LANTHANIDE-BASED HALIDE SYSTEMS: A FASCINATING ROUTE FROM MULTITECHNIQUE DATA ACQUISITION TO DATA PREDICTION

Marcelle Gaune-Escard
Ecole Polytechnique, France

L. Rycerz
Wroclaw University of Technology, Poland

S. Gadzuric
University of Novi Sad, Serbia & Montenegro

W. Gong
Central South University, China

M.F. Butman
Ivanovo State University of Chemical Technology, Russia

S.A. Kuznetsov
Kola Science Centre RAS, Russia

ABSTRACT

The lanthanide trihalides have been the subject of investigations for many years. The physicochemical properties of the compounds they form, for instance with the alkali halides, can be examined and correlated in a way which is unique since the lanthanides regularly vary along the series they form in the periodic table.

Lanthanide metal halides as also the systems they form with alkali metal halides were recently the subject of focused and renewed interest. While the lanthanide fluorides or chlorides and related systems have been investigated in the past in relation with different applications, mostly nuclear in the 1950s and 1960s, very little existed until recently on their bromide and iodide counterparts.

These systems are of technological importance in several fields of which optical and scintillation devices, high-temperature energy-saving light sources (metal-halide lamps), etc., are just a few examples. They also characterize by several features making them challenging objects of fundamental interest.

Several experimental techniques were used complementarily to acquire the corresponding physicochemical data that are also required for process development.

From there a fascinating route opened from data acquisition to data correlation and ultimately to data prediction for still unknown compounds.

INTRODUCTION

Rare earth metals and alloys based on a rare earth and a light or transition metal are gaining increased importance, particularly in the fields of magnetism, energy and advanced technology [36, 37]. The use of molten salts, as reaction media, provides a unique opportunity for the electrowinning and electrorefining of high purity rare earth metals, as well as for the electrochemical synthesis of their alloys [12, 52, 80, 89].

The lanthanide halides have been the subject of investigations for many years. Their physicochemical properties as also those of the compounds they form, for instance with the alkali halides, can be examined and correlated in a way which is unique since the lanthanides vary regularly along the series they form in the periodic table.

Lanthanide metal halides as also the systems they form with alkali metal halides were recently the subject of focused and renewed interest. While the lanthanide fluorides or chlorides and related systems have been investigated in the past in relation with different nuclear applications, they are still currently investigated in the present context of pyrochemical separations (novel fuel cycles for future reactor systems, innovative waste management strategies, etc.) [13].

The pyrochemical reprocessing of nuclear fuel is presently considered as a promising option for the proposed advanced fuel cycles [8, 40, 59]. New concepts for partitioning and transmutation (P&T) [40] strategies are being explored, e.g. efficient separation of the Minor Actinides (MAs) from the fission products (FPs), and their destruction by transmutation [40, 61, 77, 55]. During the electrochemical separation process of the FPs, special attention must be paid to the lanthanides (Lns); chemically similar to the actinides, they constitute a neutronic poison that could reduce the efficiency of the transmutation process. Therefore, after several separation cycles, the molten salt has to be decontaminated from Lns [29, 73].

These reprocessing methods, as any molten salt-based process, can be rationalized and optimized only through a full understanding of the Ans and Lns chemistry in molten salts and of mechanisms regulating the electrolytic extraction via liquid or solid metallic cathodes, and oxide selective dissolution/precipitation [2, 3, 7].

The determination of the thermodynamic, structural, and spectral characteristics of lanthanide halides is a complex research problem of high-temperature chemistry, which has been tackled by a large number of research teams (e.g. see reviews [27, 38, 62, 71]. These fundamental efforts are related to a variety of practical implications in addition to those nuclear applications quoted above. In particular, data on lanthanide trihalides are crucial for growing pure and doped LnX_3 crystals, which are extensively used in optical [60] and scintillation [41] devices, and for simulation of high-temperature processes in energy-saving light sources (metal-halide lamps) [54].

All these features make the lanthanide halide-based melts challenging objects of fundamental interest. The present paper highlights how several experimental techniques were used complementarily to acquire the corresponding physicochemical data (enthalpy/temperature of phase transition, heat capacity, electrical conductivity [71], standard potential and diffusion coefficients [45, 46, 47, 48, 49, 50, 51], structure [85, 88] also mandatory for process development.

From there a fascinating route opened from data acquisition to data correlation [71] and ultimately to data prediction for those still unknown compounds [15, 81, 82, 83], under press. This latter goal makes use of informatics tools and data mining techniques applied to the large data sets in the molten salt database [14, 86] and of the above research results.

Mass Spectrometry and Calorimetry

In many applications the lanthanide tribromides are of primary importance [41, 54, 60]. In the recent studies for instance of $LaBr_3$ [4] and $LuBr_3$ [5] the thermodynamics of molecular and ionic vaporization were investigated using the Knudsen effusion mass spectrometry.

Very recent works, reporting data on $CeBr_3$ [57] and Cs_3CeCl_6 [6] exemplify how a multitechnique approach permitted more insight on the global properties of these compounds.

The saturated vapor pressure over $CeBr_3$ has been measured earlier by integral methods such as the Knudsen effusion [28, 77], the boiling point [53] and the torsional effusion [87] methods.

The purpose of the work [57] was to (i) determine the fraction of oligomer molecules in the vapor phase under equilibrium vaporization (the Knudsen method) and free vaporization (the Langmuir method) conditions, (ii) refine the enthalpy of sublimation of $CeBr_3$ in the form of monomers and determine the enthalpy of sublimation in the form of oligomers using a new unified set of thermodynamic functions for the condensed and gaseous states and obtain the thermodynamic characteristics of molecules in the gas phase, (iii) determine the activation energies of sublimation, (iv) analyze the composition of and ratio between charged species in vaporization fluxes in two vaporization regimes and determine the thermodynamic characteristics of ions. This novel approach consisted in a complex study of the thermodynamic and kinetic characteristics of the vaporization of $CeBr_3$ accompanied by an analysis of both molecular and ionic vapor components.

The molecular and ionic composition of the vapor over crystalline $CeBr_3$ under Knudsen and Langmuir conditions was studied by high-temperature mass spectrometry. It was established that in both vaporization regimes the molecular vaporization fluxes consist of the $CeBr_3$ monomers and the Ce_2Br_6 dimers.

The sublimation enthalpies of $CeBr_3$ to the monomers and dimers as also the standard formation enthalpies of the $CeBr_3$ and Ce_2Br_6 molecules were calculated using an updated set of thermodynamic functions.

The thermal emission of the $CeBr_4$– and Ce_2Br_7– ions had been detected for the first time, these ions being emitted both by the surfaces of crystalline and molten lanthanide halides.

Several compounds may exist in the LnX_3-MX mixtures (Ln=lanthanide, X=halide, M=alkali metal). These systems have relatively simple phase diagrams when they include the lighter alkali metal halides (LiX and NaX), while those with KX, RbX and CsX exhibit generally several compounds of stoichiometry M_3LnX_6, M_2LnX_5 and MLn_2X_7. The stability of these compounds depends both on the nature of cations (lanthanide Ln, alkali M) and anions X [65, 66, 75]. We have paid much attention to the M_3LnX_6 stoichiometric compounds that exist in most LnX_3-MX systems and have a more extended stability range than those of other stoichiometry [16, 17, 19, 20, 64, 68, 69, 71]. These congruently melting compounds were found to exist also in the $CeCl_3$-MCl systems (M=K, Rb and Cs) [73].

A new approach coupling Differential Scanning Calorimetry and the thermionic emission technique of the Knudsen Effusion Mass Spectrometry was developed for the thermodynamic characterization of the M_3LnX_6 stoichiometric compounds that exist in most LnX_3-MX systems. It was successfully applied to Cs_3CeCl_6 [6].

As established earlier, this compound is metastable at ambient temperature [73, 74]. It undergoes a solid-solid state transition at 676 K and melts congruently at 1078 K with the respective enthalpies 7.8 ± 0.4 and 67.4 ± 0.8 kJ mol^{-1} [65, 75]. Its formation enthalpy from the system components – CsCl and $CeCl_3$ – was determined as -26.0 kJ/mol at 298.15 K [69] by solution calorimetry.

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

Heat capacity was measured by differential scanning calorimetry with a Setaram DSC 121 operated in a stepwise mode. This so-called *step method* has been described [65, 66] previously. Results are presented in Figure 1.

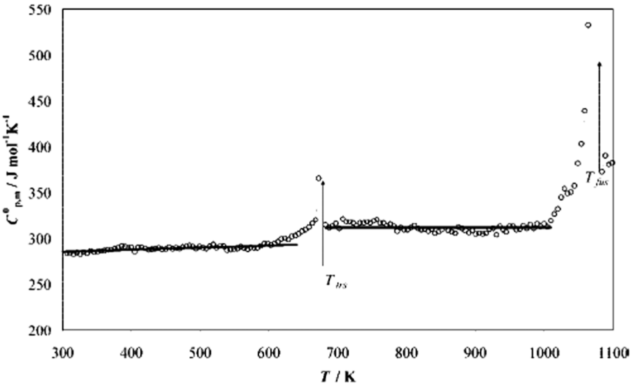

Figure 1: Molar heat capacity $C^o_{p.m}$ of Cs_3CeCl_6: open circles – mean values from experimental results, broken line – global heat capacity, solid lines – polynomial fitting of experimental results

The measurements of thermodynamic activity in the two-phase field {Cs_3CeCl_6(s) + liquid} were carried out with the $CeCl_3$-CsCl mixture of composition x(CsCl) = 0.70 by Knudsen Effusion Mass Spectrometry. The technique of thermionic emission current ratio was used [78] for this purpose.

These data enabled experimental derivation of the absolute entropy of Cs_3CeCl_6 at 298.15 K and were used to calculate the whole set of thermodynamic functions for solid and liquid compound together with the Gibbs free energy and the enthalpy variation with temperature of the compound formation reaction $CeCl_{3(s,l)} + 3\ CsCl_{(s,l)} = Cs_3CeCl_{6(s,l)}$.

Electrochemistry and Calorimetry

Electroreduction of $EuCl_3$ in alkali chloride melts was studied by different electrochemical methods (Linear sweep voltammetry (LSV) and cyclic voltammetry (CV). It was found that at a sweep rate of $\nu \leq 0.1$ V s-1 the electroreduction of Eu(III) to Eu(II) is reversible and electrochemical transient techniques can be used [42, 80] for the determination of the formal standard redox potentials E*Eu(III)/Eu(II). The formal standard potentials

$E^*Eu(II)/Eu$, were determined from open-circuit potentiometry data.
The electrochemistry of the redox process: Eu(III) + e- ↔ Eu(II), in NaCl-KCl melts in the temperature range 973-1123 K on glassy carbon electrode has been studied in detail previously [43, 44]. A similar electrochemical behavior was obtained for the KCl and CsCl melts.

The diffusion coefficients (*D*) for the chloride complexes of Eu(III) and Eu(II) in KCl and CsCl melts were determined as also the activation energies for diffusion (ΔU) of Eu(III) and Eu(II). Smaller values of *D* were obtained when the cation in the second coordination sphere changes from Na^+ to Cs^+. Similar changes in *D* values are well known [48]. They are due to the decrease of the counter-polarizing effect of cations from Na^+ to Cs^+, resulting in a decrease of metal-ligand bond length. Diffusion coefficients decrease when the europium oxidation state increases while the activation energies for diffusion increase. Thus *D* decreases and ΔU increases with increasing ionic moment of the diffusing species. These results are in agreement with numerous data showing that diffusion coefficients and activation energies for diffusion of complexes strongly depend on the oxidation state of the central atoms [49].

The formal standard potentials $E^*_{Eu(III)/Eu(II)}$ in alkali chloride melts were obtained from the diffusion coefficients coupled to the cathodic Ep_c and anodic Ep_a peak potentials and $E_{1/2}$ half-wave potential, according to the theory of linear sweep and steady state voltammetry [11], the following relation is valid for the reversible electrochemical reduction.

Then the Gibbs energy for the reaction: $EuCl_3$(sol.) ↔ $EuCl_2$(sol.) +1/2 Cl_2(g.), was calculated.

The redox potential was found to shift toward more negative values with increasing alkali metal ionic radius. This is due to the greater stabilization of Eu(III) complexes as compared with the Eu(II) complexes, occurring with the radius increase of alkali metal cation in the sequence sodium, potassium and caesium in the melt.

Open-circuit potentiometric method was used for the determination of formal standard potentials of $E^*Eu(II)/Eu$ in alkali chloride melts (Figure 2). Indeed, prior and systematic investigations had shown that it was not possible to use cyclic voltammetry to determine the electroreduction peak value for: Eu(II) + 2e- → Eu, because the potentials of the above discharge processes and those of cations of alkali metals are very similar.

The $E^*_{Eu(III)/Eu}$ and $E^*_{Eu(II)/Eu}$ formal standard potentials values were calculated as also the equilibrium constants (K^*) of the metal-salt reaction: 2Eu(III)+Eu ↔ 3Eu(II), in the different melts.

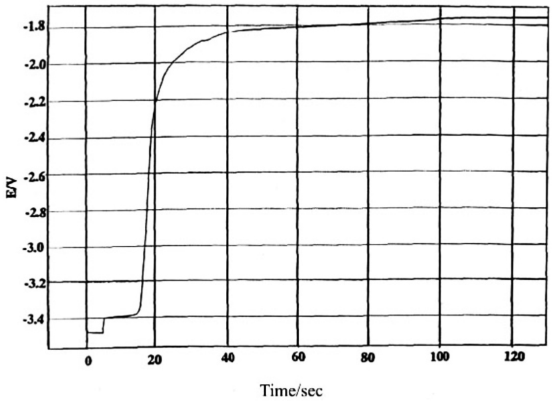

Figure 2: Open-circuit potential delay of molybdenum electrode after cathodic polarization in NaCl-KCl-$EuCl_2$ melt. Time of polarization: 5 sec. Current density: 360 mA cm^{-2}. Temperature: 1000 K. Concentration of $EuCl_2$: $8.61 \oplus 10^{-5}$ mol cm^{-3}. Reference electrode: Cl_2/Cl^-.

The resulting equations for the Gibbs energies clearly indicated that the Eu(II) species can only exist from the contact of metallic europium with the NaCl-KCl (KCl, CsCl)-$EuCl_3$ melts. Calorimetric investigations were conducted on the $EuCl_2$-MCl systems (M=Na, K, Rb) by direct calorimetry in a Calvet type calorimeter by using the ampoule break-off technique [18]. Negative mixing enthalpies were observed for all systems (Figure 3) over the whole composition range [9, 10].

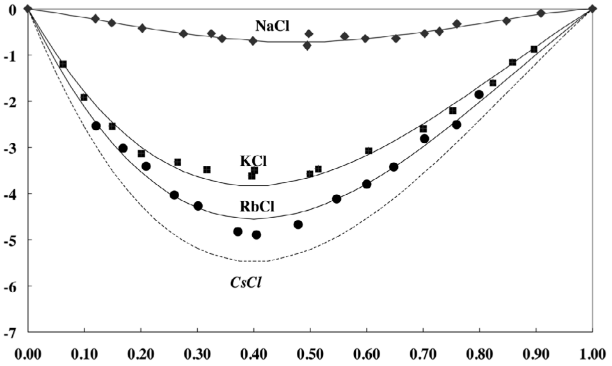

Figure 3: Molar enthalpies of mixing $\Delta_{mix}H_m$ of MCl-$EuCl_2$ liquid binary systems at 1138 K. Dashed line: calculated

It was concluded that the electrochemical reduction of Eu(III) in alkali chloride melts occurs via two successive reversible stages involving transfer of one and two electrons. The influence of the second coordination sphere on the diffusion coefficients of Eu(III) and Eu(II) was studied in alkali chloride melts. The formal standard potentials of E*Eu(II)/Eu, E*Eu(III)/Eu and formal redox potentials of E*Eu(III)/Eu(II) were calculated from open-circuit potentiometry and linear sweep voltammetry data. Some thermodynamic properties for dilute solutions of EuCl2, and EuCl3 in alkali chloride melts were obtained. The relative partial molar enthalpy of mixing EuCl2 with alkali chloride melts was determined by electrochemical techniques, and the values from electrochemical measurements are in fairly good agreement with data obtained by the calorimetric method [51].

Phase Diagram Calculation

Phase diagram calculations were performed on a number of lanthanide halide-based systems [22, 23, 24]. A recent paper [26] reports as an example the critical thermodynamic description of the KBr-$TbBr_3$ system that was carried out by the CALPHAD method. The thermodynamic parameters of the KBr and $TbBr_3$ compounds were taken from the SGTE database and authors' previous assessment [62, 66, 68] respectively. Those relative to the KBr-$TbBr_3$ system were optimized in this study by using both the already published experimental information together with a new and complementary experimental determination regarding the K_3TbBr_6 compound. A two-sublattice ionic solution model $(K^+)_P$ $(Br^-, TbBr_6^{-3}, TbBr_3)_Q$ was adopted to describe the liquid phase. This description of the KBr-$TbBr_3$ system is fully consistent with the whole set of experimental thermodynamic properties.

The calculated phase diagram is reported below (Figure 4).

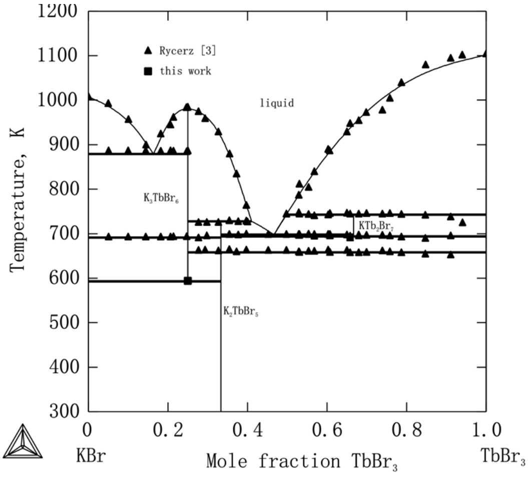

Figure 4: Calculated $KBr–TbBr_3$ phase diagram compared with the measured data [26, 67]

Molten Salts Data

Molten salt technology is a catch-all phrase that include some very diverse technologies; electro-chemistry, heat transfer, chemical oxidation/reduction baths, and nuclear reactors. All of these technologies are linked by the general characteristics of molten salts that can function as solvents, have good heat transfer characteristics, function like a fluid, can attain very high temperatures, can conduct electricity and also may have chemical catalytic properties. The Janz molten salt database [30, 31, 32, 33, 34, 35] is the most comprehensive compilation of property data about molten salts available today and is widely used for both fundamental and applied purposes. Databases are traditionally viewed as *static* documents, which are used in a *search and retrieval* mode. These static data can be transformed by informatics and data mining tools into a dynamic dataset for analysis of the properties of the materials and for making predictions. While this approach has revealed successful in the chemical and bio-chemical sciences in searching for and establishing structure-property relationships, it is not widely used in the materials science community. Since the design of the original molten salt database was not oriented towards this informatics goal, it was essential to evaluate this dataset in terms of data mining standards. Two techniques were used – a projection (*Principal Components Analysis*) and a predictive method (*Partial Least Squares*) – in conjunction with fundamental knowledge acquired from long-term practice of molten salt chemistry [15, 83].

Principal Component Analysis is a technique to reduce the information dimensionality. It relies on the fact that most of the descriptors are inter-correlated and these correlations in some instances are high [1, 81]. The complex tasks of prediction or classification are made easier in this compressed space. Partial Least Squares (PLS) is a multivariate predictive technique with distinct advantages over the classical multiple regression and principal component regression approaches. The use of PLS techniques is well established in many fields such as psychology, chemometrics, process control, biology and economics. The details on PCA and PLS are reported in [82, 83].

Using the data sets obtained during our thermodynamic investigations of lanthanide halides, we explored the impact of a multivariate analysis of seven descriptors on ΔH_{form} and ΔG_{form} behavior [84]. Principal Component Analysis (PCA) was applied to a data set consisting of a 744x7 matrix called *training set* hereafter. The seven descriptors were implemented as a function of temperature available for nineteen rare earth halides (equimolar weight, atomic number, electronegativity difference between cation and anion (ΔE), cationic charge/radius ratio (Z_c/r_c), temperature of melting, ΔH_{form} and ΔG_{form}).

Partial Least Squares (PLS) method was used to predict ΔH_{form} and ΔG_{form} for those lanthanide halides that have not been investigated yet. The prediction was performed for the following compounds, named as test set: $YbBr_2$, YbI_2, EuI_2, $SmCl_2$, $SmBr_2$, SmI_2, $CeBr_3$, $PrBr_3$, $SmBr_3$, $EuBr_3$, $GdBr_3$, $DyBr_3$, $TmBr_3$ and $YbBr_3$.

Figure 5 and Figure 6 show predicted against experimental values of ΔH_{form} and ΔG_{form}, respectively, for the training set. The large R^2 values 89.97% and 87.51% were obtained, respectively, indicating a high level of confidence for these predictions.

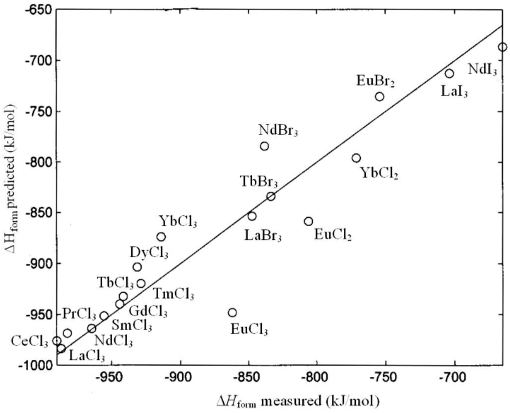

Figure 5: Predicted vs. experimental ΔH_{form} values for the training set of data

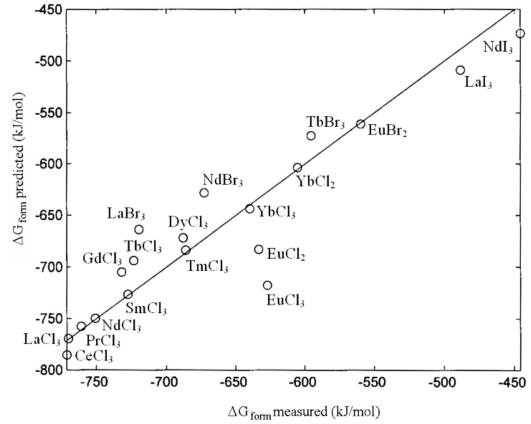

Figure 6: Predicted vs. experimental ΔG_{form} values for the training set of data

CONCLUSIONS

The physicochemical characterization of lanthanide halide-based systems is a multifaceted problem.

A few examples were given to illustrate the benefits that arise from multitechnique approaches for understanding processes.

Data correlation statistical techniques make it possible to obtain comprehensive information with the ultimate goal of properties prediction.

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