

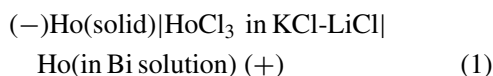
Thermodynamic properties of dilute holmium in liquid bismuth

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The implementation of partitioning and transmutation (P&T) is intended to reduce the inventories of actinides and long-lived fission products in nuclear waste. Aqueous separation techniques (such as the 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 one element at a time. A possible grouping of certain elements could result in a compact, economic and non-proliferative recycling process, as well as a simplified overall management. Pyrochemical processing based on liquid-liquid extraction using molten salt and liquid metal is a potential technology for the group separation of lanthanides and actinides in the irradiated fuel reprocessing industry [1, 2]. In order to facilitate this group separation process, the thermodynamic behavior of lanthanides and actinides in molten salt and liquid metal must be determined. 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 [3–5]. The main aim of this work was to determine the thermodynamic properties associated with the formation of liquid Ho-Bi alloys at low Ho concentration using the electromotive force (EMF) measurement.

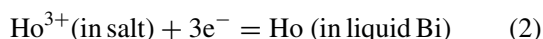
The following galvanic cell was designed to measure the EMF values between the metallic Ho and Ho solute in Bi solution [3].



The pure Ho electrode was prepared by welding a tantalum lead to a small rod of 99.9% pure Ho metal. The alloy electrode was prepared by directly dissolving a small piece of pure Ho metal in 99.999% pure Bi. The electrolyte was KCl-LiCl eutectic with purity of 99.9% (mole ratio of lithium and potassium = 51/49). The HoCl₃ in KCl-LiCl eutectic was directly extracted from the Bi phase. The experiments were carried out in a glove-box filled with purified argon. Measurements were performed in the temperature range from 790 to 1080 K. After the desired temperature was achieved, the pure lanthanide electrode was immersed into the molten salt phase, and the EMF between the pure Ho electrode and liquid alloy electrode was measured with an electrometer. After immersing the pure Ho electrode, the value of EMF was monitored continuously for more

than 10 min until it stabilized. The temperature was controlled within $\pm 1^\circ\text{C}$. At each level of temperature, the concentration of Ho in Bi phase was changed several times, and the mole fraction of Ho in Bi was analyzed by ICP-AES (ICPS-1000III, Shimadzu Co. Ltd.).

In general, Ho in chloride melts in contact with Bi was trivalent [6]. The following equilibrium between the salt phase and Ho-Bi solution was thus attained.



According to the Nernst's equation, the electromotive force, ΔE , between lanthanide metal and lanthanide in bismuth can be expressed as the following equation [4, 5, 7].

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

where, $\Delta G^{\text{fusion}}(\text{Ho})$ is the fusion energy of metallic Ho, which can be deduced from literature [8]; R is the gas constant; T is the absolute temperature (K); F is the Faraday constant; $a_{\text{Ho-Bi}}$ is the activity of metallic Ho in Bi solution, where $a_{\text{Ho-Bi}} = x_{\text{Ho}} \times \gamma_{\text{Ho}}$; x_{Ho} is the mole fraction of Ho in Bi solution; and γ_{Ho} is the activity coefficient of Ho in Bi solution. Then γ_{Ho} can be obtained according to Equation (3), using the values of ΔE , x_{Ho} and T obtained in this study. The dilute solution of Ho in Bi was treated as a regular solution, the heat of formation of liquid Ho-Bi alloys ($\Delta H_{\text{Ho-Bi}}^M$) can be obtained from γ_{Ho} by thermodynamic deductions [7, 9, 10].

$$\begin{aligned} \Delta H_{\text{Ho-Bi}}^M &= 2.3x_{\text{Ho}}RT \log \gamma_{\text{Ho}} \\ &\quad + 2.3x_{\text{Bi}}RT \log \gamma_{\text{Bi}} \end{aligned} \quad (4)$$

where, x_{Bi} is the concentration of Bi in Bi phase, and γ_{Bi} is the activity coefficient of Bi. When $x_{\text{Ho}} \ll 0.1$ in our experiments, $\gamma_{\text{Bi}} = 1$. Then $\Delta H_{\text{Ho-Bi}}^M$ can be obtained using the experimental values of x_{Ho} and γ_{Ho} as

$$\Delta H_{\text{Ho-Bi}}^M = 2.3x_{\text{Ho}}RT \log \gamma_{\text{Ho}} \quad (5)$$

The EMF values measured over the 790–1080 K ranges were plotted in Fig. 1. The observed EMF (ΔE) shows

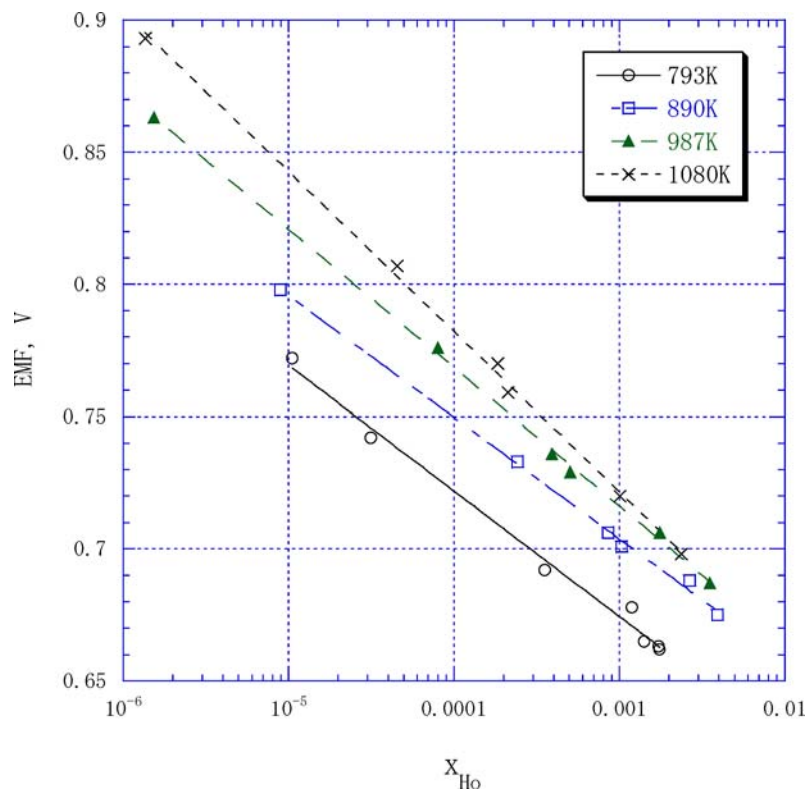


Figure 1 Concentration dependence of the EMF determined for Ho.

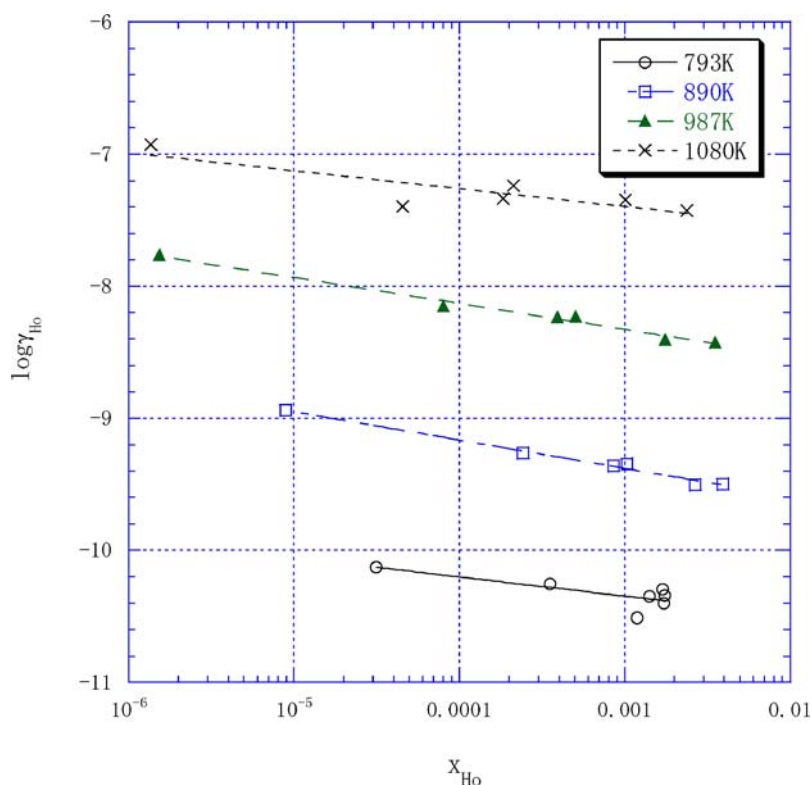


Figure 2 Concentration dependence of the activity coefficients of Ho.

a roughly linear dependence on $\log \gamma_{\text{Ho}}$, suggesting that ΔE approximately obeys Equation (3). The line slopes drawn in Fig. 1 were those of the theoretical slopes ($\frac{2.3RT}{3F}$) that were obtained by applying the least-square fitting method to the experimental data of every temperature. This means that the dilute solutions of Ho 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 Equation (3) is not absolutely constant over the tested concentration range, and that γ_{Ho} may depend on the concentration. Fig. 2 shows the variation of $\log \gamma_{\text{Ho}}$ as a function of composition (x_{Ho}). The errors of $\log \gamma_{\text{Ho}}$, involving all errors associated with measurement, were about 10% for $x_{\text{Ho}} = 10^{-6}$ to 3% for $x_{\text{Ho}} = 10^{-2}$. The activity coefficient increased with increasing temperature. In Fig. 2, a slight dependence of $\log \gamma_{\text{Ho}}$ on $\log x_{\text{Ho}}$ is clearly observed. This might be attributed to such a

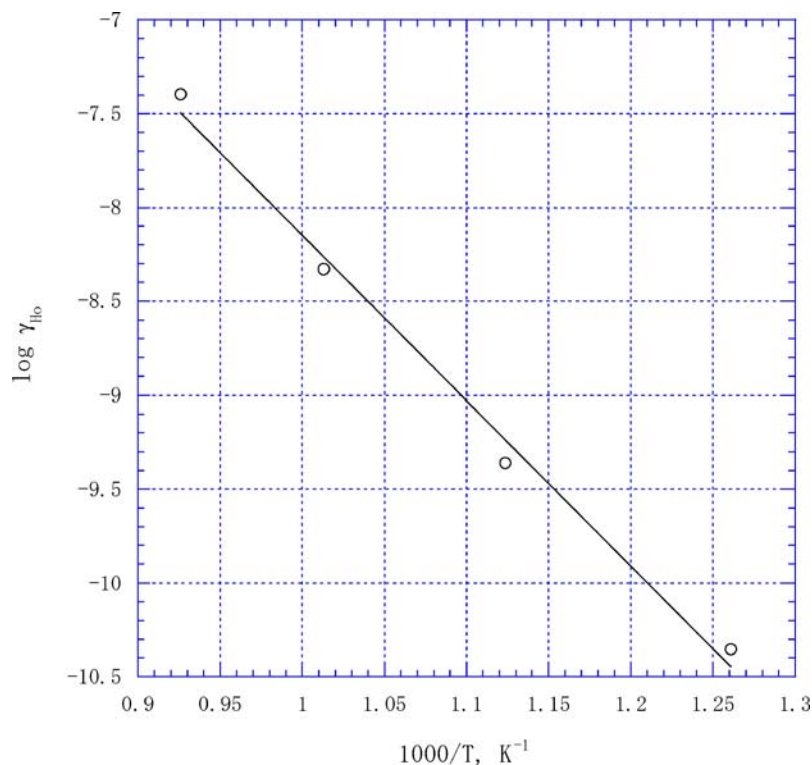


Figure 3 Temperature dependence of the activity coefficient.

phenomenon as a weak interaction among the solute clusters, but it could not be identified in this paper due to the limited experimental data.

The activity coefficient increased considerably as temperature increased. In order to evaluate the temperature dependency, mole fraction $x_{\text{Ho}} = 0.001$ was chosen as the representative concentration to calculate $\log \gamma_{\text{Ho}}$. A linear dependence of $\log \gamma_{\text{Ho}}$ on $1/T$ was found, as shown in Fig. 3. The line in Fig. 3 reflects

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

$$\log \gamma_{\text{Ho}} = 0.656 - \frac{8803.9}{T} \quad (6)$$

$\log \gamma_{\text{Ho}}$ at any desired temperature can be calculated by Equation (6) in order to calculate the $\Delta H_{\text{Ho-Bi}}^M$. Fig. 4 shows the experimental $\Delta H_{\text{Ho-Bi}}^M$ as a function of

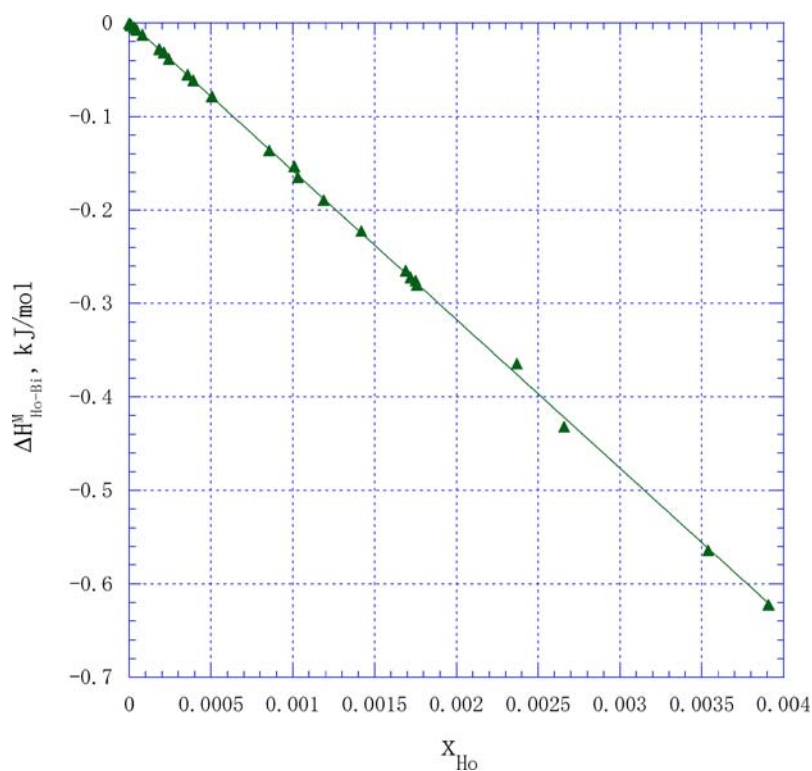


Figure 4 Variation of $\Delta H_{\text{Ho-Bi}}^M$ as a function of x_{Ho} .

x_{Ho} . A linear dependence of $\Delta H_{\text{Ho-Bi}}^M$ on x_{Ho} was observed as well, suggesting a small tendency for clustering of Ho and Bi in the experimental concentration and temperature ranges. The linear relationship between the experimental $\Delta H_{\text{Ho-Bi}}^M$ and x_{Ho} shown in Fig. 4 can be expressed by

$$\Delta H_{\text{Gd-Bi}}^M = -159.04 x_{\text{Ho}} \text{ (kJ/mol)} \quad (7)$$

The partial molar excess Gibbs free energy changes of Ho dissolved in Bi solution ($\Delta \bar{G}_{\text{Ho}}^{\text{ex}}$) can be deduced as follows [7, 9, 10]:

$$\Delta \bar{G}_{\text{Ho}}^{\text{ex}} = 2.3 RT \log \gamma_{\text{Ho}} \quad (8)$$

and

$$\Delta \bar{G}_{\text{Ho}}^{\text{ex}} = \Delta \bar{H}_{\text{Ho}}^{\text{ex}} - T \Delta \bar{S}_{\text{Ho}}^{\text{ex}} \quad (9)$$

Where $\Delta \bar{H}_{\text{Ho}}^{\text{ex}}$ is the partial excess enthalpy change of Ho dissolved in Bi solution; and $\Delta \bar{S}_{\text{Ho}}^{\text{ex}}$ is the corresponding excess entropy change. Combining Equations (8) and (9), the following equation is produced:

$$\log \gamma_{\text{Ho}} = \frac{-\Delta \bar{S}_{\text{Ho}}^{\text{ex}}}{2.3R} + \frac{\Delta \bar{H}_{\text{Ho}}^{\text{ex}}}{2.3RT} \quad (10)$$

According to Equations (6) and (8), the molar excess formation free energy at 873 K and for $x_{\text{Ho}} = 0.001$ was calculated as

$$\Delta \bar{G}_{\text{Ho}}^{\text{ex}} = -157.40 \text{ kJ/mol} \quad (11)$$

Combining Equations (6) and (10), $\Delta \bar{H}_{\text{Ho}}^{\text{ex}}$ and $\Delta \bar{S}_{\text{Ho}}^{\text{ex}}$ were obtained as

$$\Delta \bar{H}_{\text{Ho}}^{\text{ex}} = -168.57 \text{ kJ/mol} \quad (12)$$

$$\Delta \bar{S}_{\text{Ho}}^{\text{ex}} = -12.56 \text{ J} \cdot \text{K}^{-1} \text{ mol}^{-1} \quad (13)$$

In summary, the thermodynamic properties of small amounts of Ho (10^{-6} to 10^{-2} in molar fraction) diluted in Bi solution were determined by EMF measurement in the temperature range from 790 to 1080 K. The temperature and composition dependences of the activity coefficients were investigated, and then the values of $\Delta H_{\text{Ho-Bi}}^M$, $\Delta \bar{G}_{\text{Ho}}^{\text{ex}}$, $\Delta \bar{H}_{\text{Ho}}^{\text{ex}}$ and $\Delta \bar{S}_{\text{Ho}}^{\text{ex}}$ were determined. A considerable increase of the activity coefficient with increasing temperature was observed over the Ho concentration ranges studied.

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