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THE ESTIMATION OF THE THERMODYNAMIC PROPERTIES OF TERNARY ALLOYS FROM BINARY DATA USING THE SHORTEST DISTANCE COMPOSITION PATH

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ABSTRACT

A new composition path, $X_i - X_j = \text{constant}$, is suggested for the semi-empirical calculation of the thermodynamic properties of ternary 'substitutional' solutions from binary data, when the binary systems show deviations from the regular solution model. A comparison is made between the results obtained for integral and partial properties using this composition path and those calculated employing other composition paths suggested in literature. It appears that the best estimate of the ternary properties is obtained when binary data at compositions closest to the ternary composition are used.

INTRODUCTION

Chemical thermodynamics is frequently used in the evaluation of high temperature equilibria encountered in the production and refining of metals and alloys. Methods for the estimation of the properties of ternary and multicomponent solutions from information on corresponding binary systems have therefore received considerable attention. A detailed review of available models for the prediction of the thermodynamic properties in multicomponent systems is given by Ansara[1] and Spencer et al.[2]. The regular and quasichemical solution models lead to symmetric integral properties of mixing in binary alloys. A reveiw of experimental data on alloys[3] indicates that only a limited number of systems exhibit this behaviour. Many semi-empirical formulations have therefore been developed, which are based on the equation derived by Meijering[4] for the excess free energy of mixing of a regular ternary solution:

$$\Delta G^{E}_{ABC} = X_A X_B \alpha_{AB} + X_B X_C \alpha_{BC} + X_C X_A \alpha_{CA} \tag{1}$$

where $\alpha_{AB} = \Delta G^{E}_{AB}/N_A N_B = ZN^{\circ}\,[E_{AB} - (E_{AA} + E_{BB}/2)]$, etc., X_i is the ternary mole fraction, N_i is the binary mole fraction of component i, Z is the coordination number,

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N° is the Avagadro's number and E_{AB} is the energy of an A–B bond. From eqn (1) the partial property of component A can be obtained as,

$$\Delta\bar{G}^{E}_{A(A+B+C)} = \Delta\mu^{E}_{A(A+B+C)} = \alpha_{AB}X_B(X_B+X_C)+\alpha_{AC}X_C(X_B+X_C)-X_BX_C\alpha_{BC} \tag{2}$$

Since α is not a constant independent of composition for most alloys, it has been replaced by experimentally determined binary values of ΔG^E along certain composition paths. In Fig. 1 several such composition paths from the ternary composition to the bounding binary systems are shown.

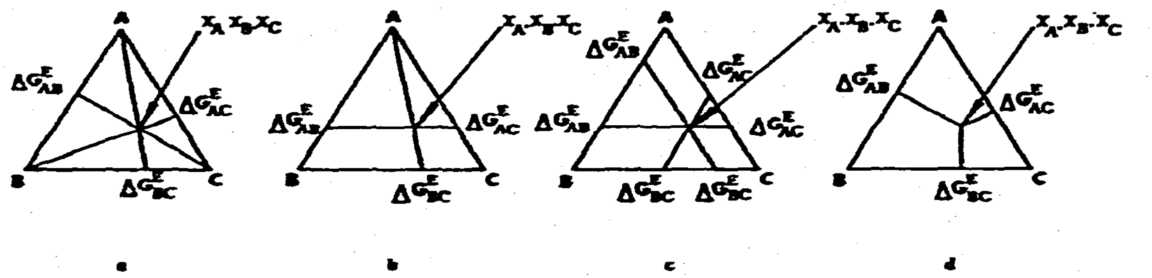


Fig. 1. Composition paths relating the ternary alloy to constituent binary alloys: (a) composition path of constant X_A/X_B, X_B/X_C and X_A/X_C (Kohler); (b) composition path of constant X_A and X_B/X_C (Toop); (c) composition path of constant X_A, X_B and X_C (Colinet); (d) the shortest distance composition path along which (X_A-X_B), (X_B-X_C) and (X_A-X_C) are constant.

(I) THE KOHLER EQUATION

Kohler[5] suggested that the excess free energy of mixing in a ternary system A+B+C may be expressed by the equation,

$$\Delta G^{E}_{ABC} = (1-X_A)^2[\Delta G^{E}_{BC}]_{X_B/X_C}+(1-X_B)^2[\Delta G^{E}_{AC}]_{X_A/X_C}+ \\ +(1-X_C)^2[\Delta G^{E}_{AB}]_{X_A/X_B} \tag{2}$$

The binary compositions, at which the binary excess free energy terms are taken, are shown in Fig. 1(a). This equation has also been rederived by Olson and Toop[6], and extended to multicomponent systems by Kehiaian[7]. The property of component A is given by

$$\Delta\mu^{E}_{A(A+B+C)} = [(1-X_B)\Delta\mu^{E}_{A(A+C)}+X_B(1-X_B)\Delta G^{E}_{AC}]_{X_A/X_C}+ \\ +[(1-X_C)\Delta\mu^{E}_{A(A+B)}+X_C(1-X_C)\Delta G^{E}_{AB}]_{X_A/X_B}- \\ -(1-X_A)^2[\Delta G^{E}_{BC}]_{X_B/X_C} \tag{3}$$

By expressing α_{AB} etc. in terms of a power series in N_A/N_B,

$$\alpha_{AB} = A_0+A_1(N_A/N_B)+A_2(N_A/N_B)^2+\dots$$

and substituting in eqn (1), one obtains an alternate form of eqn (2) as,

$$\Delta G^{E}_{ABC} = X_A X_B[A_0 + A_1(X_A/X_B) + A_2(X_A/X_B)^2 + \ldots] + \\ + X_B X_C[A_0^1 + A_1^1(X_B/X_C) + A_2^1(X_B/X_C)^2 + \ldots] + \\ + X_A X_C[A_0^{11} + A_1^{11}(X_A/X_C) + A_2^{11}(X_A/X_C)^2 + \ldots] \quad (4)$$

which may be more useful for computer calculations.

(2) THE TOOP EQUATION

Based on the composition paths shown in Fig. 1(b), Toop[8] has expressed the excess free energy of mixing by the relation,

$$\Delta G^{E}_{ABC} = \left[\frac{X_B}{1-X_A}\Delta G^{E}_{AB} + \frac{X_C}{1-X_A}\Delta G^{E}_{AC}\right]_{X_A} + (1-X_A)^2[\Delta G^{E}_{BC}]_{X_B/X_C} \quad (5)$$

Since the composition paths connecting the ternary point to the binary compositions are not symmetric, the values calculated using this equation for non-regular ternary alloys depend on the choice of component A. If for a ternary system the equation is used with each metal as component A, different values for ΔG^{E}_{ABC} are obtained for the same composition of the alloy. If the data for the binary systems A+B and A+C are expressed as a power series in N_A and the data for the binary B+C as a power series in N_B/N_C then eqn (5) can also be expressed as,

$$\Delta G^{E}_{ABC} = X_A X_B[f_0 + f_1 X_A + f_2 X_A^2 + \ldots] + X_A X_C[f_0^1 + f_1^1 X_A + f_2^1 X_A^2 + \ldots] + \\ + X_B X_C[A_0^1 + A_1^1(X_B/X_C) + A_2^1(X_B/X_C)^2 + \ldots] \quad (6)$$

The partial excess free energy or the excess chemical potential of component A can be expressed as

$$\Delta\mu^{E}_{A(A+B+C)} = \left[\frac{X_B}{1-X_A}\Delta\mu^{E}_{A(A+B)} + \frac{X_C}{1-X_A}\Delta\mu^{E}_{A(A+C)}\right]_{X_A} - \\ - (1-X_A)^2[\Delta G^{E}_{BC}]_{X_B/X_C} \quad (7)$$

(3) THE COLINET EQUATION

Colinet[9] has established a relationship to express thermodynamic properties of mixing for a multicomponent system by the following equation,

$$\Delta G^{E} = \frac{1}{2}\sum_{i=1}^{i=m-1}\sum_{j=i+1}^{j=m}\frac{X_i}{1-X_j}[\Delta G_{ij}]_{X_j} \quad (8)$$

The geometry used is shown in Fig. 1(c); the composition paths correspond to constant mole fractions of A, B, and C.

THE SHORTEST DISTANCE COMPOSITION PATH

It is reasonable to assume that the estimated ternary property would be in better agreement with experimental values if the binary values incorporated into eqn (1) correspond to binary compositions closest to the ternary point. The composition path, $X_i - X_j = \text{constant}$, shown in Fig. 1(d), represents the shortest distance connecting any ternary composition to the respective binary compositions. This composition path corresponds to perpendiculars drawn from any ternary point to the sides of the equilateral triangle. From the geometry of the triangle it can be shown that along the path $X_B - X_C = \text{constant}$,

$$N_B = X_B + \frac{X_A}{2}$$

$$N_C = X_C + \frac{X_A}{2} \tag{9}$$

and so on. Rewriting eqn (1) in terms of binary values along the new composition paths, one obtains,

$$\begin{aligned}\Delta G^E_{ABC} = {} & \frac{X_A X_B}{\left(X_A + \frac{X_C}{2}\right)\left(X_B + \frac{X_C}{2}\right)} [\Delta G^E_{AB}]_{X_A - X_B = k} + \\ & + \frac{X_B X_C}{\left(X_B + \frac{X_A}{2}\right)\left(X_C + \frac{X_A}{2}\right)} [\Delta G^E_{BC}]_{X_B - X_C = k'} + \\ & + \frac{X_C X_A}{\left(X_C + \frac{X_B}{2}\right)\left(X_A + \frac{X_B}{2}\right)} [\Delta G^E_{AC}]_{X_A - X_C = k''}\end{aligned} \tag{10}$$

Similarly the excess chemical potential of the component A may be obtained by substituting,

$$\begin{aligned}\Delta\mu^E_{A(A+B+C)} = {} & X_B(X_B + X_C)\left[\frac{\Delta\mu^E_{A(A+B)}}{\left(X_B + \frac{X_C}{2}\right)^2}\right]_{X_A - X_B = k} + \\ & + X_C(X_B + X_C)\left[\frac{\Delta\mu^E_{A(A+C)}}{\left(X_C + \frac{X_B}{2}\right)^2}\right]_{X_A - X_C = k''} - \\ & - X_B X_C \left[\frac{\Delta G^E_{BC}}{\left(X_B + \frac{X_A}{2}\right)\left(X_C + \frac{X_A}{2}\right)}\right]_{X_B - X_C = k'}\end{aligned} \tag{11}$$

For computer applications the binary data may be expressed as a power series in $(N_A - N_B)$ etc. and eqn (10) may be rewritten in the form,

$$\begin{aligned}\Delta G^E_{ABC} = {} & X_A X_B[B_0 + B_1(X_A - X_B)_2 + B_2(X_A - X_B)^2 + \ldots] + \\ & + X_B X_C[B'_0 + B'_1(X_B - X_C) + B'_2(X_B - X_C)^2 + \ldots] + \\ & + X_A X_C[B''_0 + B''_1(X_A - X_C) + B''_2(X_A - X_C)^2 + \ldots] \qquad (12)\end{aligned}$$

since along the proposed composition path $N_A - N_B = X_A - X_B$, etc.

COMPARISON OF THE SEMI-EMPIRICAL EQUATIONS

At the present time, it does not seem possible to make a theoretical evaluation of the systematic differences obtained for a given excess function using the models described above. An alternate approach is to compare by numerical calculation the values obtained from the models for a given ternary system with experimental data. The same values for the properties of the three limiting binary systems are used in the different models. The first system chosen to test the models is Cd + Bi + Pb, for which closely agreeing free energy measurements have been reported by two groups of

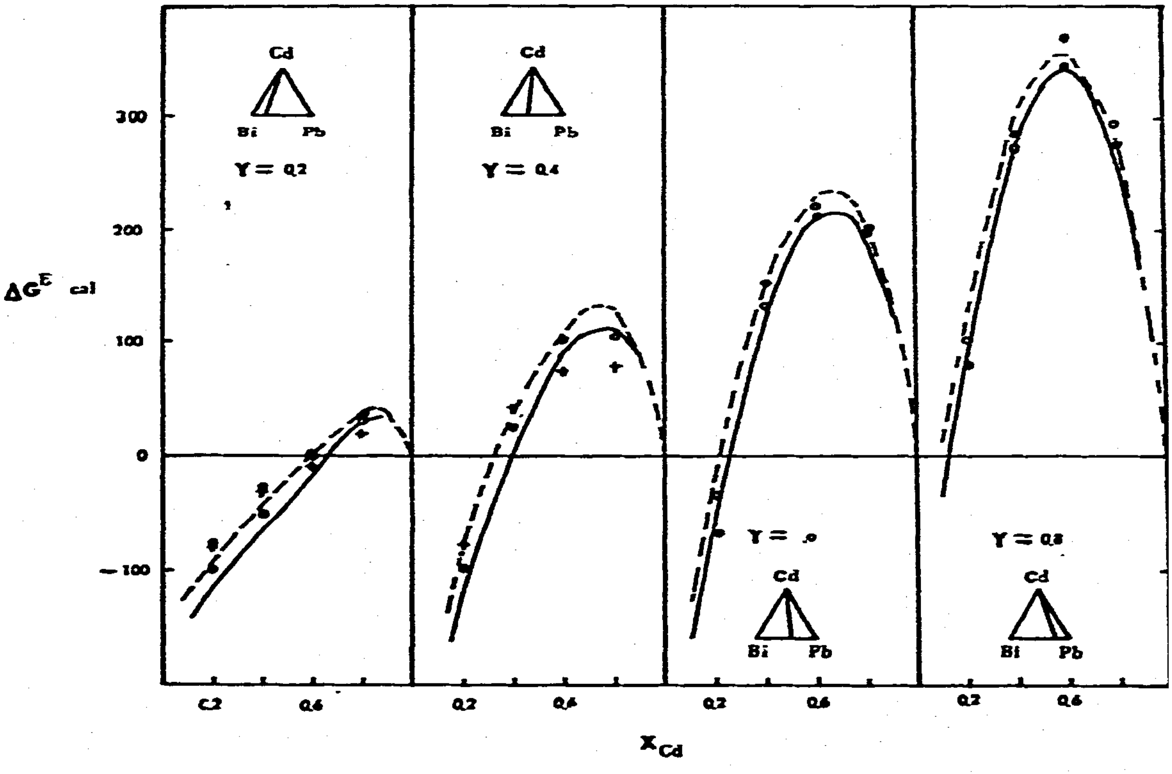


Fig. 2. Integral excess free energy for liquid Cd–Bi–Pb solutions at 760 K. Experimental data: O Elliott and Chipman[10]; ———, Moser and Zabdyr[11]. Calculated values: – – –, along path of constant $(X_i - X_j)$ suggested in this study; ●, Kohler model; +, Toop model.

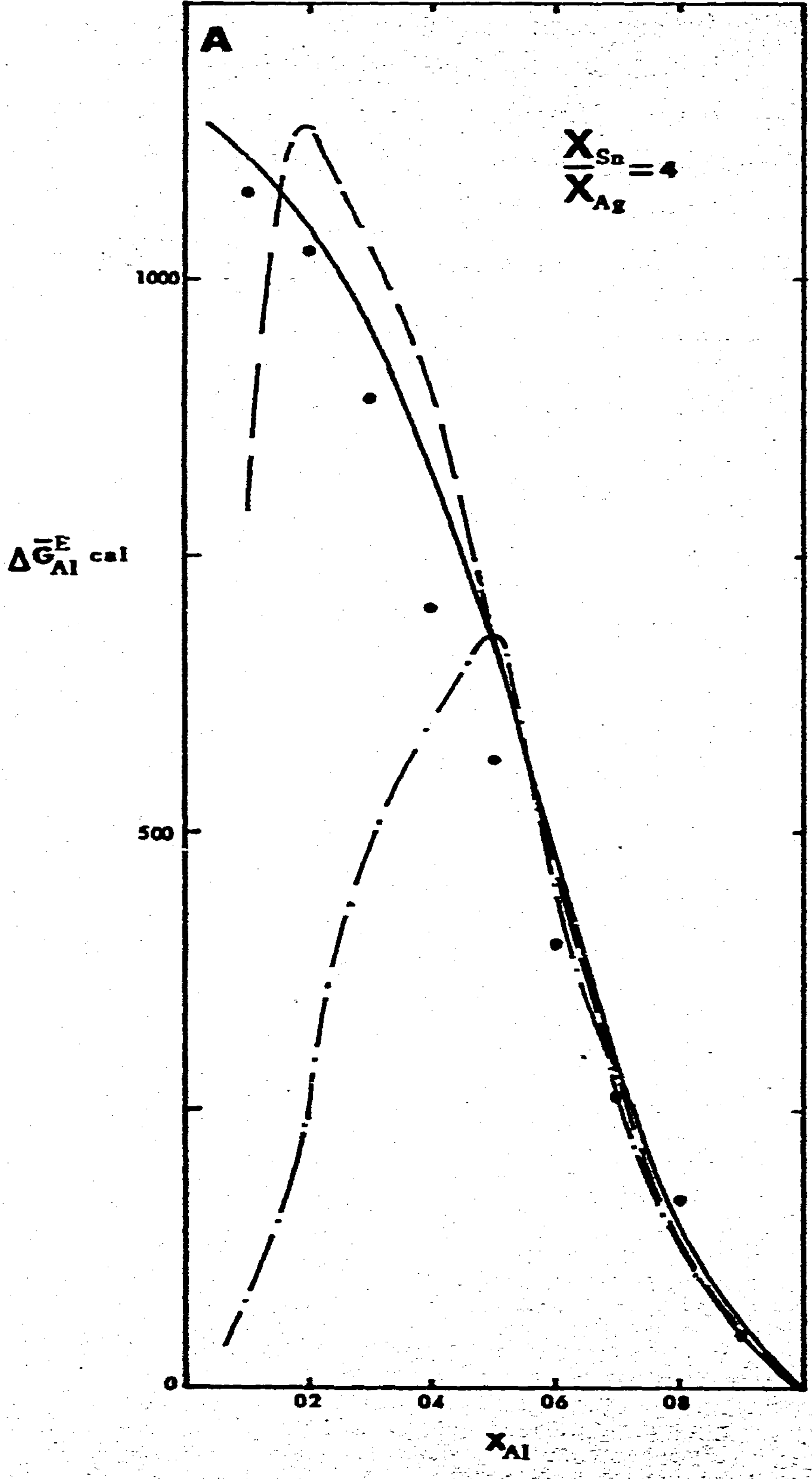
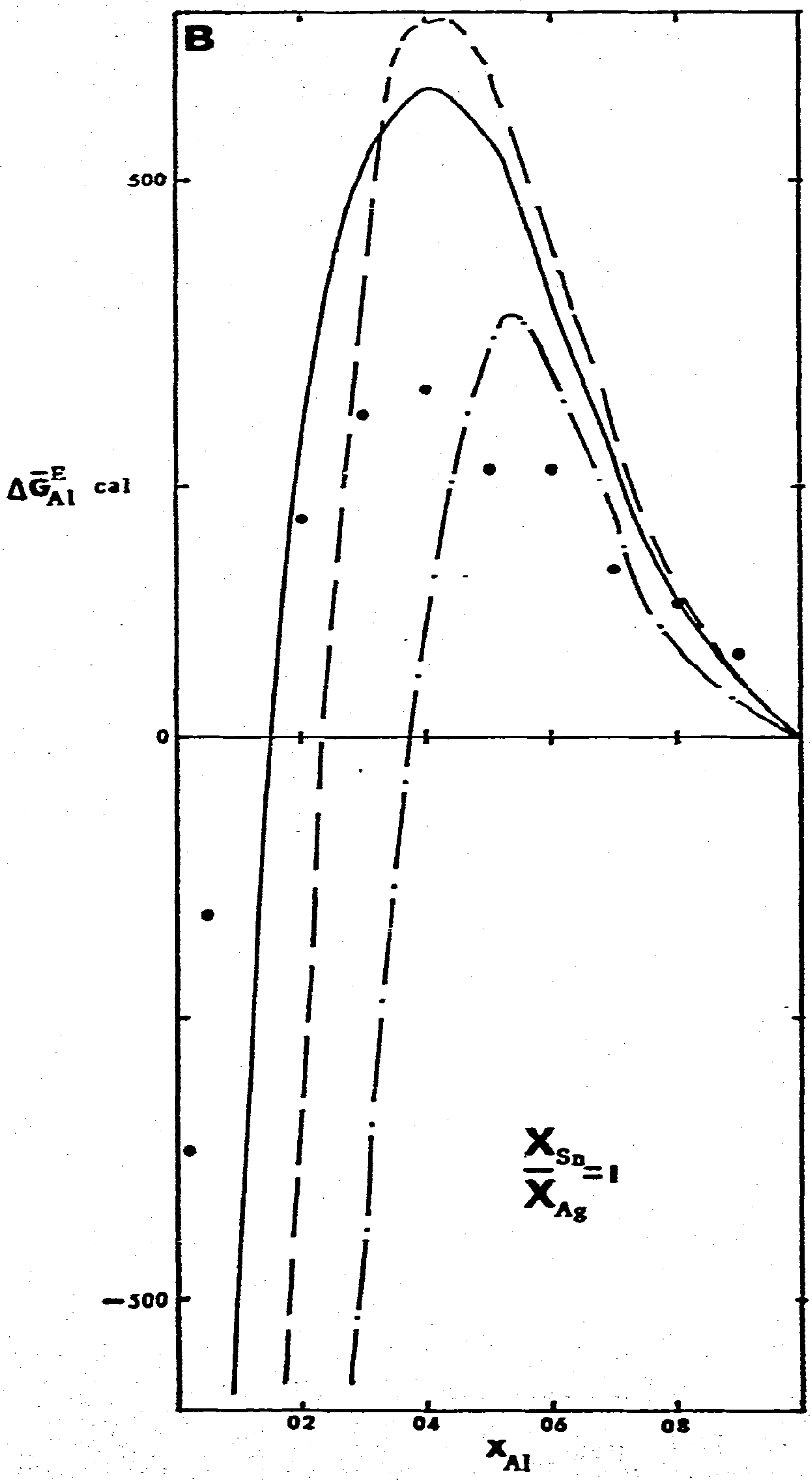


Fig. 3. (See legend on p. 204).



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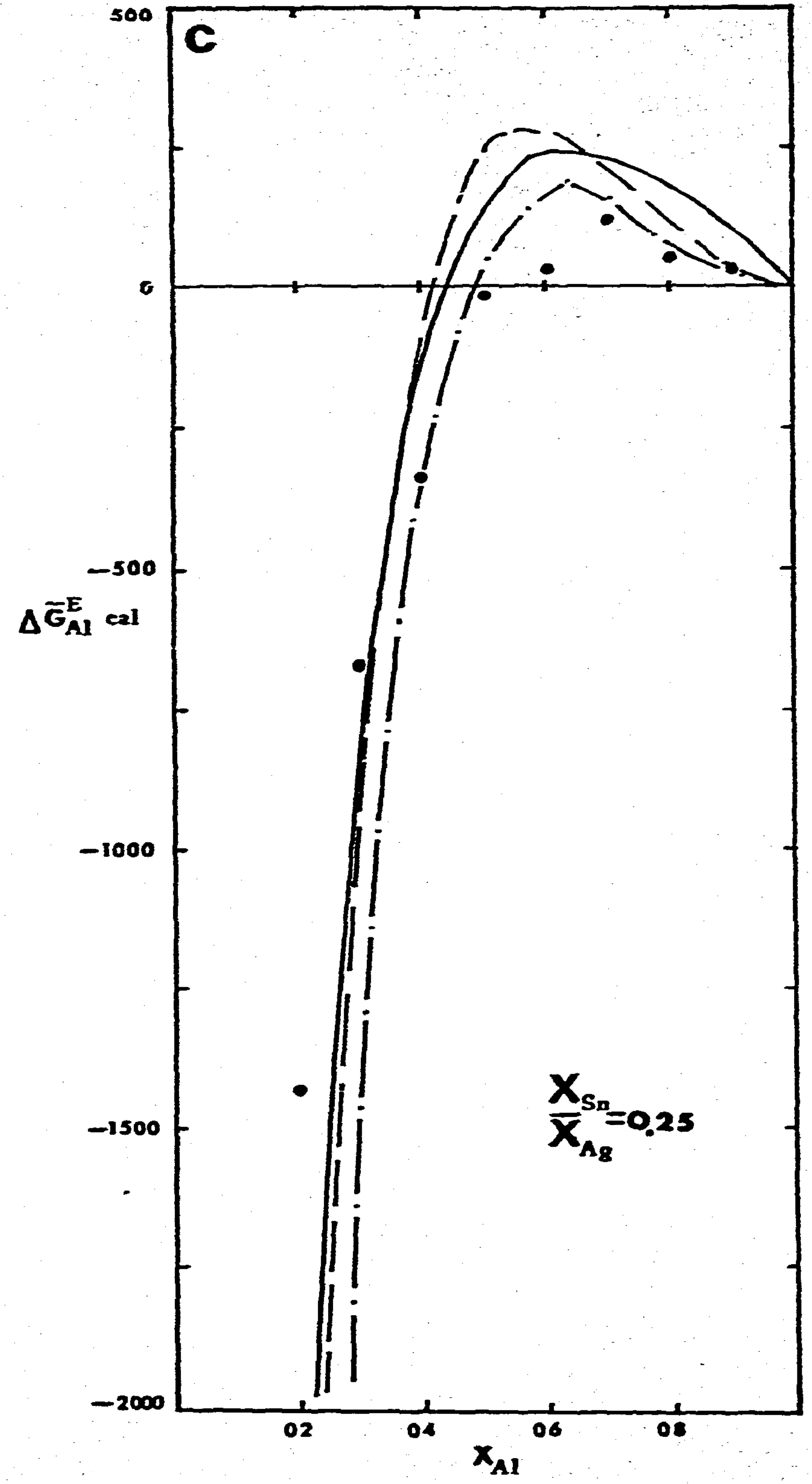

Fig. 3. Partial excess free energy of aluminium in the ternary system Al–Ag–Sn at 1273 K. ●, Experimental data[14]. Calculated values: – – –, Kohler's model; –·–·, Toop's model; ———, model based on shortest distance composition path.

investigators[10,11]. The binary systems Bi+Pb[12] and Cd+Bi[11] have negative excess free energies of mixing, while the system Cd+Pb[13] has positive excess free energy of mixing. Of these three binary systems, only the Bi+Pb system conforms to the regular solution model. The excess free energies of mixing in the three systems have numerical values less than 520 cal g-at^{-1}. The values for the three binary systems and the ternary system were measured in the same laboratory using similar methods. The experimental values for the excess free energy of mixing for the ternary alloys are compared in Fig. 2 with those calculated using the different models, along paths of constant, $X_{\mathrm{Bi}}/X_{\mathrm{Pb}} = y$. The comparison suggests that eqn (10), corresponding to the shortest distance composition path, produces a small but significant improvement in the predicted values. For low affinity systems formed mainly from low melting metals such as Cd+Bi+Pb, all of the proposed models based on eqn (1) predict values that are in good agreement with experimental data. For higher affinity alloys the agreement between the estimated and experimental values is less satisfactory, especially for the partial properties. In Fig. 3(a, b, c) the excess chemical potential of Al in the Al+Ag+Sn system calculated using the different models is compared with values obtained from direct e.m.f. measurements by Massart et al.[14] on concentration cells of the type $\mathrm{Al/Al^{3+}}$, KCl–LiCl/$\mathrm{Al_{alloy}}$. Since these investigators did not measure the properties of the binary Ag–Sn system, the values suggested by Kubaschewski and Alcock[15] are used in the calculations. Although none of the models discussed in this communication are in exact accord with experiment, the shortest distance composition path provides the best estimate, especially for dilute alloys. It may be pointed out that in both the ternary systems chosen for illustration, the component metals have different valencies.

DISCUSSION

One of the advantages of the composition paths defined by, $X_i - X_j =$ constant, is that the partial properties may be derived algebraically from integral properties, when the latter is expressed as a power series;

$$\Delta G^{\mathrm{E}}_{(\mathrm{A+B})} = N_{\mathrm{A}} N_{\mathrm{B}} \sum_{n=0,1,\ldots} B_n (N_{\mathrm{A}} - N_{\mathrm{B}})^n \tag{13}$$

$$\Delta \bar{G}^{\mathrm{E}}_{\mathrm{A(A+B)}} = \Delta \mu^{\mathrm{E}}_{\mathrm{A(A+B)}} = N_{\mathrm{B}}^2 \left\{ B_0 + \sum_{n=1,2,\ldots} B_n [(2n+1) N_{\mathrm{A}} - N_{\mathrm{B}}] (N_{\mathrm{A}} - N_{\mathrm{B}})^{n-} \right\} \tag{14}$$

When $N_{\mathrm{A}} = N_{\mathrm{B}} = 0.5$, all terms on the right-hand side of eqn (13) except the first one vanish. Because of this property fewer terms are required to fit the experimental data over the whole composition range than when power series in N_{A} or $N_{\mathrm{A}}/N_{\mathrm{B}}$ are employed.

For systems with strong interactions the quasichemical model would be more appropriate. Since few binary systems are fully described by the quasichemical model with only one parameter, the binary quasichemical terms in the ternary expressions would have to be replaced by the real experimental binary values along certain composition paths. Hagemark[16] has formulated a quasichemical ternary expression along the composition path used in Kohler's model (Fig. 1(a)). This expression contains all the "regular solution" terms of the Kohler equation and an additional non-radom ternary mixing term. Similar quasichemical equations formulated along the shortest distance composition path suggested in this paper will be discussed in a separate communication. There are also certain advantages in reformulating the ternary and quaternary Gibbs–Duhem equations along the composition path proposed in this study.

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