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# Higher-order correlation effects on thermodynamic properties of liquid Hg–Na alloys determined by EMF measurements

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**Abstract.** The electromotive force (EMF) of liquid Hg–Na alloys was measured in detail below 15 at. % Na as functions of Na concentration and of temperature. On the basis of observed EMF values, thermodynamic functions of mixing were obtained at 398 K and 448 K. At 2–8 at. % Na anomalous changes were observed in the concentration dependence curve of the excess partial molar entropy,  $\bar{S}_{P,i}^E$  ( $i = \text{Na or Hg}$ ), and on that of the partial molar enthalpy of Na,  $\bar{H}_{P,\text{Na}}^E$ . These anomalies indicate higher-order correlation effects arising from the characteristic changes in the concentration derivatives of  $n$ -body ( $n \geq 2$ ) correlation function  $g_{\alpha\beta\gamma\dots}^{(n)} (\partial g_{\alpha\beta\gamma\dots}^{(n)} / \partial c_i)_{V,T,c_{j(\neq i)}}$ , which could be derived explicitly to be the function of the higher-order  $(n + 1)$ -body correlation function  $g_{\alpha\beta\gamma\dots}^{(n+1)}$ .

## 1. Introduction

For liquid Hg-based alloys containing the alkali metals Tl or In, in the dilute solute concentration range, anomalous behaviours have been observed in the concentration dependence curve (CDC) of temperature derivative of electrical resistivity  $\rho$ ,  $\partial\rho/\partial T$ , and thermoelectric power  $Q$ ,  $\partial Q/\partial T$  (Itami *et al* 1982, 1983, 1984), and on the CDC of the thermal expansion coefficient  $\alpha_p$  (Sato *et al* 1982, Morikawa *et al* 1986, 1987). These temperature derivative anomalies have been interpreted as being derived from higher-order correlation (HOC) effects of anomalous behaviours of higher-order correlation functions that were included in the theoretical expression of each property (Itami *et al* 1982).

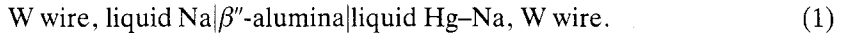
In a recent paper (Morikawa *et al* 1986) on liquid Hg–Tl and Hg–In alloys it was found that broad humps appeared at a few at. % of the solute (Tl or In) on the CDC of the excess partial molar entropy of the solute,  $\bar{S}_{P,\text{Sol}}^E$ . Values were obtained from the compilation by Hultgren *et al* (1973); their data were obtained by electromotive force (EMF) measurements. We also suggested a close relation between the humps and HOC effects. From this point of view it is interesting to study the excess partial molar entropy of component  $i$  ( $i = \text{Na or Hg}$ ) of liquid Hg–Na alloys,  $\bar{S}_i^E$ , because the Hg–Na system typically shows HOC effects on electronic properties (Fielder 1967, Itami *et al* 1986) and  $\alpha_p$  (Morikawa *et al* 1987), and the EMF can be measured accurately as a function of Na concentration. This is controlled precisely by the coulombic titration using a  $\beta''$ -alumina separator (Hsueh and Bennion 1971, Ishiguro *et al* 1982).

The structure and thermodynamic properties of liquid Hg–Na alloys have already been discussed with the use of results of EMF measurements (Iverson and Recht 1967, Antoin 1967, Ishiguro *et al* 1982). Nonetheless, we need accurate EMF values in the Hg-rich region as functions of concentration and temperature in more detail to discuss HOC effects on the concentration dependence of  $\bar{S}_i^E$  ( $i = \text{Na}$  or  $\text{Hg}$ ) of this system.

In this study, such detailed EMF measurements of liquid Hg–Na alloys were made in the Hg-rich region and the results are discussed from the point of view of HOC effects based on the theoretical expression of entropy due to the cluster expansion theory of Faber (1972). The theoretical expression of the concentration derivative of  $n$ -body correlation functions at constant volume, which play an important role in this study, were explicitly derived as a function of  $(n + 1)$ -body correlation functions (see Appendix).

## 2. Experimental

The EMF of liquid Hg–Na alloys was measured using a  $\beta''$ -alumina concentration cell, in which the  $\beta''$ -alumina of a  $\text{Na}^+$  selective conductor was set as a separator (see Tamaki and Cusack 1977). The schematic layout of the EMF cell was as follows:



The  $\beta''$ -alumina tube was purchased from Nippon Tokusyu Togyo Co Ltd. The purities of mercury and sodium were 99.997% and 99.98%, respectively. Details of the cell assembly will be shown elsewhere.

The EMF measurements were carried out for 28 samples with different concentrations below 15 at. % Na in a vacuum. The Na concentration in the alloys was changed by coulombic titration with a constant current. The concentrations thus determined were in good agreement with that determined by the chemical analysis using acid-based titration. The coulombic titration time was adjusted by a countdown digital timer with a precision of 0.01 s. The current density was kept below  $0.004 \text{ A cm}^{-2}$ .

The EMF was measured by a digital voltmeter (YEW model 2051A precision digital multimeter) at 25 temperatures between 373 K and 473 K. The temperature was controlled within  $\pm 0.03 \text{ K}$  in a silicone oil bath.

## 3. Experimental results

Figure 1 shows several examples of the temperature dependence of the observed EMF for liquid Hg–Na alloys. The EMF was detected with a precision of  $\pm 0.02 \text{ mV}$ . The results are in good agreement with previous ones. Detailed descriptions of the present experimental numerical data as functions of temperature and concentration will be given elsewhere.

## 4. Procedure for evaluating thermodynamic functions

The observed value of EMF,  $\epsilon$ , is related to the partial molar Gibbs free energy of Na relative to the pure liquid Na,  $\Delta\bar{G}_{\text{P,Na}}$ , as follows:

$$\Delta\bar{G}_{\text{P,Na}} = -F\epsilon \quad (2)$$

where  $F$  is the Faraday constant.

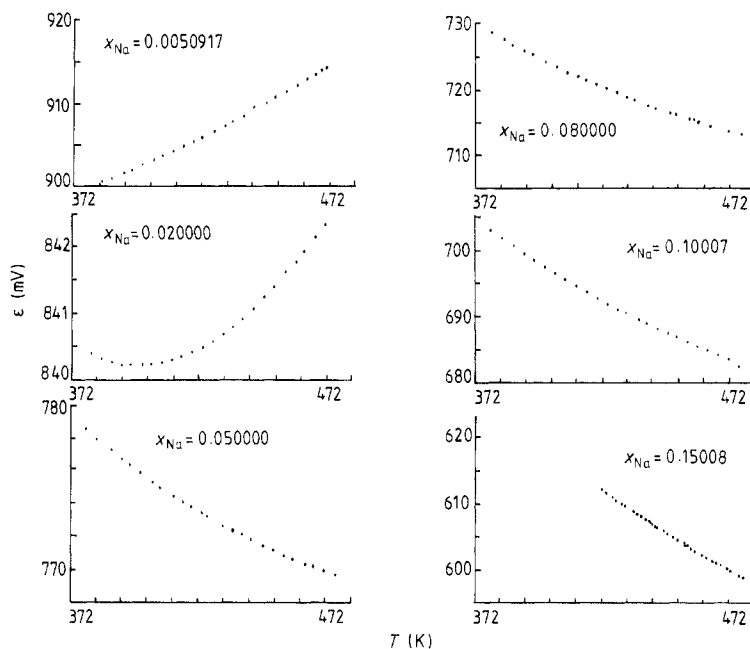


Figure 1. Examples of temperature dependence of observed EMF for liquid Hg–Na alloys.

Excess partial molar quantities—the excess partial molar Gibbs free energy, entropy and enthalpy of Na,  $\bar{G}_{P,Na}^E$ ,  $\bar{S}_{P,Na}^E$  and  $\bar{H}_{P,Na}^E$ —were calculated using relation (2), as follows:

$$\bar{G}_{P,Na}^E = \Delta\bar{G}_{P,Na} - RT \ln x_{Na} = RT \ln \gamma_{Na} \quad (3)$$

$$\bar{S}_{P,Na}^E = - \left( \frac{\partial \bar{G}_{P,Na}^E}{\partial T} \right)_{P, c_{Na}, c_{Hg}} = -R \ln \gamma_{Na} - RT \left( \frac{\partial \ln \gamma_{Na}}{\partial T} \right)_P \quad (4)$$

$$\bar{H}_{P,Na}^E = \bar{G}_{P,Na}^E + T\bar{S}_{P,Na}^E = -RT^2 \left( \frac{\partial \ln \gamma_{Na}}{\partial T} \right)_P \quad (5)$$

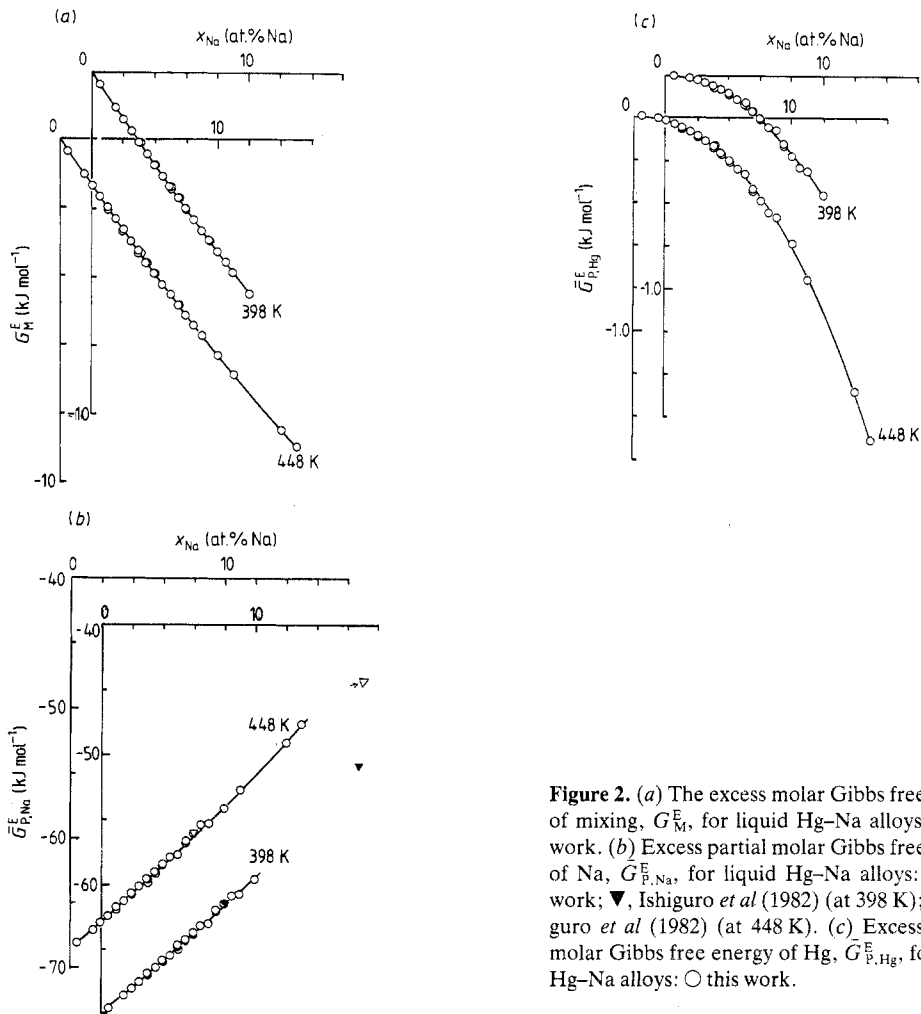
where  $\gamma_{Na}$  is the activity coefficient of Na,  $x_i$  is the atomic fraction of species  $i$  ( $i = \text{Na}$  or Hg),  $c_i$  the mole number of species  $i$ ,  $T$  the absolute temperature,  $P$  the pressure and  $R$  the gas constant.

From the Gibbs–Duhem relation we can obtain the excess (integrated) quantity of the system per mole,  $A_M^E$ , and its partial molar quantity of Hg,  $\bar{A}_{P,Hg}^E$ , for a given property  $A$  (the Gibbs free energy  $G$ , entropy  $S$ , or enthalpy  $H$ ) by the following relations

$$A_M^E(x_{Na}) = (1 - x_{Na}) \int_0^{x_{Na}} \frac{\bar{A}_{P,Na}^E(x'_{Na})}{(1 - x'_{Na})^2} dx'_{Na} \quad (6)$$

$$\bar{A}_{P,Hg}^E(x_{Na}) = [A_M^E(x_{Na}) - x_{Na}\bar{A}_{P,Na}^E(x_{Na})]/(1 - x_{Na}) \quad (7)$$

where  $\bar{A}_{P,Na}^E$  is the excess partial molar quantity of Na. The calculation was carried out using the experimental equation for  $\bar{A}_{P,Na}^E(x_{Na})$ , which was obtained by the least-squares method on the basis of the present observed values of  $\varepsilon$ .

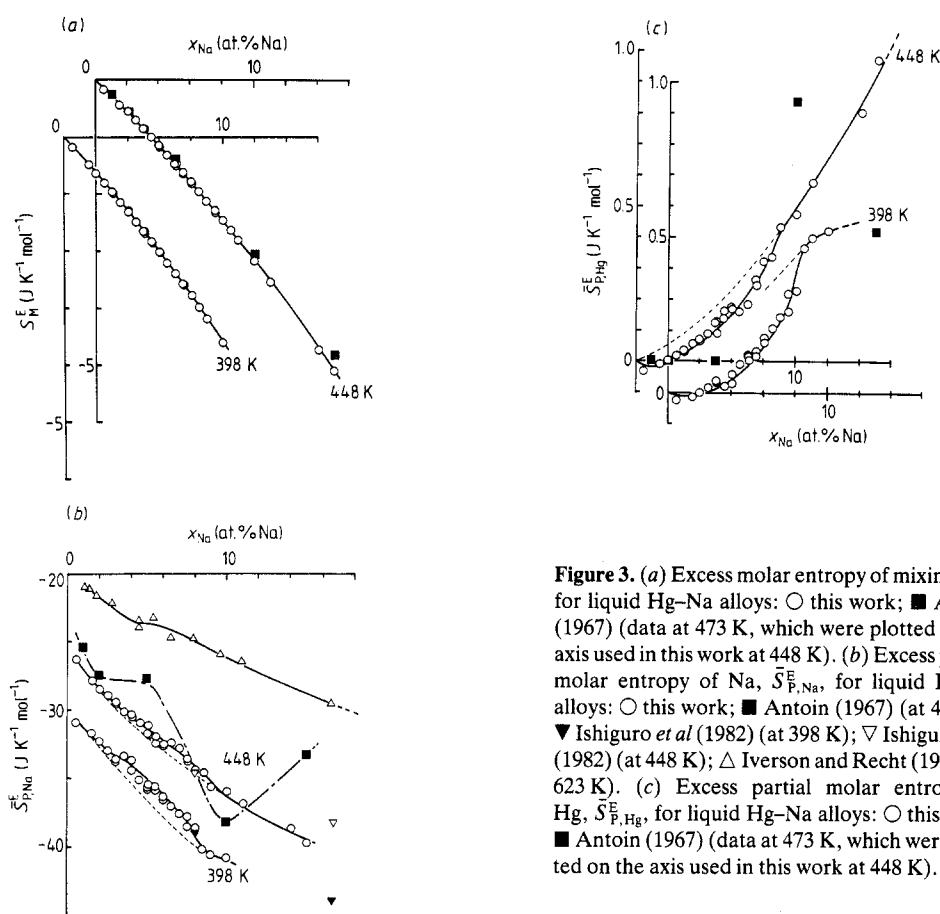


**Figure 2.** (a) The excess molar Gibbs free energy of mixing,  $G_M^E$ , for liquid Hg–Na alloys: ○ this work. (b) Excess partial molar Gibbs free energy of Na,  $\bar{G}_{P,\text{Na}}^E$ , for liquid Hg–Na alloys: ○, this work; ▼, Ishiguro *et al* (1982) (at 398 K); ▽ Ishiguro *et al* (1982) (at 448 K). (c) Excess partial molar Gibbs free energy of Hg,  $\bar{G}_{P,\text{Hg}}^E$ , for liquid Hg–Na alloys: ○ this work.

## 5. Results

The  $\ln \gamma_{\text{Na}}$ , evaluated from equations (2) and (3) using the experimental values of  $\varepsilon$ , could be expressed as a fourth-order polynomial function of  $T$  at each concentration. Coefficients in these polynomials were determined by the least-squares method for 10 experimental values of  $\ln \gamma_{\text{Na}}$  within  $\pm 15$  K around the temperature of interest, namely 398 K or 448 K. In figure 1 are shown typical examples of  $\varepsilon$  for liquid Hg–Na alloys as a function of temperature. Figures 2(a)–(c) indicate smooth changes in the CDCs of  $G_M^E$ ,  $\bar{G}_{P,\text{Na}}^E$  and  $\bar{G}_{P,\text{Hg}}^E$ , respectively.

Figure 3(a) shows that the CDC of  $S_M^E$  changes monotonously.  $\bar{S}_{P,\text{Na}}^E$  and  $\bar{S}_{P,\text{Hg}}^E$  are plotted in figures 3(b) and (c), respectively. Figure 3(b), in which previous data are also plotted, shows that the present values of  $\bar{S}_{P,\text{Na}}^E$  are in good agreement with those of Ishiguro *et al* (1984), at least in the concentration range studied here. It should be noted that spoon-shaped depressions are found at 2–8 at. % Na on the CDC of  $\bar{S}_{P,\text{Hg}}^E$ , (figure 3(c)); the depth of these spoons are substantial compared with the range of experimental error (less than  $\pm 0.04$  J K<sup>-1</sup> mol<sup>-1</sup> at 5 at. % Na). Moreover, broad upheavals are



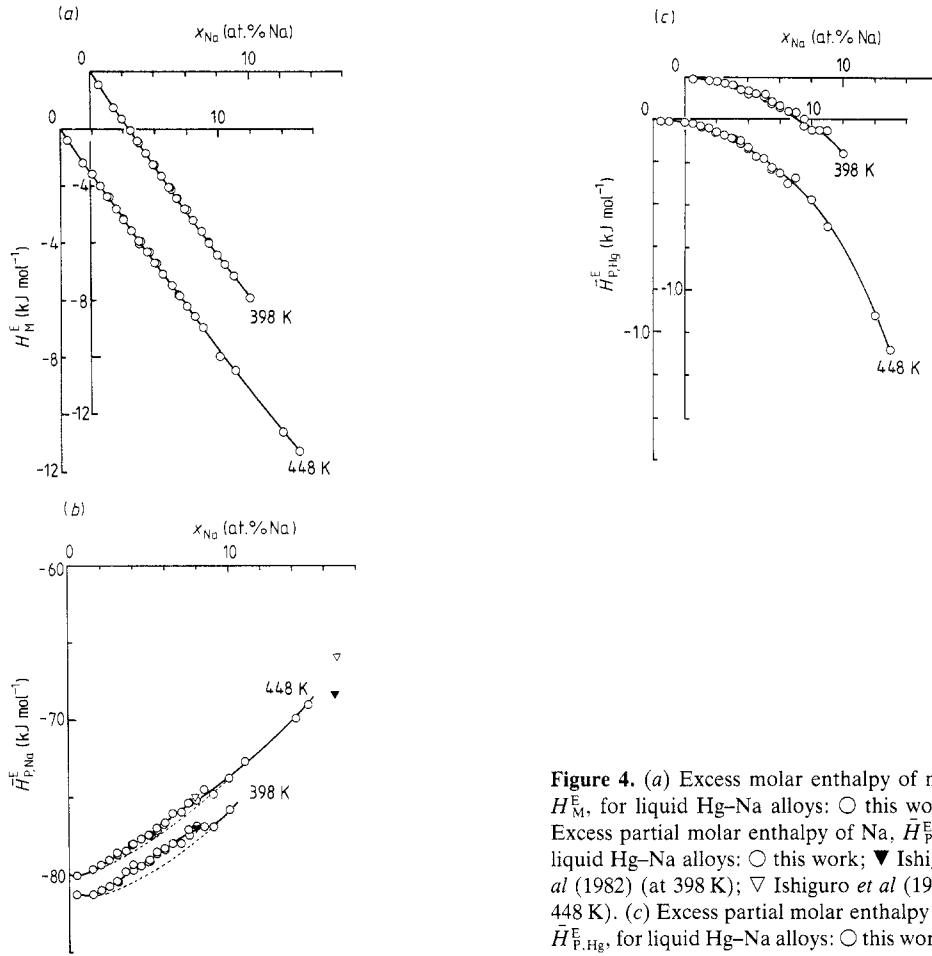
**Figure 3.** (a) Excess molar entropy of mixing,  $S_M^E$ , for liquid Hg–Na alloys:  $\circ$  this work;  $\blacksquare$  Antoin (1967) (data at 473 K, which were plotted on the axis used in this work at 448 K). (b) Excess partial molar entropy of Na,  $S_{P,Na}^E$ , for liquid Hg–Na alloys:  $\circ$  this work;  $\blacksquare$  Antoin (1967) (at 473 K);  $\blacktriangledown$  Ishiguro *et al* (1982) (at 398 K);  $\nabla$  Ishiguro *et al* (1982) (at 448 K);  $\triangle$  Iverson and Recht (1967) (at 623 K). (c) Excess partial molar entropy of Hg,  $S_{P,Hg}^E$ , for liquid Hg–Na alloys:  $\circ$  this work;  $\blacksquare$  Antoin (1967) (data at 473 K, which were plotted on the axis used in this work at 448 K).

observed in the CDC of  $\bar{S}_{P,Na}^E$  at 2–8 at.% Na, as shown in figure 3(b). The height of the upheavals also exceeds the range of experimental error (less than  $\pm 0.1 \text{ J K}^{-1} \text{ mol}^{-1}$  at 5 at.% Na). We note that such upheavals of  $\bar{S}_{P,Na}^E$  were also observed around 5 at.% Na in previous data (Antoin 1967, Iverson and Recht 1967), and the origin of these upheavals may be common to that of humps at a few at.% solute (In or Tl) observed on the CDC of  $\bar{S}_{P,In}^E$  for liquid Hg–In alloys and on that of  $\bar{S}_{P,Tl}^E$  for liquid Hg–Tl alloys, which were shown in figure 3 of Morikawa *et al* (1987).

Figure 4(a) indicates that the CDC of  $H_M^E$  decreases smoothly. In figure 4(b), broad upheavals also appear at 2–8 at.% Na for  $\bar{H}_{P,Na}^E$  at 398 K and 448 K. The range of experimental error for  $\bar{H}_{P,Na}^E$  is less than  $\pm 0.07 \text{ kJ mol}^{-1}$  at 5 at.% Na. Errors in  $\bar{H}_{P,Na}^E$  are therefore small enough to consider upheavals in the CDC of  $\bar{H}_{P,Na}^E$  as substantial anomalies. In figure 4(c), the tendency to form a depression may be observed on the CDC of  $\bar{H}_{P,Hg}^E$  at 8 at.% Na at 398 K, although this is within the reproducibility of the experimental points (see, e.g., the two points at  $x_{Na} = 0.075$ ).

## 6. Discussion and conclusions

The characteristic aspects of figures 2–4 are (a) spoon-shaped depressions on the CDC of the excess molar entropy of Hg,  $\bar{S}_{P,Hg}^E$  and upheavals observed on those of  $\bar{S}_{P,Na}^E$ , (b) the



**Figure 4.** (a) Excess molar enthalpy of mixing,  $H_M^E$ , for liquid Hg–Na alloys:  $\circ$  this work. (b) Excess partial molar enthalpy of Na,  $\bar{H}_{P,Na}^E$ , for liquid Hg–Na alloys:  $\circ$  this work;  $\blacktriangledown$  Ishiguro *et al* (1982) (at 398 K);  $\nabla$  Ishiguro *et al* (1982) (at 448 K). (c) Excess partial molar enthalpy of Hg,  $\bar{H}_{P,Hg}^E$ , for liquid Hg–Na alloys:  $\circ$  this work.

tendency of upheavals on the CDC of  $\bar{H}_{P,Na}^E$ , (c) smooth changes in the CDC of integrated quantities such as  $G_M^E$ ,  $S_M^E$  and  $H_M^E$ .

### 6.1. Anomalies for $\bar{S}_{P,1}^E$ ( $I = Na$ or $Hg$ )

It is necessary to give the theoretical expression of the excess partial molar entropy of component 1 ( $I = Na$  or  $Hg$ ). Using the definition of the excess entropy of mixing  $S^E$  and the excess molar entropy  $S_M^E$ , the excess partial molar entropy  $\bar{S}_{P,1}^E$  can be written as follows:

$$\bar{S}_{P,1}^E = (\partial S^E / \partial c_1)_{P,T,c_2} \quad (8)$$

$$= S_M^E + (c_1 + c_2)(\partial S_M^E / \partial c_1)_{P,T,c_2} \quad (9)$$

where

$$S_M^E = S^E / (c_1 + c_2) = S_M^{\text{Alloy}} - \sum_i x_i (S_{i,M}^0 - R \ln x_i). \quad (10)$$

In these equations  $S_M^{\text{Alloy}}$  is the molar entropy of alloys and  $S_{i,M}^0$  is that of component  $i$  in

the pure state. The expression of entropy of a multi-component liquid was given by Faber (1972) based on the cluster expansion method. Following this approach, the molar entropy of a binary liquid,  $S_M^{\text{Alloy}}$ , can be given as

$$S_M^{\text{Alloy}} = - \sum_i R x_i \ln x_i + \sum_i x_i S'_{i,M} + \sum_i \sum_j x_i x_j S'_{ij} + \sum_i \sum_j \sum_k x_i x_j x_k S'_{ijk} + \dots \quad (11)$$

with

$$- \frac{S'_{ij}}{N k_B} = \frac{N^2}{2! V^2} \int g_{ij}^{(2)}(|\mathbf{R}_{\alpha_i \beta_j}|) \ln g_{ij}^{(2)}(|\mathbf{R}_{\alpha_i \beta_j}|) d\mathbf{R}_{\alpha_i \beta_j} \quad (12)$$

$$- \frac{S'_{ijk}}{N k_B} = \frac{N^3}{3! V^3} \int d\mathbf{R}_{\alpha_i \beta_j} d\mathbf{R}_{\beta_j \gamma_k} g_{ijk}^{(3)}(\mathbf{R}_{\alpha_i \beta_j}, \mathbf{R}_{\beta_j \gamma_k}) \times \ln \frac{g_{ijk}^{(3)}(\mathbf{R}_{\alpha_i \beta_j}, \mathbf{R}_{\beta_j \gamma_k})}{g_{ij}^{(2)}(|\mathbf{R}_{\alpha_i \beta_j}|) g_{jk}^{(2)}(|\mathbf{R}_{\beta_j \gamma_k}|) g_{ik}^{(2)}(|\mathbf{R}_{\alpha_i \gamma_k} - \mathbf{R}_{\alpha_i \beta_j}|)} \quad (13)$$

In these equations,  $k_B$  is the Boltzmann constant;  $N (= (c_1 + c_2) \times N_A; N_A$  is Avogadro's number) is the total number of particles of the system contained in the volume  $V$ ;  $S'_{i,M}$  is the entropy of component  $i$  in the pure state, which has the same  $N$  particles in the same volume as in the alloy state, and  $g_{ijk}^{(3)}$  is the three-body correlation function among species  $i, j$  and  $k$ , and  $\mathbf{R}_{\alpha_i \beta_j}$  in  $g_{ij}^{(2)}(|\mathbf{R}_{\alpha_i \beta_j}|)$  is equal to  $\mathbf{R}_{\alpha_i} - \mathbf{R}_{\beta_j}$ , where  $\mathbf{R}_{\alpha_i}$  represents the position of  $\alpha_i$ th ion of species  $i$ . Equations (11)–(13) indicate that  $S_M^E$  depends on  $n$ -body ( $n \geq 2$ ) correlation functions. The mole number derivative of  $S_M^E$ , the second term of equation (9), is written as

$$\left( \frac{\partial S_M^E}{\partial c_1} \right)_{P,T,c_2} = \left( \frac{\partial S_M^{\text{Alloy}}}{\partial c_1} \right)_{P,T,c_2} - \sum_i \left( \frac{\partial}{\partial c_1} [x_i (S'_{i,M} - R \ln x_i)] \right)_{P,T,c_2} \quad (14)$$

where

$$\left( \frac{\partial S_M^{\text{Alloy}}}{\partial c_1} \right)_{P,T,c_2} = \left( \frac{\partial S_M^{\text{Alloy}}}{\partial c_1} \right)_{V,T,c_2} + \gamma_V \bar{V}_{P,1} \quad (15)$$

In equation (15), the partial molar volume of species 1,  $\bar{V}_{P,1}$ , was derived as a function of pair-correlation functions by Buff and Brout (1955). Note that the thermal pressure coefficient  $\gamma_V$  is connected to the temperature derivative of pair-correlation function  $g_{ij}^{(2)}$  ( $\partial g_{ij}^{(2)} / \partial T$ ) $_V$ , which is expressed with three- and four-body correlation functions (Itami *et al* 1982).

From equation (11), the first term of equation (15) takes the form

$$\begin{aligned} \left( \frac{\partial S_M^{\text{Alloy}}}{\partial c_1} \right)_{V,T,c_2} = & - \left[ \frac{\partial}{\partial c_1} \left( \sum_i R x_i \ln x_i \right) \right]_{V,T,c_2} + \sum_i \left[ \left( \frac{\partial x_i}{\partial c_1} \right)_{V,T,c_2} S'_{i,M} \right] \\ & + \sum_i \sum_j \left[ \left( \frac{\partial x_i x_j}{\partial c_1} \right)_{V,T,c_2} S'_{ij} + x_i x_j \left( \frac{\partial S'_{ij}}{\partial c_1} \right)_{V,T,c_2} \right] \\ & + \sum_i \sum_j \sum_k \left[ \left( \frac{\partial x_i x_j x_k}{\partial c_1} \right)_{V,T,c_2} S'_{ijk} + x_i x_j x_k \left( \frac{\partial S'_{ijk}}{\partial c_1} \right)_{V,T,c_2} \right] + \dots \quad (16) \end{aligned}$$

In this equation the mole number ( $c_1$ ) derivatives of  $x_i, x_i x_j, x_i x_j x_k$ , etc., can be easily evaluated using the definition  $x_i = c_i / (c_1 + c_2)$ . Equation (16) indicates that the mole



number derivative of  $S_M^{\text{Alloy}}$  is also a function of the mole number derivatives of the  $n$ -body ( $n \geq 2$ ) correlation functions  $g_{ijk\dots}^{(n)}$ ,  $(\partial g_{ijk\dots}^{(n)}/\partial c_1)_{V,T,c_2}$ , in addition to the  $n$ -body ( $n \geq 2$ ) correlation functions themselves.

Here we remember the characteristic features of the present experimental results for the entropy of liquid Hg–Na alloys. These are the smooth variations in  $S_M^E$  and the anomalous behaviours of  $\bar{S}_{P,\text{Na}}^E$  and  $\bar{S}_{P,\text{Hg}}^E$ . As can be seen from equation (11), anomalous behaviours of  $S_M^E$  may be derived from terms with  $S'_{ij}$ ,  $S'_{ijk}$ , etc., if they are present. Therefore, it may be assumed that  $S'_{ij}$ ,  $S'_{ijk}$ , etc., may change smoothly with variations in  $x_{\text{Na}}$ . On the other hand, both partial molar entropies,  $\bar{S}_{P,\text{Na}}^E$  and  $\bar{S}_{P,\text{Hg}}^E$ , can be expressed theoretically by the  $\gamma_{\text{Na}}$  term and mole number derivatives  $(\partial S'_{ij}/\partial c_1)_{V,T,c_2}$ ,  $(\partial S'_{ijk}/\partial c_1)_{V,T,c_2}$ , etc., in addition to  $S'_{ij}$ ,  $S'_{ijk}$ , etc., themselves (see equations (15) and (16)). Therefore, these anomalous behaviours of  $\bar{S}_{P,\text{Na}}^E$  and  $\bar{S}_{P,\text{Hg}}^E$  may result from the mole number derivatives  $(\partial S'_{ij}/\partial c_1)_{V,T,c_2}$ ,  $(\partial S'_{ijk}/\partial c_1)_{V,T,c_2}$ , etc., in addition to the  $\gamma_{\text{Na}}$  term. The  $(\partial g_{ijk\dots}^{(n)}/\partial c_1)_{V,T,c_2}$  in these mole number derivatives can be considered to be a generating function of higher correlation functions  $g_{|n_1+1|n_2|}^{(n+1)}$  and  $g_{|n_1|n_2+1|}^{(n+1)}$  (see Appendix). The  $V_{\text{Na}}$  also contains HOC functions, such as three- and four-body correlation functions, as described above. Therefore, anomalies in  $\bar{S}_{P,\text{Na}}^E$  and  $\bar{S}_{P,\text{Hg}}^E$  may be derived from the anomalous behaviours of these HOC functions. Needless to say,  $S_M^E$  itself contains HOC functions, as can be seen in equations (11)–(13), and anomalies should be present if the anomalous behaviours are present in the HOC functions. However, from the experimental point of view, the partial quantity  $\bar{S}_{P,\text{Na}}^E$  is measured first and the integrated quantity  $S_M^E$  is evaluated by the integration operation of equation (6). Because of this integration operation, rather small anomalies in  $\bar{S}_{P,\text{Na}}^E$  may disappear in  $S_M^E$ . Anyway, the  $\bar{S}_{P,\text{Na}}^E$  and the  $\bar{S}_{P,\text{Hg}}^E$  containing the  $V_{\text{Na}}$  and the generating function of HOC functions  $(\partial g_{ijk\dots}^{(n)}/\partial c_1)_{V,T,c_2}$  are more abundant in informations of HOC functions than  $S_M^E$ .

## 6.2. Anomalous trends for $\bar{H}_{P,\text{Na}}^E$

The excess partial molar enthalpy of 1 ( $1 = \text{Na}$  or  $\text{Hg}$ ) is defined by

$$\bar{H}_{P,1}^E = \Delta \bar{H}_{P,1} = \left( \frac{\partial \Delta H}{\partial c_1} \right)_{P,T,c_2} = \left( \frac{\partial H^{\text{Alloy}}}{\partial c_1} \right)_{P,T,c_2} - \sum_i \left( \frac{\partial c_i H_{i,M}^0}{\partial c_1} \right)_{P,T,c_2} \quad (17)$$

where  $H_{i,M}^0$  is the enthalpy per mole of component  $i$  in the pure state, and  $H^{\text{Alloy}}$  is the enthalpy per mole of the alloys.  $(\partial H^{\text{Alloy}}/\partial c_1)_{P,T,c_2}$  can be expressed in the same way as equation (15), as follows:

$$\left( \frac{\partial H^{\text{Alloy}}}{\partial c_1} \right)_{P,T,c_2} = \left( \frac{\partial E^{\text{Alloy}}}{\partial c_1} \right)_{V,T,c_2} + T\gamma_V \bar{V}_{P,1}. \quad (18)$$

$E^{\text{Alloy}}$  in equation (18) is the internal energy of liquid alloys, expressed as

$$E^{\text{Alloy}} = \frac{3}{2} Nk_B T + Nu_g + \frac{1}{2} (N^2/V) \sum_i \sum_j \sum_{\alpha} \sum_{\beta} x_i x_j \int u_{ij}(|\mathbf{R}_{\alpha\beta_j}|) g_{ij}^{(2)}(|\mathbf{R}_{\alpha\beta_j}|) d\mathbf{R}_{\alpha\beta_j} \quad (19)$$

where  $u_g$  is the structure-independent energy of the system, and  $u_{ij}(\mathbf{R})$  is the pair potential of the  $i$ - $j$  pair.

From equations (18) and (19) it is easy to show that  $(\partial E^{\text{Alloy}}/\partial c_1)_{V,T,c_2}$  is the function of  $[\partial g_{ij}^{(2)}(\mathbf{R})/\partial c_1]_{V,T,c_2}$ . Note that the excess enthalpy of mixing under constant pressure,

$H^E$ ,  $H^E = \Delta H = \Delta E + p\Delta V$ , contains information on only the pair-correlation functions, because  $\Delta E$  and  $\Delta V$  are properties which are represented only by pair-correlation functions (Buff and Brout 1955). The smooth concentration dependence of  $H_M^E$  in figure 4(a) indicates that these pair-correlation functions may change smoothly with increases in Na concentration. Therefore, the hump in the CDC of  $\bar{H}_{P,Na}$  may come from  $[\partial g_{ij}^{(2)}(R)/\partial c_1]_{V,T,c_2}$  in the first term of equation (18) and  $[\partial g_{ij}^{(2)}(R)/\partial T]_V$  in  $\gamma_V$  (see equation (18)), in which HOC functions are included as described above.

No anomaly is found for  $\bar{G}_{P,1}^E$ , although the excess partial Gibbs free energy  $\bar{G}_{P,1}^E$  is connected with  $\bar{H}_{P,1}^E$  and  $\bar{S}_{P,1}^E$ , both of which are functions of the HOC functions. The HOC effects on  $\bar{G}_{P,1}^E$  may be eliminated by the mutual cancellation between the HOC effects on  $\bar{H}_{P,1}^E$  and those on  $\bar{S}_{P,1}^E$ .

### Acknowledgment

The authors thank Mr T Kiya for preparing the cell used.

### Appendix: The mole-number derivative of $n$ -body correlation function

Buff and Brout (1955) derived the concentration derivative of the  $n$ -body correlation function  $g_{|n_1|n_2|\dots|n_\nu|}^{(n)}$  at constant pressure for the  $\nu$ -component system. Here we describe the derivation of the concentration derivative of the  $n$ -body correlation function  $g_{|n_1|n_2|}^{(n)}$  at constant volume on the basis of their method for the two-component system;  $n_i$  is the number of particles of species  $i$  ( $i = 1$  or  $2$ ) included in the assembly with  $n$  particles of interest (i.e.,  $n = n_1 + n_2$ ), and  $|n_i|$  denotes an array of  $n_i$  letters of 'i'. For example,  $g_{|n_1|n_2|}^{(3)}$  means  $g_{111}^{(3)}$  when  $n_1 = 3$  and  $n_2 = 0$ , and  $g_{112}^{(3)}$  when  $n_1 = 2$  and  $n_2 = 1$ .

First we consider the binary mixture containing  $N_1$  particles of species 1 and  $N_2$  particles of species 2 in volume  $V$ . If the system is large enough to consider the limit  $V \rightarrow \infty$  and of  $N_1 + N_2 = N \rightarrow \infty$  despite a finite number density  $N/V$ , the  $n$ -body correlation function of the grand canonical ensemble for a binary mixture is defined by

$$g_{|n_1|n_2|}^{(n)} = (\rho_1^{n_1} \rho_2^{n_2})^{-1} \frac{1}{\Xi} \sum_{N \geq 2} \frac{z_1^{N_1}}{(N_1 - n_1)!} \frac{z_2^{N_2}}{(N_2 - n_2)!} \times \int \dots \int \prod_{i=1}^2 \prod_{s_i=n_i+1}^{N_i} dV_{s_i} \exp[-U_i\{N\}\beta] \quad (\text{A1})$$

where  $\rho_i$  is the number density of species  $i$ ,  $\beta = 1/k_B T$  and  $U_i\{N\}$  is the total energy of the system with  $N$  particles.  $\Xi$  is the grand canonical partition function expressed as

$$\Xi = \sum_{N \geq 0} \frac{Z_1^{N_1} z_2^{N_2}}{N_1! N_2!} \int \dots \int \prod_{i=1}^2 \prod_{s_i=1}^{N_i} dV_{s_i} \exp[-U_i\{N\}\beta]. \quad (\text{A2})$$

In equations (A1) and (A2)  $z_i$  is the activity of species  $i$  defined by

$$z_i = \frac{\exp[\mu_i\beta]}{(h^2\beta/2\pi m_i)^{3/2}} \quad (\text{A3})$$

where  $\mu_i$  is the chemical potential of species  $i$  with mass  $m_i$ , and  $h$  is Planck's constant.

Considering  $g_{|n_1|n_2|}^{(n)}$  to be a function of  $V$ ,  $\beta$ ,  $\beta\mu_1$  and  $\beta\mu_2$ , the differentiation of  $g_{|n_1|n_2|}^{(n)}$  by the number density of species 1,  $\rho_1$ , at constant volume leads to the following form

$$\left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \rho_1} \right|_{\beta, V, \rho_2} = \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \beta\mu_1} \right|_{\beta, \beta\mu_2} \left. \frac{\partial \beta\mu_1}{\partial \rho_1} \right|_{\beta, V, \rho_2} + \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \beta\mu_2} \right|_{\beta, \beta\mu_1} \left. \frac{\partial \beta\mu_2}{\partial \rho_1} \right|_{\beta, V, \rho_2}. \quad (\text{A4})$$

Using the Gibbs–Duhem relation equation (A4) can be rewritten as

$$\left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \rho_1} \right|_{\beta, V, \rho_2} = \rho_2 \left. \frac{\partial \beta\mu_2}{\partial \rho_1} \right|_{\beta, V, \rho_2} \left( \frac{1}{\rho_2} \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \beta\mu_2} \right|_{\beta, \beta\mu_1} - \frac{1}{\rho_1} \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \beta\mu_1} \right|_{\beta, \beta\mu_2} \right). \quad (\text{A5})$$

In equation (A5), the derivative of  $g_{|n_1|n_2|}^{(n)}$  by  $\beta\mu_i$  ( $i = 1$  or  $2$ ) can be written as

$$\begin{aligned} \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \beta\mu_i} \right|_{\beta, V, \{\beta\mu_j\}'} &= \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial z_i} \right|_{\beta, V, \{z_j\}'} \left. \frac{\partial z_i}{\partial \beta\mu_i} \right|_{\beta, V, \{\beta\mu_j\}'} \\ &= n_i g_{|n_1|n_2|}^{(n)} - \sum_{j=1}^2 n_j (\delta_{ji} + \rho_i G_{ji}) g_{|n_1|n_2|}^{(n)} + \rho_i \int dV_{n_i+1} (g_{|n_1|n_2|i}^{(n+1)} - g_{|n_1|n_2|}^{(n)}) \end{aligned} \quad (\text{A6})$$

with

$$G_{ij} = \int d\mathbf{R}_{\xi_j \alpha_j} [g_{ij}^{(2)}(|\mathbf{R}_{\xi_j \alpha_j}|) - 1]. \quad (\text{A7})$$

In these equations, the subscript  $\{\beta\mu_j\}'$  (or  $\{z_j\}'$ ) indicates that the differentiation by  $\beta\mu_i$  (or  $z_i$ ) should be performed at constant values of set  $\{\beta\mu_j\}'$  (or  $\{z_j\}'$ ) except for  $\beta\mu_i$  (or  $z_i$ ). The  $dV_{n_i+1}$  indicates the volume element of space coordinates of the  $(n_i + 1)$ th ion of species  $i$ , and  $\mathbf{R}_{\xi_j \alpha_j}$  in  $g_{ij}^{(2)}(|\mathbf{R}_{\xi_j \alpha_j}|)$  is equal to  $\mathbf{R}_{\xi_j} - \mathbf{R}_{\alpha_j}$ , where  $\mathbf{R}_{\xi_j}$  indicates the position vector of the  $\xi_j$ th ion of species  $j$ . The symbol  $|n_1|n_2|i$  indicates  $|n_1 + 1|n_2|$  if  $i = 1$  and  $|n_1|n_2 + 1|$  if  $i = 2$ .

On the other hand, the derivative of  $\rho_i$  has been obtained by Buff and Brout (1955) as follows:

$$\left. \frac{\partial \rho_i}{\partial \beta\mu_k} \right|_{\beta, V, \{\beta\mu_l\}'} = \rho_i \delta_{ki} + \rho_k \rho_i \int [g_{ki}(|\mathbf{R}_{\gamma_k \alpha_i}|) - 1] d\mathbf{R}_{\gamma_k \alpha_i}. \quad (\text{A8})$$

Substitution of equations (A6) and (A8) into (A5) leads to

$$\begin{aligned} \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \rho_1} \right|_{\beta, V, \rho_2} &= \frac{(N_A/V)\rho_2 G_{12}}{(1 + \rho_1 G_{11})(1 + \rho_2 G_{22}) - \rho_1 \rho_2 G_{12}^2} \\ &\times \left[ \int dV_{n_1+1} \{g_{|n_1+1|n_2|}^{(n+1)} - n_1 (g_{11}^{(2)} - g_{12}^{(2)}) g_{|n_1|n_2|}^{(n)}\} \right. \\ &\left. - \int dV_{n_2+1} \{g_{|n_1|n_2+1|}^{(n+1)} - n_2 (g_{22}^{(2)} - g_{21}^{(2)}) g_{|n_1|n_2|}^{(n)}\} \right] \end{aligned} \quad (\text{A9})$$

where  $g_{|n_1|n_2|}^{(n)}$  is constant in these integrals.

Moreover, using the relation between the mole number  $c_1$  and the number density  $\rho_1$  ( $c_1 = \rho_1 V / N_A$ ), equation (A9) can be rewritten as the mole number derivative of  $g_{|n_1|n_2|}^{(n)}$  as follows:

$$\left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial c_1} \right|_{\beta, V, c_2} = \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \rho_1} \right|_{\beta, V, \rho_2} \left. \frac{\partial \rho_1}{\partial c_1} \right|_{\beta, V} = \frac{N_A}{V} \left. \frac{\partial g_{|n_1|n_2|}^{(n)}}{\partial \rho_1} \right|_{\beta, V, \rho_2} \quad (\text{A10})$$

where  $N_A$  is Avogadro's number. In the text, the discussion was made on the basis of equation (A10).

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