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MODEL ANALYSIS OF MIXING ENTHALPIES IN THE Cd–Tl–In TERNARY SYSTEM

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ABSTRACT

Three different solution models have been used to describe the experimental data for mixing enthalpies for liquid Cd–Tl–In alloys. All models require that an additional ternary term of the form, $\alpha_{ABC} \cdot x_A \cdot x_B \cdot x_C$, be added to the summation of the binary mixing enthalpies of the constituent systems in order to obtain satisfactory agreement between experimental and calculated values.

INTRODUCTION

In the past several years interest in the calculation of the thermodynamic properties of ternary systems from the data for the base-binary systems has increased considerably. This has arisen principally because of the difficulties associated with experimental measurements in the ternary systems and because of the vast number of data points needed to adequately describe the surface configuration of the selected thermodynamic property. It would be of considerable advantage to have available analytical expressions which would allow calculation of the entire ternary mixing enthalpy surface from a limited number of ternary data points. Several models are available for this type of analysis and most have been described by Ansara[1]. It was the purpose of this work to apply three different models to the mixing enthalpies for the Cd–Tl–In system and compare the calculated results with the experimental data of Predel and Berka[2].

MODEL ANALYSIS

In the analysis and calculation of ternary mixing enthalpies from the binary data it is customary to assume that the ternary data are adequately represented by the sum of the base binary data at the appropriate alloy composition. That this is not always the case has been illustrated by Sharkey et al.[3] who have shown, in the development

of the modified quasi-chemical model and its subsequent application, that a ternary interaction term of the type $C_1 x_A x_B x_C$ occurs. Here C_1 is a constant and x_A, x_B and x_C are mole fractions of A, B, and C. It is not surprising that a term of this type exists. From strictly a physical standpoint it is expected that the addition of a third atom, C, to a binary liquid solution of A and B will perturb the A–B bond energy and thus lead to a term with the above form. Likewise the addition of B to A–C and A to B–C will produce similar perturbations of the primary bond energy in the base binaries leading to additional terms of the same form. In the simplest approximation these three terms can be combined into a single ternary interaction term. Subsequently this term can be determined from experimental data and the remaining ternary mixing enthalpy surface calculated.

In this work three different models have been used to determine analytical expressions for the binary systems Cd–Tl, Cd–In and Tl–In. These are, the regular solution model of Hildebrand[4], the sub-regular solution model of Hardy[5], and the modified quasi-chemical model of Sharkey et al.[3]. With these models the mixing enthalpies can be expressed by the following three equations

$$\Delta H_R^M = \alpha_1 x_A x_B \tag{1}$$

$$\Delta H_{SR}^M = \alpha_1 x_A x_B^2 + \alpha_2 x_A^2 x_B \tag{2}$$

and

$$\Delta H_{SRP}^M = \alpha_1 x_A x_B^2 + \alpha_2 x_A^2 x_B - \alpha_3 x_A^2 x_B^2 \tag{3}$$

where $A_1 = \alpha_1$, $A_2 = \alpha_2 - \alpha_3 - \alpha_1$ and $A_3 = \alpha_3$.

In these equations x_A and x_B denote the atom fractions of A and B, respectively, and the α_i terms are constants determined by a least-squares fit of the data expressed in the form of $\Delta H/x_A x_B$. If one expresses the function $\Delta H/x_A x_B$ as a second degree polynominal in x_A, the following equation results

$$\frac{\Delta H^M}{x_A x_B} = A_1 + A_2 x_A + A_3 x_A^2 \tag{4}$$

This equation yields the coefficients for the regular model for $A_2 = A_3 = 0$, the sub-regular model for $A_3 = 0$ and the modified quasi-chemical model if A_1, A_2 and A_3 are non-zero values. This equation is quite easily handled by a computer to yield resultant values of the α_i coefficients for each model from a least-squares fit of the experimental data.

The ternary mixing enthalpies can be expressed by the following equation for each model

$$\Delta H_{ternary}^M = \Sigma \Delta H_{binary}^M + \alpha_{ABC} x_A x_B x_C \tag{5}$$

It has been shown by Sharkey et al.[3] that the ternary interaction term must appear if a deviation from a random atom distribution occurs. Since this is the case for a number of binary metallic systems the same is expected to be true for the ternary systems. If the system does have a random distribution of atom types then the α_{ABC}

coefficient approaches zero and the ternary mixing enthalpy is adequately expressed by the sum of the binary mixing enthalpies. For the Cd–Tl–In system the z_{ABC} term has been determined for each model from the experimental data of Predel and Berka[2].

The initial step in this analysis was to determine the analytical coefficients for the three binary systems using each model. The reported data for Cd–In[6] and Cd–Tl[7] by Predel and Berka as well as the data on Tl–In calculated by Berka[8] have been used since these data were obtained under the same conditions as the Cd–Tl–In data[2]. For the Cd–Tl system the following set of equations was obtained

$$\Delta H_R^M = 1970\, x_{Cd}x_{Tl} \tag{6}$$

$$\Delta H_{SR}^M = 2415\, x_{Cd}x_{Tl}^2 + 1525\, x_{Cd}^2x_{Tl} \tag{7}$$

$$\Delta H_{SHP}^M = 2848\, x_{Cd}x_{Tl}^2 + 1958\, x_{Cd}^2x_{Tl} - 2604\, x_{Cd}^2x_{Tl}^2 \tag{8}$$

where ΔH^M values are given in cal/g-atom. Similar equations for Cd–In and Tl–In are given below.

$$\Delta H_R^M = 1618\, x_{Cd}x_{In} \tag{9}$$

$$\Delta H_{SR}^M = 2164\, x_{Cd}x_{In}^2 + 1073\, x_{Cd}^2x_{In} \tag{10}$$

$$\Delta H_{SHP}^M = 2119\, x_{Cd}x_{In}^2 + 1028\, x_{Cd}^2x_{In} + 270\, x_{Cd}^2x_{In}^2 \tag{11}$$

$$\Delta H_R^M = 549\, x_{Tl}x_{In} \tag{12}$$

$$\Delta H_{SR}^M = 686\, x_{Tl}x_{In}^2 + 412\, x_{Tl}^2x_{In} \tag{13}$$

$$\Delta H_{SHP}^M = 668\, x_{Tl}x_{In}^2 + 395\, x_{Tl}^2x_{In} + 103\, x_{Tl}^2x_{In}^2 \tag{14}$$

From the z_3 coefficient in the SHP equation it is apparent that only the Cd–Tl system exhibits a gross deviation from random behavior.

For each model the ternary mixing enthalpy was first calculated using only the sum of the binary expressions. The results of these calculations are shown in Figs. 1–9 for 3 different Tl/In ratios. Only in the case of a Tl/In ratio of 9 is the agreement between the calculated curve and experimental data satisfactory. The maximum difference appears at a Tl/In ratio of 1. Since the sum of the binary systems does not give satisfactory agreement with the experimental data the ternary coefficient, z_{ABC}, given in eqn. (5) was calculated using each different model. This was done in the following manner. The ternary mixing enthalpy at the composition $x_{Cd} = 0.5$ was calculated using the sum of the binary terms for the 6 available quasi-binary sections of different Tl/In ratios. This was then subtracted from the measured mixing enthalpy and the result divided by the corresponding mole fraction product, $x_{Cd}x_{Tl}x_{In}$. The

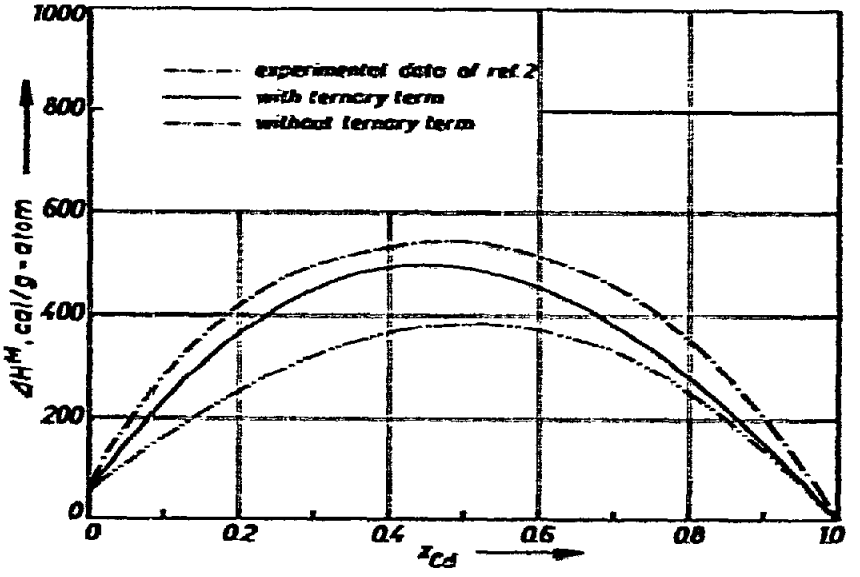

Fig. 1. Regular model calculation for $x_{Tl}/x_{In} = 1/9$.

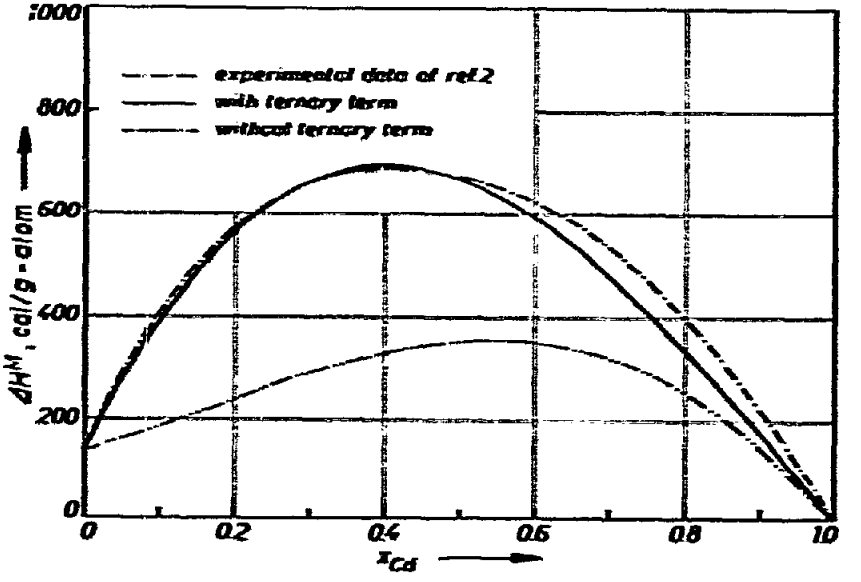

Fig. 2. Regular model calculation for $x_{Tl}/x_{In} = 1$.

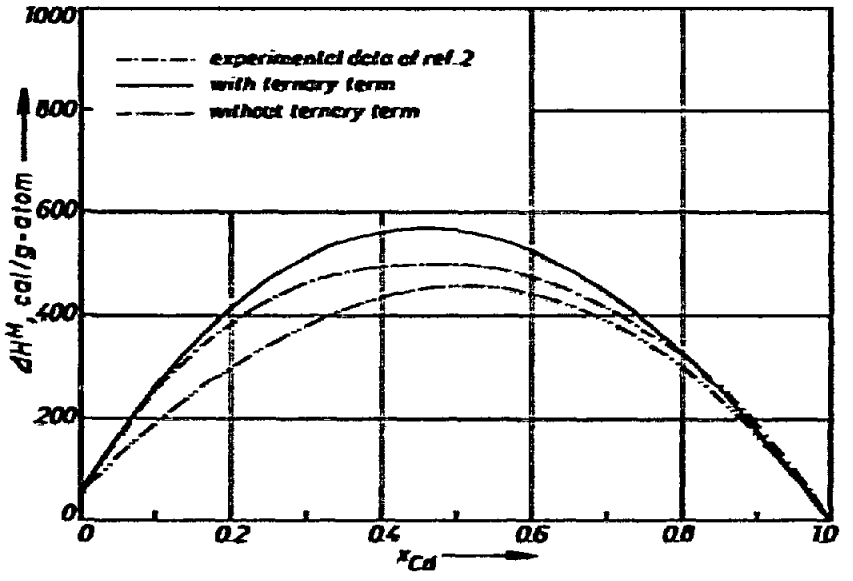

Fig. 3. Regular model calculation for $x_{Tl}/x_{In} = 9$.

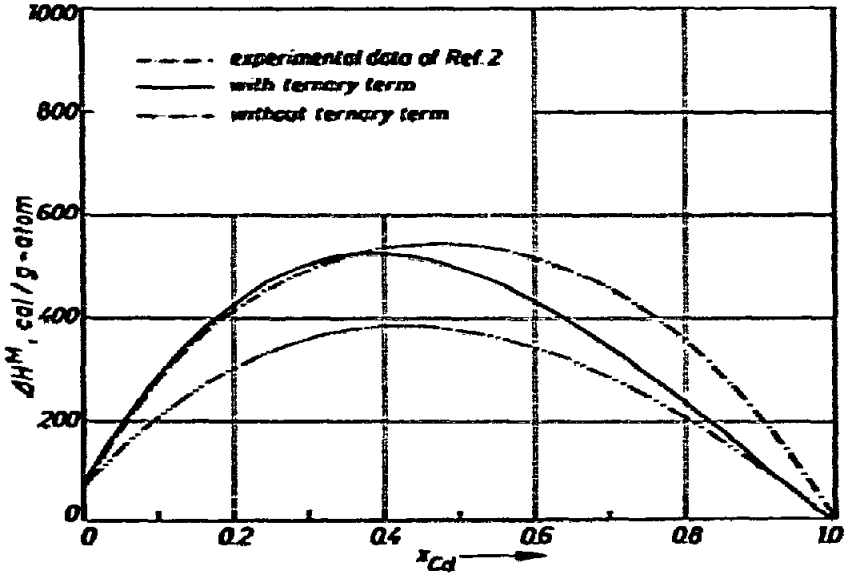

Fig. 4. Sub-regular model calculation for $x_{Tl}/x_{In} = 1/9$.

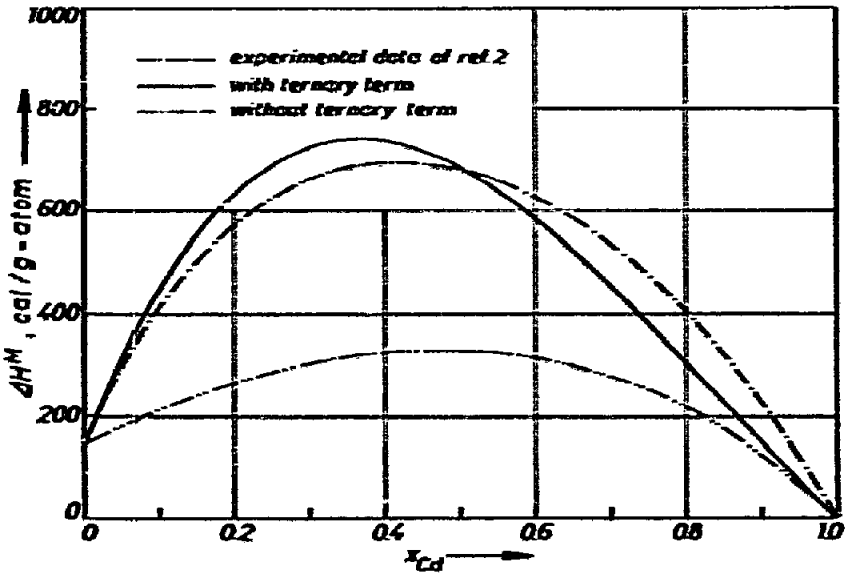

Fig. 5. Sub-regular model calculation for $x_{Tl}/x_{In} = 1$.

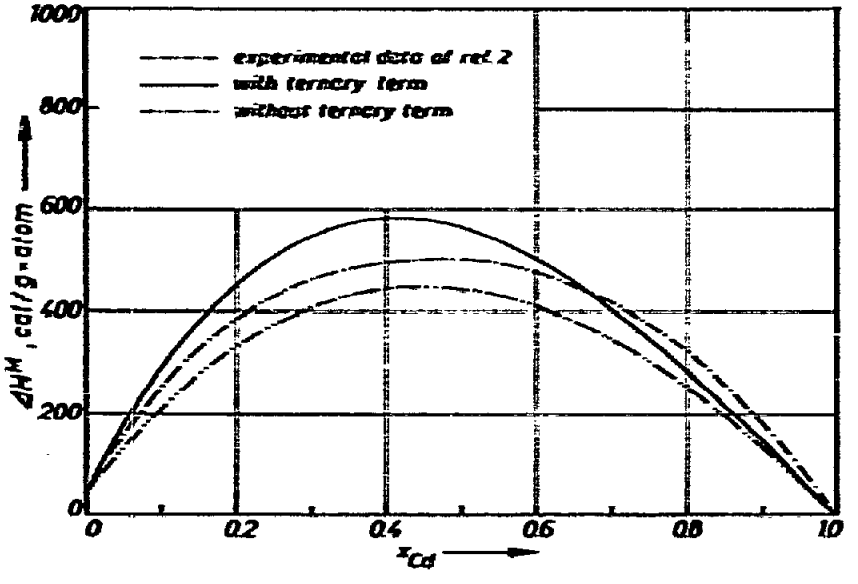

Fig. 6. Sub-regular model calculation for $x_{Tl}/x_{In} = 9$.

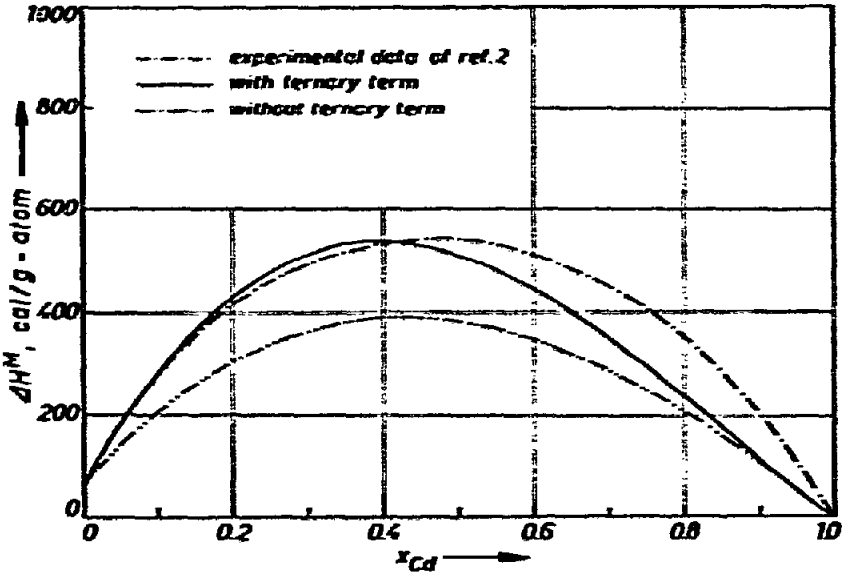

Fig. 7. Modified quasi-chemical model calculations for $x_{Tl}/x_{In} = 1.9$.

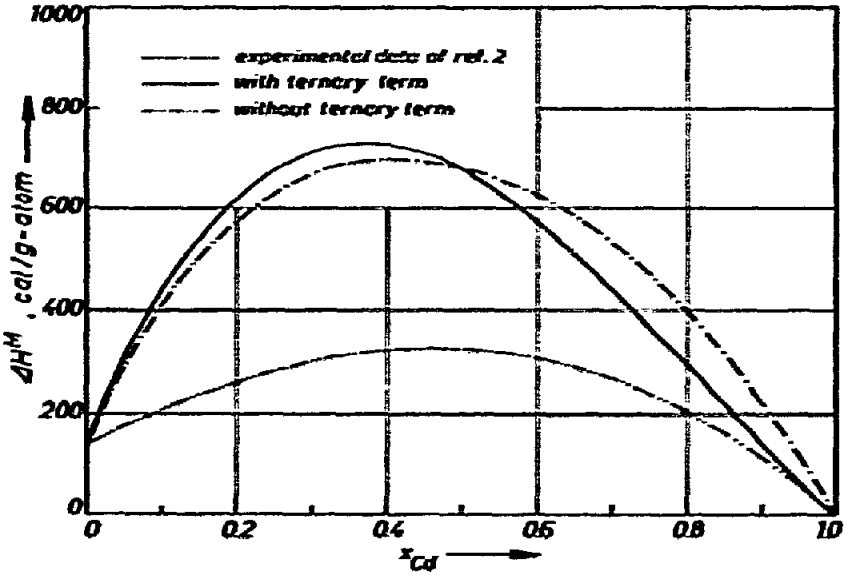

Fig. 8. Modified quasi-chemical model calculations for $x_{Tl}/x_{In} = 1$.

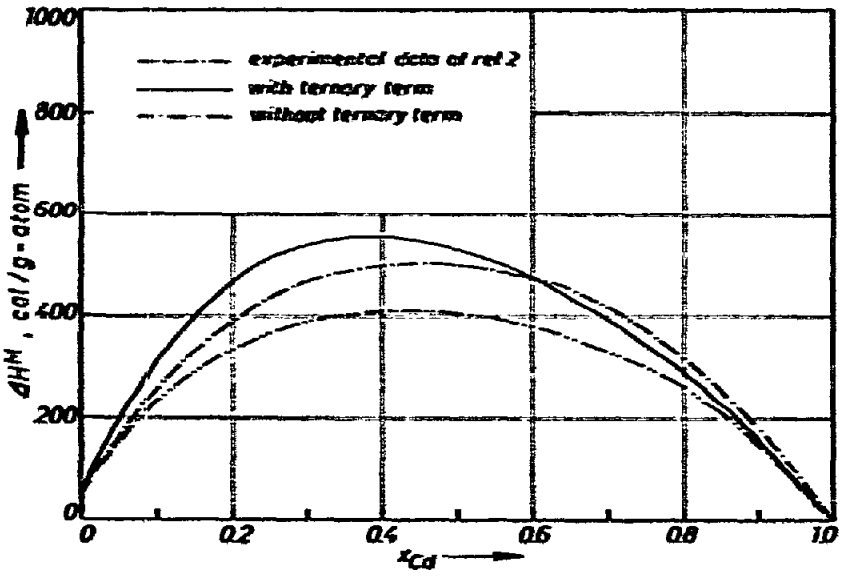

Fig. 9. Modified quasi-chemical model calculations for $x_{Tl}/x_{In} = 9$.

six coefficients obtained in this way were then averaged to yield a single interaction parameter. The resulting numbers, in cal/g-atom, are given below.

$$\alpha^{R}_{ABC} = 10066;\ \alpha^{SR}_{ABC} = 11233;\ \alpha^{SHP}_{ABC} = 11614 \qquad (15)$$

With the exception of the Tl/In ratio of 9 the individual coefficients differ by less than 15% from the average value.

The mixing enthalpies calculated using the above coefficients are compared to the experimental data and the calculations without the ternary term in Figs. 1–9. It is obvious that the addition of the ternary term yields much better agreement for all three models. However, it is not possible to differentiate among the three models since all three agree with the experimental data to approximately the same degree. In order to obtain a perspective of the mixing enthalpy surface a computer program was written which would plot the ternary data. The experimental data are shown in Fig. 10 and the calculated data from the three models in Figs. 11–13. From these figures it is obvious that the experimental data go through a maximum at about $x_{Cd} = 0.4$ for a Tl/In ratio of 1 while the model calculations without a ternary interaction term show a minimum in the mixing enthalpy surface.

On the basis of the above analysis it is concluded that the mixing enthalpies in the Cd–Tl–In system are adequately described with any of the three models considered but a ternary interaction term must be included.

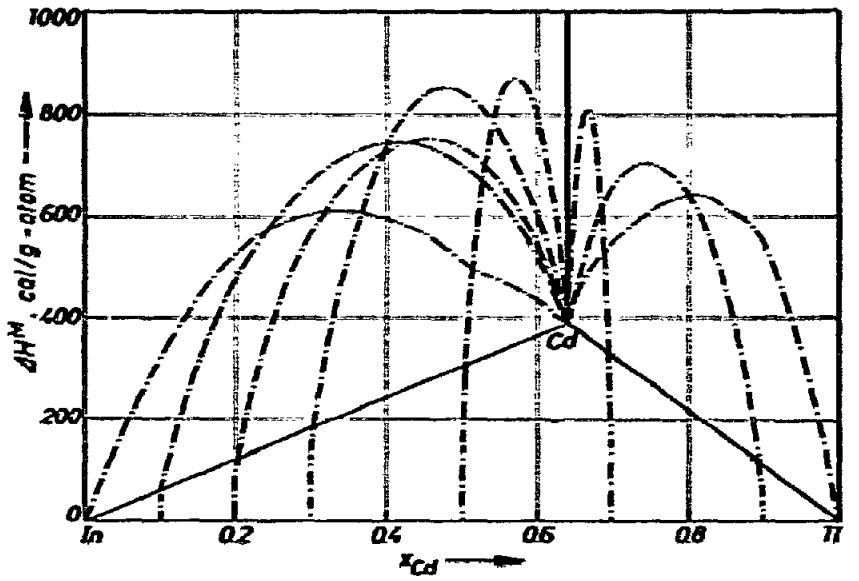

Fig. 10. Experimental data for Cd–Tl–In alloys (ref. 2).

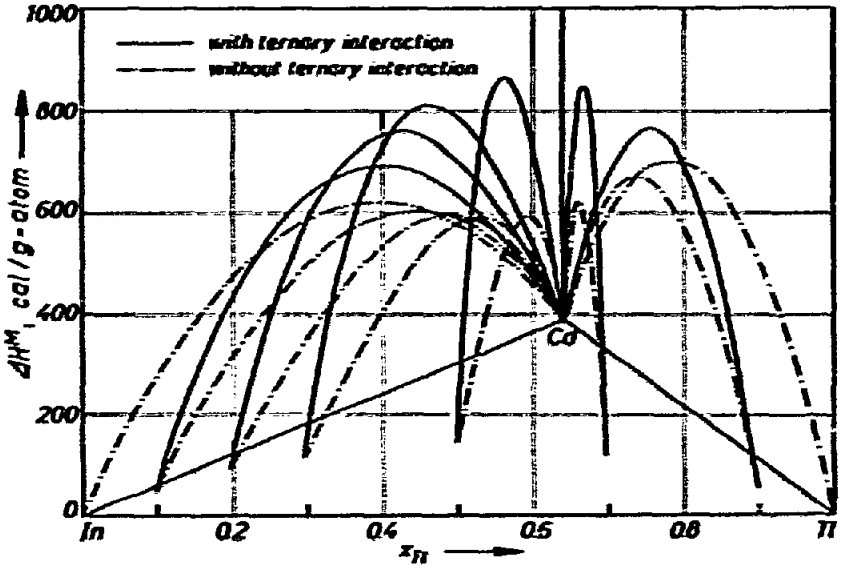

Fig. 11. Ternary mixing enthalpies for Cd–Tl–In calculated using the regular solution model.

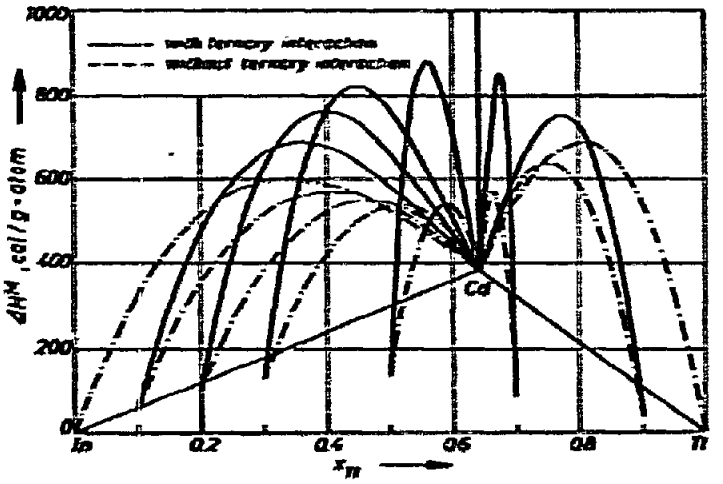

Fig. 12. Ternary mixing enthalpies for Cd–Tl–In calculated using the sub-regular solution model.

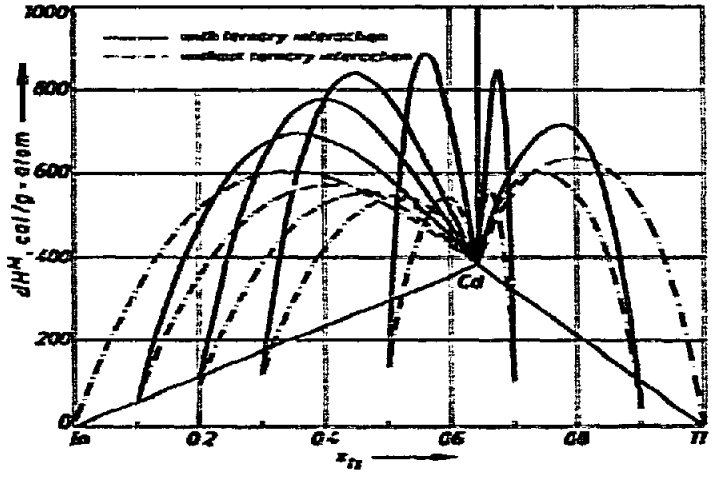

Fig. 13. Ternary mixing enthalpies for Cd–Tl–In calculated using the modified quasi-chemical model.

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