Thermodynamic properties of fission products in liquid bismuth

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Abstract: The thermodynamic properties of fission products in molten salt and liquid metal have a great influence on the disposal of nuclear waste in the nuclear fuel cycle industrial system. This paper attempts to extract useful thermodynamic information from the only few experimental activities of lanthanides (Ce, Pr, La) in liquid Bi at different temperatures. The molecular interaction volume model (MIVM) was adopted to model and predict some temperature-dependent thermodynamic functions, including activity, infinite dilute activity coefficient, and molar excess Gibbs energy. The minor average of $\Delta G$ error indicated that assuming $\varepsilon_{ji} - \varepsilon_{ii}$ is a constant is reasonable. On this basis, the natural logarithm of the interaction coefficients and the natural logarithm of the infinite dilute activity coefficient of lanthanides (Ce, Pr, La) in the Bi-based metal melt, these two parameters, show the linear relationship with the reciprocal of temperature. The reasonable agreement of the modeled thermodynamic parameters with the existing experimental data verified that the MIVM is quite convenient and reliable, which can provide guidance for separating fission products from molten salt reactors.

1. Introduction
The secure disposal of nuclear waste is an important part of the utilization of nuclear energy. The pyrochemical reprocessing of spent nuclear fuels has been seen as a means of disposing of nuclear waste [1], which offers the potential for the separation of fission products in the short cooling time of irradiated fuel with more compact facilities in the future [2]. To improve this separation technique, it is highly important to accurately know the thermodynamic behavior of fission products dissolved in molten salt or liquid metal [3].

The low melting point of liquid bismuth and its immiscibility with molten salts make it widely used to separate fission products from molten salt reactors [4]. The separation performance of fission products is significantly affected by their thermodynamic properties in liquid bismuth. For example, the separation efficiency and the distribution of fission products are greatly influenced by their activity coefficients in liquid bismuth [5, 6]. In the past few decades, massive studies about the activity coefficients of fission products in liquid bismuth have been carried out [1, 2, 5-8]. Lanthanides are important components of fission products. However, because of the high melting point of lanthanides, the available data are still finite about the thermodynamic properties of lanthanides in the liquid bismuth. Recently, the CALPHAD method was used to describe the thermodynamic properties of Bi-Pr, Bi-Ce, and Bi-Er [4], which formulation requires knowledge of the presence and composition of an complex in the binary alloys and uses more fitting parameters. The Miedema model [9], which is widely used, can calculate the heat of formation of any binary alloy except O, S, and Te, using the
molar volume, electronegativity and electron density of constituent elements of the melt. On the basis of the Miedema model, the activity and activity coefficient of the binary alloy components can be calculated according to the thermodynamic relationship.

The molecular interaction volume model (MIVM) can describe the thermodynamic properties of liquid binary, ternary and multicomponent alloy systems under the precondition of nearly ideal alloys, with fewer fitting parameters [10-12], which was extracted from the statistical thermodynamics by Tao [13]. In recent years, lots of works demonstrated that the MIVM can also be used to simulate the activity coefficients of an alloy system, and the predicted results show a large negative deviation from the ideal state [14, 15]. According to the experimental activity of low-level lanthanides (Ce, Pr, La) dissolved in liquid Bi [1, 2, 16], which were measured by the electromotive force measurement method at several temperatures, the significant negative deviations from Raoult’s law (the activity of element is much less than its content) point to a strong interparticle interaction between the components of binary lanthanides–bismuth systems.

In the present paper, the primary goal of our investigation was to model the little experimental data of low-level lanthanides (Ce, Pr, La) dissolved in liquid Bi [1, 2, 15] to acquire the complete theoretical activity curve of lanthanides in liquid Bi as a function of temperature and to predict the thermodynamic properties of the liquid binary alloy at different temperatures. The accuracy of predicting thermodynamic performance will be evaluated by comparing it with other experimental data. The second goal was to explore the temperature effect on the infinite dilute activity coefficient and molar excess Gibbs energy of lanthanides in liquid bismuth.

2. Molecular interaction volume model
Unlike gas and solid molecules, the movement of liquid molecules is a non-random migration from one molecular cell to another [10, 11], which causes a phenomenon that each molecule migrates into an adjacent cavity as a central molecule. The MIVM is built on the assumption that liquid molecules can pass freely through a cell space, and adjacent atoms are relative to each other, interchangeable, movable, and have similar cells [10, 11]. Derived with mathematic calculation, the molar excess Gibbs energy $G^E$ of the liquid binary alloy $i$–$j$ is given by

$$G^E = RT \left( x_i \ln \frac{V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} + x_j \ln \frac{V_{mj}}{x_j V_{mj} + x_i V_{mi} B_{ij}} - \frac{x_i x_j}{2} \left( \frac{Z_i B_{ji} \ln B_{ji} + Z_j B_{ij} \ln B_{ij}}{x_i + x_j B_{ji}} \right) \right)$$  \(1\)

where $R$ is the ideal gas constant, $T$ is the temperature of the mixture, $x_i$ and $x_j$ are the molar fractions of $i$ and $j$, $V_{mi}$ and $V_{mj}$ are the molar volume of $i$ and $j$, $Z_i$ and $Z_j$ are the first coordination number of $i$ and $j$ in the liquid state, $B_{ji}$ and $B_{ij}$ are the pair-potential energy interaction parameters, which is defined by the following formula

$$B_{ji} = \exp \left( -\frac{\epsilon_{ji}}{kT} \right)$$  \(2\)

where $k$ is the Boltzmann constant and $\epsilon_{ji}$ is the pair potential energy of a central atom $i$ and its first nearest neighbor $j$.

Based on equation (1), the activity of the components $i$ was calculated by the following mathematical expression

$$\ln \alpha_i = \ln \frac{x_i V_{mi}}{x_i V_{mi} + x_j V_{mj} B_{ji}} + x_j \left( \frac{V_{mj} B_{ji}}{x_j V_{mj} + x_i V_{mi} B_{ij}} - \frac{V_{mi} B_{ij}}{x_i V_{mi} + x_j V_{mj} B_{ji}} \right) - \frac{x_j^2}{2} \left( \frac{Z_i B_{ji} \ln B_{ji} + Z_j B_{ij} \ln B_{ij}}{x_i + x_j B_{ji}} \right)$$  \(3\)
The values of the physical parameters, $V_m$ and $Z$, for the metals of interest in the present study are taken from references [17] and [18]. To determine the value of $B_{ji}$ and $B_{ij}$, the activity of $i$ in binary alloy, $\alpha_i$, was fitted with the equation (3) at a given temperature. The experimental activities were obtained by the electromotive force measurement in references [19]. The optimal values of $B_{ji}$ and $B_{ij}$ are obtained by minimizing the error $\text{err} = \sqrt{\sum_{i=1}^{n} \left( \ln(\alpha_{i,\text{exp}}) - \ln(\alpha_{i,\text{MIVM}}) \right)^2} / n$, in which $n$ is the number of experimental data points.

When $x_i$ approaches 0, the infinite dilution activity coefficient $\gamma_i^0$ obtained from equation (3) can be expressed as:

$$\ln \gamma_i^0 = 1 - \ln \left( \frac{V_m B_{ji}}{V_m} \right) - \frac{V_m B_{ij}}{V_m} - \frac{1}{2} \left( Z_i \ln B_{ji} + Z_j \ln B_{ij} \right)$$

(4)

### 3. Results and discussion

#### 3.1. Theoretical activity of low-level lanthanides in liquid bismuth

The activity of a component is an important thermodynamic parameter that relates closely with the minimum Gibbs energy needed in any proposed process of extracting or refining pure metals from its metal solutions [20]. The experimental activities of low-level Ce in binary Ce–Bi liquid alloy were taken from the electromotive force measurement by Dong, et al. [2] within the temperature interval from 735 to 937K, as shown in figure 1(a). For liquid Pr–Bi and La–Bi, the experimental data were quoted from Ref. [1] and [16], as shown in figure 1(b) and (c), respectively. These experimental activities at different temperatures were fitted with equation (3) in order to determine the values of the interaction coefficients between lanthanides and bismuth, $B_{BiX}$ and $B_{XBi}$, as listed in table 1. Here, X is a lanthanide of interest, Ce, Pr and La, respectively. By using MIVM presented in the previous sections, the corresponding theoretical activities for these three alloys were also calculated by equation (3) using the determined interaction coefficients, and the activity curves were shown in figure 1(a)–(c).
Figure 1. Activity of lanthanides in liquid Bi at the different temperature.

Figure 1(a) is the activity of Ce vs. the concentration of Ce in the liquid alloys at 735K, 797K, 887K and 937K, respectively. Figure 1(b) is the activity of Pr vs. the concentration of Pr in the liquid alloys at 810K, 910K, 1010K and 1110K, respectively. Figure 1(c) is the activity of La vs. the concentration of La in the liquid alloys at 723K, 821K, 923K and 975K, respectively. The triangles, circles, and squares denote the experimental values at different temperatures quoted from Ref. [2], [1] and [16], respectively. The solid lines denote theoretical values from the MIVM.

Table 1. The values of $B_{BX}$ and $B_{XBi}$ of liquid X–Bi alloy at the different temperatures, with the error in the modeled partial Gibbs free energy of X. X is a lanthanide of interest, Ce, Pr and La, respectively.

| X | T(K) | $B_{BX}$ | $B_{XBi}$ | average of $\Delta G_{MX} - \Delta G_X$ (10^{-21}J) | average of error (kJ/mol) |
|---|-----|---------|---------|---------------------------------|------------------------|
| Ce | 735 | 1.8     | 49.2    | 5.9647                           | ±0.12                  |
|    | 797 | 1.4     | 49.1    | -3.7025                          | ±0.33                  |
|    | 887 | 1.7     | 24.8    | -6.4983                          | ±0.98                  |
|    | 937 | 1.1     | 31.9    | -1.2330                          | ±0.63                  |
|    | 910 | 0.5     | 84.9    | 1.7516                           | ±1.15                  |
| Pr | 1010| 0.5     | 33.0    | 9.6656                           | ±1.90                  |
|    | 1110| 0.5     | 23.4    | 10.6226                          | ±3.96                  |
|    | 723 | 2.4     | 27.6    | -8.7390                          | ±1.74                  |
|    | 923 | 1.4     | 34.3    | -4.2878                          | ±1.91                  |
|    | 975 | 1.8     | 20.2    | -7.9124                          | ±0.93                  |

As shown in figure 1, it can be noted that these curves calculated by MIVM reproduced fairly well the experimental values of activity at the indicated temperatures. To assess the perfection of the fitting, the average error in the partial Gibbs free energy of lanthanides is also given, which is defined as

$$
\Delta G_{MIVM} - \Delta G_{exp} = RT \ln \frac{\alpha_{MIVM}}{\alpha_{exp}}
$$

In table 1, the maximal difference was ±3.96 kJ/mol between the modeled and the experimental
$\Delta \bar{G}$. The good consistency between the predicted and experimental values justifies the use of the MIVM for this study.

3.2. Predicted activity and $G^E$ of low-level lanthanides in liquid bismuth assuming that $\varepsilon_{BiX} - \varepsilon_{XX}$ is a constant

Through analysis of Tao’s model, the temperature dependence of $B_j$ and $\varepsilon_j$ can be seen from equation (2). The temperature dependence of the interaction coefficients was verified for Ca–Sb [21] and Ca–Bi [15]. In this paper, the value of $\varepsilon_{BiX} - \varepsilon_{XX}$ for lanthanides (Ce, Pr, La) in liquid Bi was calculated by using the equation (2) and the average value of $\varepsilon_{BiX} - \varepsilon_{XX}$ were also shown in table 1. $X$ is a lanthanide of interest, Ce, Pr and La, respectively. The average value of $\varepsilon_{BiX} - \varepsilon_{XX}$ at different temperatures was considered as a constant. Thus, the relationship between the interaction coefficients and temperature originated from the equation (2) can be expressed as

$$\ln B_{BiCe} = \frac{315.04}{T}$$  \hspace{1cm} (6)

$$\ln B_{BiPr} = \frac{-665.42}{T}$$  \hspace{1cm} (7)

$$\ln B_{BiLa} = \frac{499.80}{T}$$  \hspace{1cm} (8)

For lanthanides (Ce, Pr, La) in liquid Bi, the values of the interaction parameters of binary liquid alloys at 723K, 773K and 900K can be predicted according to equation (6) – (8), as listed in table 2. The variation with temperature of $V_m$ and $Z$ was taken into consideration for Bi during the calculation of the interaction parameters at 723K, 773K and 900K, whereas these two parameters at its melting point were reused for lanthanides (Ce, Pr, La), ignoring their temperature dependence. The experimental activities of lanthanides (Ce, Pr, La) in liquid Bi at 723K and 773K were measured by Kurata et al [8]. The predicted activities at 723K and 773K match the experimental data, as plotted in figure 2. In table 2, the maximal difference was $\pm 7.45$ kJ/mol between the predicted and the experimental $\Delta \bar{G}$. This good agreement verifies the accuracy of the MIVM for low-level lanthanides in liquid bismuth.

Table 2. The calculated values of $B_{BiX}$ and $B_{XBi}$ of liquid X–Bi alloy at the different temperatures, with the error in the predicted partial Gibbs free energy of X. X is a lanthanide of interest, Ce, Pr and La, respectively.

| X   | T(K) | $B_{BiX}$ | $B_{XBi}$ | average of $\Delta \bar{G}$ | error (kJ/mol) |
|-----|------|-----------|-----------|----------------------------|----------------|
| Ce  | 723  | 1.5       | 64.7      | $\pm 4.46$                 |                |
|     | 773  | 1.5       | 49.4      | $\pm 1.22$                 |                |
|     | 900  | 1.4       | 28.5      |                            |                |
|     | 723  | 0.4       | 135.4     | $\pm 2.85$                 |                |
| Pr  | 773  | 0.4       | 98.5      | $\pm 2.78$                 |                |
|     | 900  | 0.5       | 51.6      |                            |                |
|     | 723  | 1.8       | 66.5      | $\pm 7.45$                 |                |
| La  | 773  | 1.8       | 50.7      | $\pm 2.03$                 |                |
|     | 900  | 1.68      | 29.18     |                            |                |

Based on the hypothesis that $\varepsilon_{BiX} - \varepsilon_{XX}$ is a constant, the molar excess Gibbs energy $G^E$ at 900K was calculated according to the equation (1) - (3) and it is gratifying to note that the predicted values indicated in figure 3 are in quite good consistency with the results cited from Ref. [22].
The feasibility of taking $\varepsilon_{BiX} - \varepsilon_{XX}$ as a constant is proven by the consistency between the predicted activity and $G^E$ and the experimental values, shown in figure 2 and figure 3.

3.3. Temperature dependence of the infinite dilute activity coefficient

To more accurately grasp the factors affecting the separation of lanthanides from liquid bismuth, knowledge of the infinite dilute activity coefficient is a significant consideration for evaluating the thermodynamic and kinetic behavior of lanthanides in liquid Bi. It is a pity that only a small amount of data is utilizable for the infinitely dilute activity coefficient of lanthanides in liquid Bi. Using the MIVM, the infinite dilute activity coefficient of lanthanides (Ce, Pr, La) in Bi-based melts can be obtained calculated by equation (4). The relationship between the natural logarithm of the calculated infinite dilute activity coefficient of lanthanides (Ce, Pr, La) in the Bi-based metal melt and the reciprocal of temperature of interest is drawn in figure 4. Fitting the results of MIVM, a linear relationship can be obtained between the two parameters, shown in figure 4, which is indicated by equation (9) - (11).

$$\ln \gamma^0_{Ce} = - \frac{25733}{T} + 2.41$$ \hspace{1cm} (9)

$$\ln \gamma^0_{Pr} = - \frac{26010}{T} + 3.73$$ \hspace{1cm} (10)

$$\ln \gamma^0_{La} = - \frac{20670}{T} - 3.90$$ \hspace{1cm} (11)
Figure 2. Predicted activity of low-level lanthanides in liquid Bi at 723K and 773K assuming $\varepsilon_{\text{BiX}} - \varepsilon_{\text{XX}}$ is a constant.

Figure 2(a) is the activity of low-level Ce vs. the concentration of Ce in the liquid alloys. Figure 2(b) is the activity of Pr vs. the concentration of low-level Pr in the liquid alloys. Figure 2(c) is the activity of La vs. the concentration of low-level La in the liquid alloys. The solid circle were cited from [8].

Figure 3. Molar excess Gibbs energy of lanthanides (Ce, Pr, La) in liquid Bi at 900K. $x$ is the concentration of lanthanides in the liquid alloys. The circles denote the values cited from Ref. [22]. The line denotes theoretical values from the MIVM.

For completeness, the Miedema model was also used to calculate the value of $\ln \gamma^x$, which is also shown in figure 4. This consistency among the calculated values obtained by different models offers evidence of the correctness of the associated thermodynamic modeling aspects. Although there is a lack of relevant experimental data, the thermodynamic properties of lanthanides in the Bi-based metal melt can be inferred based on this conclusion.
Figure 4. The linear relationship between $\ln \gamma^0$ for lanthanides in liquid Bi and the reciprocal of temperature.

Figure 4(a) is the $\ln \gamma^0$ of Ce vs. temperature. Figure 4(b) is the $\ln \gamma^0$ of Pr vs. temperature. Figure 4(c) is the $\ln \gamma^0$ of La vs. temperature.

4. Conclusion

Molecular interaction volume model (MIVM) is of great value in simulating the thermodynamic functions of dilute fission products in liquid bismuth. The calculated values of activity and molar excess Gibbs energy agree well with the experimental results for low-level lanthanides (Ce, Pr, La) in liquid Bi. In the calculation of MIVM, it is reasonable to regard $\varepsilon_{ji} - \varepsilon_{ii}$ as a constant, and the relationship between the interaction parameters and the reciprocal of temperature is obtained, expressed as: $\ln B_{BiCe} = 315.04 / T$, $\ln B_{BiPr} = -665.42 / T$ and $\ln B_{BiLa} = 499.80 / T$. The influence of temperature on the infinite dilute activity coefficient is presented by the equations: $\ln \gamma^0_{Ce} = -25733 / T + 2.41$, $\ln \gamma^0_{Pr} = -26010 / T + 3.73$ and $\ln \gamma^0_{La} = -20670 / T - 3.90$. Good consistency of results has come to light between the calculated results and the considerations of the Miedema model. The results obtained in this paper confirm that MIVM is credible for calculating the thermodynamic
activities of liquid binary lanthanides–bismuth systems. On the basis of these conclusions, precisely predicting the thermodynamic properties of high melting point lanthanides will provide a theoretical basis for the safe disposal and recycling of nuclear waste.

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