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Boundary Phase Stability and Critical Phenomena in Higher Order Solid Solution Systems II

Conditions for Critical Points and Approximate Solutions

By

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Mit 6 Abbildungen

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The thermodynamic treatment of double-pseudobinary solutions of the type $(A_xB_y)_{r_0}(M_uN_v)_{s_0}$ presented in a preceding publication was extended to include the conditions defining the critical points for the asymmetric case ($r_0 \neq s_0$) and approximations for the spinodal and binodal surface near the critical solution point.

Closed solutions for the coordinates of the critical points were obtained only for systems with ideal mixing behavior, and the isothermal binodal and spinodal near the critical solution point in such systems are adequately approximated by circles and ellipses, respectively. An axes ratio of $\sqrt{3}$ is nearly independent of the relative sublattice abundance and the major effect of changes in the ratio $\frac{s_0}{r_0}$ is a rotation of the binodal by an angle $\operatorname{tg} \alpha = \sqrt{\frac{s_0}{r_0}}$.

The principal features of nonideal regular systems for temperatures close to the critical solution point are described by expressions derived from small term expansions of the conditional equations, but generalizations are not possible to the same extent as for the case with ideal boundary systems. The results are discussed and the application of the equations demonstrated on model examples.

Introduction

In a preceding publication[1] the stability conditions, as well as the equations describing the binodal and spinodal surfaces in double-pseudobinary solid solutions $(A_xB_y)_{r_0}(M_uN_v)_{s_0}$ were derived and the symmetrical case, characterized by equal abundance of the two sublattices ($r_0 = s_0 = 1$), discussed in greater detail. In particular, it was demonstrated, that critical phenomena in such systems can be induced by proper choice of the stabilities of the binary boundary phases and thus are not by necessity bound to nonideal mixing behavior. The close formal relationships between the binary regular solution model and the formulation for the double pseudobinary solution with ideal mixing behavior, in which the role of the interaction coefficient is taken by the free energy difference

$$\Delta\Delta\, G_f = \Delta\, G_{f,\, A_{r_0}M_{s_0}} + \Delta\, G_{f,\, B_{r_0}N_{s_0}} - \Delta\, G_{f,\, A_{r_0}N_{s_0}} - \Delta\, G_{f,\, B_{r_0}M_{s_0}},$$

is noteworthy, particularly in view of the fact, that the regular solution appears as the zeroth order approximation of a statistical model limited to only nearest neighbor interactions[2]. The double-pseudobinary solution thus appears to be an ideal model case for examining the statistical approach and we hope to report on this subject at a later date.

Our primary concern in the discussion here will be to extend the thermodynamic treatment to include the asymmetric ($r_0 \neq s_0$) case of the double-pseudobinary solid solution, to obtain additional relations characterizing the critical points in such systems, and to derive useful approximations for the description of the phase phenomena in the vicinity of the critical solution point.

I. Conditions for the Critical Point

Consider the double-pseudobinary solid solution

$$(A_xB_y)_{r_0}\,(M_uN_v)_{s_0}$$

with the integral free energy

$$G = r_0\,(x\mu_A + y\mu_B) + s_0\,(u\mu_M + v\mu_N),$$

μ_i = thermodynamic potential of component i.

Noting the form of the derivatives,

$$\left(\frac{\partial G}{\partial x}\right)_u = r_0\,(\mu_A - \mu_B)$$

$$\left(\frac{\partial G}{\partial u}\right)_x = s_0\,(\mu_M - \mu_N),$$

we define thermodynamic potentials Ω and θ by *Legendre* transformation of G according to (T, p = const):

$$\Omega\,(u, \mu_A - \mu_B) = G - x\left(\frac{\partial G}{\partial x}\right)_u$$

$$\theta\,(x, \mu_M - \mu_N) = G - u\left(\frac{\partial G}{\partial u}\right)_x .$$

Since

$$\left(\frac{\partial^2 \Omega}{\partial u^2}\right)_{\mu_A - \mu_B} = \frac{G_{xx}\,G_{uu} - (G_{xu})^2}{G_{xx}}$$

and

$$\left(\frac{\partial^2 \theta}{\partial x^2}\right)_{\mu_M - \mu_N} = \frac{G_{xx}\,G_{uu} - (G_{xu})^2}{G_{uu}},$$

the condition for stability in terms of the transformed functions is now specified by

$$\left(\frac{\partial^2 \Omega}{\partial u^2}\right)_{\mu_A - \mu_B} \geqslant 0 \text{ and } \left(\frac{\partial^2 \theta}{\partial x^2}\right)_{\mu_M - \mu_N} \geqslant 0.$$

Considering that

$$\left(\frac{\partial \Omega}{\partial u}\right)_{\mu_A - \mu_B} = (\mu_M - \mu_N)$$

and

$$\left(\frac{\partial \theta}{\partial x}\right)_{\mu_M - \mu_N} = (\mu_A - \mu_B)$$

we observe, that the system will always be stable if $(\mu_M - \mu_N)_{\mu_A - \mu_B}$ and $(\mu_A - \mu_B)\,\mu_M - \mu_N$ increase monotonically with u and x, resp. Conversely, unstable states are characterized by monotonically decreasing functions $[\mu_M - \mu_N]\,(u)$ and $[\mu_A - \mu_B]\,(x)$, and the boundary between stable and unstable states (spinodal) are characterized by the extrema of these functions, i.e.

$$\left(\frac{\partial\,(\mu_M - \mu_N)}{\partial u}\right)_{\mu_A - \mu_B} = \left(\frac{\partial^2 \Omega}{\partial u^2}\right)_{\mu_A - \mu_B} = 0 \qquad (1\,\mathrm{a})$$

$$\left(\frac{\partial\,(\mu_A - \mu_B)}{\partial x}\right)_{\mu_M - \mu_N} = \left(\frac{\partial^2 \theta}{\partial x^2}\right)_{\mu_A - \mu_B} = 0. \qquad (1\,\mathrm{b})$$

The transition between stable and unstable states at the critical solution point is thus marked by an inflection point and we obtain as additional condition ($T, p = \text{const}$):

$$\left(\frac{\partial^3 \Omega}{\partial u^3}\right)_{\mu_A - \mu_B} = 0 \text{ and } \left(\frac{\partial^3 \theta}{\partial x^3}\right)_{\mu_M - \mu_N} = 0. \tag{2}$$

Conditions (1) and (2) are sufficient to define the critical points of the system.

The third derivatives of Ω and θ in terms of the derivatives of the free energy G are given by

$$\left(\frac{\partial^3 \Omega}{\partial u^3}\right)_{\mu_A - \mu_B} = G_{uuu} - 3\, G_{uux} \left(\frac{G_{xu}}{G_{xx}}\right) + 3\, G_{uxx} \left(\frac{G_{xu}}{G_{xx}}\right)^2 - G_{xxx} \left(\frac{G_{xu}}{G_{xx}}\right)^3 \tag{3a}$$

$$\left(\frac{\partial^3 \theta}{\partial x^3}\right)_{\mu_M - \mu_N} = G_{xxx} - 3\, G_{xxu} \left(\frac{G_{xu}}{G_{uu}}\right) + 3\, G_{xuu} \left(\frac{G_{xu}}{G_{uu}}\right)^2 - G_{uuu} \left(\frac{G_{xu}}{G_{uu}}\right)^3. \tag{3b}$$

In order to apply equations (1) and (2), it is necessary to express G in terms of the independent thermodynamic parameters of the system. For the description we choose the regular solution model with two independent interaction coefficients ε_M and ε_i for the two sublattices (A, B) and (M, N), resp.[1]. The ideal case is then given by $\varepsilon_M = \varepsilon_i = 0$. With these assumptions, the integral free energy of the solid solution system becomes

$$\begin{gathered} G = xuG^0_{A_{r_0}M_{s_0}} + yuG^0_{B_{r_0}M_{s_0}} + xvG^0_{A_{r_0}N_{s_0}} + yvG_{B_{r_0}N_{s_0}} + G^{mix}, \\ \frac{G^{mix}}{RT} = r_0 \left(\frac{\varepsilon_M}{RT} xy + x \ln x + y \ln y\right) + s_0 \left(\frac{\varepsilon_i}{RT} uv + u \ln u + v \ln v\right), \end{gathered} \tag{4}$$

with the derivatives

$$\begin{aligned} G_{xx} &= RTr_0 \left(-2\, \varepsilon_M + \frac{1}{x} + \frac{1}{y}\right) \\ G_{xxx} &= RTr_0 \left(-\frac{1}{x^2} + \frac{1}{y^2}\right) \\ G_{xxu} &= G_{uux} = 0 \\ G_{xu} &= \Delta\Delta\, G_f \\ G_{uu} &= RTs_0 \left(-2\, \varepsilon_i + \frac{1}{u} + \frac{1}{v}\right) \\ G_{uuu} &= RTs_0 \left(-\frac{1}{u^2} + \frac{1}{v^2}\right). \end{aligned}$$

Since the mixed derivatives G_{xxu} and G_{uux} are zero, conditions (3 a) and (3 b) for the critical point reduce to:

$$(G_{xx})^3\, G_{uuu} = G_{xxx}\, (G_{xu})^3$$

and

$$(G_{uu})^3\, G_{xxx} = G_{uuu}\, (G_{xu})^3.$$

Substitution of the derivatives of G into the above expressions and rearrangement of the terms results in the relations:

$$r_0\, s_0^2 \left(\frac{x-y}{u-v}\right) \frac{1}{x^2\, y^2\, uv} \left(1 - \frac{2\,\varepsilon_i\, uv}{RT}\right)^3 = \left(\frac{\Delta\Delta\, G_F}{RT}\right)^3$$

$$r_0^2\, s_0 \left(\frac{u-v}{x-y}\right) \frac{1}{u^2\, v^2\, xy} \left(1 - \frac{2\,\varepsilon_M\, xy}{RT}\right)^3 = \left(\frac{\Delta\Delta\, G_F}{RT}\right)^3.$$

Combining both equations and substituting the pseudobinary critical temperatures for the interaction coefficients,

$$\varepsilon_M = 2\, RT_{c_1};\quad \varepsilon_i = 2\, RT_{c_2},$$

and further introducing the reduced temperatures

$$\bar{T}_1 = \frac{T}{T_{c1}};\quad \bar{T}_2 = \frac{T}{T_{c2}},$$

we obtain the equation in its final form:

$$r_0\, \frac{xy}{(x-y)^2} \left(1 - \frac{4\,xy}{\bar{T}_1}\right)^3 = s_0\, \frac{uv}{(u-v)^2} \left(1 - \frac{4\,uv}{\bar{T}_2}\right)^3. \tag{5}$$

Relation (5), together with the spinodal calculated from (1):

$$\left(\frac{1}{4\,xy} - \frac{1}{\bar{T}_1}\right) \left(\frac{1}{4\,uv} - \frac{1}{\bar{T}_2}\right) = \frac{1}{\bar{T}_3^2}$$

$$\Delta\Delta\, G_f = 4\, RT_{c3} \sqrt{r_0 s_0};\quad \bar{T}_3 = \frac{1}{\bar{T}_{c3}}, \tag{6}$$

define the coordinates of the critical points of the regular double-pseudobinary solid solution $(A_xB_y)_{r_0}\, (M_uN_v)_{s_0}$ at the temperature T.

For calculation purposes, but especially for carrying out small term expansions for approximations, it is convenient to shift the origin of the concentration coordinates to the center of the composition quadrangle. We substitute:

$$x = \frac{1}{2} + s;\quad u = \frac{1}{2} + t,$$

and conditional equations (5) and (6), rewritten in the new coordinates s and t, become then:

$$r_0\left(\frac{1-4s^2}{s^2}\right)\left(1-\frac{1-4s^2}{\overline{T}_1}\right)^3=s_0\left(\frac{1-4t^2}{t^2}\right)\left(1-\frac{1-4t^2}{\overline{T}_2}\right)^3 \tag{7}$$

$$\left(\frac{1}{1-4s^2}-\frac{1}{\overline{T}_1}\right)\left(\frac{1}{1-4t^2}-\frac{1}{\overline{T}_2}\right)=\frac{1}{\overline{T}_3^2}. \tag{8}$$

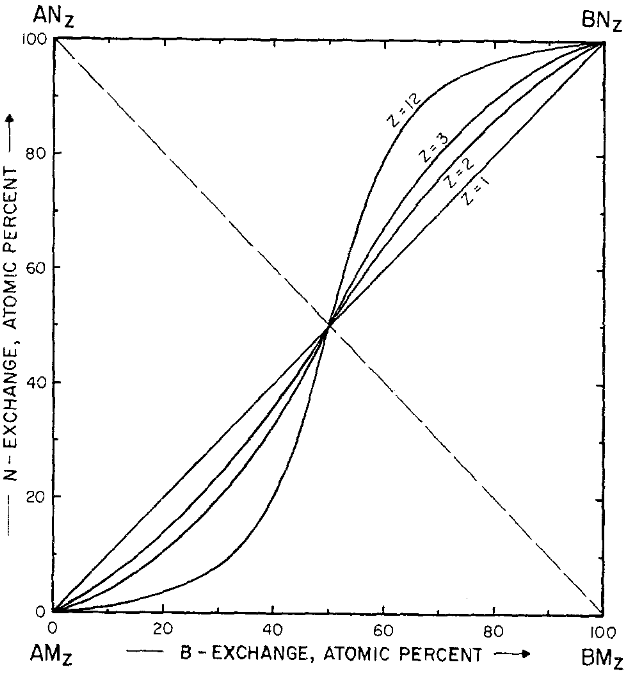

Fig. 1. Plot of the function:

$$r_0\frac{xy}{(x-y)^2}\left(1-\frac{4xy}{\overline{T}_1}\right)^3=s_0\frac{uv}{(u-v)^2}\left(1-\frac{4uv}{\overline{T}_2}\right)^3$$

for different parameter values $z=\left(\frac{s_0}{r_0}\right)$

II. Calculation of the Coordinates of the Critical Points and Approximate Solutions for the Binodal and Spinodal near the Critical Solution Point

A. *Ideal Boundary Systems*

For this particular case we have

$$T_{c_1}=T_{c_2}=0 \text{ and } T_{c_3}=T_c.$$

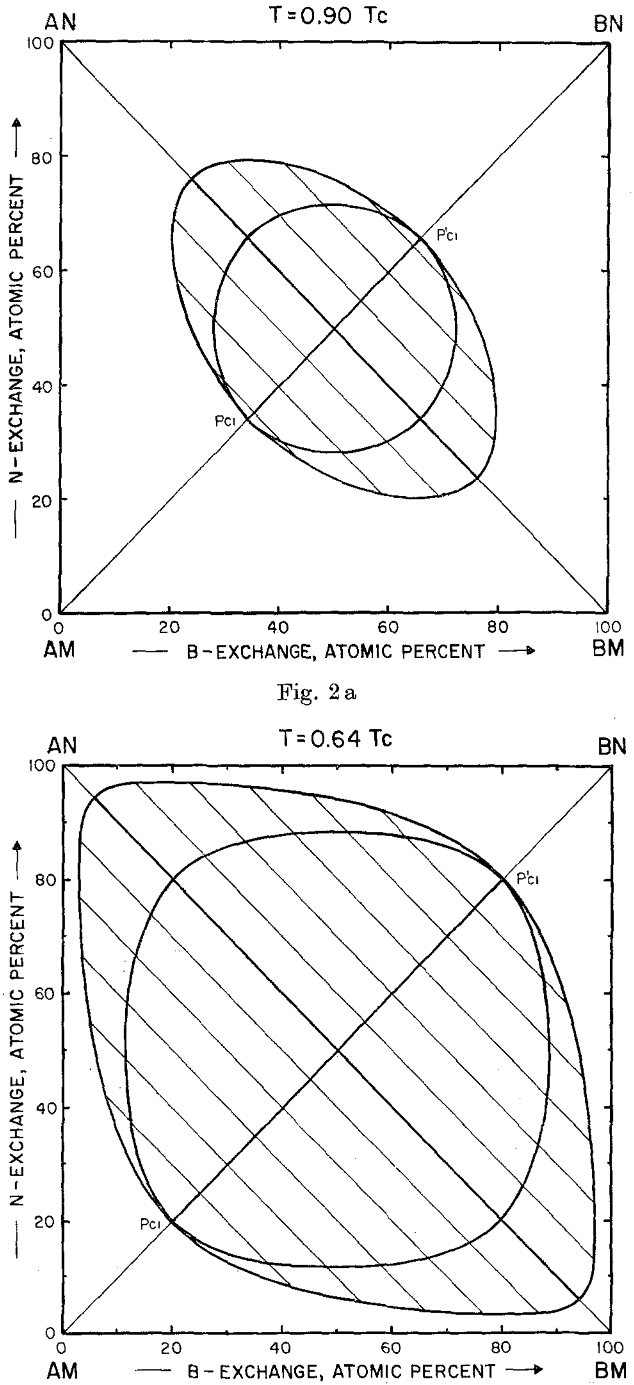

Fig. 2a

Fig. 2b

Fig. 2. Binodal and spinodal curves for the ideal symmetric, $r_0 = s_0$, double-pseudobinary solid solution; (a) $\overline{T} = 0.90$; (b) $\overline{T} = 0.64$

Because condition (7) does not contain any other variables but the concentrations and the sublattice abundance factors s_0 and r_0, and can be presented in the form

$$R\left(x, u, \frac{s_0}{r_0}\right) = 0\,,$$

the critical points are conveniently located graphically as the intersection points of parametric plots of condition (7), Fig. 1, with the spinodal at the desired value of $\bar{T}$. Since the shape of the spinodal remains unaffected by the sublattice abundance factors and is roughly circular at temperatures not too far from the critical solution point, the principal effect of variations in $z = \frac{s_0}{r_0}$ is a partial revolution of the binodal around the (fixed) binodal. This behavior is shown in graphs 2 through 4 for values of z of 1, 3, and 12. The spinodals for these examples were calculated using equation (8), and the binodals from the relations[1]:

$$(u' - u'') = \bar{T}\frac{r_0}{4\sqrt{r_0 s_0}} \ln \frac{x''}{y''} \cdot \frac{x'}{y'} \tag{9a}$$

$$(x' - x'') = \bar{T}\frac{s_0}{4\sqrt{r_0 s_0}} \ln \frac{u''}{v''} \cdot \frac{v'}{u'} \tag{9b}$$

$$(x''u'' - x'u') = \frac{\bar{T}}{4\sqrt{r_0 s_0}}\left(r_0 \ln \frac{y''}{y'} + s_0 \ln \frac{v''}{v''}\right). \tag{9c}$$

Examining the boundaries in Fig. 2 through 4, it will be noted that the principal dimensions of the binodal near the critical solution point are also largely unaffected by the choice of z and are roughly elliptical in shape.

Solving equations (7) and (8) for t and s yields the coordinates of the critical points:

$$s^2 = \frac{2\,r_0 - (r_0 - s_0)\,\bar{T}^2}{8\,r_0}\left[1 - \sqrt{1 - \frac{4\,r_0^2\,(1 - \bar{T}^2)}{[(r_0 - s_0)\,\bar{T}^2 - 2\,r_0]^2}}\right] \tag{10a}$$

$$t^2 = \frac{2\,s_0 - (s_0 - r_0)\,\bar{T}^2}{8\,s_0}\left[1 - \sqrt{1 - \frac{4\,s_0^2\,(1 - \bar{T}^2)}{[(s_0 - r_0)\,\bar{T}^2 - 2\,s_0]^2}}\right] \tag{10b}$$

From a small term expansion of (10 a) and (10 b) for the vicinity of the critical solution point we immediately get the next lower approximation

$$s^2 = \frac{1}{4}\left(\frac{r_0}{r_0 + s_0}\right)(1 - \overline{T}^2)\left[1 + \left(\frac{r_0}{r_0 + s_0}\right)^2 (1 - \overline{T}^2)\right] \qquad (11\,\mathrm{a})$$

$$t^2 = \frac{1}{4}\left(\frac{s_0}{r_0 + s_0}\right)(1 - \overline{T}^2)\left[1 + \left(\frac{s_0}{r_0 + s_0}\right)^2 (1 - \overline{T}^2)\right] \qquad (11\,\mathrm{b})$$

Table 1. *Comparison between the Exact Location of the Critical Points (equation* 10) *and Coordinates Obtained from the Zeroth Order Approximation* (12) *at* $\overline{T} = 0.90$

	s (±)		t (∓)	
z	Exact	From Approx. (12)	Exact	From Approx. (12)
2	0.132	0.126	0.180	0.178
3	0.115	0.109	0.190	0.189
12	0.066	0.063	0.210	0.209

or, discarding the first order temperature correction terms in the square brackets, the zeroth order approximation:

$$s^2 \simeq \frac{1}{4}\left(\frac{r_0}{r_0 + s_0}\right)(1 - \overline{T}^2) \qquad (12\,\mathrm{a})$$

$$t^2 \simeq \frac{1}{4}\left(\frac{s_0}{r_0 + s_0}\right)(1 - \overline{T}^2). \qquad (12\,\mathrm{b})$$

The agreement between the exact coordinates of the critical points calculated from relations (10) and those determined from the zeroth order approximation (12) for $\overline{T} = 0.90$ is quite good, as evidenced by the data presented in Table 1. The slope of the critical tie lines, obtained as

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Fig. 3. Binodal and spinodal curves for an ideal asymmetric double-pseudobinary solid solution with

$$z = \left(\frac{s_0}{r_0}\right) = 3 \quad \text{(a)} \quad \overline{T} = 0.90 \quad \text{(b)} \quad T = 0.64$$

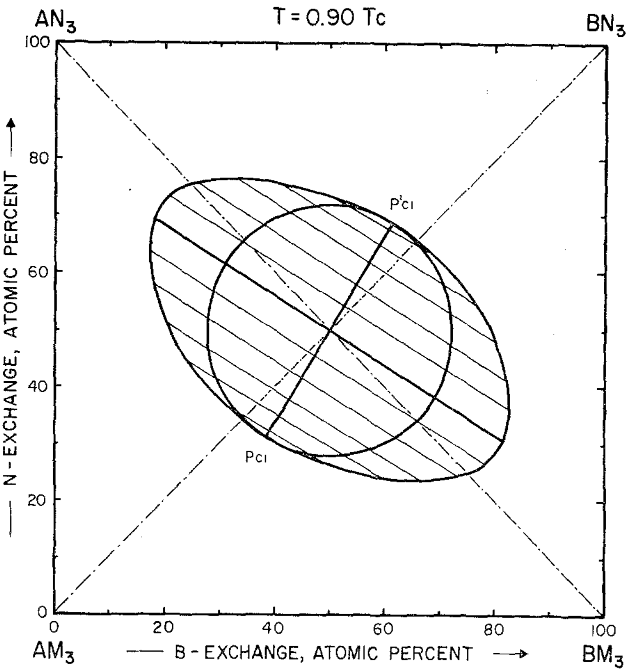

AN_3
T = 0.90 Tc
BN_3
100
80
60
40
20
0
N - EXCHANGE, ATOMIC PERCENT →
P'_{c1}
P_{c1}
0
20
40
60
80
100
AM_3
— B - EXCHANGE, ATOMIC PERCENT →
BM_3

Fig. 3 a

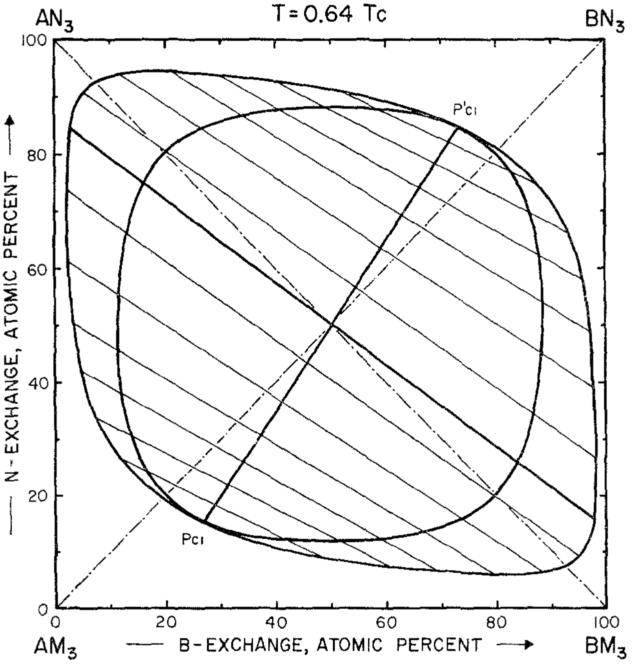

AN_3
T = 0.64 Tc
BN_3
100
80
60
40
20
0
N - EXCHANGE, ATOMIC PERCENT →
P'_{c1}
P_{c1}
0
20
40
60
80
100
AM_3
— B - EXCHANGE, ATOMIC PERCENT →
BM_3

Fig. 3 b

slope of the binodal at the critical points, and the slope of the line through both critical points (minor axis) are given by:

$$S = \left(\frac{\mathrm{d}t}{\mathrm{d}s}\right)_{P_c} = \left(\frac{\mathrm{d}v}{\mathrm{d}y}\right)_{P_c} \cong -\sqrt{\frac{r_0}{s_0}}\left[1 + \frac{1}{2}\left(\frac{r_0 - s_0}{r_0 + s_0}\right)(1 - \overline{T}^2)\right] \tag{13}$$

$$S' = \frac{t}{s} \cong \sqrt{\frac{s_0}{r_0}}\left[1 + \frac{1}{2}\left(\frac{r_0 - s_0}{r_0 + s_0}\right)(1 - \overline{T}^2)\right]. \tag{14}$$

The first order temperature correction terms contained in the square brackets of (13) and (14) are small at temperatures close to T_c and can be neglected for approximate calculations. We thus find the critical tie lines to be roughly perpendicular to the line connecting the critical points.

From the binodal (9) we further obtain for the end points of the tie line through the symmetry center s, t (0,0) the approximations

$$s_1 \simeq \pm \frac{\sqrt{3}}{2}\sqrt{\left(\frac{s_0}{r_0 + s_0}\right)(1 - \overline{T}^2)} \tag{15a}$$

$$t_1 \simeq \mp \frac{\sqrt{3}}{2}\sqrt{\left(\frac{r_0}{r_0 + s_0}\right)(1 - \overline{T}^2)} \tag{15b}$$

and from these coordinates the slope of the major axis:

$$S_1 = \frac{t_1}{s_1} \cong -\sqrt{\frac{r_0}{s_0}}. \tag{16}$$

In the limit, the major axis has thus the same slope as the critical tie lines.

Table 2 gives a comparison between the exact values of the coordinates and those calculated with the aid of approximations (15) for $z = 2$, 3, and 12. As can be seen from the data, agreement between the exact and calculated values is not as good as in the approximation for the critical points, but still satisfactory. In particular, equations (15) predict major axes which are systematically too long and a closer approximation would therefore have to include higher order terms in the expansion of the equation for the binodal.

Fig. 4. Binodal and spinodal curves for an ideal asymmetric double-pseudobinary solid solution with

$$z = \left(\frac{s_0}{r_0}\right) = 12 \quad \text{(a)} \quad \overline{T} = 0.90 \quad \text{(b)} \quad \overline{T} = 0.64$$

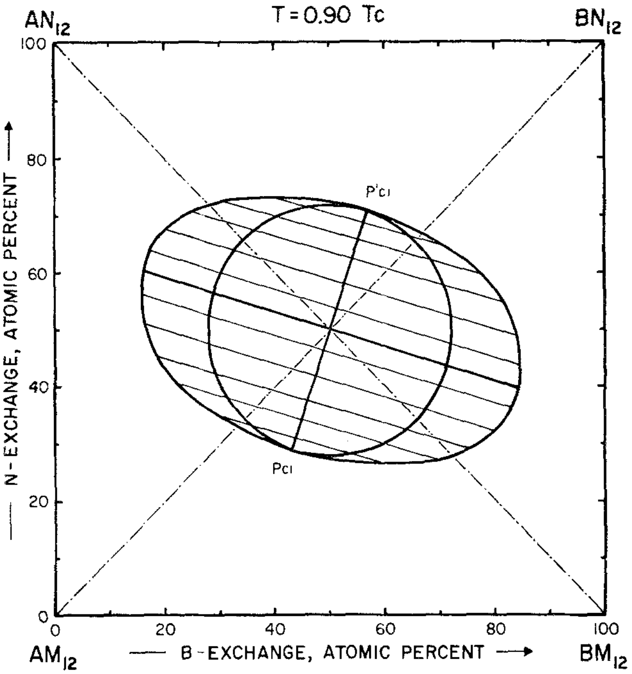

T=0.90 Tc
AN12
BN12
AM12
BM12
P'c1
Pc1
N-EXCHANGE, ATOMIC PERCENT
B-EXCHANGE, ATOMIC PERCENT
0
20
40
60
80
100

Fig. 4a

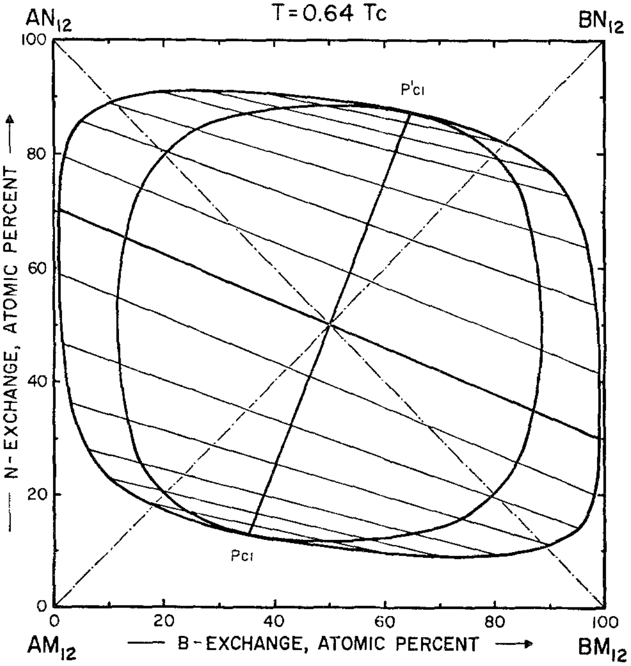

T=0.64 Tc
AN12
BN12
AM12
BM12
P'c1
Pc1
N-EXCHANGE, ATOMIC PERCENT
B-EXCHANGE, ATOMIC PERCENT
0
20
40
60
80
100

Fig. 4b

From relations (12) and (15) we obtain for the dimensions of the minor and major axis

$$d^2_{\text{minor}} = (1 - \bar{T}^2)$$

$$d^2_{\text{major}} = 3\,(1 - \bar{T}^2).$$

A nearly constant axes ratio of $\sim\sqrt{3}$ is thus in agreement with the qualitative inspection of the boundaries in Figs. (2 a), (3 a), and (4 a).

Table 2. *Comparison between the Exact Coordinates of the Tie Line through s, t, (0.0) and Values Calculated from the Zeroth Approximation* (15) *at* $T = 0.90\,T_c$

z	s_1 ($\pm$)		t_1 ($\mp$)	
	Exact	From Approx. (15)	Exact	From Approx. (15)
2	0.297	0.308	0.218	0.218
3	0.312	0.327	0.190	0.189
12	0.338	0.363	0.107	0.105

The approximate equations for the spinodal and binodal at temperatures not too far from the critical solution point are then:

$$\xi^2 + \eta^2 \simeq \frac{1}{4}(1 - \bar{T}^2) \;\ldots\ldots\; \text{spinodal} \tag{17}$$

$$\frac{\xi^2}{3} + \eta^2 \simeq \frac{1}{4}(1 - \bar{T}^2) \;\ldots\ldots\; \text{binodal.} \tag{18}$$

The new rectangular coordinate system (ξ, η) is obtained by rotation of the coordinate system (s, t) by an angle α given by $\operatorname{tg}\alpha = \sqrt{\frac{s_0}{r_0}}$. Ap-

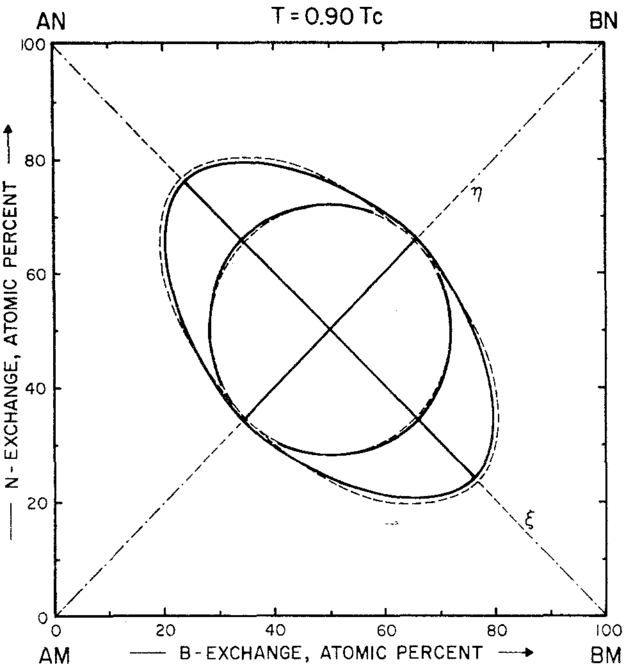
Fig. 5. Approximated (broken lines) binodals and spinodals of ideal double-pseudobinary solid solutions at $T = 0.90\,T_c$. Solid lines show exact boundaries. Approximate solutions:

Spinodal: $\xi^2 + \eta^2 = \frac{1}{4}(1 - \bar{T}^2)$

Binodal: $\frac{\xi^2}{3} + \eta^2 = \frac{1}{4}(1 - \bar{T}^2)$

$\operatorname{tg}\,\alpha = \sqrt{\frac{s_0}{r_0}}$

(a) $z = 1$; (b) z — 12


T = 0.90 Tc
AN
BN
AM
BM
η
ξ
100
80
60
40
20
0
0
20
40
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80
100
— N - EXCHANGE, ATOMIC PERCENT →
— B - EXCHANGE, ATOMIC PERCENT →

Fig. 5a

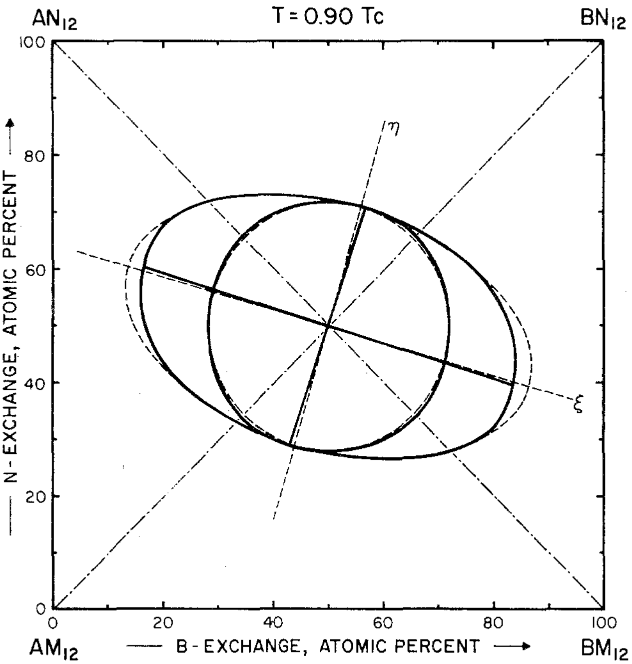
T = 0.90 Tc
AN₁₂
BN₁₂
AM₁₂
BM₁₂
η
ξ
100
80
60
40
20
0
0
20
40
60
80
100
— N - EXCHANGE, ATOMIC PERCENT →
— B - EXCHANGE, ATOMIC PERCENT →

Fig. 5b

proximations calculated from (17) and (18) for two different ratios $\left(\frac{s_0}{r_0}\right)$, together with computer-calculated, exact, boundaries are depicted in Figs. (5 a) and (5 b).

B. *Nonideal Boundary Systems*

In view of the involved arithmetic, it proved impractical to carry the approximations for the nonideal case beyond that of zeroth order; the only exception being the slope of the critical tie lines, for which more tractable expressions could be developed.

Approximate solution of equations (7) and (8) by small term expansion ($1 - \overline{T}$, s, $t \ll 1$) yields the coordinates of the critical points:

$$s^2 \simeq \frac{1}{4} \cdot \frac{r_0 (1 - \overline{T}_1^{-1})^3}{r_0 (1 - \overline{T}_1^{-1})^2 + s_0 (1 - \overline{T}_2^{-1})^2} \left[1 - \overline{T}_3^2 (1 - \overline{T}_1^{-1}) (1 - \overline{T}_2^{-1})\right] \tag{19a}$$

$$t^2 \simeq \frac{1}{4} \cdot \frac{s_0 (1 - \overline{T}_2^{-1})^3}{r_0 (1 - \overline{T}_1^{-1})^2 + s_0 (1 - \overline{T}_2^{-1})^2} \left[1 - \overline{T}_3^2 (1 - \overline{T}_1^{-1}) (1 - \overline{T}_2^{-1})\right], \tag{19b}$$

from which we immediately obtain the slope of the line through the critical points to:

$$S' = \frac{t}{s} \simeq \sqrt{\frac{s_0}{r_0}} \left(\frac{1 - \overline{T}_2^{-1}}{1 - \overline{T}_2^{-1}}\right)^{3/2} . \tag{20}$$

Small terms expansion and differentiation of the regular binodal[1] yields for the slope at the critical point:

$$S = \left(\frac{\mathrm{d}t}{\mathrm{d}s}\right)_{P_c} = \left(\frac{\mathrm{d}v}{\mathrm{d}y}\right)_{P_c} \simeq - \sqrt{\frac{r_0}{s_0}} \cdot \left(\frac{1 - \overline{T}_1^{-1}}{1 - \overline{T}_2^{-1}}\right)^{1/2} (1 + K) \tag{21}$$

in which the first order correction term K is given by

$$K = \frac{1}{2} \frac{\left[r_0 (1 - \overline{T}_1^{-1})^2 - s_0 (1 - \overline{T}_2^{-1})^2\right] \left[1 - (1 - \overline{T}_1^{-1}) (1 - \overline{T}_2^{-1}) \overline{T}_3^2\right]}{r_0 (1 - \overline{T}_1^{-1})^2 + s_0 (1 - \overline{T}_2^{-1})^3} .$$

For $\overline{T}_1{}^{-1}$, $\overline{T}_2{}^{-1} \rightarrow 0$, and $\overline{T}_3 \rightarrow \overline{T}$ (ideal solution), expression (21) becomes

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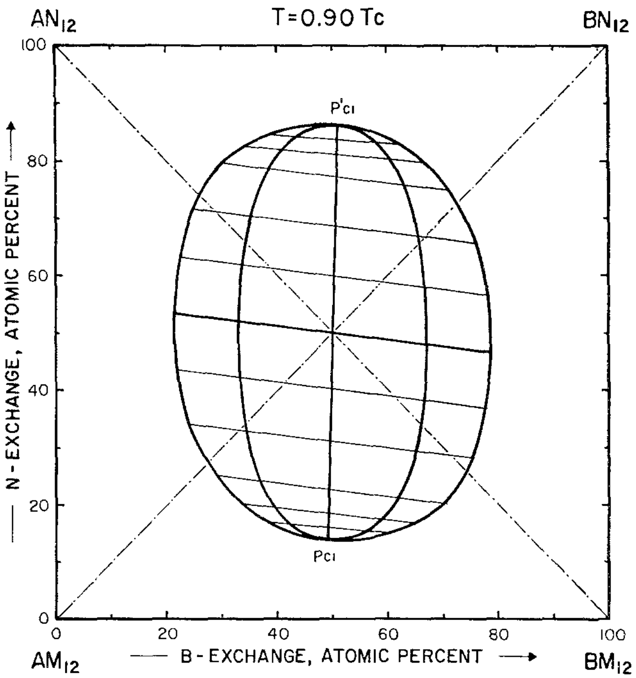
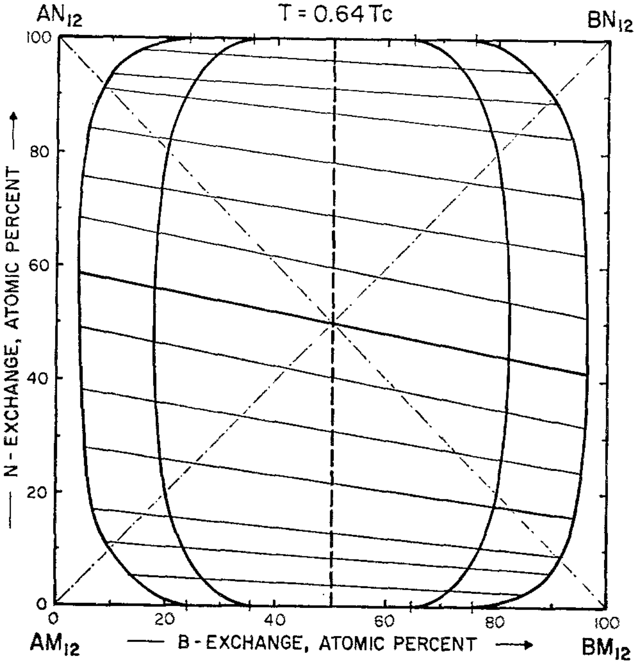
Fig. 6. Binodal and spinodal lines of a regular asymmetric, double-pseudobinary solid solution ($z = 12$), calculated with $T_{c_1} = - T_{c_2} = T_{c_3}$.
(a) $\overline{T} = 0.90$; (b) $\overline{T} = 0.64$



AN12
T=0.90 Tc
BN12
P'c1
Pc1
N - EXCHANGE, ATOMIC PERCENT
B - EXCHANGE, ATOMIC PERCENT
AM12
BM12
0
20
40
60
80
100

Fig. 6 a



AN12
T = 0.64 Tc
BN12
N - EXCHANGE, ATOMIC PERCENT
B - EXCHANGE, ATOMIC PERCENT
AM12
BM12
0
20
40
60
80
100

Fig. 6 b

identical with (13). From the binodal we also calculate the slope of the tie line through the symmetry center s, t (0,0) to:

$$S_1 = \frac{t_1}{s_1} = -\sqrt{\frac{r_0}{s_0}}\left(\frac{1-\bar{T}_1^{-1}}{1-\bar{T}_2^{-1}}\right)^{1/2}$$

Comparison of (20), (21), and (22) reveals that, in the lowest order approximation, the critical tie line is parallel to the tie line through s, t (0,0), but that the principal axes are not perpendicular to each other if $\bar{T}_1$ and $\bar{T}_2$ are dissimilar. The effect of nonideal behavior is shown on particular model examples for $\bar{T} = 0.90$ and 0.64 in Figs. 6a and 6b, which were calculated assuming regular solution behavior of the boundary systems and critical temperatures of $T_{c_1} = -T_{c_2} = T_{c_3}$. The critical solution temperature, needed for the calculation of the reduced temperatures, was derived from the relation[1],

$$T_c = \frac{T_{c1}+T_{c2}}{2} + \frac{1}{2}\sqrt{(T_{c1}-T_{c2})^2 + 4\,T_{c_3}^2}.$$

Discussion

The foregoing thermodynamic treatment permits several generalizations concerning the phase equilibrium features of double-pseudobinary solid solutions:

First, we find that phase separation in solid solutions with ideal, or weakly nonideal, boundary systems is principally controlled by the stability of the boundary phases. Although the relative abundance of the sublattices does affect critical solution temperature and orientation of the binodal and tie lines, its influence on extent and shape of the miscibility gap at equivalent temperatures is only minor. Unequal sublattice abundance ($r_0 \neq s_0$) and nonideal sublattice solid solution behavior causes a slanting of the tie lines in the direction of the boundary systems with the higher sublattice weight factors and less positive deviations from ideality. A point of practical interest concerns the prediction that the mutual solubilities are higher in the less stable boundary phase pair, and that the solubilities along the composition line connecting the higher stability boundary phase pair are expected to be very small below $\bar{T} = 0.5$.

Although the conditional equations for the critical point derived in Section I have general validity, the particular nonideal solution model chosen for the description of the model examples has principal limitations: An example is the breakdown of the model for $\Delta\Delta\, G_f = 0$, since under these circumstances the critical solution temperature would be given by either T_{c_1}, or T_{c_2}, whichever is higher, and the solution at T_c would become critical along the entire concentration line $x = 1/2$, or $u = 1/2$. For the thermodynamic description of double-pseudobinary solid solutions with substantial, and dissimilar, nonideal behavior of the boundary systems, a four-parameter[1] equation for the regular solution,

$$G^{mix} = \varepsilon_1\, uxy + \varepsilon_2\, vxy + \varepsilon_3\, xuv + \varepsilon_4\, yuv + G^{mix(ideal)}$$

should provide a more reasonable approximation of the actual conditions. The interaction parameters ε_i can be estimated from the miscibility gaps in the corresponding pseudobinary boundary systems, or from the measured tie line distributions in pseudoternary systems with miscibility gaps[3].

While it will not prove difficult to assess the applicability of the equations developed in this paper to solid solutions based on simple ordered structures, careful consideration has to be given to cases where intermixing occurs simultaneously on several non-equivalent crystal sites occupied by the same set of components, say (A, B), or where the occupational interchange between the two sublattices is substantial. To exemplify the situation, we consider a solid solution

$$(A_xB_y)_z(M, N),$$

in which the components A and B are distributed among n nonequivalent crystal sites: z_1 equivalent sites 1, z_2 sites 2, ... etc., with $\sum_n z_i = z$. Uniform distribution of A and B on the different sublattice sites will only be assured if they are all energetically equivalent with respect to occupation by A and B. If this is not the case, we have to consider the formation of internal partition equilibria of the form

$$(A_{x'}B_{y'})_{z_1} — (A_{x''}B_{y''})_{z_2} — \dots,$$

and analyze the composition of each sublattice in order to be able to describe the integral free energy of the system. At least in principle, coexisting sublattice compositions (tie lines of the homogeneous partition equilibrium) can be determined by diffraction techniques and thermodynamically evaluated using essentially the same methods as for heterogeneous phase equilibria[4]. For the limiting case of large energy separations (strongly preferential occupation of the sublattice sites), the system is divided into n subsystems, e.g.

$$(A_{x'}\, B_{y'})_{z_1}\, A_{z_2}, A_{z_3} \dots A_{z_n}\, (M, N) \qquad 0 \leqslant y_B \leqslant \frac{z_1}{z}$$

$$B_{z_1}\, (A_{x''}\, B_{y''})_{z_2}\, A_{z3} \dots A_{z_n}\, (M, N) \qquad \frac{z_1}{z} \leqslant y_B \leqslant \frac{z_1 + z_2}{z} \dots \text{etc.}$$

each of which may have a critical point and closed loop binodals.

Acknowledgements

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References

[1] *E. Rudy*, J. Less Common Metals **33** (1), 43 (1973).

[2] Compare, for example, *T. L. Hill*, Statistical Mechanics. New York: McGraw-Hill. 1956.

[3] *E. Rudy*, *H. Nowotny*, *F. Benesovsky*, *R. Kieffer*, and *A. Neckel*, Mh. Chem. **91**, 176 (1960).

[4] *E. Rudy*, Z. Metallkde. **54**, 112 (1963).