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Letter to the Editors

Gibbs free energy of formation of liquid lanthanide–bismuth alloys

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Abstract

The linear free energy relationship developed by Sverjensky and Molling provides a way to predict Gibbs free energies of liquid Ln–Bi alloys formation from the known thermodynamic properties of aqueous trivalent lanthanides (Ln^{3+}). The Ln–Bi alloys are divided into two isostructural families named as the $LnBi_2$ (Ln = La, Ce, Pr, Nd and Pm) and LnBi (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb). The calculated Gibbs free energy values are well agreed with experimental data.

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1. Introduction

Pyrochemical process based on the liquid–liquid extraction using molten salt and liquid metal is a possible technology for the group separation of lanthanides and actinides in the irradiated fuel reprocessing industry [1,2]. In order to evaluate the effectiveness of the extraction and separation by this technique, the thermodynamic activities of lanthanides dissolved in liquid metal have to be carefully studied. Our previous works [1,3,4] and other research [5] deduced the standard Gibbs free energy of some lanthanides dissolved in liquid bismuth, however, some lanthanides are not measured yet. On the other hand, the systematic variations of Gibbs free energy along the lanthanide series are still insufficient. Finding such systematic variations is of quite useful for estimating Gibbs free energy of formation for those lanthanides when experimentally based values are unavailable. Once we applied a simplified linear relation of standard Gibbs free energy with the 2/3 power of the metallic volumes of lanthanides, which was determined by the least-squares fitting of the reported values for some trivalent lanthanides. However, this linear relation still has a large uncertainty [4]. Thus, the purpose of this paper is to apply the widely known linear free energy relationship developed by Sverjensky and Molling to predict the Gibbs free energies of formation for the liquid Ln–Bi alloys from the known thermodynamic properties of aqueous trivalent cations (Ln^{3+}).

2. Application of the linear free energy relationship

Sverjensky and Molling [6] have developed an empirically based linear free energy equation applicable to cations of any charge, radius or chemical types, which allows estimate of the free energy of solids with uncertainties of less than ±4.18 kJ/mol. This equation is directly analogous to the linear free energy relations of Hammett and others for aqueous organic reactions, but applies instead to crystalline solids [7,8]. The equation has been successfully applied to experimentally derived standard Gibbs free energy of formation of isostructural families of divalent oxides, hydroxides, carbonates, fluorides, chlorides and sulphates [6].

The lanthanides have the similar ionic radii and charge. When small amount of Ln was dissolved in liquid Bi (mole fraction less than 0.01), two isostructural

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types of Ln–Bi alloys are formed from the reported phase diagrams [9]; one intermetallic compound type is LnBi (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb), and the other is $LnBi_2$ (Ln = La, Ce, Pr, Nd and Pm). There is less information about the valence of lanthanides in liquid Ln–Bi alloys. In order to apply the Serverjensky–Molling equation, the studied lanthanides are reasonably treated as trivalent (Ln^{3+}) [10,11]. Here, we present a parallel application of Sverjensky–Molling equation to Ln–Bi alloys. Following the procedures of Serverjensky–Molling equation, the linear free energy correlation for Ln–Bi alloys is expressed as [6]

$$\Delta G_{f,Ln-Bi} = a \times \Delta G^0_{n,Ln^{3+}} + b + \beta \times \gamma_{Ln^{3+}}, \quad (1)$$

where the coefficients a, b and β characterize the particular structure of Ln–Bi alloys, $\Delta G_{f,Ln-Bi}$ denotes the formation free energy of Ln–Bi alloys at 873 K in this study, and $\gamma_{Ln^{3+}}$ is the crystallographic ionic radius of Ln^{3+} cations. The coefficients a, b and β can be determined by regression if the formation free energy of three or more Ln–Bi alloys at 873 K are known. The parameter $\Delta G^0_{n,Ln^{3+}}$ is the standard non-solvation energy from a radius-based correction to the standard free energy of formation of aqueous cation Ln^{3+}, which is calculated using

$$\Delta G^0_{n,Ln^{3+}} = \Delta G^0_{f,Ln^{3+}} - \Delta G^0_{a,Ln^{3+}}, \quad (2)$$

where $\Delta G^0_{n,Ln^{3+}}$ is the non-solvation energy of Ln^{3+}; $\Delta G^0_{f,Ln^{3+}}$ the standard free energy of formation of aqueous cation Ln^{3+}; and $\Delta G^0_{a,Ln^{3+}}$ the standard free energy of solvation of aqueous cation Ln^{3+}.

The $\Delta G^0_{a,Ln^{3+}}$ can be calculated from conventional Born solvation coefficients for aqueous cations ($\omega_{Ln^{3+}}$) and the dielectric constant of water (ε: 78.47 at 25 °C and 1 bar) according to the following equation:

$$\Delta G^0_{a,Ln^{3+}} = \omega_{Ln^{3+}}\left(\frac{1}{\varepsilon} - 1\right), \quad (3)$$

In turn, the conventional Born solvation coefficients are calculated from the equation

$$\omega_{Ln^{3+}} = \omega^{abs}_{Ln^{3+}} - 3\omega^{abs}_{H^+}, \quad (4)$$

where $\omega^{abs}_{H^+}$ is absolute Born solvation coefficient of H^+ (225.17 kJ/mol), $\omega^{abs}_{Ln^{3+}}$ is the absolute Born solvation coefficient obtained from effective electrostatic radii of the aqueous cation ($\gamma_{e,Ln^{3+}}$) used in Eqs. (5) and (6)

$$\omega^{abs}_{Ln^{3+}} = (166.027) \times 3^2/(\gamma_{e,Ln^{3+}}), \quad (5)$$

$$\gamma_{e,Ln^{3+}} = \gamma_{Ln^{3+}} + 3(0.94). \quad (6)$$

The standard solvation energies and non-solvation energies of Ln^{3+} can be calculated based on the above equations, and the results are listed in Table 1. Table 1 also gives the values of $\gamma_{Ln^{3+}}$ and the experimental values of $\Delta G_{f,Ln-Bi}$. The regression analysis for the coefficients a, b and β according to Eq. (1) using the experimental $\Delta G_{f,Ln-Bi}$ values in Table 1 gives:

$LnBi_2$ (Ln = La, Ce, Pr, Nd and Pm):

$a = 1.23$, $b = -1097.30$ kJ/mol,

$\beta = 577.39$ kJ mol^{-1} Å^{-1}.

LnBi (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb):

$a = 0.47$, $b = 35.32$ kJ/mol,

$\beta = -385.25$ kJ mol^{-1} Å^{-1}.

Table 1
Ionic radii, thermodynamic data for aqueous cations, and predicted Gibbs free energy of Ln–Bi alloys formation[a]

Ln	$\gamma_{Ln^{3+}}$ (Å)	Ln^{3+}, aqueous (kJ/mol)			$\Delta G_{f,Ln-Bi}$ (kJ/mol) (873 K)			
		$\Delta G^0_{a,Ln^{3+}}$	$\Delta G^0_{f,Ln^{3+}}$	$\Delta G^0_{n,Ln^{3+}}$	$LnBi_2$		LnBi	
					Expt.	Calc.	Expt.	Calc.
La	1.032	−934.78	−688.00	246.79	−199.13	−198.37		
Ce	1.010	−943.99	−676.00	267.99	−184.10	−185.04		
Pr	0.990	−952.45	−681.00	271.45	−191.68	−192.34		
Nd	0.983	−955.43	−672.00	283.43	−180.67	−181.67		
Pm	0.970	−961.00	−663.00	298.00	–	−171.29		
Sm	0.958	−966.17	−677.00	289.17			−195.89	−196.97
Eu	0.947	−970.94	−576.00	394.94			−141.02	−142.70
Gd	0.938	−974.87	−660.00	314.87			−173.02	−177.11
Tb	0.921	−982.33	−668.00	314.33			−166.22	−170.82
Dy	0.912	−986.31	−664.00	322.31			−169.74	−163.57
Ho	0.901	−991.20	−675.00	316.20			−162.15	−162.23
Er	0.890	−996.12	−673.00	323.12			−153.78	−154.72
Tm	0.880	−1000.61	−671.00	329.61			–	−147.79
Yb	0.868	−1006.04	−639.00	367.04			–	−125.47

[a] Radii of the cations and the values of $\Delta G^0_{a,Ln^{3+}}$ are from [10].

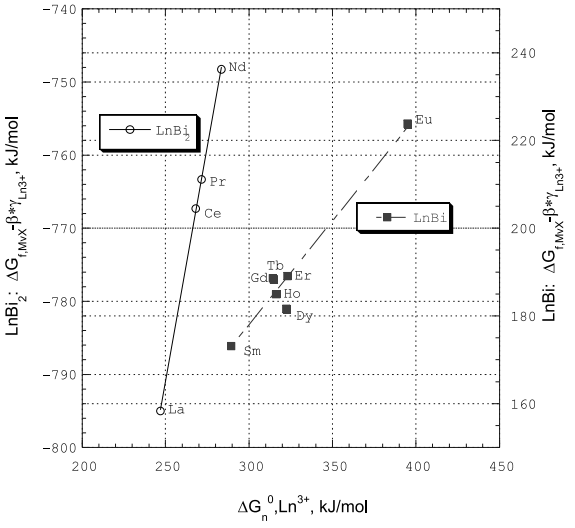

Fig. 1. Linear free energy relationship of Eq. (7) for LnBi and $LnBi_2$.

According to Eq. (1) and the above coefficients a, b and β, together with other constants in Table 1, the values of Gibbs free energy of formation of Ln–Bi alloys at 873 K were calculated, which are listed in Table 1. The calculated Gibbs free energy values agree well with the experimental data. The discrepancy of $LnBi_2$ type between calculated and experimental value is less than 1.0 kJ/mol. The worst discrepancy of LnBi type is for Dy (6.17 kJ/mol), while others are within ±5.0 kJ/mol. Eq. (1) can be rearranged as the following equation:

$$\Delta G_{\mathrm{f,Ln\text{–}Bi}} - \beta \times \gamma_{\mathrm{Ln^{3+}}} = a \times \Delta G^{0}_{\mathrm{n,Ln^{3+}}} + b, \qquad (7)$$

Then the linear free energy correlation can be expressed as Eq. (7). This linear relationship is illustrated in Fig. 1, which demonstrated that the Sverjensky–Molling equation was applicable to liquid Ln–Bi alloys.

The coefficient a characterizes the interaction between the remainder anions [6]. The regression results show a large difference of coefficient a between $LnBi_2$ and LnBi types, which implies the different coordination numbers of $LnBi_2$ and LnBi. Although the predicted values need to be confirmed by experiments, the linear free energy relationship provides a useful tool for predicting unknown thermodynamic properties from a limited number of available data. It is suggested that this linear free energy relationship may also be available for the actinide–metal alloys, where many of the Gibbs free energy data are still unavailable because of the experimental difficulty in handling radioactive actinides.

3. Conclusion

Sverjensky–Molling equation successfully described the standard Gibbs free energy of formation of liquid Ln–Bi alloys formed by dissolving small amount of lanthanide in liquid bismuth. The coefficients for the structural family for $LnBi_2$ (Ln = La, Ce, Pr, Nd and Pm) are: $a = 1.23$, $b = -1097.30$ kJ/mol, and $\beta = 577.39$ kJ mol^{-1} Å^{-1}; and for the family of LnBi (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb) are: $a = 0.47$, $b = 35.32$ kJ/mol, and $\beta = -385.25$ kJ mol^{-1} A^{-1}. The discrepancy between calculated and observed free energies is within ±5.0 kJ/mol, except for Dy of 6.17 kJ/mol.

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