ fluoride complex,¹⁰⁻¹¹ which can be reduced in metallic Ln:



To predict the reduction potential of the electroactive species, Nernst law is used:

$$E_{\text{LnF}_6^{3-}/\text{Ln}} = E_{\text{LnF}_6^{3-}/\text{Ln}}^0 + \frac{RT}{3F} \ln \frac{a_{\text{LnF}_6^{3-}}}{a_{\text{F}^-}^6} \quad [3]$$

where a_i the activity of the i species

As the fluoride activity value a_{F⁻} for a selected solvent is constant but unknown, thermodynamic data determined in the article are only valid in LiF-CaF₂. However, this method for determining thermodynamic parameters is universal and can be extended to other solvent systems.

Nernst potential measurements.—The goal is to experimentally measure the equilibrium potential of Ce(III)/Ce redox couple and to

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Table I. LiF/Li reduction potentials in the LiF-CaF₂ eutectics for different temperature in V vs. F₂/F⁻.

T °K	ΔG° kJ/mol	E° LiF/Li V vs. F ₂ /F ⁻	a _{LiF} in LiF-CaF ₂	E LiF/Li V vs. F ₂ /F ⁻
1113	509.385	-5.279	0.797865	-5.300
1153	506.396	-5.248	0.798332	-5.270
1193	503.627	-5.219	0.798770	-5.242
1233	500.88	-5.190	0.799182	-5.214

compare it with thermodynamic data (to estimate the main parameters a , γ , E° ...).

In this study, the designated reference electrode is F₂/F⁻, currently used and convenient for thermodynamic calculation in fluoride-based salts.

Solvent.—A platinum wire immersed in the solution was used as a quasi-reference electrode. Because of its potential relative stability, potentials were referenced to an internal reference, the solvent reduction potential:



The Nernst potential of the LiF/Li is then:

$$E_{\text{LiF/Li}} = E_{\text{LiF/Li}}^0 + \frac{RT}{F} \ln a_{\text{LiF}} \quad [5]$$

where F the Faraday constant (96500 C/mol), T the absolute temperature (°K), R the ideal gas constant (8.314 J/K/mol) and a_{LiF} the activity of LiF in LiF-CaF₂.

HSC 6.1 database was used to calculate the LiF/Li standard potential, E° (LiF/Li), referred to F₂/F⁻ potential and the LiF activity was estimated thanks to the FactSage software (FTSalt database) for LiF-CaF₂ eutectic composition at a defined temperature.

From these data, the evaluation of $E_{\text{LiF/Li}}$ vs F₂/F⁻ is then possible and the different values are gathered in Table I.

Solute.—To accurately measure the Ce(III)/Ce equilibrium potential (ΔE_{exp}), the work done on dynamic reference electrodes was used to create an in-situ redox system. A short electrolysis on tungsten was realized to cover the electrode of metallic cerium, and then a relaxation curve of the cathode potential, corresponding to an equilibrium potential measurement, was recorded. The electrode potential in the relaxation part is then the equilibrium potential of Ce(III)/Ce couple.

Afonichkin et al.¹² and Duran-Klie et al.¹³ worked on the electrolysis parameters, where intensity and polarization duration were optimized. From these publications, polarization duration was fixed at 35 s and the intensity at 0.1 A. To avoid the lithium co-deposition, the electrolysis was manually stopped during the experiment when the electrode potential tends to the lithium deposition one. The global curve of the electrode potential (V vs. LiF/Li) versus time is presented in Figure 1: the first part represents the polarization curve and the second one the relaxation curve.

An horizontal plateau of few seconds (<10 s) is observed and corresponds to the equilibrium potential ΔE_{exp} between the deposited metallic Ce and Ce(III) in the salt versus Li⁺/Li. Then, ΔE_{exp} is then referred to F₂/F⁻ potential with Equation 6 for each temperature:

$$E\left(\text{V}/\text{F}_2/\text{F}^- \right) = E_{\text{LiF/Li}}\left(\text{V}/\text{F}_2/\text{F}^- \right) + \Delta E_{\text{exp}}\left(\text{V}/\text{LiF}/\text{Li} \right) \quad [6]$$

where $E_{\text{LiF/Li}}$ is the potential of the lithium fluoride reduction calculated as previously described (Table I) in V vs. F₂/F⁻, ΔE_{exp} is the potential of the cerium redox couple in V vs. LiF/Li and E is the potential of cerium reduction in V vs. F₂/F⁻.

This in-line measurement of the cerium redox couple potential was found to be accurate enough (± 5 mV) and very reproducible for Nernst potential measurement.

Thermodynamic definition of a system.—In thermodynamics, a reference state and a composition scale has to be firstly defined.

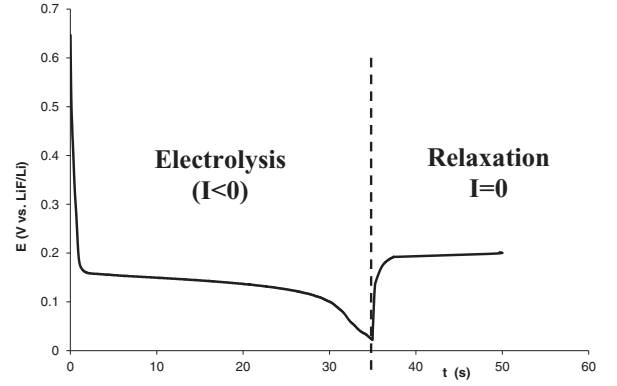


Figure 1. Electrolysis at -100 mA during 35 s in LiF-CaF₂-CeF₃ (0.18 mol/L) and its relaxation curve at T = 1113 K. Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt.

Different reference states were used in this publication and are defined below:

- The liquid reference state: the solute is considered as a pure liquid at working temperature. This reference state is noted L.
- The solid reference state: the solute is considered as a pure solid at working temperature. This reference state is noted S.
- The infinite dilution state: the solute is considered as a single molecule completely surrounded by solvent and is noted ID. No solute-solute interactions are taken into account.

It must be emphasized that the definition of the reference state is purely arbitrary and as such can be entirely hypothetical, i.e. corresponding to no physical reality. Thus, the definition of the activity coefficient depends on the composition scale adopted as well as on the reference state.

Concerning the composition scales for miscible mixture, the composition of the liquid mixture can be expressed as a molarity C (mol/L), a molality m (mol/kg) or a molar fraction x . Unlike the molarity, molar fraction and molality have to advantage to be independent of temperature. From these composition scales, it come that the solute activity is defined as:

$$a_{C,i} = \gamma_{C,i} (C_i/C^{\text{ref}}) \quad [7]$$

$$a_{m,i} = \gamma_{m,i} (m_i/m^{\text{ref}}) \quad [8]$$

$$a_{x,i} = \gamma_{x,i} (x_i/x^{\text{ref}}) \quad [9]$$

where γ is the activity coefficient, C^{ref} is the reference molarity (1 mol/L), m^{ref} is the reference molality (1 mol/kg), and x^{ref} is the reference molar fraction¹ of the solute. These reference states in solution are hypothetical ideal states of unit value to keep the activities dimensionless.

Standard potential determination.—Theoretical thermodynamic values were extracted from FactSage and HSC 6.1 database, where the composition scale is the molar fraction.

Liquid reference state.—HSC 6.1 software allows the standard Gibbs enthalpy $\Delta G^{0,L}$ of the reaction presented below to be determined, where the solute is considered as pure compound in a liquid state.

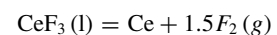
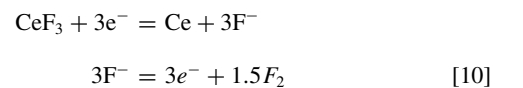


Table II. Standard Gibbs energies and standard potentials of CeF₃/Ce couple in the liquid reference state at different temperatures.

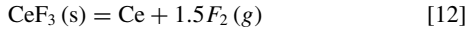
T °K	ΔG ^{o,L} kJ/mol	E ^{0,L} V / F ₂ /F ⁻
1113	1392.929	-4.811
1153	1384.639	-4.783
1193	1376.405	-4.754
1233	1368.224	-4.726

As F₂/F⁻ couple is the reference system, its potential is set to zero: it comes that the standard potential of CeF₃/Ce can be determined from Equation 11 in V vs. F₂/F⁻:

$$\Delta G^{0,L} = -nFE^{0,L} \quad [11]$$

Standard potential in liquid reference state E^{0,L} of CeF₃/Ce is then directly calculated from thermodynamic database and expressed in V vs. F₂/F⁻ by fixing the physical state of the solute (Table II).

Solid reference state.—The standard Gibbs enthalpy ΔG^{0,S} of reaction 12 in the solid reference state is extracted from FactSage database (not available in HSC):



Values of E^{0,S} in V vs. F₂/F⁻ are in Table III.

Infinite dilution reference state.—In this reference system, the solute composition can be expressed as a molarity C (mol/L), a molality m (mol/kg) or a molar fraction x. The standard potential is then dependent on the composition scale, defining E^{0,C}_{ID}, E^{0,m}_{ID}, and E^{0,x}_{ID}. The methodology for determining E⁰_{ID} is presented with the molarity, but is valid for both molality and molar fraction.

In the molarity composition scale, the solute activity is defined in Equation 7. According to Nernst law, the reduction potential of CeF₃ into Ce is expressed as:

$$E_{\text{CeF}_3/\text{Ce}} = E_{\text{ID CeF}_3/\text{Ce}}^{0,C} + \frac{RT}{3F} \ln \gamma_{\text{CeF}_3}^C + \frac{RT}{3F} \ln C_{\text{CeF}_3} \quad [13]$$

It comes:

$$E_{\text{CeF}_3/\text{Ce}} - \frac{RT}{3F} \ln C_{\text{CeF}_3} = E_{\text{ID CeF}_3/\text{Ce}}^{0,C} + \frac{RT}{3F} \ln \gamma_{\text{CeF}_3}^C \quad [14]$$

At infinite dilution, C_{CeF₃} tends toward 0 and γ to 1, the extrapolation of the experimental value of (E_{CeF₃/Ce} - $\frac{RT}{3F} \ln C_{\text{CeF}_3}$) versus C_{CeF₃} is equal to the CeF₃/Ce standard potential E^{0,C}_{ID}.¹⁴ This graph is presented in Figure 2 at different temperatures.

Standard potentials in LiF-CaF₂ at infinite dilution were determined between 1113 and 1233 K and their linear variations with the temperature are plotted in Figure 3. The linear relationships are presented below for the different composition scales:

$$E_{\text{ID CeF}_3/\text{Ce}}^{0,x} = 8.05 \cdot 10^{-4} T - 5.787$$

$$E_{\text{ID CeF}_3/\text{Ce}}^{0,m} = 7.05 \cdot 10^{-4} T - 5.781$$

Table III. Standard Gibbs energies and standard potentials of CeF₃/Ce couple in the solid reference state at different temperatures.

T °K	ΔG ^{o,S} kJ/mol	E ^{0,S} V / F ₂ /F ⁻
1113	1417.572	-4.897
1153	1408.101	-4.864
1193	1398.666	-4.831
1233	1389.270	-4.799

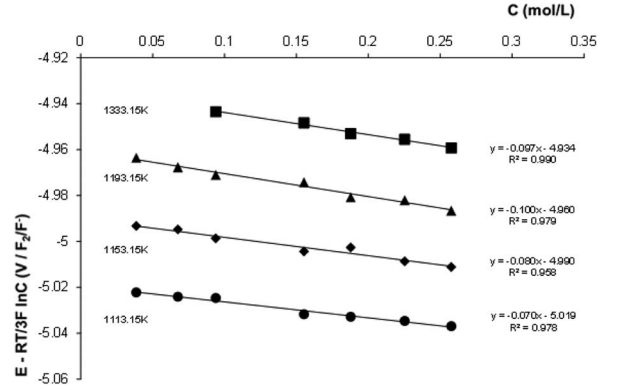


Figure 2. Determination of standard potential in infinite dilution reference state and molarity composition scale of Ce^{III}/Ce couple in LiF-CaF₂ eutectic mixture at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

$$E_{\text{ID CeF}_3/\text{Ce}}^{0,C} = 7.1 \cdot 10^{-4} T - 5.809$$

where T is the absolute temperature in K and E⁰_{ID} the standard potential at infinite dilution in V vs. F₂/F⁻.

This linearity indicates that the standard enthalpy ΔH^o and the standard entropy ΔS^o are not temperature-depend in our temperature range and can be calculated from Equation 15:

$$E_{\text{CeF}_3/\text{Ce}}^0 = -\frac{\Delta H_{\text{CeF}_3}^0}{nF} + T \frac{\Delta S_{\text{CeF}_3}^0}{nF} \quad [15]$$

Identical values are obtained, whatever the composition scale, and the average of the 3 values gives:

$$\Delta S_{\text{CeF}_3}^0 = -204.8 \text{ J/K/mol}$$

$$\Delta H_{\text{CeF}_3}^0 = -1681.8 \text{ kJ/mol}$$

Activity coefficient determination.—Knowing the standard potential, the activity coefficient can be determined by mixing the definition of the activity (Equations 7, 8, and 9) and the Nernst equation (Equation 13):

$$\gamma^Y = \exp \left[\frac{3F}{RT} (E - E^{0,Y} - \frac{RT}{3F} \ln Y) \right] \quad [16]$$

where Y is either C, m or x.

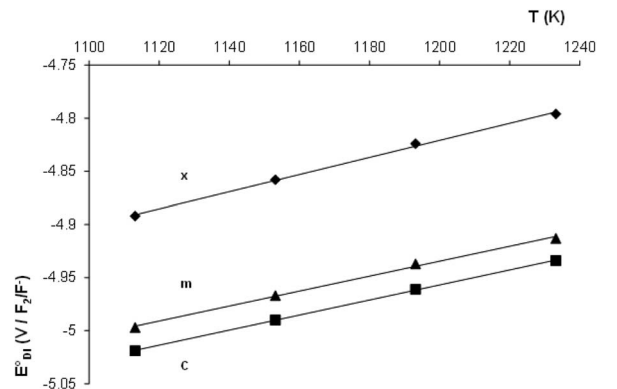


Figure 3. Linear relationships between the temperature and the standard potential of Ce^{III}/Ce in the different composition scales at infinite dilution reference state in LiF-CaF₂ eutectic mixture.

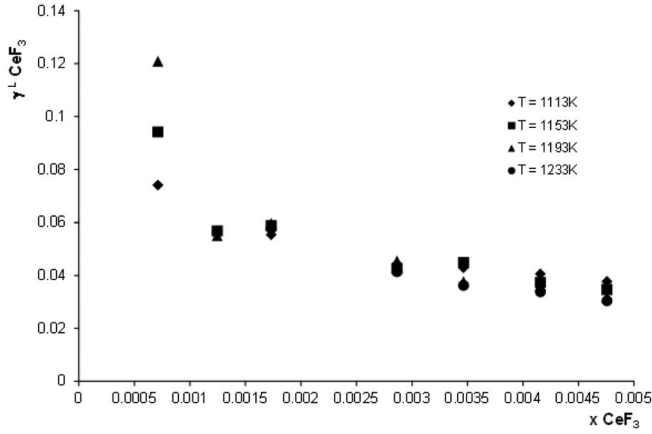


Figure 4. Evolution of the activity coefficient in liquid reference state versus cerium fluoride molar fraction at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

Liquid reference state.—The standard potential E_L^0 of the electrochemical system was previously determined in the molar fraction composition scale and the activity coefficient was estimated thanks to Equation 16. Data are represented in Figure 4 at different temperatures.

A slight decrease of the activity coefficient is observed with an increase of CeF_3 molar fraction. It can also be noted in this reference state that γ^L is almost independent of the temperature (except for the most diluted solution).

Solid reference state.—Using the same methodology, data obtained for the solid reference state are gathered in Figure 5 at 1113 K, 1153 K, 1193 K and 1233 K.

A decrease of γ^S is observed when x_{CeF_3} increases. Moreover, the activity coefficient in the solid reference state depends on the temperature: the higher the temperature is, the lower γ^S is.

Infinite dilution reference state.—In the previous, the standard potentials of CeF_3/Ce were determined for the different composition scales at infinite dilution. Using the appropriate E^0 , activity coefficients γ^{ID} in a defined composition scale were calculated and presented in Figures 6, 7, and 8 for the molar fraction, the molality, and the molarity respectively.

Whatever the composition scale, the same trend is observed: the activity coefficients decrease with an increase of CeF_3 in the solution.

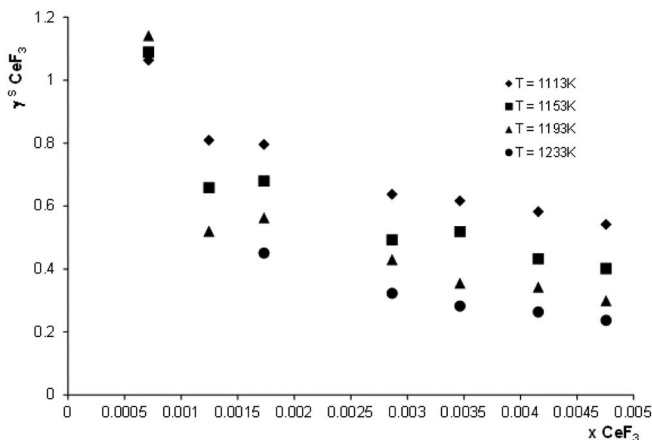


Figure 5. Evolution of the activity coefficient in solid reference state versus cerium fluoride molar fraction at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

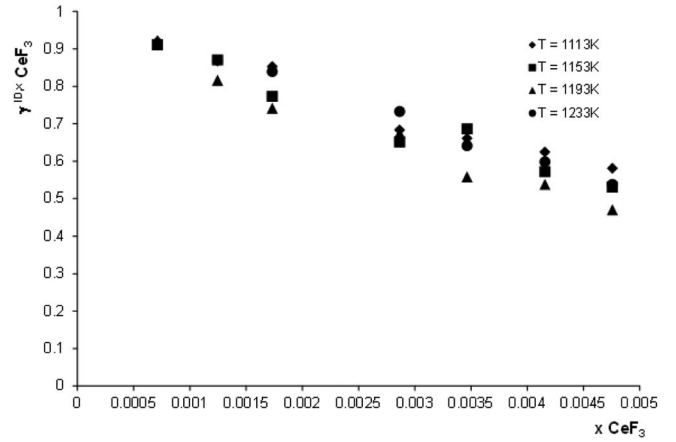


Figure 6. Evolution of the activity coefficient at infinite dilution reference state in the molar fraction composition scale versus cerium fluoride molar fraction at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

γ values vary randomly with the temperature and no tendency can be extracted from our results. However, the properties of infinite dilution solutions are respected where γ^{ID} tends to 1 when CeF_3 amount tends to zero. In our experiments, the solution can be considered as an ideal solution ($\gamma = 1$) for $m < 0.02$ mol/kg.

Change of reference state.—The calculation of γ was developed for different reference states and these activity coefficients are interconnected. In the molar fraction composition scale, the Nernst potential in the different reference states can be written:

$$E = E_{\text{ID}}^0 + \frac{RT}{3F} \ln x + \frac{RT}{3F} \ln \gamma^{\text{ID}} \quad [17]$$

$$E = E_L^0 + \frac{RT}{3F} \ln x + \frac{RT}{3F} \ln \gamma^L \quad [18]$$

$$E = E_S^0 + \frac{RT}{3F} \ln x + \frac{RT}{3F} \ln \gamma^S \quad [19]$$

Combining these equations, and in the specific case of infinite dilution ($x \rightarrow 0$)

$$\frac{\gamma^L}{\gamma^{\text{ID}}} = \exp \left[\frac{3F}{RT} (E_{\text{ID}}^0 - E_L^0) \right] = \text{constant} = \gamma_{\infty}^L \quad [20]$$

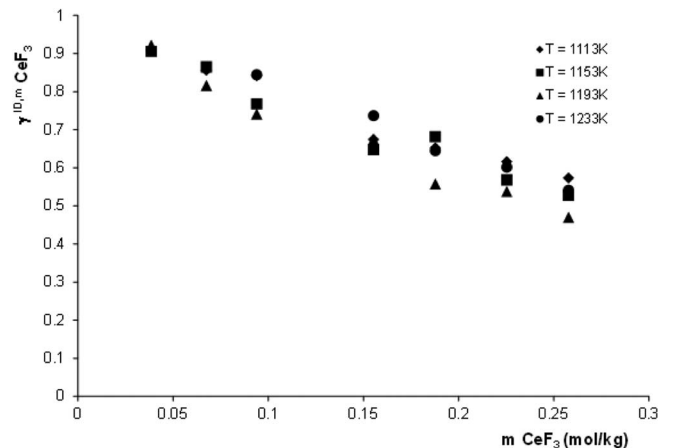


Figure 7. Evolution of the activity coefficient at infinite dilution reference state in the molality composition scale versus cerium fluoride molality (mol/kg) at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

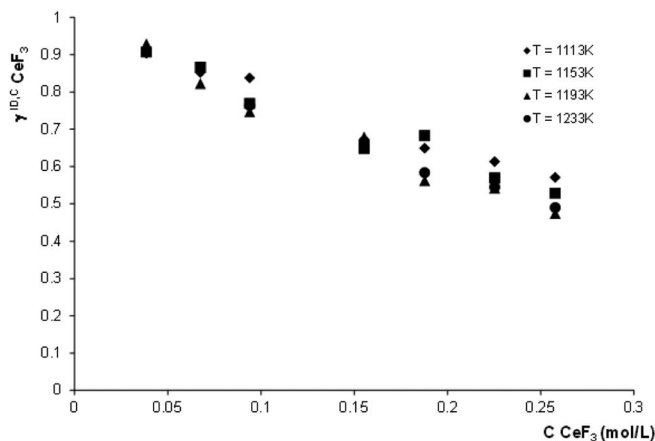


Figure 8. Evolution of the activity coefficient at infinite dilution reference state in the molarity composition scale versus cerium fluoride molarity (mol/L) at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

$$\frac{\gamma^S}{\gamma^{ID}} = \exp \left[\frac{3F}{RT} (E_{ID}^0 - E_S^0) \right] = \text{constant} = \gamma_{\infty}^S \quad [21]$$

These gamma values (γ_{∞}^L and γ_{∞}^S) can be used to change the reference state from infinite dilution to solid or liquid reference states and are presented in Table IV at different temperatures.

Conclusions

From electrochemical measurements and a thermodynamic database, it was possible to accurately determine thermodynamic properties of CeF₃ in LiF-CaF₂ solution at different temperatures. Calculations of CeF₃/Ce standard potentials as well as activity coefficients were performed in the liquid, in the solid, and in the infinite dilution reference state, and for different composition scales (molar

Table IV. Infinite activity coefficient in solid and liquid reference states for cerium fluoride in LiF-CaF₂ media at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

T °K	$\gamma_{\infty,L}$	$\gamma_{\infty,S}$
1113	0.0650	0.9330
1153	0.0654	0.7562
1193	0.0675	0.6373
1233	0.05655	0.4409

fraction, molarity, and molality) and temperatures. Moreover, constants to change the reference state from infinite dilution to liquid and solid reference states were also calculated at different temperatures. This general methodology can also be used with other electroactive species and for different solvents.

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