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Prediction of the formation enthalpies of Bi–Cd–Ga–In–Pb–Sn–Zn liquid alloys by binary infinitely dilute enthalpies

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ABSTRACT

The molecular interaction volume model (MIVM) is used to predict the formation enthalpies of Bi–Cd–Ga–In–Sn–Zn and Bi–Cd–Ga–In–Pb–Sn–Zn liquid alloys, using only the infinitely dilute enthalpies of binary systems and the coordination numbers of the constituent elements in liquid alloys. In addition, the infinitely dilute enthalpies of binary system were obtained by Miedema's theory without requiring experimental data. The results are compared with the experimental data and calculated values using the Hoch–Arpshofen model (HAM), the results indicate that the model is reliable as well as being convenient.

1. Introduction

The knowledge of the formation enthalpies of multicomponent alloys is important for providing important thermodynamic information in materials science and metallurgical engineering. A great deal of binary data has been so far compiled as monographs for example Hultgren et al. [1]. More than 200 binary systems were studied by Kleppa's group providing an unrivalled set of enthalpy data [2]. The experimental thermodynamic study of a multicomponent system is very time consuming since a great number of measurements are necessary. Therefore, theoretical predicting is a significant and effective approach to obtain thermodynamic properties of alloys, especially for multicomponent ones. During the past decades, various methods based on the properties of pure elements have been developed for estimating the formation enthalpies of a limited number of alloys [3–10]. The Hoch–Arpshofen model (HAM) is suitable for the description of the concentration dependence of thermodynamic state functions particularly the formation enthalpy of liquid alloys [11,12]. The molecular interaction volume model (MIVM) is obtained on a physical basis [13], it is a two-parameter model that is able to predict some component activities and enthalpies in liquid alloys [14,15]. Both HAM and MIVM are based on the matter structure and predict the thermodynamic properties of alloys from the principles of statistical mechanics. The prediction method of the two models that only uses the formation enthalpies of binary systems is more convenient and available than either the HAM or the MIVM models.

In a preceding paper [16], the formation enthalpies of Cd–Ga–In–Sn–Zn alloys and its constitutive subsystems were calculated using only the infinitely dilute enthalpies of binary systems. The purpose of this work is to apply the MIVM to Bi–Cd–Ga–In–Sn–Zn and Bi–Cd–Ga–In–Pb–Sn–Zn liquid alloys. Also infinitely dilute enthalpies of the binary system were obtained using the Miedema model without requiring experimental data. The predicted values are compared with experimental data and also values calculated by the HAM to verify the usefulness of the method.

2. Models

2.1. Molecular interaction volume model

According to MIVM [13], the molar excess Gibbs energy G_m^E of the multicomponent can be expressed as:

$$\frac{G_m^E}{RT} = \sum_{i=1}^{n} x_i \ln \frac{V_{mi}}{\sum_{j=1}^{n} x_j V_{mj} B_{ji}} - \frac{1}{2}\sum_{i=1}^{n} Z_i x_i \left(\frac{\sum_{j=1}^{n} x_j B_{ji} \ln B_{ji}}{\sum_{k=1}^{n} x_k B_{ki}} \right) = -\frac{S_m^E}{R} + \frac{H_m^E}{RT} \quad (1)$$

where Z_i is the nearest molecule or first coordination number, x_i, x_j and x_k are the molar fractions; and B_{ij} and B_{ji} are the pair-potential

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Table 1
The related parameters of the components [17–19].

i	V_{mi} (cm^3/mol)	ΔH_{mi} (kJ/mol)	σ_i ($\times 10^{-8}$ cm)	r_{0i} ($\times 10^{-8}$ cm)
Bi	$20.80\,[1+1.17\times10^{-4}\,(T-544)]$	10.88	3.38	2.68
Cd	$14.0\,[1+1.50\times10^{-4}\,(T-594)]$	6.40	3.14	2.72
Ga	$11.4\,[1+0.92\times10^{-4}\,(T-303)]$	5.59	2.71	2.31
In	$16.3\,[1+0.97\times10^{-4}\,(T-430)]$	3.26	3.33	2.64
Pb	$19.4\,[1+1.24\times10^{-4}\,(T-600)]$	4.81	3.50	2.70
Sn	$17.0\,[1+0.87\times10^{-4}\,(T-505)]$	7.20	3.26	2.59
Zn	$9.94\,[1+1.5\times10^{-4}\,(T-693)]$	7.28	2.79	2.30

energy interaction parameters defined as,

$$B_{ij}=\exp\left[\frac{-(\varepsilon_{ij}-\varepsilon_{jj})}{kT}\right],\quad B_{ji}=\exp\left[\frac{-(\varepsilon_{ji}-\varepsilon_{ii})}{kT}\right] \tag{2}$$

where ε_{ii}, ε_{jj} and ε_{ij} are the i–i, j–j, and i–j pair-potential energies, $\varepsilon_{ij}=\varepsilon_{ji}$, k is the Boltzmann constant, and T is the absolute temperature. Then the molar formation enthalpy of the multicomponent can be expressed as

$$\frac{\Delta H_m^M}{RT}=-\frac{1}{2}\sum_{i=1}^{n}Z_i x_i\left(\frac{\sum_{j=1}^{n}x_j B_{ji}\ln B_{ji}}{\sum_{k=1}^{n}x_k B_{ki}}\right) \tag{3}$$

So the formation enthalpy of binary mixture $i-j$ is:

$$\frac{\Delta H_m^M}{RT}=-\frac{1}{2}\left[Z_i x_i\left(\frac{x_j B_{ji}\ln B_{ji}}{x_i+x_j B_{ji}}\right)+Z_j x_j\left(\frac{x_i B_{ij}\ln B_{ij}}{x_i B_{ij}+x_j}\right)\right] \tag{4}$$

In order to determine the required binary parameters B_{ij} and B_{ji}, the infinitely dilute enthalpies of the binary liquid alloys and the related parameters of their components must be obtained. The related parameters of pure metals [17–19] are shown in Table 1. The coordination number Z_i of liquid metals can be predicted from their atomic parameters, molar volumes, melting points and melting enthalpies [17]. The infinitely dilution enthalpies of binary liquid alloys [1,20–22] and the required binary parameters B_{ij} and B_{ji} are shown in Table 2, respectively.

The parameters B_{ij} and B_{ji} can be determined by the procedure as follows.

The partial molar formation enthalpy of component i is obtained from Eq. (3)

$$\frac{\Delta\bar{H}_i^M}{RT}=-\frac{1}{2}\left[\frac{Z_i\sum_{j=1}^{n}x_j B_{ji}\ln B_{ji}}{\sum_{l=1}^{n}x_l B_{li}}+\sum_{j=1}^{n}\frac{Z_j x_j B_{ij}}{\sum_{l=1}^{n}x_l B_{lj}}\times\left(\ln B_{ij}-\frac{\sum_{t=1}^{n}x_t B_{tj}\ln B_{tj}}{\sum_{l=1}^{n}x_l B_{lj}}\right)\right] \tag{5}$$

When x_i or x_j approaches zero, the infinitely dilution enthalpies $\Delta\bar{H}_i^\infty$ and $\Delta\bar{H}_j^\infty$ are derived from Eq. (5),

$$\frac{\Delta\bar{H}_i^\infty}{RT}=-\frac{1}{2}(Z_i\ \ln B_{ji}+Z_j B_{ij}\ \ln B_{ij}) \tag{6}$$

$$\frac{\Delta\bar{H}_j^\infty}{RT}=-\frac{1}{2}(Z_j\ \ln B_{ij}-Z_i B_{ji}\ \ln B_{ji}) \tag{7}$$

It is shown that the values of B_{ij} and B_{ji} can be obtained from Eqs. (6) and (7) by using the Newton–Raphson methodology if $\Delta\bar{H}_i^\infty$ and $\Delta\bar{H}_j^\infty$ are known. When the values of B_{ij} and B_{ji} are known at one temperature, it is possible to calculate the values of B_{ij} and B_{ji} at the required temperatures from Eq. (2) in which the pair-potential energy interaction parameters $(\varepsilon_{ij}-\varepsilon_{jj})/kT$ and $(\varepsilon_{ji}-\varepsilon_{ii})/kT$ may be assumed to be independent of temperature. Substituting the corresponding B_{ij} and B_{ji} into Eq. (3), the formation enthalpies of liquid alloys have been calculated.

Table 2
The values of Z_i, Z_j, B_{ij} and B_{ji} of the binary alloys i–j at the required temperatures.

i–j	T (K)	$\Delta\bar{H}_i^\infty$ (kJ/mol)	$\Delta\bar{H}_j^\infty$ (kJ/mol)	B_{ij}	B_{ji}	Z_i	Z_j
Bi–Cd [1]	773	8.37	2.82	1.1746	0.5662	8.25	11.05
Bi–Ga [20]	873	13.38	10.62	0.8858	0.6992	8.03	7.58
Bi–In [1]	900	−6.63	−5.77	1.4867	0.5894	7.97	10.16
Bi–Pb [1]	700	−3.49	−3.46	1.4397	0.6094	8.44	10.25
Bi–Sn [1]	600	0.42	0.42	0.9911	0.9907	8.77	9.64
Bi–Zn [1]	873	26.15	13.58	0.9214	0.4496	8.03	10.47
Cd–Ga [21]	700	15.82	9.83	0.6568	0.8182	11.30	7.88
Cd–In [1]	800	4.71	7.74	0.7096	1.1046	10.97	10.30
Cd–Pb [1]	773	9.33	15.90	0.6011	1.0170	11.05	10.09
Cd–Sn [1]	773	6.57	9.35	0.7066	1.0030	11.05	8.48
Cd–Zn [1]	800	8.83	8.79	0.8791	0.8765	10.97	10.66
Ga–In [22]	623	5.15	4.68	0.9309	0.8168	8.01	10.59
Ga–Pb[a]	–	16.25	21.56	0.5744	0.7435	–	–
Ga–Sn [22]	750	3.31	3.82	0.8659	1.0002	7.80	8.52
Ga–Zn [1]	750	9.21	5.44	1.0117	0.6073	7.80	10.81
In–Pb [1]	673	4.00	4.00	0.9311	0.9317	10.50	10.32
In–Sn [1]	700	−0.85	−0.94	0.8891	1.1207	10.46	8.61
In–Zn [1]	700	17.99	10.96	0.9599	0.5769	10.46	10.96
Pb–Sn [1]	1050	5.69	6.28	0.8768	0.9705	9.60	8.81
Pb–Zn [1]	926	50.52	24.06	0.7732	0.3235	9.80	10.34
Sn–Zn [1]	750	22.76	8.66	1.0317	0.4073	8.52	10.81

[a] The $\Delta\bar{H}_i^\infty$ and $\Delta\bar{H}_j^\infty$ obtained by Miedema model [6].

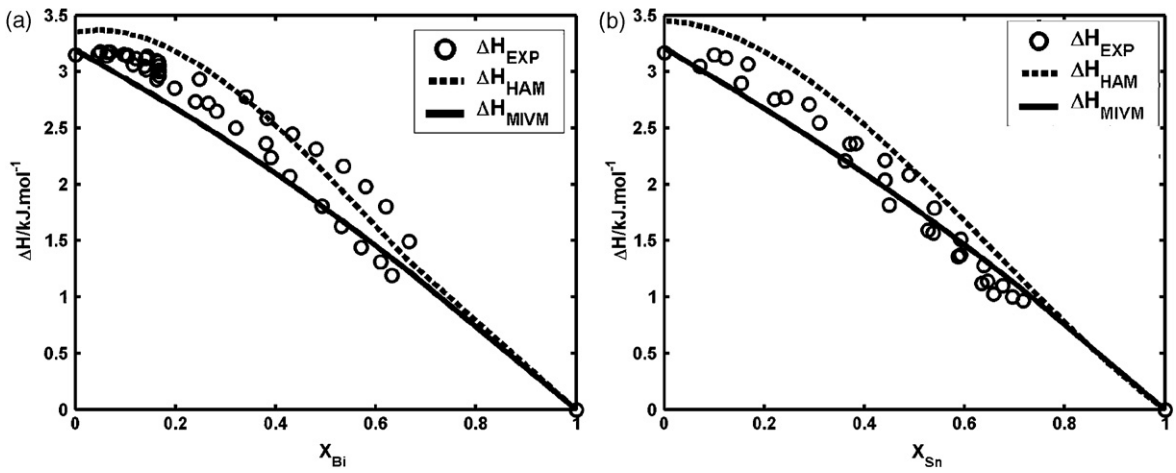

Fig. 1. Comparison of the predicted values of the MIVM and the HAM with experimental data of the Bi–Cd–Ga–In–Sn–Zn at 730 K (a) $x_{Cd} = x_{Ga} = x_{In} = x_{Sn} = x_{Zn}$, (b) $x_{Bi} = x_{Cd} = x_{Ga} = x_{In} = x_{Zn}$ [23].

2.2. Miedema model

The Miedema model is partly based on the Wigner–Seitz atomic cell theory for pure metals, this is applicable to a very large number of alloys [6]. Accordingly, the heat of mixing in a binary alloy system can be calculated by,

$$\Delta H_m^M = \frac{2px_iV_i^{2/3}x_j^s[9.4(\Delta n_{ws}^{1/3})^2 - (\Delta\phi)^2 - (r/p)]}{(n_{ws}^i)^{-1/3} + (n_{ws}^j)^{-1/3}} \quad (8)$$

where x_i, x_j are the mole fraction of metals i and j, V, ϕ and n_{ws} and the parameters, p and (r/p) are the constants determined by Miedema. The infinitely dilute enthalpy of a solution of i, $\Delta\bar{H}_i^\infty(x_i \to 0)$, can readily be derived from equation (8):

$$\Delta\bar{H}_i^\infty(x_i \to 0) = \frac{2pV_i^{2/3}[9.4(\Delta n_{ws}^{1/3})^2 - (\Delta\phi)^2 - (r/p)]}{(n_{ws}^i)^{-1/3} + (n_{ws}^j)^{-1/3}} \quad (9)$$

2.3. Hoch–Arpshofen model

The HAM was deduced from physical principles and is applicable to multicomponent systems [11,12]. For a binary system (ij), the formation enthalpies can be represented by means of the following equations:

$$\Delta H_m^M = W_{ij}n_{ij}(x_i - x_i^{n_{ij}}) \quad (10)$$

For a multicomponent solution $(i, j, k, l\ldots)$ with the molar fractions $(x_i, x_j, x_k, x_l\ldots)$, the molar enthalpy of formation is:

$$\Delta H_m^M = \sum\nolimits_{ij} W_{ij}n_{ij}x_i(1 - (1 - x_i)^{n_{ij}-1}) \quad (11)$$

The values of W_{ij} and n_{ij} are deduced from the limiting binary systems. From binary data gathered in Table 2, interaction terms (W_{ij}) and parameters (n_{ij}) were deduced and reported in the literature [23,24].

3. Results and discussion

Figs. 1 and 2 present the calculated formation enthalpies of Bi–Cd–Ga–In–Sn–Zn and Bi–Cd–Ga–In–Pb–Sn–Zn alloys at required temperatures using the MIVM, compared with the experimental data and the HAM.

From Fig. 1(a) and (b), it can be seen that the calculations by MIVM are closer to the experimental data [23] than the HAM's calculations. The MIVM is deduced from statistical thermodynamics and the basic feature of the movement of liquid molecules is nonrandom migrating. The interaction parameter B_{ij} of MIVM was obtained from the infinitely dilute enthalpies of binary systems.

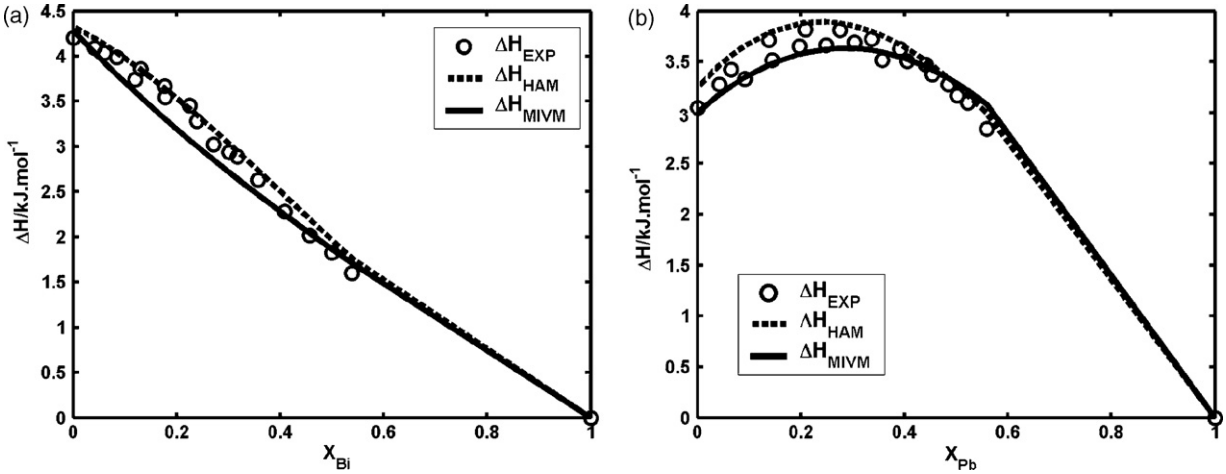

Fig. 2. Comparison of the predicted values of the MIVM and the HAM with experimental data of the Bi–Cd–Ga–In–Pb–Sn–Zn at 973 K (a) $x_{Cd} = x_{Ga} = x_{In} = x_{Pb} = x_{Sn} = x_{Zn}$, (b) $x_{Bi} = x_{Cd} = x_{Ga} = x_{In} = x_{Sn} = x_{Zn}$ [24].

Table 3
The average relative errors and the average standard errors of predicted values of formation enthalpies in the multicomponent liquid alloys.

Alloy system	T (K)	m	HAM		MIVM	
			$\pm S$ (%)	$\pm\bar{S}$ (kJ/mol)	$\pm S$ (%)	$\pm\bar{S}$ (kJ/mol)
Bi–Cd–Ga–In–Sn–Zn [23]	730	75	12.4	0.27	8.7	0.23
Bi–Cd–Ga–In–Pb–Sn–Zn [24]	973	39	4.0	0.14	4.1	0.16

The HAM is an extension of Guggenheim's treatment of solutions, combined with an adaptation of Pauling's ideas of the metallic bond [11]. The major advantage of the HAM is that by using regression analysis; one can calculate the interaction parameter W_{ij} from the measured enthalpy values. This method requires integrate binary systems experimental values and the parameter W_{ij} is an average value.

For Ga–Pb sub-system of the Bi–Cd–Ga–In–Pb–Sn–Zn system, $\Delta\bar{H}^{\infty}_{Ga} = 16.25$ kJ/mol and $\Delta\bar{H}^{\infty}_{Pb} = 21.56$ kJ/mol are calculated by the Miedema model due to the lack of the experimental data of Ga and Pb at 973K. Substituting the values for $\Delta\bar{H}^{\infty}_{Ga}$ and $\Delta\bar{H}^{\infty}_{Pb}$ into Eqs. (6) and (7), the parameters B_{ij} and B_{ji} of the MIVM can be obtained. The calculations as shown in Fig. 2 agree well with the experimental results [24]. It confirms that the prediction of formation enthalpies of multicomponent system from the present method is reasonable.

For comparing with experimental data, the average relative error is given by

$$S = \pm\frac{100}{m}\sum_{i=1}^{m}\left|\frac{\Delta H_{CAL} - \Delta H_{EXP}}{\Delta H_{EXP}}\right| \quad (12)$$

and the average standard error is expressed by

$$\bar{S} = \pm\left[\frac{1}{m}\sum_{i=1}^{m}(\Delta H_{CAL} - \Delta H_{EXP})^2\right]^{1/2} \quad (13)$$

where ΔH_{EXP} is the formation enthalpies of experimental data and ΔH_{CAL} is the calculated result by the MIVM and the HAM, respectively. m is the number of experimental data points. In Table 3, the average relative error and the average standard deviation for the formation enthalpies of Bi–Cd–Ga–In–Sn–Zn and Bi–Cd–Ga–In–Pb–Sn–Zn alloys by MIVM are ±8.7%, ±0.23 kJ/mol and ±4.1%, ±0.16 kJ/mol, respectively.

From the calculated results above it can be clearly seen that the present calculations using the MIVM are in overall agreement with experimental data, due to the accuracy of the experimental technique and the thermodynamic data of the sub-systems. The model will bring certain errors during prediction, the reason for this may arise from the predictions of correspond binary systems that will impact multicomponent systems, especially asymmetry systems. In addition, for multicomponent systems, only the binary interaction between atoms is considered and the multicomponent systems atomic interactions between the constituents are neglected when the MIVM extends to multicomponent alloy systems. On the other hand, if the strong interaction between unlike atoms and the physical properties of elements involved in alloy systems, the applicability of MIVM is not as good.

4. Conclusions

Using the properties of pure components and boundary binary systems of multicomponent liquid alloys, the formation enthalpies of multicomponent liquid alloys can be predict using the MIVM on the whole composition range. It therefore avoids empirical fitting for the pair potential energy interaction parameters. The results obtained have been compared to the experimental data and the results using HAM. The present calculations show that the model is reliable and convenient because it has a clear physical picture.

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