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Modeling and estimating the distribution of trivalent actinides and lanthanides between molten fluorides and liquid metal

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Abstract

Separation of actinides and lanthanides between a fluorinated phase rich in LiF and a metallic phase showed that the deviation (E) between the theoretical and experimental results for the trivalent actinides and lanthanides can be described using a relative ionic potential ΔPI between Li^+ and the cations An^{3+} or Ln^{3+}, such that for each of the two groups $E=\alpha\Delta PI+\beta$, where α is temperature-dependent and β varies with the nature of the system. The results obtained in the MSBR development program were analyzed to determine α at various temperatures for both series of elements, and to propose expressions for $\Delta G^\circ_f(AnF_3)$ versus temperature in the liquid phase (where An represents Np, Am, Cm or Cf). E was measured for U(III) and La(III) in the $LiF–CaF_2/Zn–Mg$ system at 720°C, and an empirical model was developed to simulate the distribution of all the trivalent actinides and lanthanides in the same system. © 1998 Elsevier Science S.A.

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1. Introduction

Experimental investigations of actinide/lanthanide separation are highly complex as they must be conducted by telemanipulation in shielded cells, which implies very long lead times and considerable expense. It is thus advantageous initially to use representative stable isotopes such as ^{238}U for the actinides and ^{139}La for the lanthanides. The authors of this work describe how the results obtained for the distribution of these two elements between a fluorinated salt phase rich in LiF and a metallic phase can be applied to a deviation estimation method to simulate the distribution of all the trivalent actinides and lanthanides. The method is used here to simulate the distribution between $LiF–CaF_2$ and Zn–Mg at 720°C.

2. Principle

The distribution of species M between two immiscible phases corresponds to the equilibrium:

$$MF_{x(\text{salt})}+\frac{x}{y}R_{(\text{metal})}\leftrightarrow M_{(\text{metal})}+\frac{x}{y}RF_{y(\text{salt})} \tag{1}$$

At a given temperature, its equilibrium constant K can be calculated by using thermodynamic data:

$$\log D_M=\frac{x}{y}\log D_R+\log K+\log\left(\frac{\gamma_R^{x/y}\cdot\gamma_{MF_x}}{\gamma_{RF_y}^{x/y}\cdot\gamma_M}\right) \tag{2}$$

in which D_M are the distribution coefficient of species M ($D_M=X_M/X_{MF_x}$). R is the reducing agent. If the activity coefficients are constant, the last term corresponds to the deviation from the ideal situation:

$$E=\frac{x}{y}\log\frac{\gamma_R^\infty}{\gamma_{RF_y}^\infty}+\log\frac{\gamma_{MF_x}^\infty}{\gamma_M^\infty} \tag{3}$$

3. Estimating the deviation E

The variation of E for different species M is related to the evolution of the $\log(\gamma_{MF_x}{}^\infty/(\gamma_M^\infty)$ term, since for elements of the same valence regardless of the species considered, the $\frac{x}{y}\log(\gamma_R^\infty/(\gamma_{RF_y}{}^\infty)$ term is the same for a given reducing agent.

Studies of molten salts by Hong and Kleppa [1] and by Ostvold [2] have shown that the enthalpy of the salt mixture depends directly on the relative ionic potential (ΔPI) of the two cations. This empirical parameter was introduced by Cartledge [3–5] as the difference in the

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ionic potentials of two cations with radii r_1 and r_2, and charges z_1 and z_2:

$$\Delta PI = \left(\frac{z_1}{r_1}\right) - \left(\frac{z_2}{r_2}\right) \qquad (4)$$

The potential value reflects the disturbance of the Coulomb interactions during the mixture of two salts; the higher the potential, the more negative the enthalpy of the mixture. A very dilute fluorinated species in the salt phase can thus be described by the ΔPI between the solvent cation and the compound cation, and by the temperature. If the behavior of a highly dilute metallic species in the metallic phase can be described by n independent parameters X_i and by the temperature, then it follows that E can be considered as a function of ΔPI, of n independent parameters X_i and of the temperature. As the variables are independent, E can be considered as a state function, and thus:

$$\frac{dE}{d\Delta PI} = \left(\frac{\partial E}{\partial \Delta PI}\right)_{T,X_{i(1\le i\le n)}} \qquad (5)$$

Within a single element series (actinides or lanthanides), we assume that the X_i values are constant. If the temperature is maintained constant for a series of experiments, it is then interesting to study the evolution of E versus ΔPI for a single element series at the same oxidation state in the salt phase.

Experimental investigations of the trivalent actinide/lanthanide distribution in fluorinated media were carried out with saline solvents in which the main component was LiF. ΔPI was thus $3/r_M - 1/r_{Li}$, and the values for each element were calculated from the ionic radii. Moriyama et al. [6] investigated the distribution of these elements between Lif–BeF$_2$ (2:1 molar) and Bi or Cd at 873 K and 1073 K using lithium as the reducing agent.

The experimental results are shown by plotting $\log D_M = f(\log D_{Li})$, allowing $\log K'_{Ln} = \log K_{Ln} + E_{Ln}$ to be measured for each lanthanide. The standard free enthalpy of formation for the fluorinated species [7–9] in the liquid state can then be used to estimate E_{Ln} for each lanthanide. The graph of $E_{Ln} = f(\Delta PI)$ plotted in Fig. 1 shows that E_{Ln} may be roughly be considered as an affine function of ΔPI; the correlation of only $r \sim 0.9$ can be attributed to measurement errors, and to the fact that the conditions of Eq. (5) are not all met (T is constant for a series of points, but the same cannot be said of the X_i variables). Nevertheless, it is assumed that an affine relation of the type $E_{Ln} = \alpha \Delta PI + \beta$ exists for the trivalent lanthanides, where α is temperature-dependent and β varies with the solvents and possible with the temperature. We measured $\alpha \sim -1.5$ at 1073 K and $\alpha \sim -2.5$ at 873 K; the mean value $\alpha \sim -2$ was therefore assumed at 720°C.

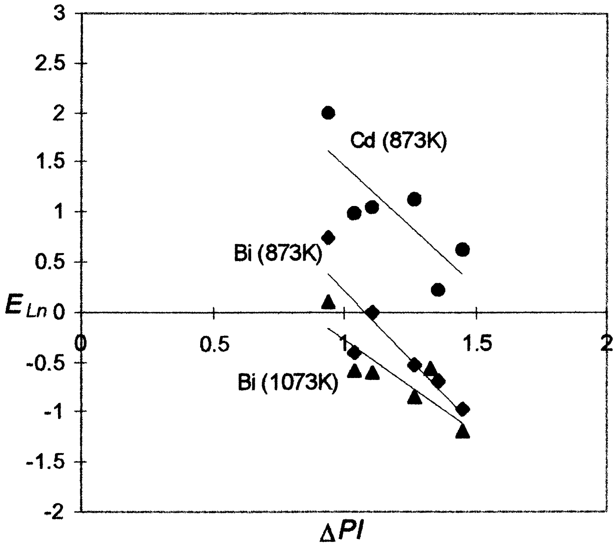

Fig. 1. E_{Ln} versus ΔPI for the trivalent lanthanides (based on experimental measures by Moriyama et al. in LiF–BeF$_2$/Bi–Li and LiF–BeF$_2$/Cd–Li).

Only experimental distribution results between LiF–BeF$_2$ and Bi–Li at 873 K are available for the trivalent actinides [6]. We have assumed that E_{An} is also an affine function of ΔPI. Thermodynamic tables indicate that only U and Pu have been sufficiently investigated to propose values for $\Delta G_f°(UF_3)$ and $\Delta G_f°(PuF_3)$ in the liquid state. Only two deviations from ideal conditions (E_U and E_{pu}) can thus be calculated from the experimental results giving $\log K'_{An} = \log K_{An} + E_{An}$. With only two points, plotting $E_{An} = f(\Delta PI)$ obviously results in a straight line. We postulate that this is the mean line that would have been obtained if all the values for $\Delta G_f°(AnF_3)$ were available; the relevant equation is $E_{An} = 13.7\Delta PI - 18.9$. Hypothetical E_{An} values may thus be calculated for the distribution of all the trivalent actinides between LiF–BeF$_2$ (2:1 molar) and Bi–Li at 873 K based on the following equilibria:

$$AnF_{3(salt)} + 3Li_{(metal)} \leftrightarrow An_{(metal)} + 3LiF_{(salt)} \qquad (6)$$

Each of the K_{An} constants can thus be calculated from the experimental results, allowing us to determine the value of $\Delta G_f°(AnF_3)$ from the classic relation:

$$\Delta G_f°(AnF_3) = RT \ln K_{An} + 3\,\Delta G_f°(LiF) \qquad (7)$$

where $\Delta G_f°(LiF) = -527.5\ kJ \cdot mol^{-1}$. Table 1 indicates the ΔPI values for the trivalent actinides with respect to

Table 1
Estimated values of equilibrium constants for liquid-phase reduction of actinide trifluorides by lithium, and standard free enthalpy of formation at 873 K

Element	ΔPI	E_{An}	$\log K_{An}$	$\Delta G_f°(AnF_3(I))$ kJ·mol^{-1}
U	1.04	−4.75	16.94	−1313.6
Pu	1.14	−3.38	14.62	−1333.4
Np	1.09	−4.04	14.56	−1339.2
Am	1.16	−2.98	14.42	−1341.5
Cm	1.19	−2.62	13.09	−1363.8
Cf	1.30	−1.11	12.58	−1372.3

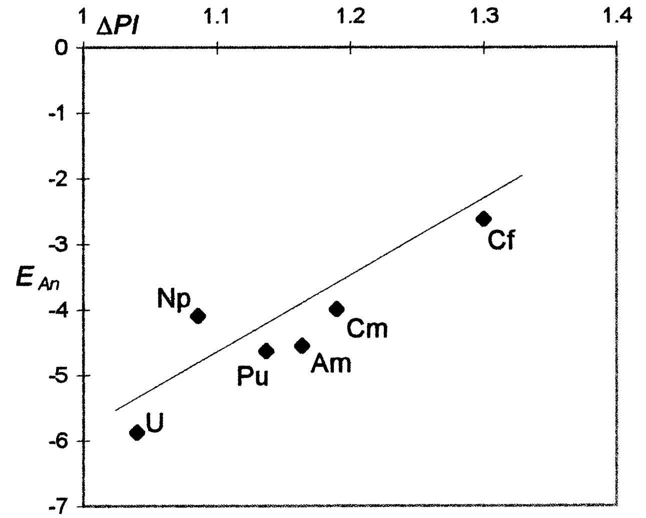

Fig. 2. E_{An} versus ΔPI for the trivalent actinides (based on experimental measures by Ferris et al. in LiF–BeF_2–ThF_4/Bi–Li at 873 K).

lithium, as well as E_{An}, $\log K_{An}$ and $\Delta G_f°(AnF_3)$ at 873 K (the values for U and Pu are taken from the literature). The free enthalpy of formation of species i is expressed by the classic relation $\Delta G_i°(T) = \Delta H_i° - T\Delta S_i°$. For UF_3(l) and PuF_3(l), the standard formation entropy values are similar (-216.5 and -218.7 $J \cdot mol^{-1}$, respectively) and it can easily be assumed that the value increases by one unit per atomic number for the actinides. The values in Table 1 can thus be substituted into Eq. (7) to estimate the standard free enthalpy of formation for the actinide trifluorides:

$$\Delta G_f°(UF_3(l)) = -1503115 + 216.5T; \quad \Delta G_f°(PuF_3(l)) = -1524300 + 218.7T$$

$$\Delta G_f°(NpF_3(l)) = -1529000 + 217T; \quad \Delta G_f°(AmF_3(l)) = -1534000 + 220T$$

$$\Delta G_f°(CmF_3(l)) = -1557000 + 221T; \quad \Delta G_f°(CfF_3(l)) = -1567000 + 223T$$

Other experimental studies of actinide transfer between LiF–BeF_2–ThF_4 (72–16–12 molar%) and Bi–Li at 873 K have been reported by Ferris et al. [10]. Here again, LiF was the principal salt component. As above, the experimental results can be used to measure $\log K'_{An} = \log K_{An} + E_{an}$. The equations of $\Delta G_f°(AnF_3(l))$ are then used to determine $\log K_{An}$. Having determined all the E_{An} values in this way, $E_{An} = f(\Delta PI)$ was then plotted (Fig. 2).

Note the very good correlation among the points for U, Pu, Am, Cm and Cf, with a slight deviation for Np. The slope of the line is 13.5 (in good agreement with the previous result) and the Y-intercept is -20.2 (the difference with the previous result can be attributed to the fact that the system itself is different: the salt composition is not the same). This very satisfactory result validates the overall hypotheses, and appears to confirm the affine relation between E and ΔPI for a given element series in the same oxidation state. The deviations from the ideal situation observed for the trivalent actinide and lanthanide distributions between a salt phase rich in LiF and a

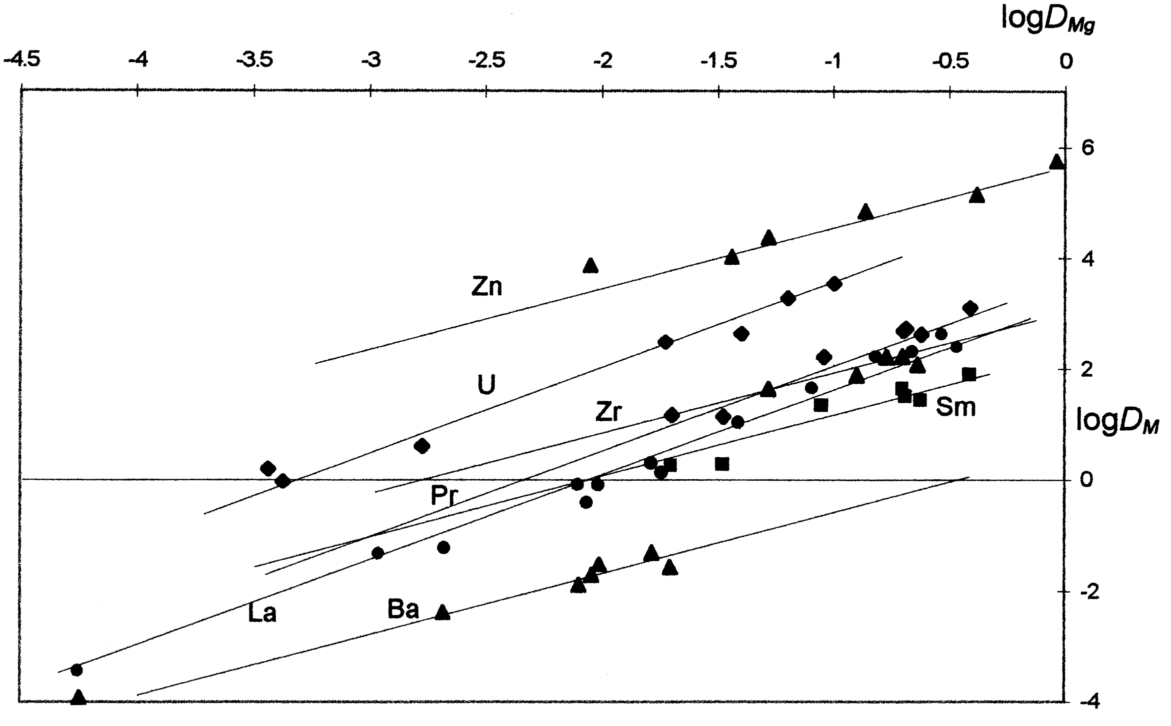

Fig. 3. Distribution of various elements between LiF–CaF_2 (4:1 molar) and Zn–Mg at 720°C.

Table 2
Measured deviation from ideal conditions for elements M between LiF–CaF_2 and Zn–Mg at 720°C

MF_x	BaF_2	LaF_3	PrF_3	SmF_2	ZrF_2	UF_3
E_M	5.7±0.4	5.3±0.5	5.0±0.4	5.9±0.3	−4.0±0.2	−0.7±0.3

Table 3
Simulated distributions of trivalent lanthanides and actinides between LiF–CaF_2 and Zn–Mg at 720°C

M	La	Ce	Pr	Nd	Gd	Tb	Dy	Ho	U	Pu	Np	Am	Cm	Cf
ΔPI	0.94	1.04	1.08	1.10	1.27	1.33	1.36	1.43	1.04	1.14	1.09	1.16	1.19	1.30
$\log K_M$	−2.3	−1.1	−1.4	−1.4	−2.2	−2.7	−1.9	−2.1	5.8	4.8	5.5	4.4	3.2	2.58
E_M	5.3	5.1	5.0	4.9	4.5	4.3	4.2	4.1	−0.7	0.4	−0.1	0.7	1.0	2.2

metallic phase at 873K may thus be expressed as $E_{Ln} = -2.5\Delta PI + \beta_{Ln}$ and $E_{An} = -13.7\Delta PI + \beta_{An}$. The values of β_{Ln} and β_{An} can be determined experimentally with one actinide and one lanthanide to calculate the results that would be obtained with the other elements.

4. Modeling the deviation *E* for the distribution of trivalent actinides and lanthanides between LiF–CaF_2 and Zn–Mg at 720°C

If the reduction of element *i* is noted $\log K_i' = \log K_i + E_i$, which is measured experimentally, Ferris et al. [11] showed that for U and Pu $\log K_U'$ and $\log K_{Pu}'$ are affine functions of the reciprocal of the temperature, and obtained the following values for the LiF–BeF_2 (2:1 molar)/Bi–Li system:

$$\log K_U' = -0.6397 + 11213/T(\mathrm{K}) \tag{8}$$

$$\log K_{Pu}' = -0.7186 + 10462/T(\mathrm{K}) \tag{9}$$

Using the equilibrium constants calculated at 720°C, α_{An} can be calculated from these expressions, yielding $\alpha_{An} = 11.3$; at 873 K, the slope of $\alpha_{An} = 13.8$, comparable to the value determined above. Hence $E_{Ln} = -2\Delta PI + \beta_{Ln}$ and $E_{An} = 11.3\Delta PI + \beta_{An}$. The values of β_{An} and β_{Ln} depend on the nature of the system, and can be determined by a single experiment assessing the distribution of a trivalent actinide and a trivalent lanthanide. We chose to perform the experiment with lanthanum-139 and uranium-238, both of which are stable isotopes and thus do not require telemanipulation. We measured the distribution of various elements between LiF–CaF_2 (4:1 molar) and Zn–Mg at 720°C using an experimental technique that has already

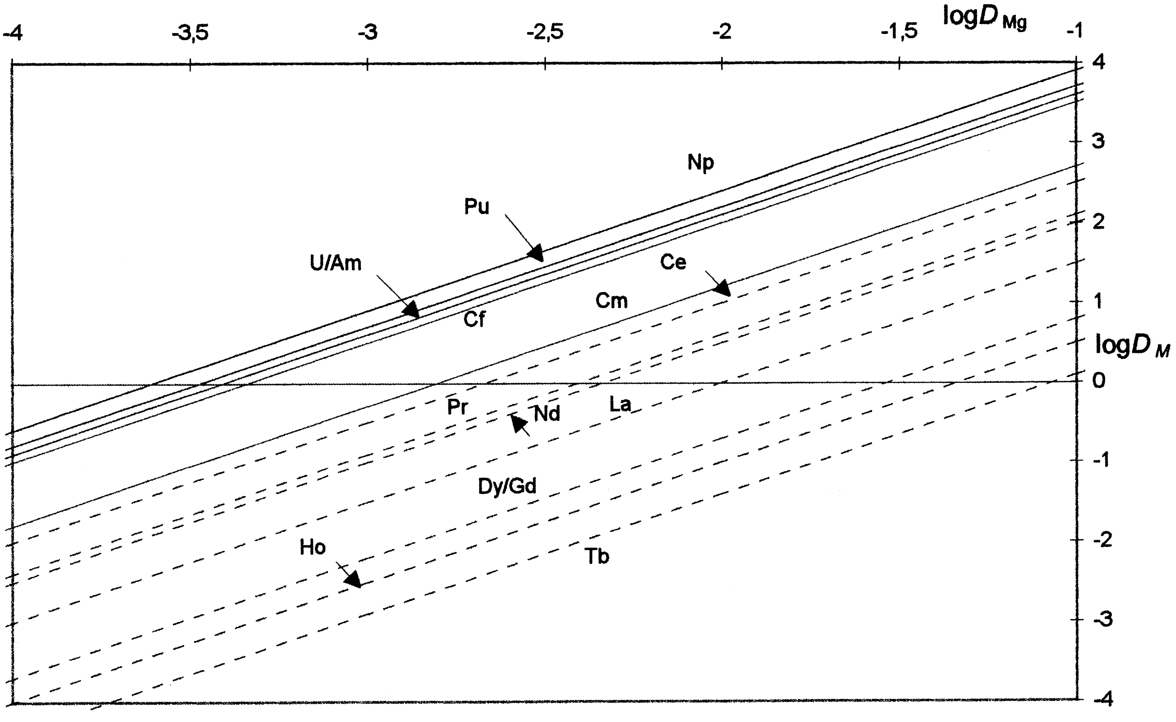

Fig. 4. Simulated distributions of trivalent lanthanides and actinides between LiF–CaF_2 and Zn–Mg at 720°C.

been described [12], and obtained the results shown in Fig. 3, showing the graph of log D_M versus log D_{Mg}. The results show that the experimental points are distributed along straight lines with a slope of $x/2$ (where x is the cation valence in the saline phase). For U and La in particular, the slopes are equal to 3/2, characterizing the +III valence of both cations. The alignment of the data points suggests that all the activity coefficients are constant, and that the deviations are constant according to the magnesium distribution. The measured deviations for each element are shown in Table 2.

The results obtained for lanthanum and uranium can be used to determine β_{Ln} and β_{An}, i.e. +7.18 and −12.45, respectively; hence the following distribution model:

$$\log D_{Ln} = {}^3/_2 \log D_{Mg} + \log K_{Ln} - 2\Delta PI + 7.18 \qquad (10)$$

$$\log D_{An} = \tfrac{3}{2} \log D_{Mg} + \log K_{An} + 11.3\Delta PI - 12.45 \qquad (11)$$

Calculating the deviation for praseodymium ($\Delta PI = 1.08$) yields $E_{Pr} = +5$, in full agreement with the experimental value (Table 2). Eq. (10) and Eq. (11) can thus be used to simulate the distribution of all the trivalent actinides and lanthanides between LiF–CaF_2 and Zn–Mg at 720°C. The results are shown in Table 3 and Fig. 4: the trivalent actinides and lanthanides clearly constitute two distinct groups of elements, although the lines for curium and cerium are relatively very close.

Separation of the trivalent actinides and lanthanides thus appears feasible in this system, but will be highly complex since the operating zone is very limited. It will be of considerable interest to test other systems in order to obtain a larger estimated Cm–Ce separation coefficient and open the way to tests with all the actinides and lanthanides.

References

[1] K.C. Hong, O. Kleppa, High Temp. Science 8 (1976) 299.

[2] T. Ostvold, Thesis, N.T.H. Trondheim, Tapir Trykk, 1971.

[3] G.H. Cartledge, J. Am. Chem. Soc. 50 (1928) 2855.

[4] G.H. Cartledge, J. Am. Chem. Soc. 50 (1928) 2863.

[5] G.H. Cartledge, J. Am. Chem. Soc. 52 (1930) 3076.

[6] H. Moriyama, T. Seshimo, K. Moritani, Y. Ito, T. Mitsugashira, J. Alloys Comp. 213–214 (1994) 354–359.

[7] I. Barin, Thermochemical Data of Pure Substances, VCH Verlags Gesellshaft, Weinheim, 1993.

[8] O. Knacke, O. Kubaschewski, K. Hesselmann, Thermodynamical Properties of Inorganic Substances, Springer-Verlag Berlin, Heidelberg, 1991.

[9] L.P. Ruzinov, B.S. Guljanickij, Ravnovesnye Prevrasoenija Retallugiceskin Reaktseij, Moskva, 1975.

[10] L.M. Ferris, J.C. Mailen, J.J. Lawrance, F.J. Smith, E.D. Nogueira, J. Inorg. Chem 32 (1970) 2019–2035.

[11] L.M. Ferris, J.C. Mailen, F.J. Smith, J. Inorg. Chem 33 (1971) 1325–1335.

[12] F. Lemort, R. Piccinato, R. Boen, M. Allibert, Electrochemical Society, Proceedings of the 9th International Conference on HTMC, 1997 May 19–23, State College Pa.