CALPHAD Vol.3, No.2, pp.109-118.
Pergamon Press Ltd. 1979. Printed in Great Britain.

SYNTHESIS OF AZEOTROPIC AND TWO TERMINAL SOLID SOLUTION TYPE BINARY DIAGRAMS

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Abstract

Synthesis of azeotropic and two terminal solid solution type phase diagrams has been carried out. Solution models used for the synthesis range from ideal to regular, quasi-chemical and surrounded atom models. In general, it is observed that the regular solution model is satisfactory, though the quasi-chemical model shows better approximation to experimentally determined diagrams. Synthesis based on the surrounded atom model shows marked deviations from that of the experimental diagrams. The discrepancy may be due to the errors in the calculations of the vibrational frequencies of the central atom for different configurations.

1. Introduction

The simplest type of solid solution interaction occurs when it is assumed that species and component mole numbers are the same. Such an assumption leads to equations which, when displayed graphically in a temperature - composition plot give a well known ascending type of solid solutions known as isomorphous systems.

Another frequently encountered solid solution type is one which exhibits a minimum in both its liquidus and solidus, the two curves touching tangentially at this minimum. Such a solid solution system is generally termed as minima type azeotrope. In this paper synthesis of these systems followed by two-terminal solid solution binary phase systems have been carried out.

2. Thermodynamic Treatment

a) Azeotropic Systems

In a binary system, when the composition of two phases in equilibrium is identical, the temperature-composition curve for each phase passes through a maximum or minimum. The systems which show this type of behaviour are many in number as evident from ASM metals Hand Book(1).

For equilibrium between two phases α and β at constant pressure in a binary system, the equations (1) and (2) are true in general.

$$S^{\alpha}\, dT + (1-x_{\alpha})\, d\mu_A + x_{\alpha}\, d\mu_B = 0 \tag{1}$$

$$S^{\beta}\, dT + (1-x_{\beta})\, d\mu_A + x_{\beta}\, d\mu_B = 0 \tag{2}$$

where μ_A and μ_B are the chemical potentials of components A and B respectively, S^{α} and S^{β} are the entropies of α and β phases respectively. Dividing through the equations (1) and (2) by dx (where x may be x_{α} or x_{β}) and on subtraction yields the equation (3)

$$-\,(S^{\alpha} - S^{\beta})\,\frac{dT}{dX} = (x_{\beta} - x_{\alpha})\,\left(\frac{d\mu_A}{dx} - \frac{d\mu_B}{dx}\right) \tag{3}$$

In equation (3), $S^{\beta} - S^{\alpha} = \delta S^{\alpha \to \beta} = \delta S_t$, the entropy change of the transformation $\alpha \to \beta$, and is equal to $(\delta H_t/T_t)$ for equilibrium transformation. Hence

$$(\delta H_T/T_t)\,\frac{dT}{dx} = (x_{\beta} - x_{\alpha})\left[\frac{d\mu_A}{dx} - \frac{d\mu_B}{dx}\right] \tag{4}$$

Under the condition that the composition of the two phases is identical at equilibrium (i.e. $x_\alpha = x_\beta$) and since δH_t is not zero, it is obvious that dT/dx is zero unless $d\mu_A/dx$ or $d\mu_B/dx$ is infinite. For vanishingly small values of x, whereby Henry's law $d\mu_B = RT\,d\ln x$, it is seen that $d\mu_B/dx$ (and similarly $d\mu_A/dx$) does approach infinity and hence this theorem is not valid in the immediate vicinity of the pure components(2). Also, it occasionally happens, in the vicinity of a strong compound or intermediate phase, that $d\mu_B/dx$ is very large, or, for practical purposes, substantially infinite, and the theorem is not valid. Hence, except in the vicinity of the pure components or of a strong compound, whenever the composition of two phases at equilibrium is identical, there is a maximum or minimum on the temperature-composition diagram.

The ideal solution model for the two α and L phases gives the following equations (5) and (6)

$$\delta G_A^{\alpha \to L} + RT \ln\,[(1-x_L)/(1-x_\alpha)] = 0 \qquad (5)$$

$$\delta G_B^{\alpha \to L} + RT \ln\,(x_L/x_\alpha) = 0 \qquad (6)$$

Applying the equations (5) and (6) to the azeotropic system in which $x_L = x_\alpha$, these equations become

$$\delta G_A^{\alpha \to L} = G_A^L - G_A^\alpha = 0 \text{ and } \delta G_B^{\alpha \to L} = G_B^L - G_B^\alpha = 0 \quad \text{or}$$

$$\delta H_A^{\alpha \to L}\,(1-\frac{T}{T_A}) = 0 \qquad (7)$$

$$\text{and} \quad \delta H_B^{\alpha \to L}\,(1-\frac{T}{T_B}) = 0 \qquad (8)$$

Since $\delta H_A^{\alpha \to L}$ and $\delta H_B^{\alpha \to L}$ terms are not equal to zero, T must be equal to T_A in equation (7) and equal to T_B in equation (8), referring to the melting points of the two pure components A and B. Since the theorem is not valid at the ends of the binary, azeotropic behaviour is not observed in ideal solution model.

Under regular solution model (5,8) for the equilibrium between two phases L and α, equations (9) and (10) are valid.

$$\delta G_A^{\alpha \to L} + RT \ln\ (1-x_L)/(1-x_\alpha) = x_\alpha^2\ W_\alpha - x_L^2\ W_L \qquad (9)$$

$$\delta G_B^{\alpha \to L} + RT \ln\,(x_L/x_\alpha) = (1-x_\alpha)^2\ W_\alpha - (1-x_L)^2\ W_L \qquad (10)$$

For $x_L = x_\alpha = x_a$, the two equations (9) and (10) become

$$\delta G_A^{\alpha \to L} = x_a^2\,(W_\alpha - W_L) \qquad (11)$$

$$\delta G_B^{\alpha \to L} = (1-x_a)^2\,(W_\alpha - W_L) \qquad (12)$$

or

$$\delta H_A^{\alpha \to L}\,(1-\frac{T_a}{T_A}) = x_a^2\,(W_\alpha - W_L) \qquad (13)$$

$$\delta H_B^{\alpha \to L} \left(1- \frac{T_a}{T_B}\right) = (1-x_a)^2 (W_\alpha - W_L) \qquad (14)$$

These two equations (13) and (14) can be simultaneously solved(10) for (x_a, T_a) which are the azeotropic composition and temperature respectively. If $W_\alpha = W_L$, equations (13) and (14) will be the same as equations (7) and (8). If $W_\alpha > W_L$, then the binary system shows a minima type of behaviour and if $W_\alpha < W_L$, the system shows a maxima type behaviour.

Under quasi-chemical model(7), for the equilibrium between L and α, equations (15) and (16) are valid.

$$\begin{aligned}\delta G_A^{\alpha \to L} &+ RT \ln [(1-x_L)/(1-x_\alpha)] \\ &= W_\alpha x_\alpha^2 \left[1 - \frac{W_\alpha}{ZRT} (1-x_\alpha) \ (3x_\alpha - 1)\right] \\ &- W_L x_L^2 \left[1 - \frac{W_L}{ZRT} (1-x_L) \ (3x_L - 1)\right] \qquad (15)\end{aligned}$$

$$\begin{aligned}\delta G_B^{\alpha \to L} &+ RT \ln (x_L/x_\alpha) \\ &= W_\alpha (1-x_\alpha)^2 \left[1 - \frac{W_\alpha}{ZRT} x_\alpha (2-3x_\alpha)\right] \\ &= W_L (1-x_L)^2 \left[1 - \frac{W_L}{ZRT} x_L (2-3x_L)\right] \qquad (16)\end{aligned}$$

For azeotropic composition and temperature $x_L = x_\alpha = x_a$ and $T = T_a$, and these two equations (15) and (16) become

$$\begin{aligned}\delta G_A^{\alpha \to L} &= (W_\alpha - W_L) \ [x_a^2 - (W_\alpha + W_L)(1-x_a) \\ &\quad (3x-1)/ZRT_a] \qquad (17)\end{aligned}$$

$$\begin{aligned}\delta G_B^{\alpha \to L} &= (W_\alpha - W_L) \ [(1-x_a)^2 - (W_\alpha + W_L) \ x_a \\ &\quad (2-3x_a)/ZRT_a] \qquad (18)\end{aligned}$$

These equations (17) and (18) are to be solved for (x_a, T_a).

Under the conditions of surrounded atom model(9) for the equilibrium between L and α, equations (19) and (20) are valid.

$$\begin{aligned}\delta G_A^{\alpha \to L} &+ RT \ln [(1-x_L)/(1-x_\alpha)] \\ &= W_\alpha x_\alpha^2 \left(1 - \frac{T}{\tau_\alpha}\right) - W_L x_L^2 \left(1 - \frac{T}{\tau_L}\right) \qquad (19)\end{aligned}$$

$$\begin{aligned}\delta G_B^{\alpha \to L} &+ RT \ln [x_L/x_\alpha] \\ &= W_\alpha (1-x_\alpha)^2 \left(1 - \frac{T}{\tau_\alpha}\right) - W_L (1-x_L)^2 \left(1 - \frac{T}{\tau_L}\right) \qquad (20)\end{aligned}$$

For the azeotropic composition and temperature $x_L = x_\alpha = x_a$ and $T = T_a$, these two equations (19) and (20) become

$$\delta G^{\alpha \to L} = (W_\alpha - W_L) \ x_a^2 - T_a \ x_a^2 \left(\frac{W_\alpha}{\tau_\alpha} - \frac{W_L}{\tau_L}\right) \qquad (21)$$

$$\delta G_B^{\alpha \rightarrow L} = (W_\alpha - W_L)\ (1-x_a)^2 - T_a\ (1-x_a)^2 \left(\frac{W_\alpha}{\tau_\alpha} - \frac{W_L}{\tau_L} \right) \tag{22}$$

These two equations (21) and (22) are to be solved for the azeotropic composition and temperature(10).

b) Two-terminal solid solutions with eutectic reaction

A two-terminal solid solution phase diagram with an invariant eutectic reaction is now considered. In this type of diagram, three phases L,α and β are present. The equilibrium relationships for obtaining the various boundaries are obtained as shown below.

To yield the phase boundaries of α/α+L and α+L/L on A-rich side, equations (5) and (6) are valid for ideal solution model, equations (9) and (10) are valid for regular solution model, equations (15) and (16) are valid for quasi-chemical model and equations (19) and (20) are valid for surrounded atom model.

To yield the phase boundaries of β/β+L and β+L/L on B-rich side for various types of models the equilibrium equations are obtained by replacing α by β in equations (5), (6), (9), (10), (15), (16), (19) and (20).

The equilibrium phase boundaries of α/α+β/β are obtained from the following equations under various models.

Ideal

$$\delta G_A^{\alpha \rightarrow \beta} + RT \ln\ [(1-x_\beta)/(1-x_\alpha)] = 0 \tag{23}$$

$$\delta G_B^{\alpha \rightarrow \beta} + RT \ln\ (x_\beta/x_\alpha) = 0 \tag{24}$$

Regular:

$$\delta G_A^{\alpha \rightarrow \beta} + RT \ln\ [(1-x_\beta)/(1-x_\alpha)] = x_\alpha^2 W_\alpha - x_\beta^2 W_\beta \tag{25}$$

$$\delta G_B^{\alpha \rightarrow \beta} + RT \ln\ (x_\beta/x_\alpha) = (1-x_\alpha)^2\ W_\alpha - (1-x_\beta)^2\ W_\beta \tag{26}$$

Quasi-chemical:

$$\begin{aligned} &\delta G_A^{\alpha \rightarrow \beta} + RT \ln\ [(1-x_\beta)/(1-x_\alpha)] \\ &= W_\alpha\ x_\alpha^2\ [1 - \frac{W_\alpha}{ZRT}\ (1-x_\alpha)\ \ (3x_\alpha-1)] \\ &- W_\beta\ x_\beta^2\ [1 - \frac{W_\beta}{ZRT}\ (1-x_\beta)\ \ (3x_\beta-1)] \end{aligned} \tag{27}$$

$$\begin{aligned} &\delta G_B^{\alpha \rightarrow \beta} + RT \ln\ (x_\beta/x_\alpha) \\ &= W_\alpha\ (1-x_\alpha)^2\ \ [1 - \frac{W_\alpha}{ZRT}\ \ x_\alpha\ (2-3x_\alpha)] \\ &- W_\beta\ (1-x_\beta)^2\ \ [1 - \frac{W_\beta}{ZRT}\ \ x_\beta\ (2-3x_\beta)] \end{aligned} \tag{28}$$

Surrounded atom model:

$$\delta G_A^{\alpha \to \beta} + RT \ln \left[(1-x_\beta)/(1-x_\alpha)\right]$$

$$= W_\alpha x_\alpha^2 \left(1 - \frac{T}{\tau_\alpha}\right) - W_\beta x_\beta^2 \left(1 - \frac{T}{\tau_\beta}\right) \quad (29)$$

$$\delta G_B^{\alpha \to \beta} + RT \ln (x_\beta/x_\alpha)$$

$$= W_\alpha (1-x_\alpha)^2 \left(1 - \frac{T}{\tau_\alpha}\right) - W_\beta (1-x_\beta)^2 \left(1 - \frac{T}{\tau_\beta}\right) \quad (30)$$

3. Results and Discussion

The systems copper-gold, nickel-palladium, columbium-molybdenum, columbium-vanadium and chromium-molybdenum have been considered. The T_o - x computation showed that (a) the liquid phase is in equilibrium with fcc phase in the case of copper-gold and nickel-palladium systems and (b) in the case of columbium-molybdenum, columbium-vanadium, and chromium-molybdenum, the liquid phase is in equilibrium with bcc phase. The synthesis of these diagrams has been carried out for all the three models of regular, quasi-chemical and surrounded-atom. The interaction parameters obtained and τ parameters calculated are presented in Tables I and II along with Debye temperatures for both liquid and solid phases(4,5,6).

TABLE 1

Interaction parameters in cal/g-atom for azeotropic systems

System A-B	e_o	e_p	e_1	e_2	e_3	e_4	W_L	W_β	W_ε	W_α
Cu-Au	0	1058	2175	0	0	0	1058	3773	3773	3773
Ni-Pd	0	2622	2137	0	0	0	2622	4759	4759	4759
Cb-Mo	0	97	834	0	0	0	97	931	931	931
Cb-V	0	144	2447	0	0	0	144	2591	2591	2591
Cr-Mo	0	1153	2137	0	0	0	1153	3290	3290	3290

TABLE II

Debye temperatures, interaction W and τ parameters for Azeotropic systems

System	Debye temperatures °K				Interaction parameters		τ parameters	
A-B	θ_A Solid	θ_A Liquid	θ_B Solid	θ_B Liquid	W Solid	W Liquid	Solid	Liquid
Cu-Au	343	208	165	115	3773	1058	806	342
Ni-Pd	450	253	274	173	4759	2622	2189	2036
Cb-Mo	275	211	450	224	931	97	651	4069
Cb-V	275	211	380	281	2591	144	4179	296
Cr-Mo	630	277	450	224	3290	1153	4890	4239

The synthesised diagrams are shown in Figures 1 to 5 and compared with experimental phase diagrams for ASM Hand Book(1) and compilation by Hansen and Anderko(3).

The synthesised solidus and liquidus of copper-gold system are below to that of experimental diagram as shown in Figure 1. The azeotropic composition is almost same. The experimental phase diagram shows an ordered fcc α' phase (Au Cu_3), an ordered fct α_1' and α_2' (Au Cu) and an ordered fcc α''' (Au_3Cu) at low temperature region. This part is not synthesised theoretically, but shown a miscibility gap corresponding to the interaction parameter of the solid solution phase.

Nickel-palladium system is shown in Figure 2 on which synthesised diagram is marked for all the models. In this case quasi-chemical model and regular solution model are almost following the experimental diagram. Here also a miscibility gap corresponding to the

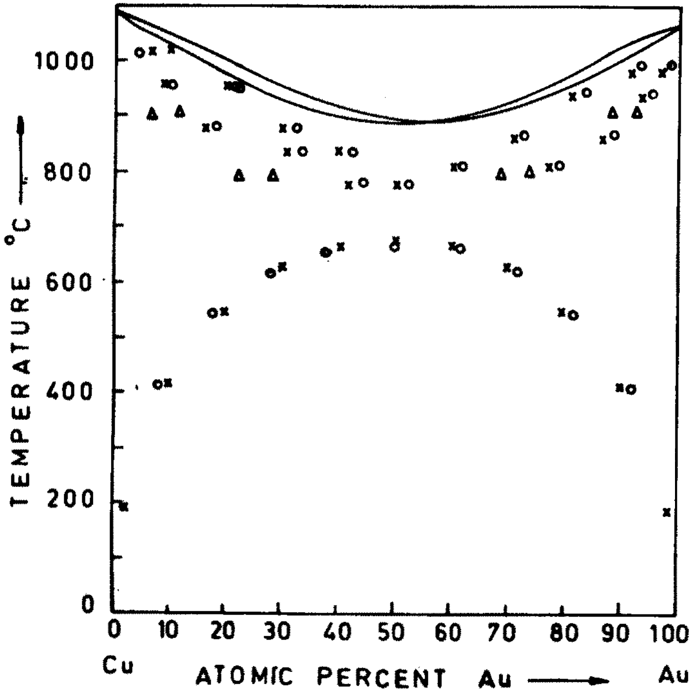

FIG. 1

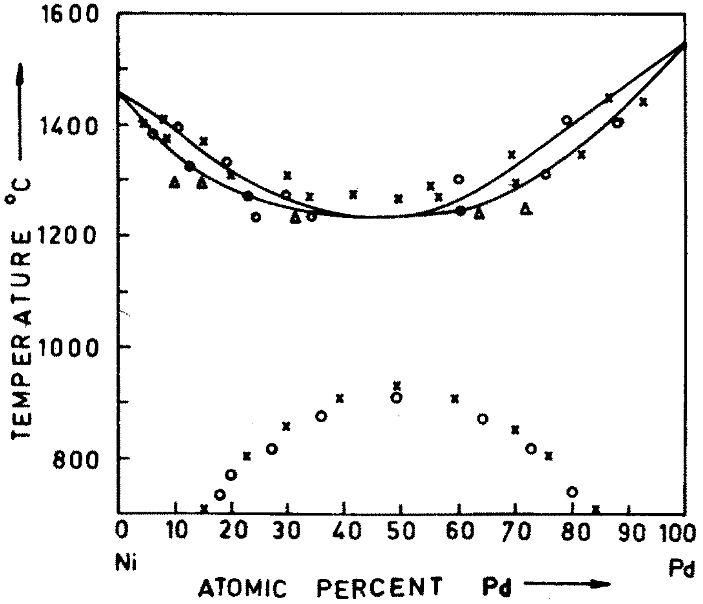

FIG. 2

SYNTHESIS OF MINIMA TYPE AZEOTROPE BINARY PHASE DIAGRAMS OF Cu-Au AND Ni-Pd

ooo_QUASI-CHEMICAL xxx_REGULAR ΔΔΔ_SURROUNDED ATOM.

—— EXPERIMENTAL

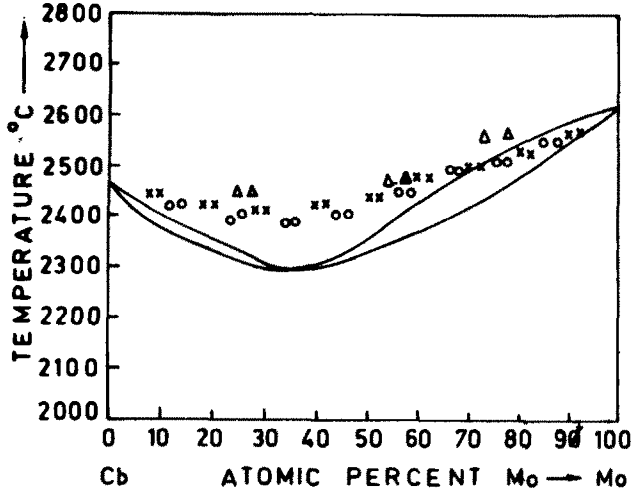

FIG. 3

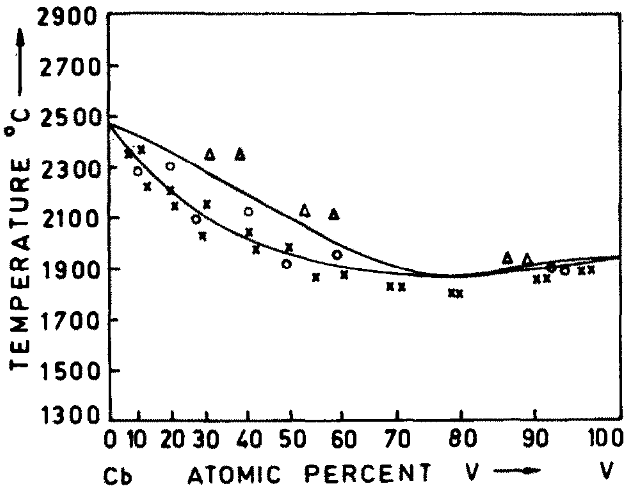

FIG. 4

SYNTHESIS OF MINIMA TYPE AZEOTROPE BINARY PHASE DIAGRAMS OF Cb-Mo AND Cb-V

ooo_QUASI-CHEMICAL xxx_REGULAR ΔΔΔ_SURROUNDED ATOM
—— EXPERIMENTAL

interaction parameter of the solid solution is shown in Figure 3 which is absent in experimental phase diagram.

The synthesised columbium-molybdenum system shown in Figure 3 is above the observed experimental diagram. But the azeotropic composition coincides with that experimentally observed.

In the case of columbium-vanadium, the synthesised solidus is in agreement with that of experimental solidus, but the synthesised liquidus is below that of the experimental as shown in Figure 4.

In Figure 5 is shown the experimental phase diagram of chromium-molybdenum. Both the experimental liquidus and solidus lines are above the synthesised ones.

The systems of silver-copper and cadium-zinc are shown in Figures 6 and 7. These diagrams have been synthesised and compared with experimental diagrams.

The interaction parameters, Debye temperatures and τ parameters are presented in Tables III and IV.

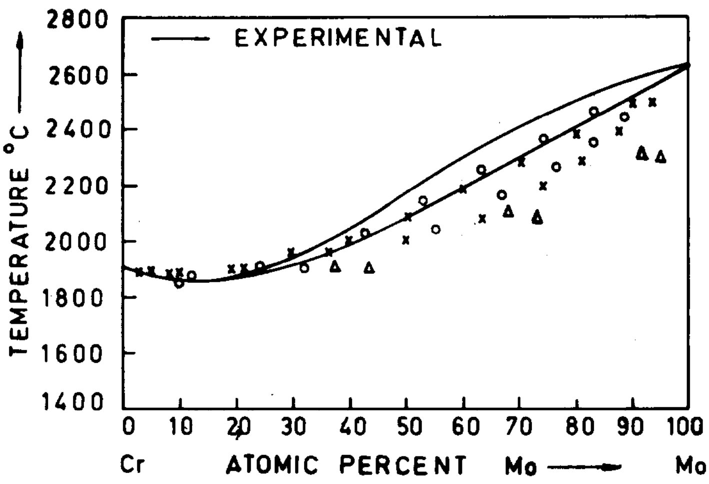

FIG. 5 _SYNTHESIS OF MINIMA TYPE AZEOTROPE BINARY PHASE DIAGRAM OF Cr - Mo

ooo_QUASI-CHEMICAL xxx_REGULAR
ΔΔΔ_SURROUNDED ATOM

TABLE III

Interaction parameters in cal/g-atom for two-terminal solid solutions with an eutectic

System A-B	e_0	e_p	e_1	e_2	e_3	e_4	W_L	W_β	W_ε	W_α
Ag-Cu	0	3380	2477	0	0	0	3380	5857	5857	5857
Cd-Zn	0	1125	865.6	0	0	0	1125	1991	1991	1991

TABLE IV

Debye temperatures,°K interaction W and τ parameters of two-terminal solid solutions

System A-B	Debye temperatures, °K				Interaction parameters		τ parameters	
	θ_A	θ_A	θ_B	θ_B	W	W		
	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid
Ag-Cu	225	136	343	208	5857	3380	2558	2110
Cd-Zn	209	89	327	117	1991	1125	1124	1691

The silver-copper synthesised diagram is in good agreement with the experimental diagram under regular solution model, but agreement with quasi-chemical model is better.

The synthesised cadmium-zinc system shows a minima type azeotropic followed by a miscibility gap whereas the experimental diagram is an eutectic with two-terminal solid solutions. This means the interaction parameter calculated for the solid solution is too small. If the parameter for the solid were larger, it would be possible to obtain the eutectic type diagram. This approach to the calculation of interaction parameter is not suited for this system.

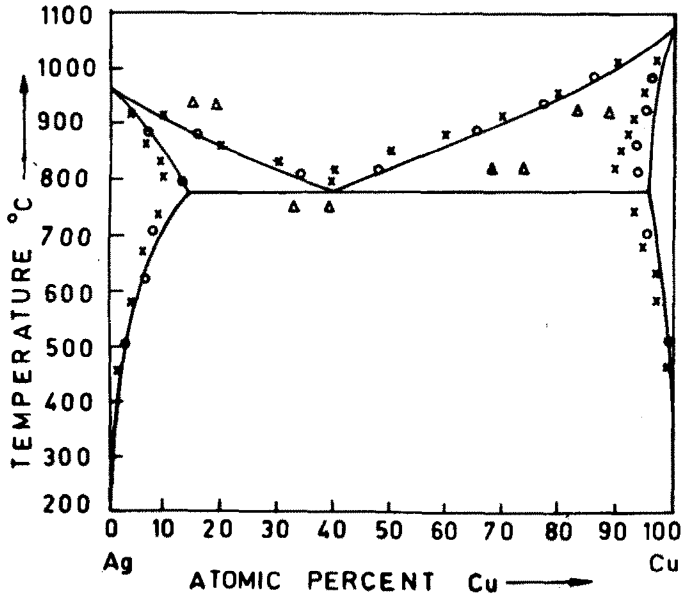

FIG. 6

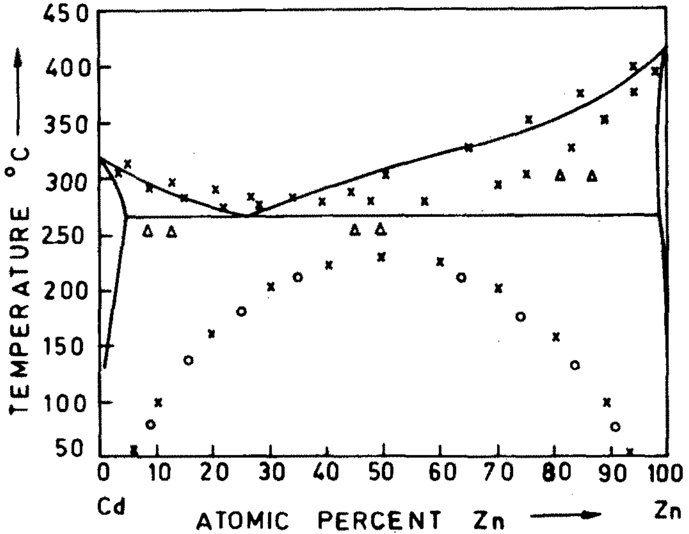

FIG. 7

SYNTHESIS OF BINARY PHASE DIAGRAMS OF EUTECTIC TYPE WITH TWO-TERMINAL SOLID SOLUTIONS OF Ag-Cu AND Cd-Zn SYSTEMS

ooo_QUASI-CHEMICAL xxx_REGULAR ΔΔΔ_SURROUNDED ATOM
—— EXPERIMENTAL

4. Conclusions

Various types of statistical thermodynamic models for ideal, regular, quasi-chemical and surrounded atom solutions were applied to minima azeotropes and two-terminal solid solution systems. In all the cases,it is found generally that the regular solution model is staisfactory. The quasi-chemical model is better than the regular solution model at first approximation. It may be possible to approach the experimental diagram more closely by considering higher order terms.

Synthesis based on the surrounded atom model shows marked deviations from that of experimental diagrams. This model may be quite satisfactory for the dilute alloys. The discrepancy may arise due to the difficulty in the calculation of the vibrational frequencies of the central atom for different configurations.

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