



## Short Communication

## Electromotive force study of lanthanum in liquid bismuth

Jian Zhang, Qing Sun, Jiawei Sheng\*

College of Materials Science and Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310032, China



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## ABSTRACT

The thermodynamics of lanthanum (La) dissolved in liquid bismuth (Bi) were determined by means of the electromotive force (EMF) measurement using a galvanic cell consisting of molten chloride and liquid bismuth at the temperature ranging from 723 K to 975 K. A considerable increase of the activity coefficient with temperature was observed for the La-Bi alloy. In addition, the activity coefficient increased slightly with the concentration of La. The values of the molar excess free energy of formation, the excess enthalpy, and the excess entropy of La dissolved in Bi were determined. The heat of formation of liquid La-Bi alloys ( $\Delta H_{La-Bi}^M$ ) was deduced from the measured activity coefficient. There is a linear dependence of experimental  $\Delta H_{La-Bi}^M$  on the La concentration.

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## 1. Introduction

In the last decades, how to satisfy the ever-increasing demand of energy has become the most pressing problem for China with its rapid economic growth. Nuclear energy is phased out in some countries, but China still has to rely on nuclear power to provide the necessary electrical energy. Besides reactor safety, a key issue for the use of nuclear energy is the reliable waste management [1, 2]. Studies of possible grouping of certain elements make it possible to achieve a compact, economic and non-proliferative recycling process and to simplify the overall management. Aqueous separation techniques (such as PUREX process) are currently employed in the nuclear fuel reprocessing industry for effective separation of minor actinides and fission products based on the separation of elements. However, PUREX process suffers from some drawbacks like limited solubility of fuel materials in acidic aqueous solutions and poor radiation stability of the organic solvents employed in the extraction process [3, 4]. In addition, a huge amount of liquid waste is produced when applying PUREX or related processes. It is therefore reasonable to investigate an alternative reprocessing method, called the pyrochemical process. The pyrochemical process of spent nuclear fuel is currently under active research and development in various countries for potential use to recover actinides from molten salts or partitioning fission products, including grouping rare earth metals into waste forms suitable for permanent disposal. Molten chloride salts play essential roles in pyrochemical process as the electrolytes for both oxide fuel reduction and metal fuel electrorefining. The use of

molten chloride salts as a separation media rather than water or organics has multiple advantages, including resistance to radiation damage and absence of neutron moderation [5–7].

Liquid Bi has broad applications in pyrochemical process in both the processing of used nuclear fuels and the partitioning of minor actinides and long-lived fission products arising out of the back-end of nuclear fuel cycles [8–11]. Waste volume minimization and separation of actinides and fission products from LiCl-KCl are areas of active research and need for improvement. In support of the establishment of this group separation process, separation of actinides from rare earths is a critical function needed for a spent fuel processing system to achieve optimal actinide recycling and minimal contamination of nuclear waste. All these applications require the fundamental data regarding behaviors of actinides and fission products in liquid Bi [7]. The extraction and separation performance of lanthanides and actinides by the pyrometallurgical extraction system mainly depends on the standard Gibbs free energy of formation of their chlorides, but their activity coefficients in both phases greatly influence the separation efficiency as well [1, 12]. Published information on the thermodynamic properties of alloys of La with Bi is inadequate. The main aim of this work was to determine the thermodynamic properties associated with the formation of liquid La-Bi alloys using the EMF measurement.

## 2. Experimental

The following galvanic cell consisting of a pure La electrode and La-Bi alloy electrode was designed to measure the EMF values between the metallic La and La solute in Bi solution [1, 12].



\* Corresponding author.

E-mail address: [jw-sheng@zjut.edu.cn](mailto:jw-sheng@zjut.edu.cn) (J. Sheng).

The pure La electrode was prepared by welding a tantalum lead to a small rod of 99.9% pure La metal. The alloy electrode was prepared by directly dissolving a small piece of pure La metal in 99.999% pure Bi. The electrolyte was ultra-dry KCl–LiCl eutectic salt with purity of 99.9% (mole ratio of lithium to potassium = 51/49). The  $\text{LaCl}_3$  in KCl–LiCl eutectic was directly extracted from the Bi phase. The experiments were carried out in a glove-box under purified argon atmosphere (oxygen level: 0.1 ppm, water level: 0.1 ppm) to prevent oxidation. Measurements were performed at temperature ranging from 723 K to 975 K. The temperature of the molten salt bath was monitored using Type K thermocouples (Omega) immersed intermittently in the salt. After the desired temperature was achieved, the pure lanthanide electrode was immersed into the molten salt phase, and the EMF between the pure La electrode and the liquid alloy electrode was measured with an electrometer. After immersing the pure La 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  $\leq 2$  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  $\pm 1$  °C. At each level of temperature, the concentration of La in Bi phase was changed several times, and the mole fraction of La in Bi was analyzed by ICP-AES (atomic emission spectroscopy) [13, 14].

### 3. Results and discussion

In general, La in chloride melts in contact with Bi was trivalent [15]. The following equilibrium between the salt phase and La–Bi solution was thus attained.



According to the Nernst's equation, the electromotive force,  $\Delta E$ , between lanthanide metal and lanthanide in bismuth can be expressed as the following equation [16–18].

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

where,  $\Delta G^{\text{fusion}}(\text{La})$  is the fusion energy of metallic La, which can be deduced from literature [19];  $R$  is the gas constant;  $T$  is the absolute temperature (K);  $F$  is the Faraday constant;  $a_{\text{La-Bi}}$  is the activity of metallic La in Bi solution, where  $a_{\text{La-Bi}} = x_{\text{La}} \times \gamma_{\text{La}}$ ;  $x_{\text{La}}$  is the mole fraction of La in Bi solution; and  $\gamma_{\text{La}}$  is the activity coefficient of La in Bi solution. Then  $\gamma_{\text{La}}$  can be obtained according to Eq. (3), using the values of  $\Delta E$ ,  $x_{\text{La}}$  and  $T$  obtained in this study.

The EMF values measured over the 723–975 K range were plotted in Fig. 1. The observed EMF shows a roughly linear dependence on  $x_{\text{La}}$ , suggesting that  $\Delta E$  approximately obeys Eq. (3). The line slopes drawn in Fig. 1 were almost the same as those of the theoretical slopes ( $\frac{2.3RT}{3F}$ ). This means that the dilute solutions of La in Bi approximately obeyed 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  $\gamma_{\text{La}}$  may depend on the concentration. Fig. 2 shows the variation of  $\log \gamma_{\text{La}}$  as a function of composition ( $x_{\text{La}}$ ). The activity coefficient depends on the temperature. In addition, a slight dependence of  $\log \gamma_{\text{La}}$  on  $x_{\text{La}}$  is clearly observed, which might be attributed to such a phenomenon as the weak interaction among the solute clusters.

The activity coefficient increased considerably as temperature increased (Fig. 2). A linear dependence of  $\log \gamma_{\text{La}}$  on  $1/T$  was found, as

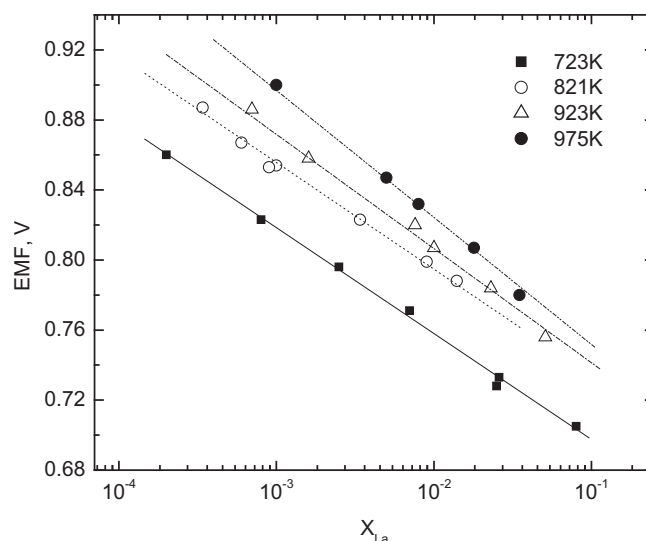


Fig. 1. Concentration dependence of the EMF determined for La in liquid Bi.

shown in Fig. 3. The line in Fig. 3 reflects the result of the least square fitting treatment, which is expressed as

$$\log \gamma_{\text{La}} = -1.876 - \frac{8758.7}{T} \quad (4)$$

Thus, the  $\log \gamma_{\text{La}}$  at any desired temperature can be calculated by Eq. (4).

The dilute solution of La in Bi was treated as a regular solution, thus, the partial molar excess Gibbs free energy changes of La dissolved in Bi solution ( $\Delta \bar{G}_{\text{La}}^{\text{ex}}$ ) can be deduced as follows [6,12,15]:

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

The temperature dependence of molar excess Gibbs free energy of formation can be expressed by

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

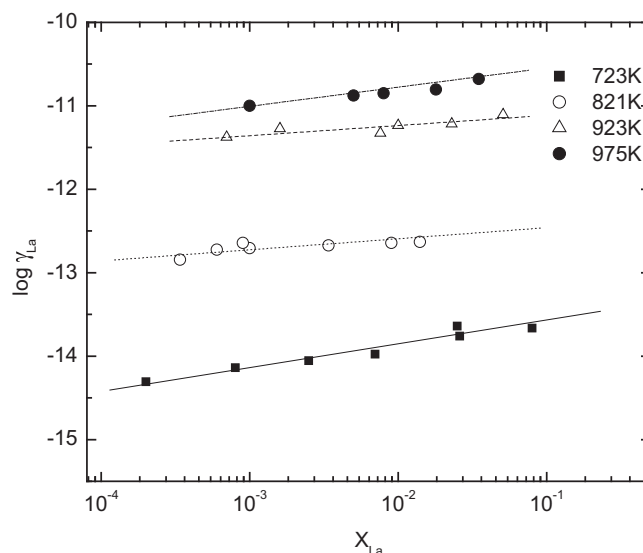


Fig. 2. Concentration dependence of the activity coefficients of La in liquid Bi.

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