

## Description of the concentration and temperature-dependent mixing enthalpy of binary metallic melts

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### Abstract

An introduction is given to different thermodynamic models for representing mixing enthalpy measurements. The TAP series and the associate model are applied and compared on the basis of the concentration and temperature-dependent mixing enthalpy of the system Mg–Pb. A new approximation method is introduced to calculate the parameters of the associate model. The number of available enthalpy values for the approximation process is systematically varied in order to simulate the flexibility of the models. From this point of view the associate model is a useful model for the representation of the mixing enthalpy and the prediction of the excess heat capacity.

*Keywords:* Binary metallic melts; Excess heat capacity; Gibbs energy of mixing; Mixing enthalpy; Thermodynamic models

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### 1. Introduction

High temperature measurements on liquid binary systems suffer from problems which restrict experimental concentration and temperature ranges, that applies especially to the mixing enthalpy. Here thermodynamic models are of special interest for describing and analysing the experimental data.

Symmetric enthalpy curves can be described by the regular [1] or subregular solution model [2]. The parameters of these models (functions, see Table 1) express the attractions between dissimilar atoms. Neither model is able to represent the tempera-

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Table 1  
Polynomial representations of the mixing enthalpy

Model	Polynomial representation of the mixing enthalpy
Regular solution	$\Delta H(M) = (x_A x_B) \beta$
Subregular solution	$\Delta H(M) = (x_A x_B) [\beta x_A + \beta_2 x_B] = (x_A x_B) [\beta_1^* + \beta_2^* x_A]$ where $\beta_1^* = \beta_1$ and $\beta_2^* = \beta_1 - \beta_2$
Quasi-chemical solution	$\Delta H(M) = (x_A x_B) \left[ \beta_1 - \frac{\beta_2}{T} x_A x_B \right] = (x_A x_B) [\beta_1^* + \beta_2^* x_A x_B]$ where $\beta_1^* = \beta_1$ , $\beta_2^* = -\frac{\beta_2}{T}$
Modified quasi-chemical solution	$\Delta H(M) = (x_A x_B) \left[ \beta_1 x_A + \beta_2 x_B - \frac{\beta_3}{T} x_A x_B \right] = (x_A x_B) \left[ \beta_1^* + \beta_2^* x_A + \beta_3^* x_A^2 \right]$ where $\beta_1^* = \beta_1$ , $\beta_2^* = \beta_1 - \beta_2 - \frac{\beta_3}{T}$ and $\beta_3^* = \frac{\beta_3}{T}$
TAP series	$\Delta H(M) = x_B \sum_{n=1}^{n=N} x_A^n \left[ \sum_{\epsilon=1}^{\epsilon=E} L_{n,1-\epsilon}^* T^{1-\epsilon} \right]$

ture-dependence. The quasichemical solution model [3] and the modified quasichemical model [4] enables the description of asymmetric enthalpy curves by the  $\alpha$  function with three parameters, wherein the temperature-dependence is represented by the parameters  $\beta_2$  and  $\beta_3$ , respectively (see Table 1). A posteriori only slight temperature dependences can be taken into consideration.

All these solution models are able to represent smooth enthalpy curves. If a sharp minimum occurs, power series with more than three parameters are necessary. On the basis of polynomial functions, Tomiska developed the thermodynamic adopted power series (TAP series) [5]. He showed in comparison with six polynomial representations for excess functions that the TAP series (presented in Table 1) was, in his opinion, the most applicable [6]. The TAP series is able to describe the temperature-dependence. Then the parameters are polynomials.  $E$  gives the number of terms used for the temperature description, where  $N$  gives the degree of the TAP series.

A physical meaning can be found [7] for most parameters in Table 1. Putting  $E = 1$  in the TAP series, these will simplify to the regular solution model if  $N = 1$ , to the subregular solution model if  $N = 2$  and to the modified quasichemical model if  $N = 3$ .

The associate model is another way of describing mixing enthalpies. Together with a new approximation technique it is presented in the following section. In the third section this model is compared with the polynomial representations of the mixing enthalpy.

## 2. Associate model for binary alloys

Gerling et al. [8] give a brief survey of the development of the model of associates. They show the variety of associate models including different assumptions. In this connection association models have two basic assumptions in common:

1. In the AB binary metallic melt regions of chemical short range order (CSRO) exist, which will be called associates ( $A_i B_j$ ).
2. The associates are in a dynamic equilibrium with the non-associated (free) atoms ( $A_f, B_f$ ).

With these conditions the binary metallic melt is interpreted as a solution of three components. Therefore the mass action law is:

$$iA_f + jB_f = A_i B_j \quad (1)$$

with the equilibrium constant:

$$K = \exp\left(-\frac{\Delta H_{A_i B_j} - T \Delta S_{A_i B_j}}{RT}\right) = \frac{X_{A_i B_j} \gamma_{A_i B_j}}{(x_{A_f})^i \cdot (x_{B_f})^j (\gamma_{A_f})^i \cdot (\gamma_{B_f})^j} \quad (2)$$

$$\ln K = [\ln x_{A_i B_j} - i \ln x_{A_f} - j \ln x_{B_f}] + \ln\left(\frac{\gamma_{A_i B_j}}{(\gamma_{A_f})^i (\gamma_{B_f})^j}\right) \quad (3)$$

where  $x_{A_i B_j} = n_{A_i B_j}/n$  is the mole fraction of the associate and  $x_{A_f} = n_{A_f}/n$  and  $x_{B_f} = n_{B_f}/n$  refer to the reactants. The numbers of moles of the reactants are  $n_{A_f} = n_A - i n_{A_i B_j}$  and  $n_{B_f} = n_B - j n_{A_i B_j}$ , wherein  $n_A$  and  $n_B$  are the initial numbers of moles of the components A and B, respectively.  $\gamma_{A_i B_j}$ ,  $\gamma_{A_f}$  and  $\gamma_{B_f}$  are the activity coefficients and  $\Delta H_{A_i B_j}$  and  $\Delta S_{A_i B_j}$  are the formation enthalpy and formation entropy of the associate.

The mixing enthalpy and mixing entropy are defined as:

$$\Delta H(M) = \frac{n_{A_f} n_{B_f}}{n} C1 + \frac{n_{A_f} n_{A_i B_j}}{n} C2 + \frac{n_{B_f} n_{A_i B_j}}{n} C3 + n_{A_i B_j} C4 \quad (4)$$

$$\Delta S(M) = -R(n_{A_f} \ln x_{A_f} + n_{B_f} \ln x_{B_f} + n_{A_i B_j} \ln x_{A_i B_j}) + n_{A_i B_j} \Delta S_{A_i B_j} \quad (5)$$

wherein C1–C3 are the parameters of the associate model and describe the interactions between

- The pure components, i.e. the free atoms ( $A_f, B_f$ ),
- The reactant  $A_f$  and the associate and
- The reactant  $B_f$  and the associate.

C4 is the formation enthalpy of the associate. Knowing the mixing enthalpy and mixing entropy, the Gibbs–Helmholtz function, Eq. (6), yields the Gibbs energy of mixing  $\Delta G(M)$ :

$$\Delta G(M) = \Delta H(M) - T \Delta S(M) \quad (6)$$

To calculate the parameters it is necessary to know the different numbers of moles (see Eq. (4)). Therefore Eqs. (3) and (4) are the basic equations for an iterative approximation treatment. Defining  $C5 = \ln K$ , the perfect differential of the mixing

enthalpy is:

$$\begin{aligned}
 d(\Delta H(M)) = & \left[ \frac{\partial \Delta H(M)}{\partial C1} \right]_{Cv} \Big|_{v=2-5} dC1 + \left[ \frac{\partial \Delta H(M)}{\partial C2} \right]_{Cv} \Big|_{v=1,3-5} dC2 \\
 & + \left[ \frac{\partial \Delta H(M)}{\partial C3} \right]_{Cv} \Big|_{v=1,2,4,5} dC3 + \left[ \frac{\partial \Delta H(M)}{\partial C4} \right]_{Cv} \Big|_{v=1-3,5} dC4 \\
 & + \left[ \frac{\partial \Delta H(M)}{\partial C5} \right]_{Cv} \Big|_{v=1-4} dC5
 \end{aligned} \tag{7}$$

or, by substituting the partial derivatives:

$$d(\Delta H(M)) = E1dC1 + E2dC2 + E3dC3 + E4dC4 + E5dC5 \tag{8}$$

wherein the parameters are given as  $C_v$  with  $v = 1-5$ .

Different approaches deal with the quotient of the activity coefficients in Eq. (2). We use the commonly accepted quasiideal statement [9–11] simplifying the quotient as unity. From this it can be seen that the fifth parameter and the mixing enthalpy itself are still functions of the number of moles of the associate. Therefore one obtains the following partial derivatives of the mixing enthalpy:

$$\begin{aligned}
 E1 = & \left[ \frac{\partial \Delta H(M)}{\partial C1} \right]_{Cv} \Big|_{v=2-5} = \left[ \frac{\partial \Delta H(M)}{\partial n_{A_i B_j}} \right]_{Cv} \Big|_{v=1-4} \left[ \frac{\partial n_{A_i B_j}}{\partial C1} \right]_{Cv} \Big|_{v=2,3,5} \\
 & + \left[ \frac{\partial \Delta H(M)}{\partial C1} \right]_{Cv, n_{A_i B_j}} \Big|_{v=2-4} = \left[ \frac{\partial \Delta H(M)}{\partial C1} \right]_{Cv, n_{A_i B_j}} \Big|_{v=2-4}
 \end{aligned} \tag{9}$$

$$\begin{aligned}
 E2 = & \left[ \frac{\partial \Delta H(M)}{\partial C2} \right]_{Cv} \Big|_{v=1,3-5} = \left[ \frac{\partial \Delta H(M)}{\partial n_{A_i B_j}} \right]_{Cv} \Big|_{v=1-4} \left[ \frac{\partial n_{A_i B_j}}{\partial C2} \right]_{Cv} \Big|_{v=1,3,5} \\
 & + \left[ \frac{\partial \Delta H(M)}{\partial C2} \right]_{Cv, n_{A_i B_j}} \Big|_{v=1,3,4} = \left[ \frac{\partial \Delta H(M)}{\partial C2} \right]_{Cv, n_{A_i B_j}} \Big|_{v=1,3,4}
 \end{aligned} \tag{10}$$

$$\begin{aligned}
 E3 = & \left[ \frac{\partial \Delta H(M)}{\partial C3} \right]_{Cv} \Big|_{v=1,2,4,5} = \left[ \frac{\partial \Delta H(M)}{\partial n_{A_i B_j}} \right]_{Cv} \Big|_{v=1-4} \left[ \frac{\partial n_{A_i B_j}}{\partial C3} \right]_{Cv} \Big|_{v=1,2,5} \\
 & + \left[ \frac{\partial \Delta H(M)}{\partial C3} \right]_{Cv, n_{A_i B_j}} \Big|_{v=1,2,4} = \left[ \frac{\partial \Delta H(M)}{\partial C3} \right]_{Cv, n_{A_i B_j}} \Big|_{v=1,2,4}
 \end{aligned} \tag{11}$$

$$E4 = \left[ \frac{\partial \Delta H(M)}{\partial C4} \right]_{Cv} \Big|_{v=1-3,5} \tag{12}$$

and

$$E5 = \left[ \frac{\partial \Delta H(M)}{\partial C5} \right]_{Cv} \Big|_{v=1-4} = \left[ \frac{\partial \Delta H(M)}{\partial n_{A_i B_j}} \right]_{Cv} \Big|_{v=1-4} \left[ \frac{\partial n_{A_i B_j}}{\partial C5} \right]_{Cv} \Big|_{v=1-3} \tag{13}$$

wherein

$$\begin{aligned} \left[ \frac{\partial \Delta H(M)}{\partial n_{A,B_i}} \right] &= C1 \frac{n(-j n_{A_i} - i n_{B_i}) - n_{A_i} n_{B_i} (1-i-j)}{n^2} \\ &+ C2 \frac{n(n_{A_i} - i n_{A,B_i}) - n_{A_i} n_{A,B_i} (1-i-j)}{n^2} \\ &+ C3 \frac{n(n_{B_i} - j n_{A,B_i}) - n_{B_i} n_{A,B_i} (1-i-j)}{n^2} \\ &+ C4 \end{aligned} \quad (14)$$

$$\left[ \frac{\partial \Delta H(M)}{\partial C1} \right]_{Cv, n_{A,B_i}} \Big|_{v=2-4} = \frac{n_{A_i} n_{B_i}}{n} \quad (15)$$

$$\left[ \frac{\partial \Delta H(M)}{\partial C2} \right]_{Cv, n_{A,B_i}} \Big|_{v=1,3,4} = \frac{n_{A_i} n_{A,B_i}}{n} \quad (16)$$

$$\left[ \frac{\partial \Delta H(M)}{\partial C3} \right]_{Cv, n_{A,B_i}} \Big|_{v=1,2,4} = \frac{n_{B_i} n_{A_i} n_{B_i}}{n} \quad (17)$$

$$\left[ \frac{\partial \Delta H(M)}{\partial C4} \right]_{Cv} \Big|_{v=1-3,5} = n_{A_i B_i} \quad (18)$$

$$\left[ \frac{\partial n_{A,B_i}}{\partial C5} \right]_{Cv} \Big|_{v=1-3} = \frac{1}{\left[ \frac{\partial C5}{\partial n_{A,B_i}} \right]_{Cv} \Big|_{v=1-3,5}} \quad (19)$$

with

$$\left[ \frac{\partial C5}{\partial n_{A,B_i}} \right]_{Cv} \Big|_{v=1-3,5} = \frac{1}{n_{A,B_i}} + \frac{i^2}{n_{A_i}} + \frac{j^2}{n_{B_i}} - \frac{(1-i-j)^2}{n} \quad (20)$$

Replacing the differentials in Eq. (8) by finite differences one obtains:

$$\Delta(\Delta H(M)) = E1\Delta C1 + E2\Delta C2 + E3\Delta C3 + E4\Delta C4 + E5\Delta C5 \quad (21)$$

with

$$\Delta(\Delta H(M)) = \Delta H(M)_{\text{exp}} - \Delta H(M)_{\text{cal}} \quad (22)$$

and

$$\Delta Cv = Cv_{(s+1)} - Cv_{(s)} \quad (23)$$

wherein  $\Delta H(M)_{\text{exp}}$  and  $\Delta H(M)_{\text{cal}}$  are the measured and the calculated mixing enthalpies. The number of steps (loops) of the iteration are given by the index  $s$ .

A stoichiometry of the associate must be assumed to start the iteration, mostly the stoichiometry of an intermetallic compound. Whenever the system has more than one or no intermetallic compounds, the obvious choice for the composition to use is the value where the curve of the mixing enthalpy exhibits a minimum. Furthermore the

number of moles of the associate must be assumed in order to calculate the equilibrium constant for the first step of the iteration. With the measured values of the mixing enthalpy, the mole fractions of the product and the reactants are available. A first fit with Eq. (4) produces a first set of parameters  $C1-C4$ . This enables the calculation of the partial derivatives ( $E1-E5$ ) and a further fit with Eq. (21) yields the differences ( $\Delta C1-\Delta C5$ ). The parameters are corrected with use of Eq. (23) and the loop starts again. This procedure is continued until the differences become zero or the least squares values of  $\Delta(\Delta H(M))$  are minimal.

Qin *et al.* [12] compared associate models with different numbers of parameters and showed that each model is able to describe the measured mixing enthalpies with its specific values of parameters, e.g. only small standard deviations occur. Applying the associate model to different measurements of the same system indicates that if the measured mixing enthalpy values differ slightly the parameters change significantly [12]. Therefore the physical meaning of the parameters should not be overinterpreted because the approximation process is always a pure mathematical treatment.

Nevertheless, the associate model including the presented approximation technique is a good tool for describing the concentration- and temperature-dependent measurements of the mixing enthalpy. Furthermore, the model enables the prediction of enthalpy data for concentration and temperature ranges which cannot be obtained by measurement. This will be shown in the following comparison of the described models.

### 3. Discussion

Choosing the system Mg–Pb as an example we compared the polynomial representation and the associate model. The mixing enthalpy of this system was measured by Sommer *et al.* [13] at  $T = 943$  K and  $T = 1033$  K over the entire concentration range and at  $T = 1233$  K in the lead-rich range up to 63 at.% magnesium. The enthalpy values (see Fig. 1) exhibit a sharp minimum at the composition of the congruent melting intermetallic compound  $Mg_2Pb$ . Furthermore, Sommer *et al.* measured the excess heat capacity at  $T = 1100$  K which deviates positively from the Neumann–Kopp rule (see Fig. 2).

Due to the sharp mixing enthalpy minimum the TAP and associate models are the favourite two for the description. To test the capabilities of the models we compared the representations of the measurements by simulating the situation that only measurements near the pure components at different temperatures are possible. The accuracy of the descriptions was tested by comparison of the predictions for the excess heat capacity. Both models enabled the calculation of the excess heat capacity,  $C_p(x_s)$ :

$$C_p(x_s) = \frac{\partial \Delta H(M)}{\partial T} \quad (24)$$

Differentiation of the polynomial description of the TAP series (see Table 1) leads to:

$$C_p(x_s) = x_B \sum_{n=1}^{n=N} x_A^n \left[ \sum_{\epsilon=1}^{\epsilon=E} (1-\epsilon) L_{n,1-\epsilon}^* T^{-\epsilon} \right] \quad (25)$$

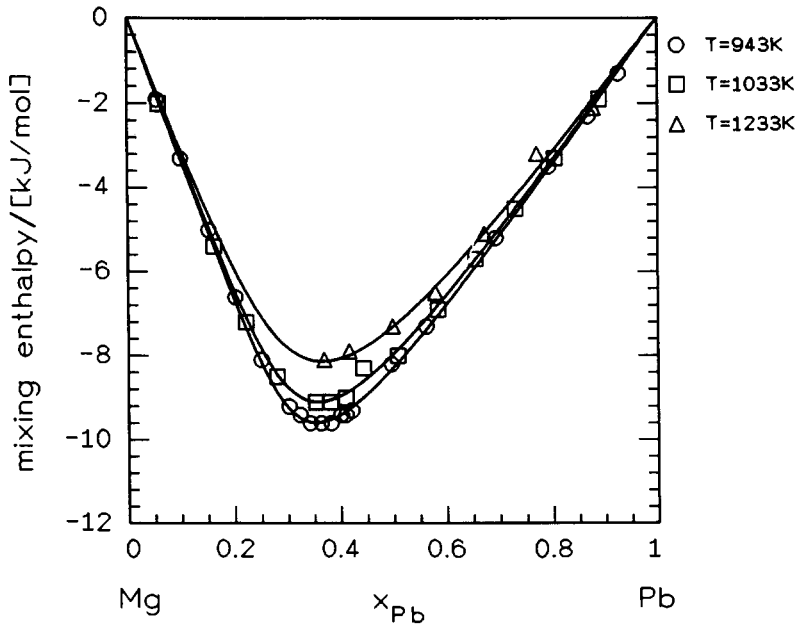


Fig. 1. Mixing enthalpies of the system Mg–Pb [13], described with the associate model, all values considered.

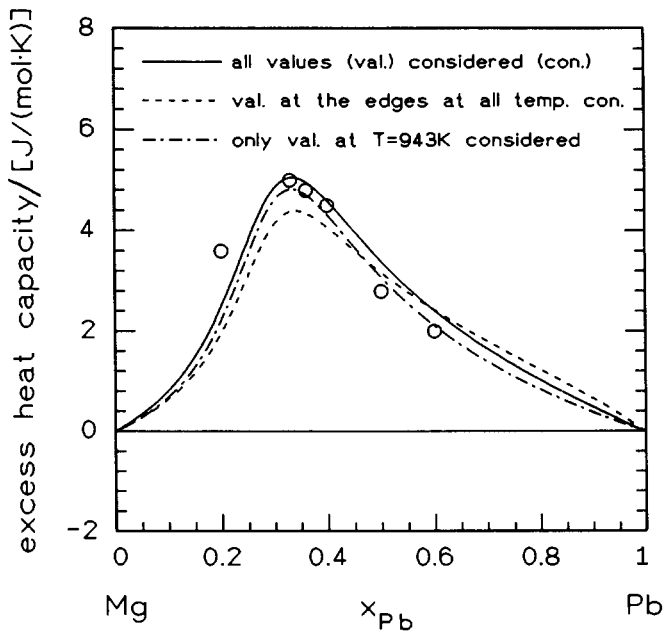


Fig. 2. Excess heat capacity of the system Mg–Pb at  $T = 1100$  K [13], curves calculated using Eq. [24] and different applications of the associate model.

Using the definition  $C_p(x,s) = (\partial \Delta H(M)/\partial T) = (\partial \Delta H(M)/\partial n_{A_i B_j})(\partial n_{A_i B_j}/\partial T)$  the excess heat capacity can be expressed by the associate model as the product of Eq. (14) and

$$\frac{\partial n_{A_i B_j}}{\partial T} = \frac{nC5}{RT^2} \left\{ \frac{1}{x_{A_i B_j}} + \frac{i^2}{x_{A_i}} + \frac{j^2}{x_{B_i}} - (1-i-j)^2 \right\}^2 \quad (26)$$

Fig. 1 shows the mixing enthalpy of the system Mg–Pb described by the associate model. All values are used to calculate the model parameters. The parameters together with the standard deviation are given in Table 2. The resulting prediction of the concentration-dependence of the excess heat capacity at  $T = 1100$  K is drawn in Fig. 2 (continuous line).

To obtain the best representation with the TAP series the degree ( $N$ ) and the number of temperature terms ( $E$ ) were varied. We used the degrees  $N = 3 \dots 6$ ; one temperature term was considered, i.e.  $E = 2$ . The polynomial functions and the standard deviation for these conditions are given in Table 3. The curves presented in Figs. 3 and 4 and their standard deviations indicate that the representations of the measurements with the TAP series are not as good as the representation given by the associate model (see Fig. 1 and Table 2). The predictions of the excess heat capacity by the different TAP series (see Fig. 5) are completely unsatisfactorily. Some segments of the curves lay below the zero line. This is an atypical behaviour for systems with an exothermic mixing enthalpy.

Mixing enthalpy measurements are frequently available only at the edge of systems. To simulate this situation we reduced the number of enthalpy values for the calculation of the parameters. The result of this comparison between the TAP series ( $N = 3$ ;  $E = 2$ ) and the associate model is shown in Fig. 6 where the fitted values are marked as full black symbols.

The TAP series is a pure mathematical treatment of the data. The approximation process does not take into consideration the correct temperature trend of the mixing enthalpy curves. Fig. 6 shows that further measurements at different temperatures do not increase the prospect of success. Therefore, the polynomial representations should be used only for measured concentrations. TAP predictions of concentration- and temperature-dependencies are unreliable.

Table 2  
Parameter and standard deviation for the different applications of the associate model

Considered values	Parameters				
	C1 in $\text{kJ mol}^{-1}$	C2 in $\text{kJ mol}^{-1}$	C3 in $\text{kJ mol}^{-1}$	$\Delta H_{A_i B_j}$	$\Delta S_{A_i B_j}$ in $(\text{J mol K})^{-1}$
All	–13.454	0.106	5.253	–39.1	–15.364
	Standard deviation: $\sigma = 0.116$				
All temp.,	–10.05	–3.56	3.74	–37.15	–10.835
	Standard deviation: $\sigma = 0.135$				
$T = 943$ K	–14.455	1.336	6.259	–39.06	–14.2705
	Standard deviation: $\sigma = 0.123$				



Table 3

Polynomial functions and standard deviation of the different TAP series ( $N = 3 \dots 6$ ),  $x = x_{\text{pb}}$ 

Part I: All mixing enthalpy values were considered

$$N = 3: \frac{\Delta H(M)}{x(1-x)} = 55.53 - \frac{0.46 \times 10^3}{T} + \left(-140 + \frac{89.84 \times 10^3}{T}\right)x + \left(118.29 - \frac{107.45 \times 10^3}{T}\right)x^2$$

Standard deviation:  $\sigma = 0.5$ 

$$N = 4: \frac{\Delta H(M)}{x(1-x)} = -57.21 + \frac{26.82 \times 10^3}{T} + \left(-179.62 + \frac{285 \times 10^3}{T}\right)x + \left(-213.62 + \frac{498.27 \times 10^3}{T}\right)x^2 + \left(67.31 - \frac{238.17 \times 10^3}{T}\right)x^3$$

Standard deviation:  $\sigma = 0.198$ 

$$N = 5: \frac{\Delta H(M)}{x(1-x)} = -60.32 + \frac{30.55 \times 10^3}{T} + \left(226.96 - \frac{342.64 \times 10^3}{T}\right)x + \left(-411.03 + \frac{739.22 \times 10^3}{T}\right)x^2 + \left(371 - \frac{610.43 \times 10^3}{T}\right)x^3 + \left(-153.78 + \frac{189.25 \times 10^3}{T}\right)x^4$$

Standard deviation:  $\sigma = 0.192$ 

$$N = 6: \frac{\Delta H(M)}{x(1-x)} = -20.03 + \frac{43.99 \times 10^3}{T} + \left(1123.94 - \frac{950.92 \times 10^3}{T}\right)x + \left(-6762.66 + \frac{6305.54 \times 10^3}{T}\right)x^2 + \left(16028.8 - \frac{15841 \times 10^3}{T}\right)x^3 + \left(-16526.56 + \frac{16887.77 \times 10^3}{T}\right)x^4 + \left(6243.6 - \frac{6481.79 \times 10^3}{T}\right)x^5$$

Standard deviation:  $\sigma = 0.13$ 

Part II: Values at all temperatures but on the edge were considered

$$N = 3: \frac{\Delta H(M)}{x(1-x)} = -296.77 + \frac{245.74 \times 10^3}{T} + \left(913.36 - \frac{887.23 \times 10^3}{T}\right)x + \left(-694.85 - \frac{708.87 \times 10^3}{T}\right)x^2$$

Standard deviation:  $\sigma = 0.307$  (in respect of the considered values)

The description of measurements with the associate model is reliable even when input data are limited in range. This reliability is confirmed by small standard deviations (see Table 2) of the fitted values to the experimental values with use of all enthalpy values. Here the prediction of the excess heat capacity is quite good. To further prove the flexibility of this model we varied the number of given values in such a way that only experimental data at one temperature ( $T = 943$  K) were taken into

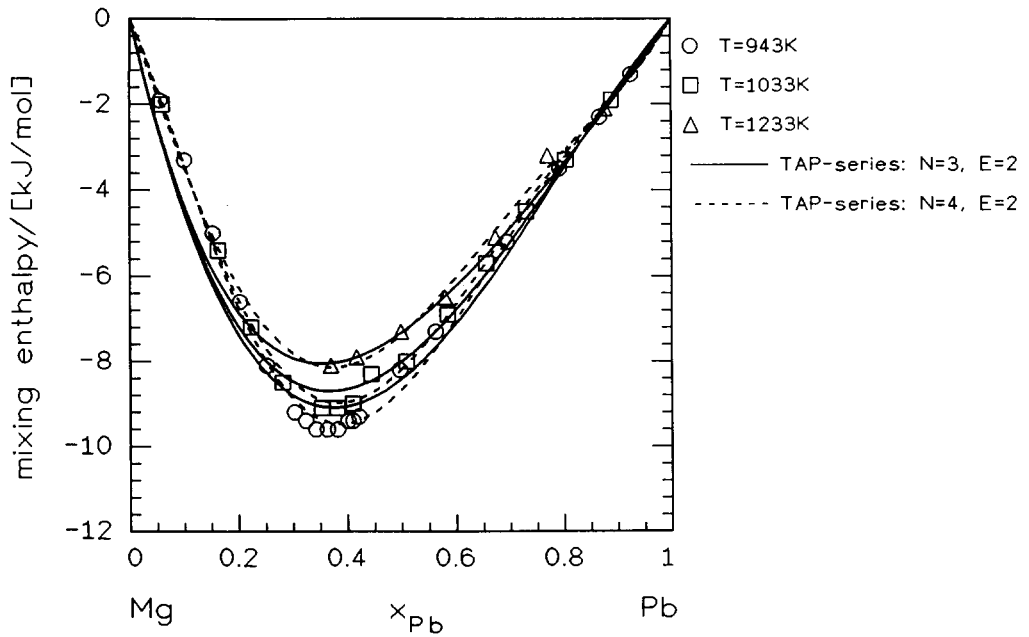


Fig. 3. Mixing enthalpies of the system Mg–Pb [13], described with different TAP series ( $N = 3$  and  $N = 4$ ).

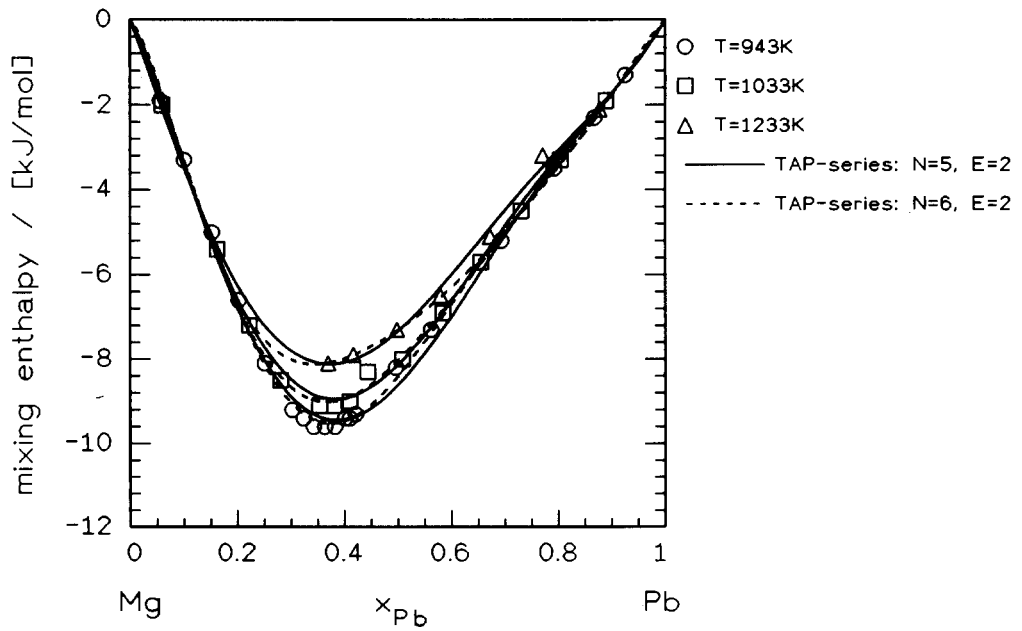


Fig. 4. Mixing enthalpies of the system Mg–Pb [13], described with different TAP series ( $N = 5$  and  $N = 6$ ).

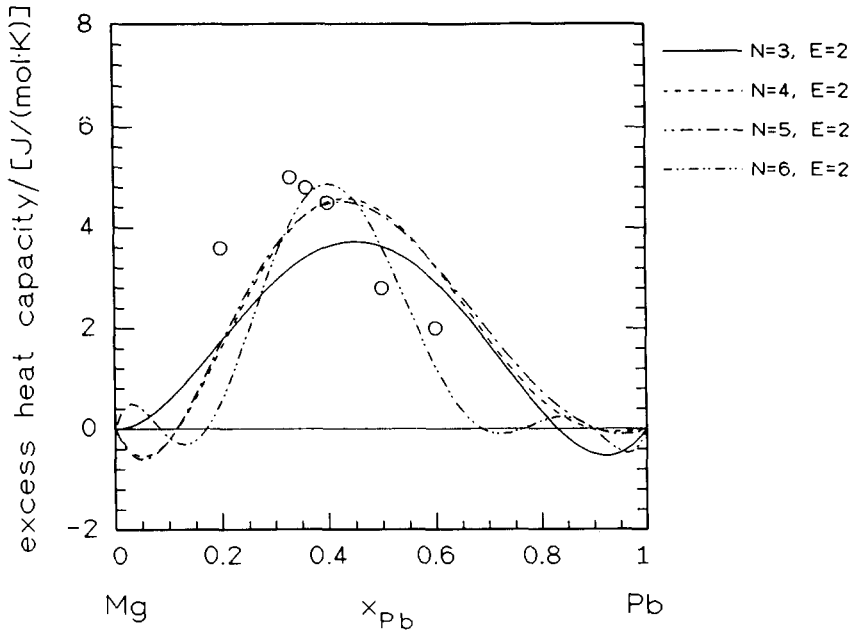


Fig. 5. Excess heat capacity of the system Mg–Pb at  $T = 1100$  K [13], curves calculated using Eq. (24) and different TAP series ( $N = 3, 4, 5, 6$ ).

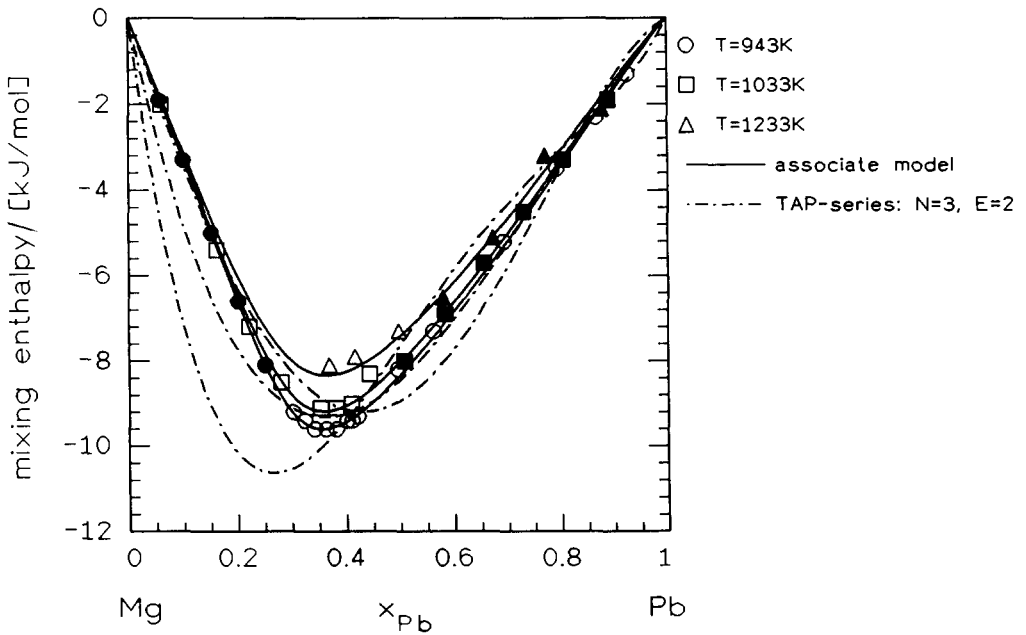


Fig. 6. Mixing enthalpies of the system Mg–Pb [13], described by the associate model and the TAP series ( $N = 3, E = 2$ ), values available during the approximation marked (fully black symbols).

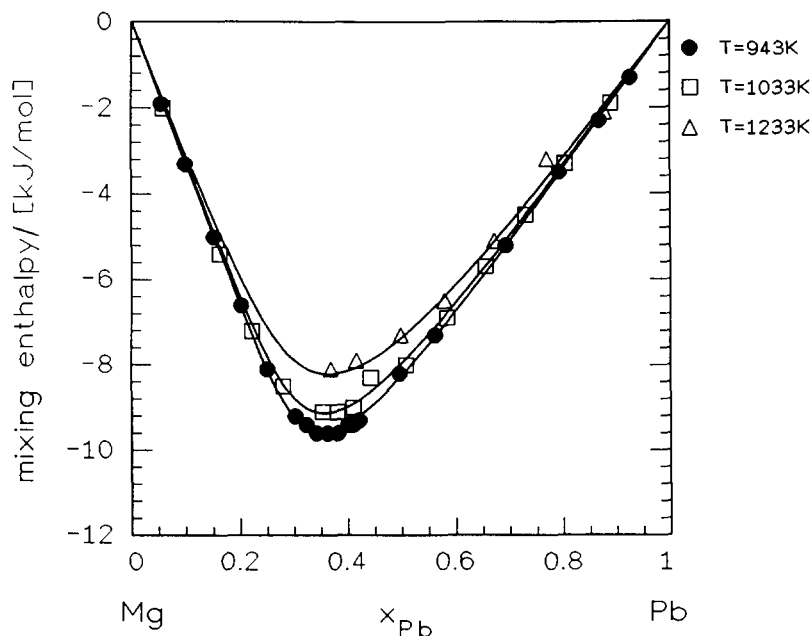


Fig. 7. Mixing enthalpies of the system Mg–Pb [13], described by the associate model, only the values at  $T = 943$  K available during the approximation (full black symbols).

account. The parameters are given in Table 2. At this temperature enthalpies are known over the entire concentration range and the position of the minimum is clear. The result is a small standard deviation (see Table 2) referring to all values and a correct description of the temperature dependence (see Fig. 7). Furthermore the prediction of the excess heat capacity is good (see Fig. 2).

The prediction of the Gibbs energy of mixing of the system is the final application of the model. Measurements of the enthalpy and the Gibbs energy of mixing ( $\Delta G(M)$ ) of the system Mg–Pb are given by Eldridge et al. [14] and Hultgren et al. [15]. Using the mixing enthalpy measurements we obtained the parameters in Table 4 and calculated

Table 4

Calculated parameters of the associate model for the system Mg–Pb, using the measurements of Eldridge et al. [14] and of Hultgren et al. [15]

Measurement	Parameters				
	C1 in $\text{kJ mol}^{-1}$	C2 in $\text{kJ mol}^{-1}$	C3 in $\text{kJ mol}^{-1}$	$\Delta H_{A_i B_j}$ in $\text{kJ mol}^{-1}$	$\Delta S_{A_i B_j}$ in $\text{J}(\text{mol K})^{-1}$
[14] $T = 822$ K	–24.41	–30.92	–27.4	–18.67	–5.014
	Standard deviation: $\sigma = 0.294$				
[15] $T = 973$ K	–24.41	–40.90	–27.4	–18.67	–5
	Standard deviation: $\sigma = 0.51$				

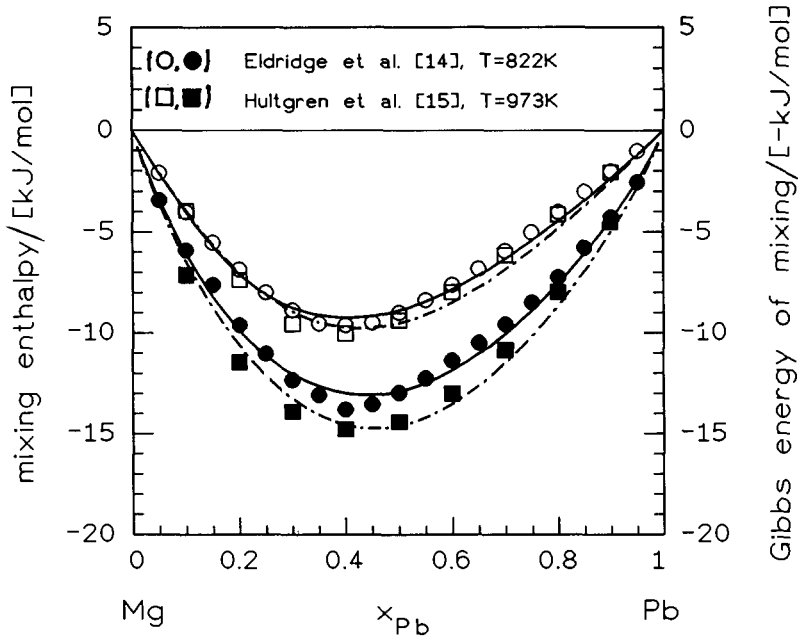


Fig. 8. Mixing enthalpies and free enthalpies of mixing (full black symbols) of the system Mg–Pb.

the Gibbs energy of mixing (see Fig. 8). The prediction of the Gibbs energy is also satisfactory.

#### 4. Conclusions

The TAP series and the associate model have been applied to mixing enthalpy measurements for the system Mg–Pb [13]. Three different situations are presented to simulate typical problems of mixing enthalpy measurements and to show how the models behave. Measurements are available (a) over the entire concentration range at different temperatures, (b) at the edges of a system at different temperatures and (c) over the entire concentration range at one temperature.

In view of the fact that the TAP series does not consider thermodynamic arrangements of a system, the series fit gives a satisfactory representation for the mixing when input data cover the entire concentration range. However prediction of the excess heat capacity is erroneous.

Excellent results are obtained with the associate model for all three simulated situations. With the parameters calculated the representation of the mixing enthalpy measurements, predictions of the excess heat capacity and of the Gibbs energy of mixing are possible and agree with the measured values. Therefore the associate model is predestined to represent mixing enthalpy measurements of liquid binary metallic systems.

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