Thermodynamic properties determination in LiF-CaF 2 using electrochemistry in high temperature fused salts: application to CeF 3

Mathieu Gibilaro, Laurent Massot, Pierre Chamelot

To cite this version:

Mathieu Gibilaro, Laurent Massot, Pierre Chamelot. Thermodynamic properties determination in LiF-CaF 2 using electrochemistry in high temperature fused salts: application to CeF 3. Journal of The Electrochemical Society, 2017, 164 (12), pp.307-311. 10.1149/2.0691712jes . hal-02134835

HAL Id: hal-02134835

https://hal.science/hal-02134835

Submitted on 20 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Open Archive Toulouse Archive Ouverte (OATAO)

OATAO is an open access repository that collects the work of some Toulouse researchers and makes it freely available over the web where possible.

This is an author's version published in: http://oatao.univ-toulouse.fr/20360

Official URL: https://doi.org/10.1149/2.0691712jes

To cite this version:

Gibilaro, Mathieu and Massot, Laurent and Chamelot, Pierre Thermodynamic properties determination in LiF-CaF 2 using electrochemistry in high temperature fused salts: application to CeF 3. (2017) Journal of The Electrochemical Society, 164 (12). 307-311. ISSN 0013-4651

Any correspondence concerning this service should be sent to the repository administrator: tech-oatao@listes-diff.inp-toulouse.fr

Thermodynamic Properties Determination in LiF-CaF$_2$ Using Electrochemistry in High Temperature Fused Salts: Application to CeF$_3$

M. Gibilaro,[*],[z] L. Massot, and P. Chamelot

Laboratoire de Génie Chimique UPS-CNRS, Université de Toulouse, Toulouse 31062, France

---

Combining thermodynamic database and electrochemical measurements, CeF$_3$ thermodynamics properties were determined between 1113 K and 1233 K in LiF-CaF$_2$ solution. First, standard potentials of CeF$_3$/Ce were calculated in different reference states: liquid and solid, and infinite dilution. Then activity coefficients of CeF$_3$ 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-sensivity 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-CaF$_2$ 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 O$_2$), 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/CaF$_2$ (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: CeF$_3$ (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$_x$/O^{2-}.[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 quiet 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.

$$2H_2O \Leftrightarrow H_3O^+ + OH^- \qquad [1]$$

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 LnF$_6$$^{3-}$ fluoride complex,[10–11] which can be reduced in metallic Ln:

$$LnF_6^{3-} + 3e^- \Leftrightarrow Ln + 6F^- \qquad [2]$$

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

$$E_{LnF_6^{3-}/Ln} = E^0_{LnF_6^{3-}/Ln} + \frac{RT}{3F}\ln\frac{a_{LnF_6^{3-}}}{a_{F^-}^6} \qquad [3]$$

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-CaF$_2$. 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

---

[*] Electrochemical Society Member.

[z] E-mail: gibilaro@chimie.ups-tlse.fr

Table I. LiF/Li reduction potentials in the LiF-CaF$_2$ eutectics for different temperature in V vs. F$_2$/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 F$_2$/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:

$$\mathrm{LiF + e^- \rightarrow Li + F^-} \qquad [4]$$

The Nernst potential of the LiF/Li is then:

$$\mathrm{E_{LiF/Li} = E^0_{LiF/Li} + \frac{RT}{F}\ln \mathit{a}_{LiF}} \qquad [5]$$

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-CaF$_2$.

HSC 6.1 database was used to calculate the LiF/Li standard potential, E° (LiF/Li), referred to F$_2$/F$^-$ potential and the LiF activity was estimated thanks to the FactSage software (FTSalt database) for LiF-CaF$_2$ eutectic composition at a defined temperature.

From these data, the evaluation of E $_{LiF/Li}$ vs F$_2$/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 F$_2$/F$^-$ potential with Equation 6 for each temperature:

$$\mathrm{E\left(V\!/_{F_2/F^-}\right) = E_{LiF/Li}\left(V\!/_{F_2/F^-}\right) + \Delta E_{exp}\left(V\!/_{LiF/Li}\right)} \qquad [6]$$

where E$_{LiF/Li}$ is the potential of the lithium fluoride reduction calculated as previously described (Table I) in V vs. F$_2$/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. F$_2$/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.

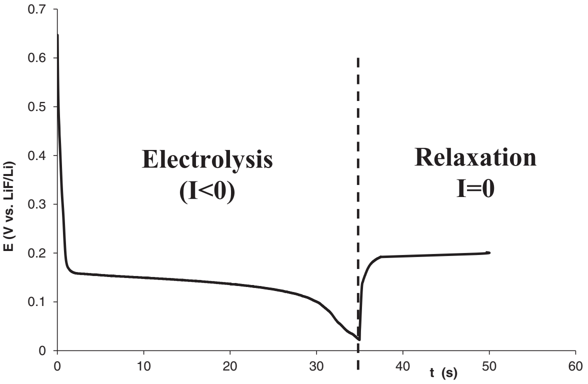

Figure 1. Electrolysis at −100 mA during 35 s in LiF-CaF$_2$-CeF$_3$ (0.18 mol/L) and its relaxation curve at T = 1113 K. Working electrode: W; Counter electrode: vitreous carbon; Quasi-reference electrode: Pt.

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:

$$\mathrm{a_{C,i}} = \gamma_{\mathrm{C,i}}\left(\mathrm{C_i/C^{ref}}\right) \qquad [7]$$

$$\mathrm{a_{m,i}} = \gamma_{\mathrm{m,i}}\left(\mathrm{m_i/m^{ref}}\right) \qquad [8]$$

$$\mathrm{a_{x,i}} = \gamma_{\mathrm{x,i}}\left(\mathrm{x_i/x^{ref}}\right) \qquad [9]$$

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 fraction[1] 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.

$$\begin{aligned} \mathrm{CeF_3 + 3e^-} &= \mathrm{Ce + 3F^-} \\ \mathrm{3F^-} &= 3e^- + 1.5F_2 \\ \mathrm{CeF_3\,(l)} &= \mathrm{Ce} + 1.5F_2\,(g) \end{aligned} \qquad [10]$$

Table II. Standard Gibbs energies and standard potentials of CeF_3/Ce couple in the liquid reference state at different temperatures.

T °K	$\Delta G^{\circ,L}$ 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 F_2/F^- couple is the reference system, its potential is set to zero: it comes that the standard potential of CeF_3/Ce can be determined from Equation 11 in V vs. F_2/F^-:

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

Standard potential in liquid reference state $E^{0,L}$ of CeF_3/Ce is then directly calculated from thermodynamic database and expressed in V vs. F_2/F^- by fixing the physical state of the solute (Table II).

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

$$CeF_3\,(s) = Ce + 1.5F_2\,(g) \qquad [12]$$

Values of $E^{0,S}$ in V vs. F_2/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 $E_{ID}^{0,C}$, $E_{ID}^{0,m}$, and $E_{ID}^{0,x}$. The methodology for determining E_{ID}^{0} 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 CeF_3 into Ce is expressed as:

$$E_{CeF_3/Ce} = E_{ID}^{0,C}{}_{CeF_3/Ce} + \frac{RT}{3F}\ln\gamma_{CeF_3}^{C} + \frac{RT}{3F}\ln C_{CeF_3} \qquad [13]$$

It comes:

$$E_{CeF_3/Ce} - \frac{RT}{3F}\ln C_{CeF_3} = E_{ID}^{0,C}{}_{CeF_3/Ce} + \frac{RT}{3F}\ln\gamma_{CeF_3}^{C} \qquad [14]$$

At infinite dilution, C_{CeF_3} tends toward 0 and γ to 1, the extrapolation of the experimental value of $(E_{CeF_3/Ce} - \frac{RT}{3F}\ln C_{CeF_3})$ versus C_{CeF_3} is equal to the CeF_3/Ce standard potential $E_{ID}^{0,C}$.[14] This graph is presented in Figure 2 at different temperatures.

Standard potentials in LiF-CaF_2 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:

$$E_{ID}^{0,x}{}_{CeF_3/Ce} = 8.05\ 10^{-4}\ T - 5.787$$

$$E_{ID}^{0,m}{}_{CeF_3/Ce} = 7.05\ 10^{-4}\ T - 5.781$$

$$E_{ID}^{0,C}{}_{CeF_3/Ce} = 7.1\ 10^{-4}\ T - 5.809$$

where T is the absolute temperature in K and E_{ID}^{0} the standard potential at infinite dilution in V vs. F_2/F^-.

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

$$E_{CeF_3/Ce}^{0} = -\frac{\Delta H_{CeF_3}^{0}}{nF} + T\frac{\Delta S_{CeF_3}^{0}}{nF} \qquad [15]$$

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

$$\Delta S_{CeF_3}^{0} = -204.8\ J/K/mol$$

$$\Delta H_{CeF_3}^{0} = -1681.8\ kJ/mol$$

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):

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

where Y is either C, m or x.

Table III. Standard Gibbs energies and standard potentials of CeF_3/Ce couple in the solid reference state at different temperatures.

T °K	$\Delta G^{\circ,S}$ 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

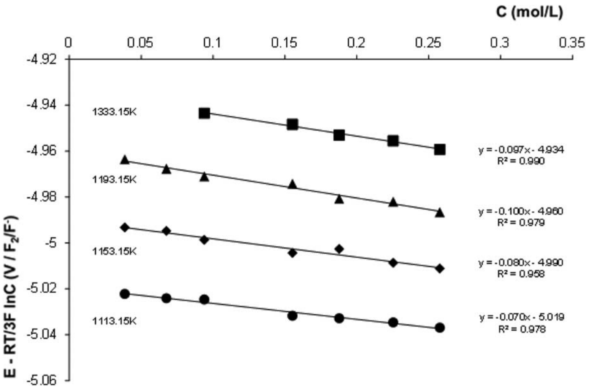

Figure 2. Determination of standard potential in infinite dilution reference state and molarity composition scale of Ce^{III}/Ce couple in LiF-CaF_2 eutectic mixture at at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

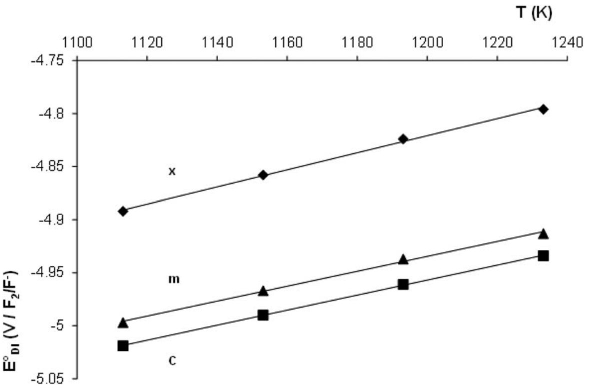

Figure 3. Linear relationships between the temperature and the standard potential of Ce^{III}/Ce in the different composition scales at infinite dilution reference state in LiF-CaF_2 eutectic mixture.

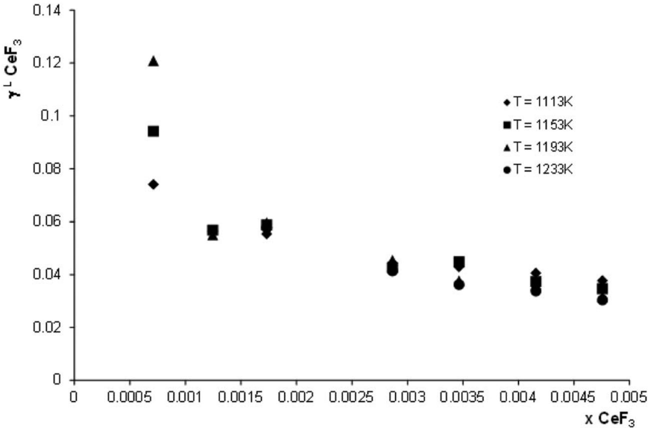

Figure 4. Evolution of the activity coefficient in liquid reference state versus cerium fluoride molar fraction at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

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°, 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. 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.

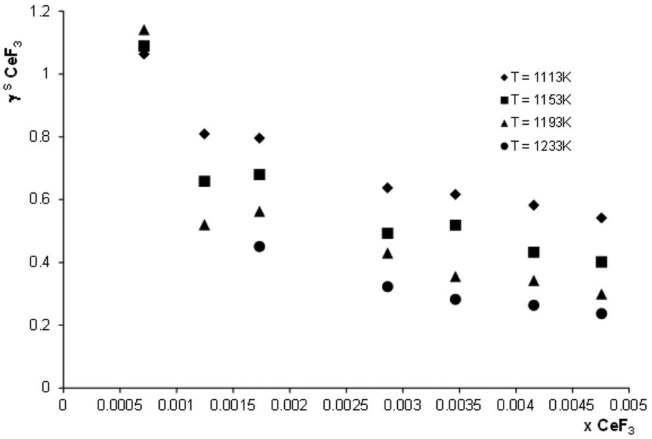

Figure 5. Evolution of the activity coefficient in solid reference state versus cerium fluoride molar fraction at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

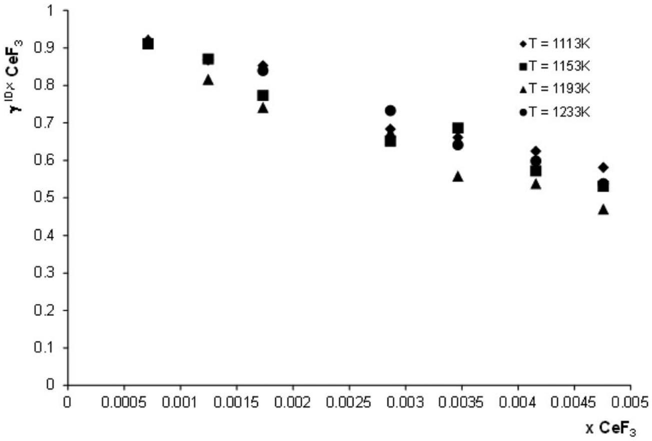

Figure 6. Evolution of the activity coefficient at infinite dilution reference state in the molar fraction composition scale versus cerium fluoride molar fraction at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

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:

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

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

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

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

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

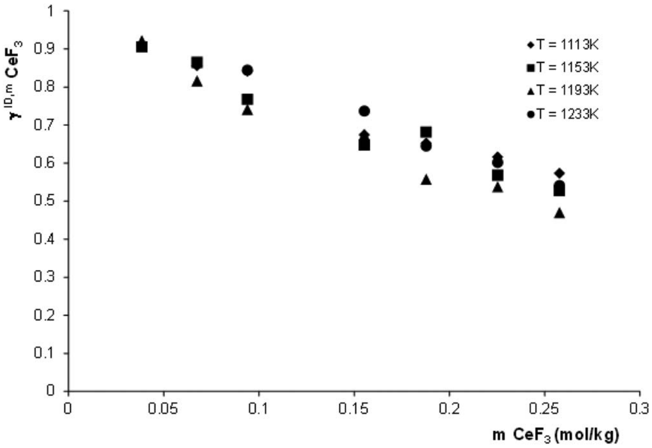

Figure 7. Evolution of the activity coefficient at infinite dilution reference state in the molality composition scale versus cerium fluoride molality (mol/kg) at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

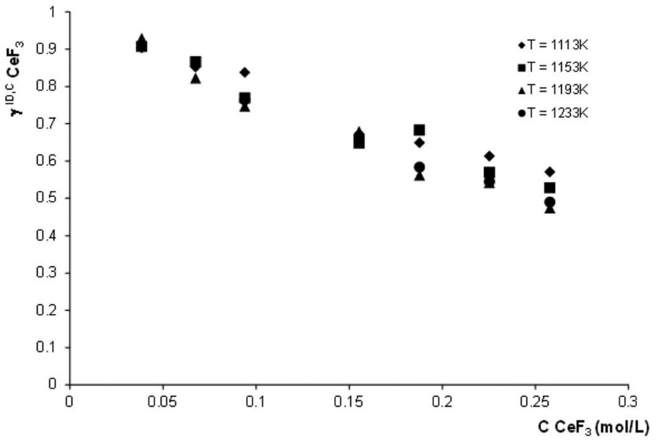

Figure 8. Evolution of the activity coefficient at infinite dilution reference state in the molarity composition scale versus cerium fluoride molarity (mol/L) at different temperatures (1113 K, 1153 K, 1193 K, and 1233 K).

$$\frac{\gamma^{S}}{\gamma^{ID}} = \exp \left. \frac{3F}{RT}\left(E^{0}_{ID} - E^{0}_{S}\right)\right] = \text{constant} = \gamma^{S}_{\infty} \qquad [21]$$

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 CeF_3 in LiF-CaF_2 solution at different temperatures. Calculations of CeF_3/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 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.

Table IV. Infinite activity coefficient in solid and liquid reference states for cerium fluoride in LiF-CaF_2 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

References

1. R. Malmbeck, C. Nourry, M. Ougier, P. Soucek, J. P. Glatz, T. Kato, and T. Koyama, *Energy Procedia*, **7**, 93 (2011).
2. A. D. Graves and D. Inman, *Nature*, **208**, 481 (1965).
3. M. Gibilaro, L. Massot, P. Chamelot, and P. Taxil, *Electrochim. Acta*, **54**(22), 5300 (2009).
4. V. Constantin, A. M. Popescu, and M. Olteanu, *J. Rare Earth*, **28**(3), 428 (2010).
5. M. Gibilaro, L. Massot, P. Chamelot, and P. Taxil, *J. Nucl. Mater.*, **382**(1), 39 (2008).
6. L. Massot Chamelot, L. Cassayre, and P. Taxil, *Electrochim. Acta*, **55**(16), 4758 (2010).
7. J. Zhang, *J. Nucl. Mater.*, **447**(1–3), 271 (2014).
8. A. L. Bieber, L. Massot, M. Gibilaro, P. Chamelot, and P. Taxil, *Electrochim. Acta*, **56**, 5022 (2011).
9. M. Kergoat, M. Gibilaro, L. Massot, and P. Chamelot, *Electrochim. Acta*, **176**, 265 (2015).
10. A.-L. Rollet, A. Rakhmatullin, and C. Bessada, *Int. J. Thermophys.*, **26**(4), 1115 (2005).
11. C. Bessada, A.-L. Rollet, A. Rakhmatullin, I. Nuta, P. Florian, and D. Massiot, *C. R. Chimie*, **9**, 374 (2006).
12. V. K. Afonichkin, A. L. Bovet, V. Ignatiev, A. V. Panov, V. G. Subbotin, A. I. Surenkov, A. D. Toropov, and A. L. Zherebtsov, *J. Fluor. Chem.*, **130**, 83 (2009).
13. G. Duran-Klie, D. Rodrigues, and S. Delpech, *Electrochim. Acta*, **195**, 19 (2016).
14. F. Lantelme and Y. Berghoute, *J. Electrochem. Soc.*, **146**(11), 4137 (1999).