

Thermodynamic investigations of liquid cerium–bismuth alloys

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Abstract The thermodynamics of the low-level Ce dissolved in liquid Bi was determined by means of the electromotive force (EMF) measurement method using a cell consisting of molten chloride and liquid Bi at the temperature ranging from 735 to 937 K. The activity coefficients of Ce in Bi were deduced from the obtained EMF results. A considerable increase in the activity coefficient with temperature was observed in the Ce concentration range studied. The values of the molar excess formation free energy, the excess enthalpy change, and the excess entropy change of Ce dissolved in Bi were determined. The heat of formation of liquid Ce–Bi alloys ($\Delta H_{\text{Ce–Bi}}^M$) was deduced from the measured activity coefficient. There is a linear dependence of experimental $\Delta H_{\text{Ce–Bi}}^M$ on the Ce concentration. The experimental results of $\Delta H_{\text{Ce–Bi}}^M$ were compared with the values predicted by the Miedema's model.

Introduction

A pyrometallurgical nuclear fuel recycle process has originally been developed by Argonne National Laboratory (ANL) for treating uranium–zirconium alloy fuel [1]. This process

included two main steps: electrorefining to extract the uranium, plutonium, and other actinides from the dissolved fuel; cathode processing to produce metal ingots from the electrorefiner products. Recently, pyrochemical separations, involving molten salt and metal media, by liquid–liquid extraction, are studied for nuclear defense and civil applications [2]. The first steps of a pyrochemical process development consist in studying the chemistry of the elements to be separated in the solvent media. The French Atomic Energy Commission (CEA) has been operating pyrochemical processes in chloride media for more than 40 years for plutonium metal preparation and recovery [2]. Actinides–lanthanides separation in fluoride molten salt and metallic Al–Cu system is also considered for spent fuel pyroprocessing by CEA in the frame of international research programs [2]. In order to understand the pyrochemical process, knowledge of thermodynamic behavior of all its constituents is very important. The efficiency of extraction and separation for lanthanides and actinides by a pyrometallurgical extraction system depends mainly on the standard Gibbs free energy of formation of their chlorides, and their activity coefficients in both phases greatly influence the separation efficiency as well [3, 4]. Up to date, the thermodynamic properties of Ce in a two-phase system of molten LiCl–KCl eutectic salt and liquid Bi were not available in the literature. Therefore, in the present study, we determined the thermodynamic properties associated with the formation of liquid Ce–Bi alloys using the electromotive force (EMF) measurement.

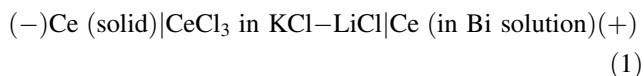
Experimental

The following galvanic cell was designed to measure the EMF values between the metallic Ce and the Ce solute in Bi solution [3].

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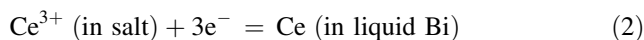


The apparatus of EMF measurement is shown in Fig. 1 [3]. The pure Ce electrode was prepared by welding a tantalum lead to a small rod of 99.9% pure Ce metal. The alloy electrode was prepared by directly dissolving a small piece of pure Ce metal in 99.999% pure Bi. The electrolyte was KCl–LiCl eutectic with purity of 99.9% (mole ratio of lithium to potassium = 51/49). The CeCl₃ in KCl–LiCl eutectic was prepared by reacting BiCl₃ in molten LiCl–KCl with Ce metal in molten Bi. The experiments were carried out in a glove-box purged with purified and dry argon to remove oxygen and humidity. The content of impurity O₂ and H₂O in the inside atmosphere was continuously maintained less than 2 ppm. Measurements were performed at temperature ranging from 735 to 937 K. After the desired temperature was achieved, the pure lanthanide electrode was immersed into the molten salt phase, and the EMF between the pure Ce electrode and the liquid alloy electrode was measured with an electrometer. After immersing the pure Ce electrode, the variation of EMF was monitored for longer than 10 min, waiting for the stabilization of EMF. In many cases, the fluctuation of EMF settled into <2 mV within 10 min after starting the measurements, and in such cases it was recognized that the electrochemical equilibrium was achieved. The temperature was controlled within ±1 °C. At each level of temperature, the concentration of Ce in Bi phase was changed several times, and the mole fraction of Ce in Bi was

analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES).

Results and discussion

In general, Ce in chloride melts in contact with Bi was trivalent [5]. The following equilibrium between the salt phase and the Ce–Bi solution was thus attained.



According to the Nernst's equation, the EMF, ΔE, between lanthanide metal and lanthanide in bismuth can be expressed as follows [3, 4, 6].

$$\begin{aligned} \Delta E &= -\frac{1}{3F} \Delta G^{fusion}(Ce) - \frac{2.3RT}{3F} \log a_{Ce-Bi} \\ &= -\frac{1}{3F} \Delta G^{fusion}(Ce) - \frac{2.3RT}{3F} \log x_{Ce} - \frac{2.3RT}{3F} \log \gamma_{Ce} \end{aligned} \quad (3)$$

where ΔG^{fusion}(Ce) is the fusion energy of metallic Ce, which can be deduced from the literature [7]; R is the gas constant; T is the absolute temperature (K); F is the Faraday constant; a_{Ce–Bi} is the activity of metallic Ce in Bi solution, where a_{Ce–Bi} = x_{Ce} × γ_{Ce}; x_{Ce} is the mole fraction of Ce in Bi solution; and γ_{Ce} is the activity coefficient of Ce in Bi solution. Then γ_{Ce} can be obtained according to Eq. 3, using the values of ΔE, x_{Ce}, and T obtained in this study.

The EMF values measured over the 735–937 K range were plotted in Fig. 2. The observed EMF shows a roughly linear dependence on log γ_{Ce}, suggesting that ΔE approximately obeys Eq. 3. The experimental data reported in the present article are within ±2% of the experimental error. The line slopes drawn in Fig. 2 were almost the same as those of the theoretical slopes (2.3RT/3F). This means that the dilute solutions of Ce in Bi approximately obeyed the Henry's law. However, it was found that the observed slopes slightly deviated from the theoretical slopes. This suggests that the third term of Eq. 3 is not absolutely constant over the tested concentration range, and that γ_{Ce} depended on the concentration.

Figure 3 shows the variation of log γ_{Ce} as a function of composition (x_{Ce}). The activity coefficients were less affected by the Ce concentrations but were greatly influenced by the temperature. The activity coefficient increased with temperature. A slight dependence of log γ_{Ce} on log x_{Ce} is clearly observed. The line slopes derived from least-square fitting were almost identical. This might be attributed to such a phenomenon as a weak interaction among the solute clusters.

The activity coefficient increased considerably with temperature. A linear dependence of log γ_{Ce} on 1/T was found, as shown in Fig. 4. The line in Fig. 4 reflects the

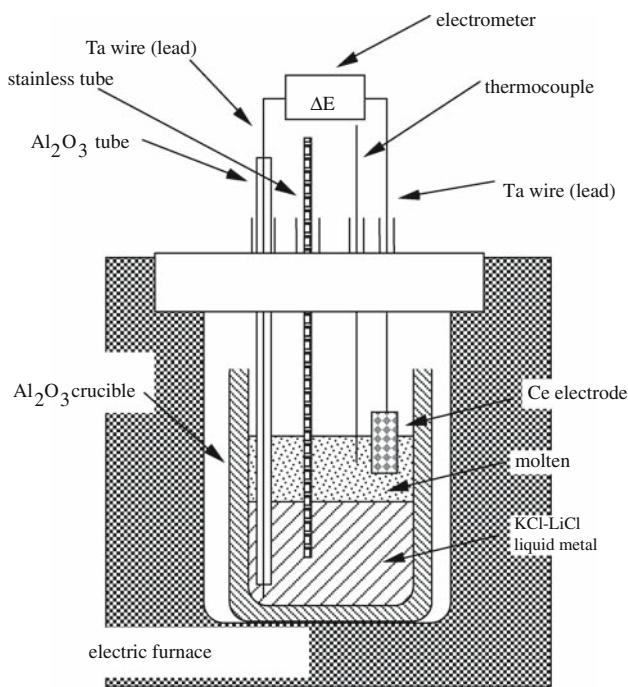


Fig. 1 Schematic diagram of the apparatus for EMF measurement

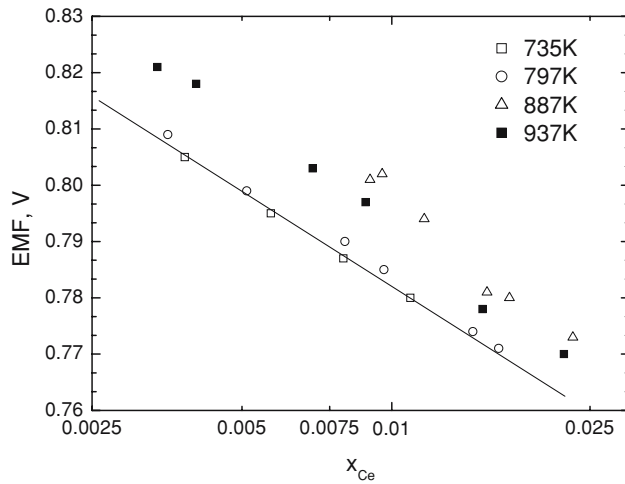


Fig. 2 Concentration dependence of the EMF determined for Ce

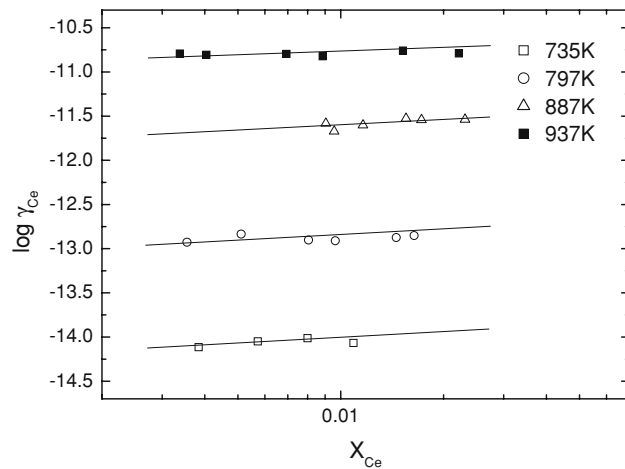


Fig. 3 Concentration dependence of the activity coefficients of Ce

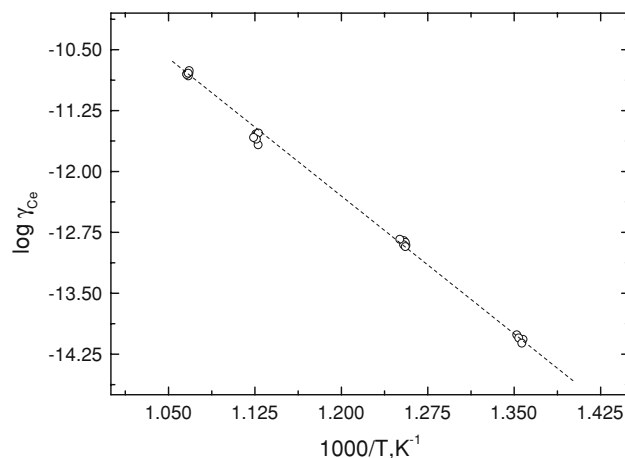


Fig. 4 Temperature dependence of the activity coefficient

result of the least square fitting treatment, which is expressed as

$$\log \gamma_{\text{Ce}} = 1.025 - \frac{11121}{T}. \quad (4)$$

Thus, the $\log \gamma_{\text{Ce}}$ at any desired temperature can be calculated from Eq. 4.

The dilute solution of Ce in Bi was treated as a regular solution, thus, the partial molar excess Gibbs free energy changes of Ce dissolved in Bi solution ($\Delta \bar{G}_{\text{Ce}}^{\text{ex}}$) can be deduced as follows [6, 8]:

$$\Delta \bar{G}_{\text{Ce}}^{\text{ex}} = 2.3 RT \log \gamma_{\text{Ce}} \quad (5)$$

and

$$\Delta \bar{G}_{\text{Ce}}^{\text{ex}} = \Delta \bar{H}_{\text{Ce}}^{\text{ex}} - T \Delta \bar{S}_{\text{Ce}}^{\text{ex}}, \quad (6)$$

where $\Delta \bar{H}_{\text{Ce}}^{\text{ex}}$ is the partial excess enthalpy change of Ce dissolved in Bi solution; and $\Delta \bar{S}_{\text{Ce}}^{\text{ex}}$ is the corresponding excess entropy change. Combining Eqs. 5 and 6, the following equation is produced:

$$\log \gamma_{\text{Ce}} = \frac{\Delta \bar{H}_{\text{Ce}}^{\text{ex}} - T \Delta \bar{S}_{\text{Ce}}^{\text{ex}}}{2.3RT} = \frac{-\Delta \bar{S}_{\text{Ce}}^{\text{ex}}}{2.3R} + \frac{\Delta \bar{H}_{\text{Ce}}^{\text{ex}}}{2.3RT}. \quad (7)$$

According to Eqs. 4 and 5, the molar excess formation free energy at 873 K was calculated as

$$\Delta \bar{G}_{\text{Ce}}^{\text{ex}} = -195.53 \text{ kJ/mol}. \quad (8)$$

Combining Eqs. 4 and 7, $\Delta \bar{H}_{\text{Ce}}^{\text{ex}}$ and $\Delta \bar{S}_{\text{Ce}}^{\text{ex}}$ were obtained as

$$\Delta \bar{H}_{\text{Ce}}^{\text{ex}} = -212.65 \text{ kJ/mol}, \quad (9)$$

$$\Delta \bar{S}_{\text{Ce}}^{\text{ex}} = -19.60 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (10)$$

The heat of formation of liquid Ce–Bi alloys ($\Delta H_{\text{Ce–Bi}}^{\text{M}}$) can be obtained from the γ_{Ce} by the thermodynamic deductions [8, 9].

$$\Delta H_{\text{Ce–Bi}}^{\text{M}} = 2.3x_{\text{Ce}} RT \log \gamma_{\text{Ce}} + 2.3x_{\text{Bi}} RT \log \gamma_{\text{Bi}}, \quad (11)$$

where, x_{Bi} is the concentration of Bi in Ce–Bi alloy, and γ_{Bi} is the activity coefficient of Bi. At the very low Ce concentration condition (such as $x_{\text{Ce}} < 0.1$ in our experiments), γ_{Bi} could be treated as 1. Then $\Delta H_{\text{Ce–Bi}}^{\text{M}}$ can be obtained using the experimental values of x_{Ce} and γ_{Ce} as

$$\Delta H_{\text{Ce–Bi}}^{\text{M}} = 2.3x_{\text{Ce}} RT \log \gamma_{\text{Ce}}. \quad (12)$$

Figure 4 shows the experimental $\Delta H_{\text{Ce–Bi}}^{\text{M}}$ as a function of x_{Ce} . As seen from this figure, a linear dependence of $\Delta H_{\text{Ce–Bi}}^{\text{M}}$ on the x_{Ce} was observed. At low concentration of Ce in Bi solution, the linear relation of experimental $\Delta H_{\text{Ce–Bi}}^{\text{M}}$ with x_{Ce} drawn in Fig. 5 can be expressed by

$$\Delta H_{\text{Ce–Bi}}^{\text{M}} = -196.60x_{\text{Ce}} \text{ (kJ/mol)}. \quad (13)$$

The semi-empirical model developed by Miedema et al. [9–12] can be used to predict the heat of formation of liquid

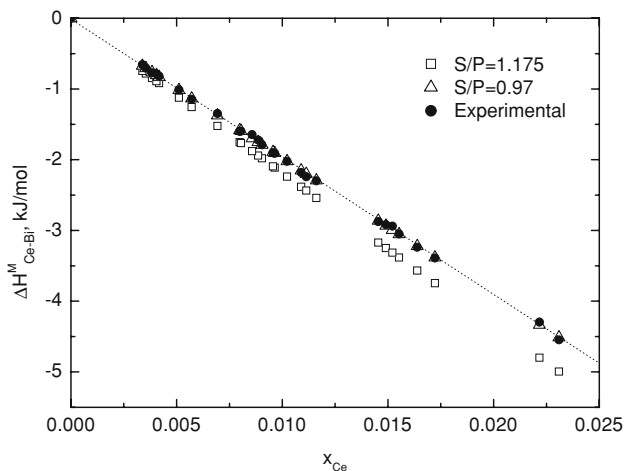


Fig. 5 Variation of $\Delta H^M_{\text{Ce-Bi}}$ as a function of x_{Ce}

metallic alloys. In the Miedema’s model, the energy effects associated with alloying or compound formation are described by changing the boundary conditions when the atomic cells are transferred from the pure metals to the alloy or compound. In the Miedema’s model, the heat of the formation of liquid Ce–Bi alloys are represented by

$$\Delta H^M_{\text{Ce-Bi}} = \Delta H^C_{\text{Ce-Bi}} C_{\text{Ce-Bi}}, \tag{14}$$

where the $\Delta H^C_{\text{Ce-Bi}}$ and $C_{\text{Ce-Bi}}$ are given by

$$\Delta H^C_{\text{Ce-Bi}} = V_{\text{Ce}}^{2/3} V_{\text{Bi}}^{2/3} \frac{2P}{n_b^{-1/3}(\text{Ce}) + n_b^{-1/3}(\text{Bi})} \times \left[-(\Delta\Phi)^2 + \frac{Q}{P} (\Delta n_b^{1/3})^2 - \frac{S}{P} \right] \tag{15}$$

$$C_{\text{Ce-Bi}} = \frac{x_{\text{Ce}} [1 + u_{\text{Ce}} x_{\text{Bi}} (\Phi_{\text{Ce}} - \Phi_{\text{Bi}})] x_{\text{Bi}} [1 + u_{\text{Bi}} x_{\text{Ce}} (\Phi_{\text{Bi}} - \Phi_{\text{Ce}})]}{x_{\text{Ce}} [1 + u_{\text{Ce}} x_{\text{Bi}} (\Phi_{\text{Ce}} - \Phi_{\text{Bi}})] V_{\text{Ce}}^{2/3} + x_{\text{Bi}} [1 + u_{\text{Bi}} x_{\text{Ce}} (\Phi_{\text{Bi}} - \Phi_{\text{Ce}})] V_{\text{Bi}}^{2/3}}, \tag{16}$$

where $V_{\text{Ce}}^{2/3}$ and $V_{\text{Bi}}^{2/3}$ are the molar volume of Ce and Bi, respectively (cm^3 , at room temperature); $n_b(\text{Ce})$ and $n_b(\text{Bi})$ electron density of Ce and Bi at the boundary of Wigner–Seitz atomic cell as derived for the pure elements in the metallic state (electrons per $(0.529 \text{ \AA})^3$); Φ_{Ce} and Φ_{Bi} the electronegativity of Ce and Bi, respectively; $\Delta\Phi$ the difference of electronegativity between Ce and Bi; and P, Q, S, u_i specific constants. Here, $\Delta n_b^{1/3} = n_b^{1/3}(\text{Ce}) - n_b^{1/3}(\text{Bi})$.

The term S/P is introduced into the expression for the heat for alloys when one of the two components is a non-transition metal [9]. The actual values of S/P in liquid Ce–Bi alloys should be based on the experimental $\Delta H^M_{\text{Ce-Bi}}$. In the present study, firstly, the value of $S/P = 1.175$ which is recommended by Alonso and March [13], is used for calculation. The parameters needed for Miedema’s model are

Table 1 Parameters for Miedema’s model

Parameters	Values
$V_{\text{Ce}}^{2/3}$	$7.76 \text{ cm}^2 \text{ mol}^{-2/3}$
$V_{\text{Bi}}^{2/3}$	$7.20 \text{ cm}^2 \text{ mol}^{-2/3}$
Φ_{Ce}	3.18 V
Φ_{Bi}	4.15 V
$n_b^{1/3}(\text{Ce})$	$1.19 (du^{1/3})^a$
$n_b^{1/3}(\text{Bi})$	$1.16 (du^{1/3})^a$
P	12.35
$\frac{Q}{P}$	0.944
$\frac{S}{P}$	1.175
u_{Ce}	0.07
u_{Bi}	0.04

^a $du = 6 \times 10^{22} \text{ electrons/cm}^3$

listed in Table 1 [10, 11, 14, 15]. Calculated values of $\Delta H^M_{\text{Ce-Bi}}$ according to the Miedema’s model are also plotted in Fig. 5 as functions of x_{Ce} , which also shows a linear relationship with x_{Ce} at lower Ce concentration conditions. It is found that the calculated values are more negative than the experimental values of $\Delta H^M_{\text{Ce-Bi}}$ in liquid phase when the literature data of $S/P = 1.175$ were used. This fact was also observed in the La–Cu and Zr–Cu systems [16]. The term of S/P in Eq. 15 is ascribed as the p – d hybridization or as a result of pressure relation of different types of valence electrons in the alloy. Since the d band of Ce is filled, there is no transfer of d electrons from the d band of Ce to the d band of Bi.

The value of $S/P = 0.97$ was regressed using experimental data of $\Delta H^M_{\text{Ce-Bi}}$ as shown in Fig. 5. Using the regressed value of $S/P = 0.97$ it is possible to predict $\Delta H^M_{\text{Ce-Bi}}$ at different x_{Ce} conditions. Figure 6 shows the calculated result of $\Delta H^M_{\text{Ce-Bi}}$ as a function of x_{Ce} at high Ce concentrations, which is expressed by

$$\Delta H^M_{\text{Ce-Bi}} = 0.058 - 203.55x_{\text{Ce}} + 202.65x_{\text{Ce}}^2. \tag{17}$$

The parabolic relation of $\Delta H^M_{\text{Ce-Bi}}$ with Ce concentration as shown in Fig. 6 demonstrates that the Ce–Bi melt can be taken as a regular solution. Regardless the physical means of constants in the Miedema’s model, it is a desirable tool to predict enthalpies of some other lanthanide–Bi alloys that experimental based values are currently unavailable.

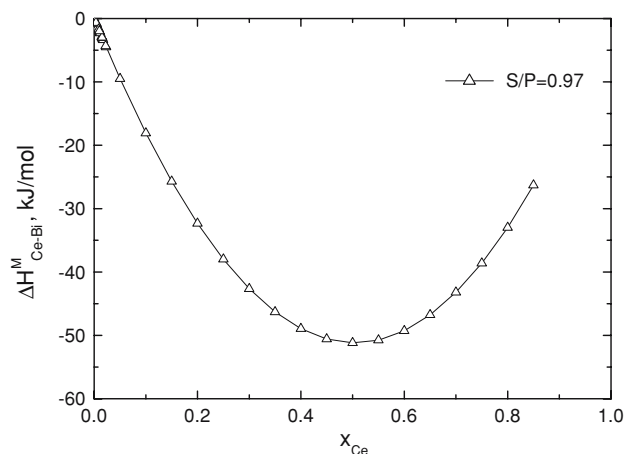


Fig. 6 Predicted ΔH_{Ce-Bi}^M as a function of x_{Ce}

Conclusion

The thermodynamic properties of small amounts of Ce diluted in Bi solution were determined by EMF measurement at temperature ranging from 735 to 937 K. The temperature and composition dependences of the activity coefficients were investigated. A considerable increase in the activity coefficient with temperature was observed over the Ce concentration ranges studied. The molar excess formation free energy, the excess enthalpy change, and the excess entropy change have been determined as $\Delta \bar{G}_{Ce}^{ex} = -195.53$ kJ/mol (at 873 K), $\Delta \bar{H}_{Ce}^{ex} = -212.65$ kJ/mol, $\Delta \bar{S}_{Ce}^{ex} = -19.60$ J K⁻¹ mol⁻¹, respectively. There is a linear relationship between the experimental ΔH_{Ce-Bi}^M and x_{Ce} . The values of ΔH_{Ce-Bi}^M were predicted by using the Miedema's model. After introducing the regressed value of $S/P = 0.97$

to the Miedema's model, the predicted data of ΔH_{Ce-Bi}^M were well agreed with the experimental values.

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