

Guidelines for Binary Phase Diagram Assessment

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The recent publication of *Binary Alloy Phase Diagrams*, 2nd ed., [90Mas] and our extensive screening of phase diagram graphics for this edition has revealed many phase diagram features, which while not explicitly violating phase diagram rules, are to a lesser or greater extent unlikely to represent thermodynamically acceptable conditions. In two previous papers, several thermodynamically improbable features or boundaries in binary phase diagrams were pointed out [91Oka2], and some unlikely thermodynamic models were shown to be unrealistic, or in error [91Oka1]. In the present paper, we discuss some of the unlikely features in more detail in order to develop a set of guidelines that may be useful for checking future proposed phase diagram boundaries, or some specific phase diagram features resulting from both experimental and theoretical work, including also phase diagram assessments.

1. Introduction

Ideally, an equilibrium phase diagram of a binary (or higher order) system should be determined experimentally. As is well known, however, in practice, a phase diagram (or some portions of it) may be very difficult to determine by experiments alone because of various unavoidable complications. For example, when certain phase boundaries are determined by thermal analysis, numerous specimens with different compositions may be needed, or very long annealing times for equilibration or phase nucleation could be involved, especially at low temperatures. Problems then arise related to temperature measurement, contamination, composition control, technique precision, and data interpretation. The same applies if diffraction techniques, metallographic phase diagram identification, or other experimental approaches are used. Accordingly, it is not unusual to see numerous portions of phase diagrams derived entirely by interpolation from other data, assumed similarities to other systems, extrapolation from adjoining regions, or just plain invention. Recently, an increasing role is also being played by thermodynamic modeling, which carries its own difficulties [91Oka1]. In all these approaches to phase diagram construction, all kinds of errors tend to compound, and it is not surprising that all too frequently the resulting phase diagram, or specific features or boundaries in it, may be invalid, distorted, or improbable.

The validity of a proposed phase diagram can often be examined from the appearance of the general pattern and the form of proposed boundaries. In three earlier reviews, [86Oka], [91Oka1], and [91Oka2] showed many examples of unlikely phase diagram features and emphasized the fact that often even though the phase rule may be satisfied, some phase boundaries

may be entirely improbable thermodynamically. Thus, it can be shown that the liquidus of a compound cannot be too asymmetric, the changing slope of a phase boundary cannot be too abrupt, initial slopes must conform to certain rules, etc. In this article, we attempt to provide a firmer quantitative basis to some of the qualitative statements in these earlier works, with the general objective of providing definitive guidelines for visually checking proposed phase boundaries and thermodynamic models.

The present approach may appear to be less rigorous in comparison with other analytical methods based on thermodynamic principles. For example, [80Pel] and [81Pel] showed that the solidus location can be determined from the liquidus location and a limited amount of thermodynamic quantities. This concept can be utilized as a criterion for examining the validity of the experimentally determined relationship between the liquidus and the solidus. More recently, [88Pel] derived equations of thermodynamic quantities of related phases to express the relationships of the ratio of phase boundary slopes at an invariant reaction. The consistency in the slopes of proposed phase boundaries can be examined accordingly. The curvatures of liquidus and solidus at the congruent melting point of an intermediate phase must satisfy the Gibbs-Konovalov rule, and those of a particular phase diagram can be calculated from the second derivative of the Gibbs energy functions of the related phases and the scale of the phase diagram [81Goo]. Any phase boundary that does not conform to this scheme is considered to be erroneous. The van't Hoff relationship for the initial slopes of the liquidus and solidus (see [91Oka2]) is another well-known rule that can be used for checking the validity of a phase diagram. However, these exact methods for checking various features of phase

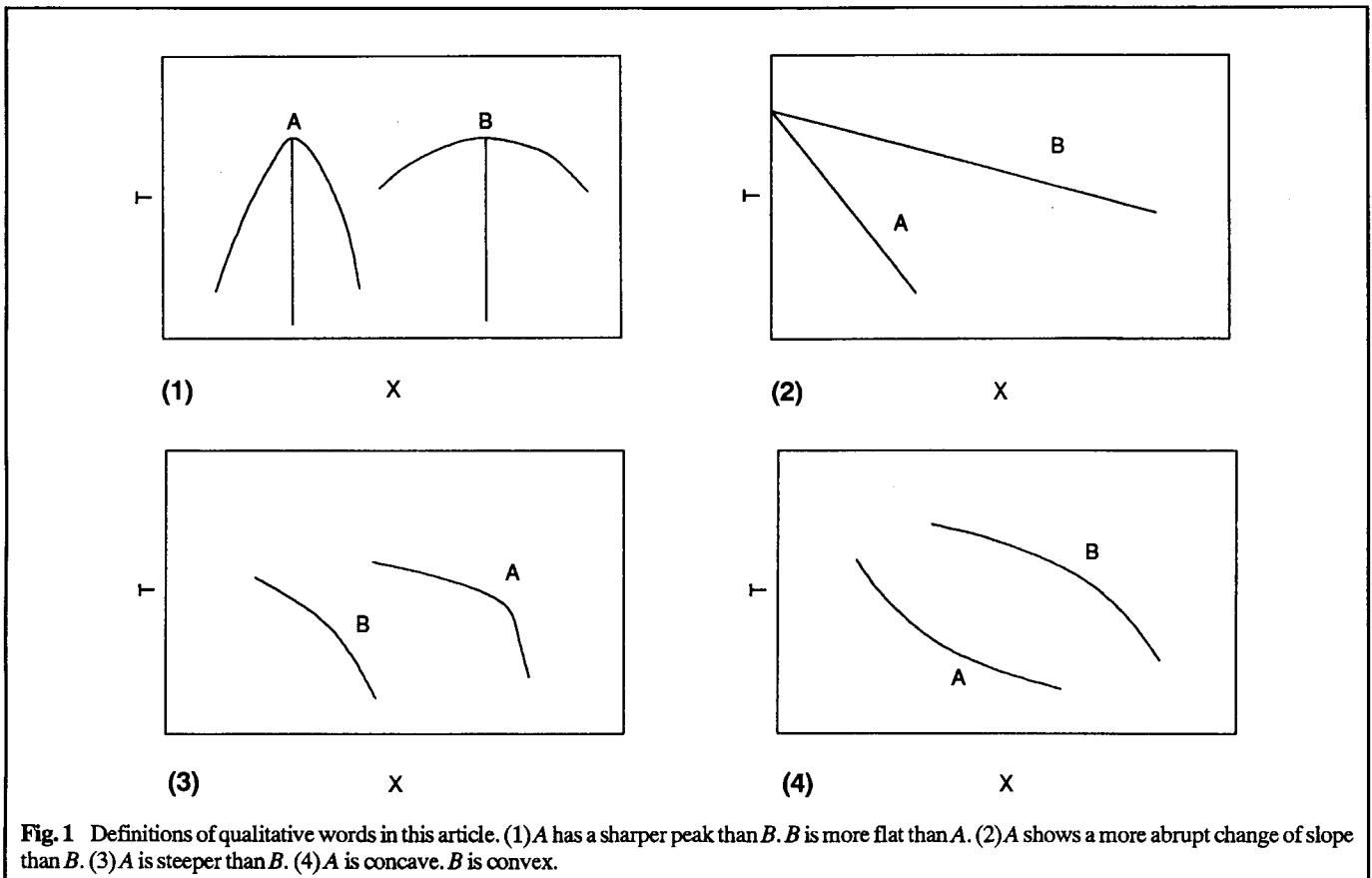


Fig. 1 Definitions of qualitative words in this article. (1) *A* has a sharper peak than *B*. *B* is more flat than *A*. (2) *A* shows a more abrupt change of slope than *B*. (3) *A* is steeper than *B*. (4) *A* is concave. *B* is convex.

diagrams have rarely been utilized in phase diagram assessments primarily because their validity can be checked only after establishing first a reliable thermodynamic model and sometimes performing extensive calculations.

The criteria described in the present article were devised to circumvent in part the difficulties associated with these more rigorous approaches. The present criteria may appear to be intuitive, but actually they too derive from thermodynamic principles and thermodynamic characteristics of phases and materials. The most remarkable advantage of the present approach over the more strict methods may be the possibility of quickly screening improbable phase diagrams or thermodynamic models by pattern recognition. A more rigorous examination may then be initiated for a given phase diagram for which anomalous features have been identified as judged from the present guidelines.

As in the earlier papers, we shall continue referring to certain curvatures of phase boundaries in somewhat qualitative terms such as "sharp," "flat," "steep," "abrupt," etc. The meaning of these words is, of course, relative, as easily perceived from the fact that the curvature of a phase boundary will vary depending on the scale selected for the phase diagram graphics. Thus, a "sharp" liquidus in our context only implies that the form of the liquidus around a certain compound-like phase appears to be more pointed at the melting point in a T - X plot than that of a neighboring phase in the same phase diagram, or more pointed than the form expected from simple thermodynamic consid-

erations. Other examples of curvature terminology are illustrated graphically in Fig. 1.

Most often, the liquid phase considered in this article will be assumed to be an ideal solution. Modest deviations from the ideal solution behavior will not affect the main points of our discussion, but special considerations are needed for the situations when the association-forming tendency in the liquid phase is very pronounced. For this reason, systems involving strongly ionic elements are beyond the scope of the present discussion. However, if the association tendency is overwhelming in the liquid phase, the compound-like phase may be regarded as an element and the present considerations will then apply.

A list of the topics considered in the present paper is given in Table 1. Their graphical representation is illustrated in Fig. 2.

2. The Form of the Liquidus (of a Compound) in the Vicinity of the Pure Element Side (Point *a* in Fig. 2)

In this section, the form of a liquidus associated with a compound-like phase, in the composition range near a pure element side (0 or 100 at. % solute) is considered. An examination of the projected metastable range of the liquidus is desirable as discussed below.

Both ends of the liquidus of an intermediate phase must eventually terminate at invariant reactions such as a eutectic or a

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peritectic. Sometimes, the proposed form of the liquidus immediately above these invariant reaction temperatures is

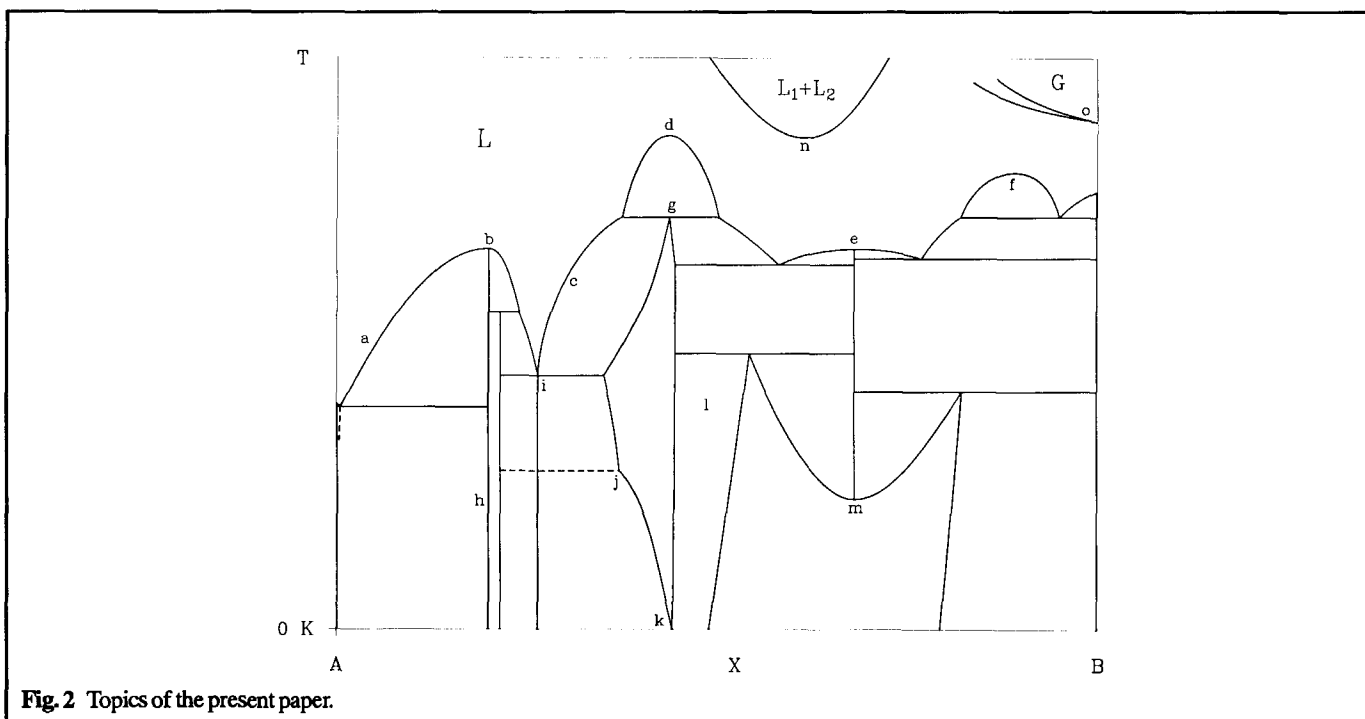
Table 1 Topics of the Present Paper

Features in Fig. 2	Topic	Discussed in section
a.....	The form of the liquidus (of a compound) in the vicinity of the pure element side	2
b.....	An unusually asymmetric liquidus	3
c.....	An unacceptably abrupt change of slope in a phase boundary	4
d.....	Flatness (or sharpness) of a miscibility gap upper boundary	5
e.....	Flatness (or sharpness) of a liquidus around a compound	6
f.....	A miscibility gap occurring close to a pure element side	7
g.....	A syntectic reaction in combination with a compound forming at lower temperatures in the same composition range	8
h.....	Two adjoining compounds having very similar compositions	9
i.....	Too much coincidence in unusual combination of phase diagram features	10
j.....	An excessive slope change associated with a polymorphic transformation occurring in a phase or a compound	11
k.....	A single-phase field having no width at 0 K	12
l.....	A two-phase field becoming increasingly wider at higher temperatures	13
m.....	A congruent transformation of a compound on cooling	14
n.....	An inverse miscibility gap	15
o.....	A too narrow G + L two-phase field	16

highly suspect even if the curvature of the liquidus appears to be normal (e.g., no abrupt change of slope is evident). The termination of the equilibrium portion of the liquidus of an intermediate phase by an invariant reaction is of course expected from the relationship between the liquid phase and the compound phase (i.e., the invariant reaction reflects the thermodynamic competition between the neighboring phases and is not connected with the form of the liquidus of the compound under consideration). It follows from this that the overall validity of a liquidus trend must be judged by taking into account also its projected metastable ranges.

In order to examine the liquidus of a compound including the metastable range, it is convenient to assume that all neighboring solid phases, including the terminal phase, can be excluded. Then, the liquidus becomes visible in its entire composition range from 0 to 100 at.%. (Only the 0 at.% side is discussed hereafter to eliminate redundancy.) Here we recall that the extrapolated liquidus cannot cross the 0 at.% solute line, because the slope of the Gibbs energy function of the liquid phase always (except at 0 K) has a negative infinity value at 0 at.% due to the $RTX \log X$ term, which derives from the contribution of the ideal entropy of mixing (Fig. 3). Accordingly, any liquidus of an intermediate phase, when extrapolated, can approach the 0 at.% line only asymptotically. Thus, for example, in order to satisfy this requirement, the liquidus of AcB_4 (Fig. 4), would have to involve a rather abrupt change of slope (as indicated with a dotted line) instead of the smooth (and incorrect) extrapolation indicated with a dashed line. * Nevertheless, the mandated accelerated change of slope

*A rather marginal example was selected for the illustration in Fig. 4. The problem becomes more pronounced when the eutectic composition is closer to 0 at.%.



is intuitively abnormal (considering only the stable and metastable liquidus and nothing else), and it would be helpful to have a clearer guideline of how much change of slope is thermodynamically reasonable.

Possible general forms of the liquidus associated with an A_3B -type compound were illustrated in [91Oka2] assuming that the liquid was an ideal solution.* Several more general situations

for a liquidus are considered below for an AB-type (50 at.%) compound melting at 1000 °C. The liquid is now assumed to be a regular solution. Of course a further deviation from a regular solution behavior would cause additional changes in the form of the liquidus, but the rate of change may be expected almost always to be a slowly changing function in any one phase. Hence, the use of a regular solution approximation may be adequate for the present purpose. (Note that the present aim is to show that a too abrupt change of slope in a liquidus near the 0 at.% line is difficult to justify thermodynamically.)

In order to examine possible variations of the curvature of a given liquidus, the curves shown in Fig. 5 were calculated for rather extreme situations. Curves a1 and a2 correspond to a situation where the interaction parameter is positive and large, i.e., $G^{ex}(L) = 18\,000X(1-X)$ J/mol. This value cannot be raised much higher because a miscibility gap then develops in the liquidus [91Oka2]. Curves c1 and c2 correspond to another extreme situation where the interaction parameter is now nega-

*When the liquid can be regarded as an ideal solution, the validity of the liquidus curve may be examined more easily by plotting $\ln X$ vs $1/T$ (Arrhenius plot), where X is the liquidus composition in atomic fraction and T is in K. If the Gibbs energy of the compound in equilibrium with the liquid varies linearly with temperature (which is a good approximation [91Oka1]), the plot should appear as a straight line at $X \ll 1$. The Arrhenius plot will be a curved line when there is any deviation from this ideal situation (nonideal liquid, substantial solubility, and at very low temperatures where the Gibbs energy of a compound cannot be approximated to vary linearly with temperature). Therefore, the question of how much can be tolerated in an abrupt change of a liquidus slope is also found in the Arrhenius plot.

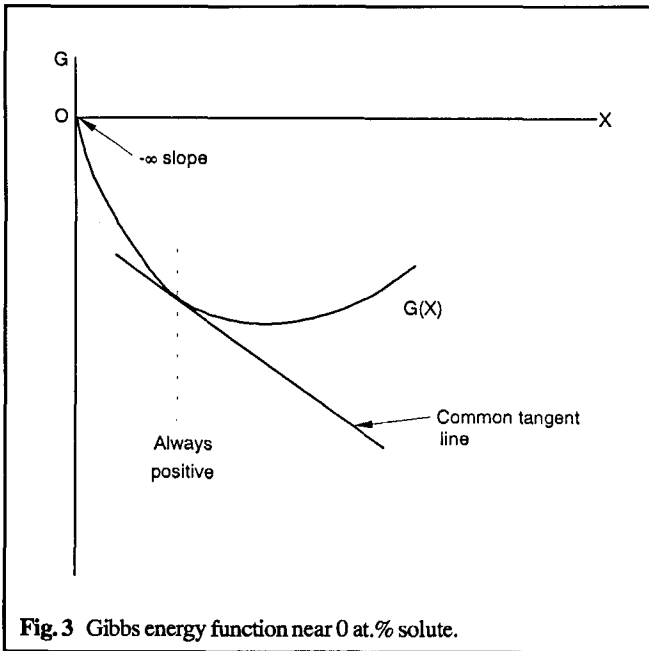


Fig. 3 Gibbs energy function near 0 at.% solute.

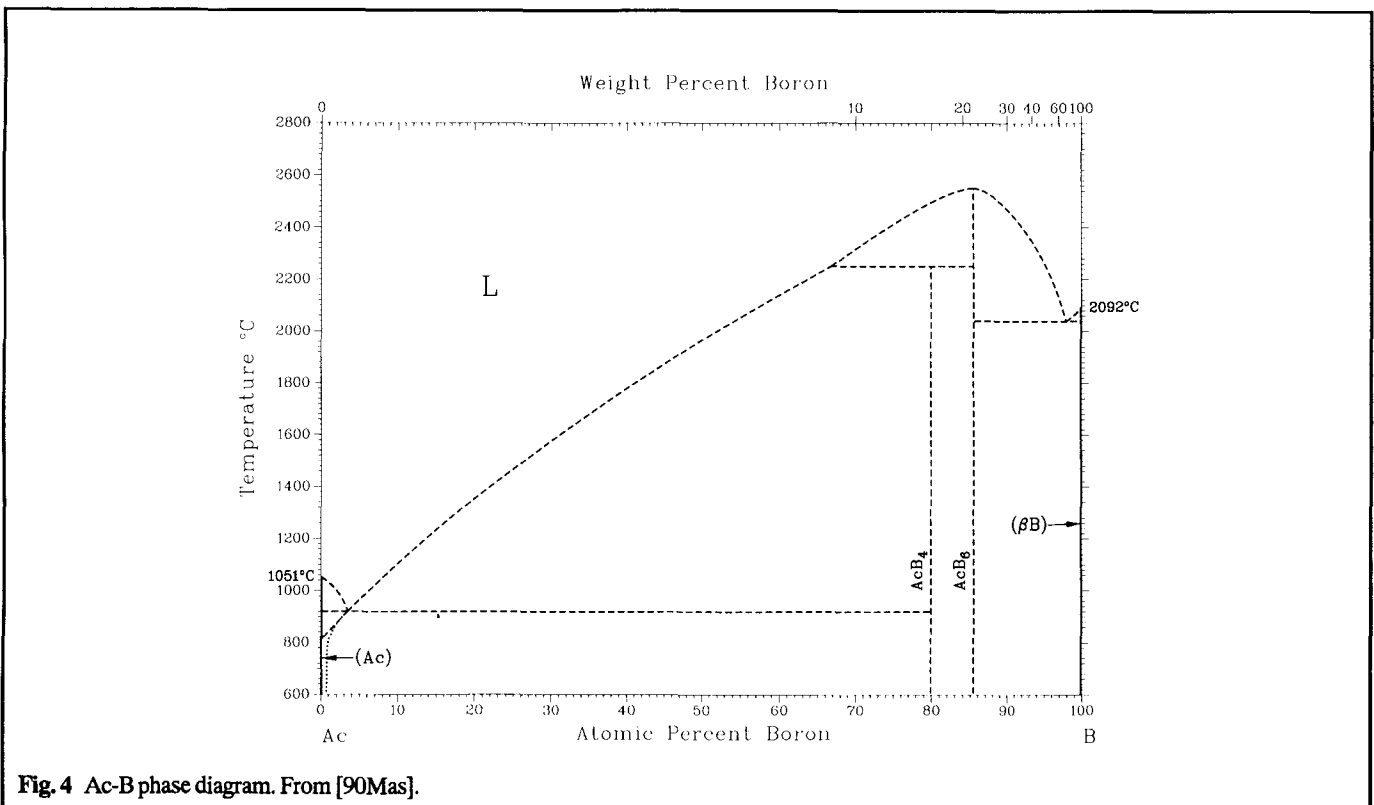


Fig. 4 Ac-B phase diagram. From [90Mas].

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tive and large, i.e., $G^{ex}(L) = -100\,000X(1 - X) \text{ J/mol}$, which is an exceptionally low value [91Oka2]. In this case, the liquidus

does not reach the 0 at.% solute line at all. For comparison, an ideal solution case is also included in Fig. 5 (b1 to b5).

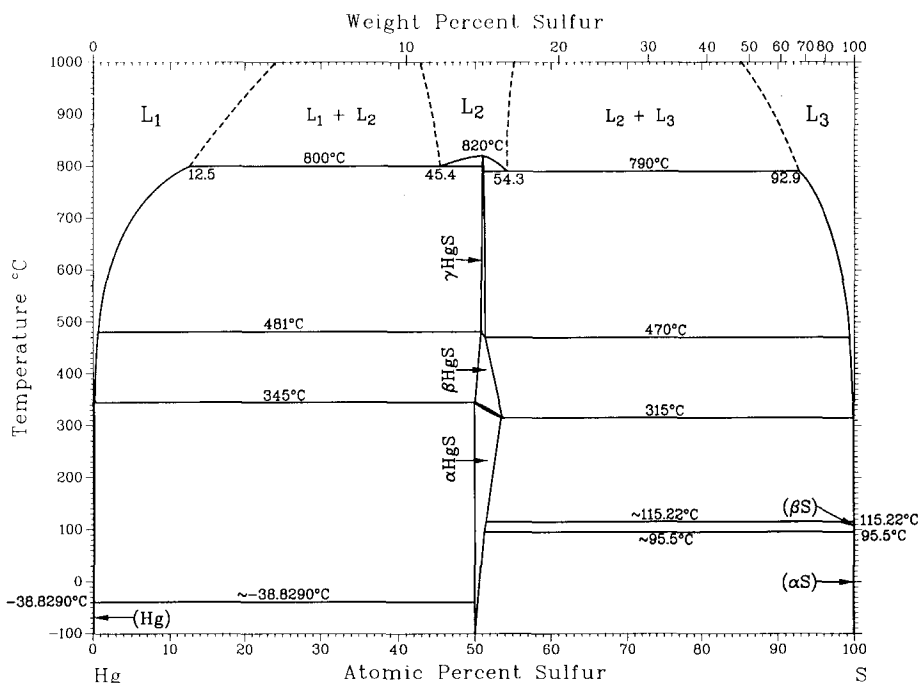


Fig. 5 Liquidus approaching 0 at.% solute.

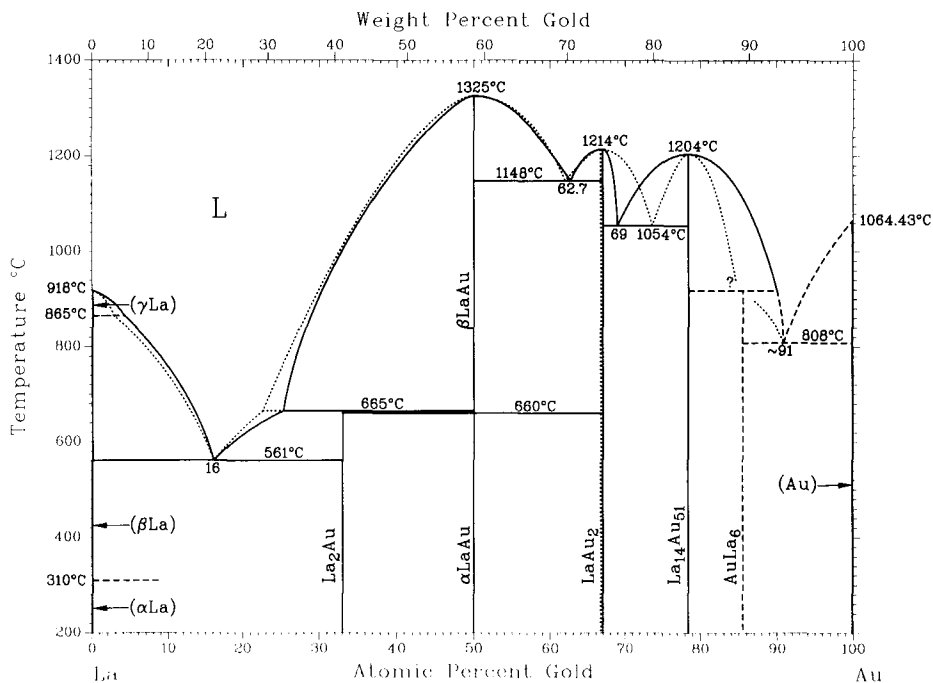


Fig. 6 La-Au phase diagram. ... is calculated. From [90Mas].

Among these curves, b4 and b5 give the apparent appearance of boundaries projecting to cross the 0% line without a downward turn, especially if the rapidly turning portion of each curve is in an actual diagram obscured from view by the liquidus of another phase, such as the terminal solid solution. However, these models correspond to rather artificial situations because the coefficients of the T term (-2 or -4) for curves b4 and b5 may be too negative for a real case, as discussed in section 6. Accordingly, it may be concluded that in a general case, a liquidus requiring an abrupt change of slope to avoid "crossing" the 0 at.% line when extrapolated, near the 0% line (as shown with a dotted line in Fig. 4), should be regarded as suspect. The remedy would be to make the equilibrium portion of the liquidus steeper near the 0 at.% line, if the modeling and the experimental data (if any) allow it.

3. Asymmetric Liquidus Curves Around Compounds (Point b in Fig. 2)

A strikingly asymmetric (and hence suspect) liquidus about a congruently melting compound in a phase diagram was already pointed out as an unlikely situation in [86Oka] and [91Oka2]. A definition of the asymmetry is of course somewhat ambiguous, but from a glance at the La-Au phase diagram (Fig. 6), for example, it is obvious that the liquidus of β LaAu is more symmetric than that of LaAu_2 . An approximate

judgment can be made by comparing the ratio of the width of the two-phase fields on each side of a compound at the same temperature. If the width on one side is either one half or double that on the other side, the asymmetry may be considered clearly unusual. In our earlier calculation of the La-Au phase diagram [87Gsc], we derived a set of almost perfectly symmetric liquidii for all observed compounds (dotted lines). The modeling is illustrated in Table 2 by the Gibbs energy functions used for the calculation of the form of the LaAu_2 liquidus.

In order to examine here the effect of further changes in this selected Gibbs energy function on the resulting asymmetry, the liquidus on the right-hand side of LaAu_2 was recalculated for various modified $\Delta_{\text{mix}}G^{\text{ex}}(\text{L})$ terms assumed for the liquid phase. In this calculation, the Gibbs energy function of LaAu_2 and its melting point are, of course, fixed. Admittedly, the transition between the two branches of the LaAu_2 liquidus, on the

Table 3 Calculated LaAu_2 Liquidus Composition at 1148 and 1054 °C

$\Delta_{\text{mix}}G^{\text{ex}}(\text{L})$, J/mol	Liquidus, at. % Au	
	1148 °C	1054 °C
$X(1-X)(-200\,000 + 95\,700X)$	72.30	75.68
$X(1-X)(-100\,000 - 54\,300X)$ (a)	71.21	73.70
$X(1-X)(-97\,488 - 58\,085X)$	71.23	73.69
$X(1-X)(0 - 204\,300X)$	70.61	72.71
$X(1-X)(100\,000 - 354\,300X)$ (b)	70.20	72.07
$X(1-X)(200\,000 - 504\,300X)$ (b)	69.91	71.61

Table 2 La-Au Thermodynamic Data

$G(\text{LaAu}_2)$	= $-38\,929 + 0.533T$ J/mol
$\Delta_{\text{mix}}G^{\text{ex}}(\text{L})$	= $X(1-X)(-97\,488 - 58\,085X)$ J/mol

(a) Almost identical to the reference curve and not shown in Fig. 7. (b) A very unlikely situation because the partial molar enthalpy for the dilute solution is strongly positive at 0% and strongly negative at 100 at.%.

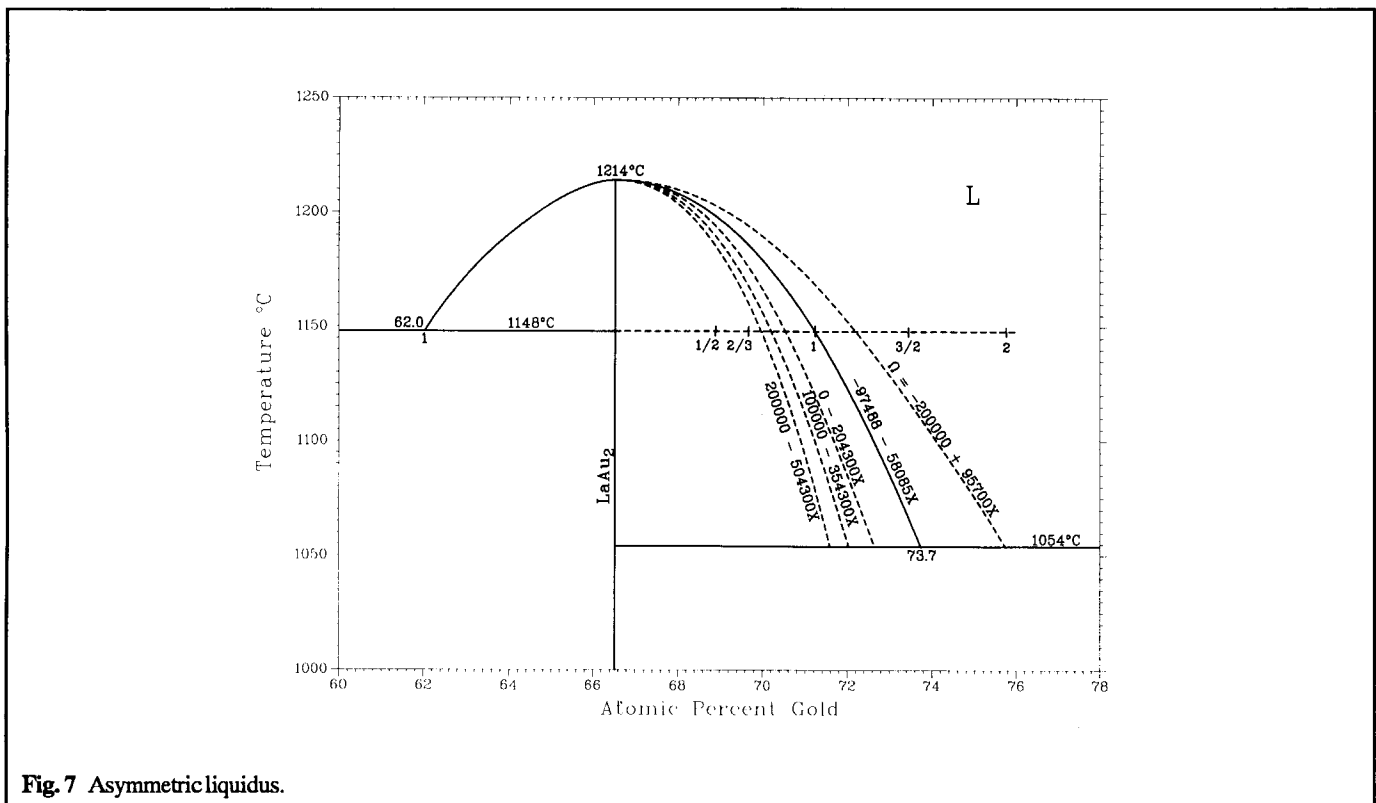


Fig. 7 Asymmetric liquidus.

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left- and right-hand sides of stoichiometry, is incompatible with the Gibbs-Konovalov rule [81Goo] because the d^2G/dX^2 value is discontinuous at the congruent point. Hence, the present modeling should be regarded as corresponding to the situation where the zero slope requirement at the congruent point may be regarded as a further subtlety that is not material to the more general examination of the liquidus behavior caused by changes in the thermodynamic properties of the liquidus as composition changes. The calculated results (Table 3) indicate that it is very difficult to generate asymmetry (Fig. 7) even when a drastic change in the thermodynamic behavior of the liquid phase is introduced, as shown by the various forms of the $\Delta_{\text{mix}}G^{\text{ex}}(\text{L})$ function in Table 3.

It appears that if the width ratio is 1:1.5 (note the scale at 1148 °C in Fig. 7), the liquidus is already fairly asymmetric. If the ratio is 1:2, the liquidus is strikingly asymmetric in the sense that an unlikely transition in the thermodynamic properties of the liquid phase would be involved in that composition range.

When checking liquidus asymmetries around compounds in a phase diagram, the above rough measure of the width ratio should be applied at several temperatures slightly away from the melting point because unessential drawing errors often cause an appearance of asymmetry very near the melting point.

Note: (1) If the liquidus is indisputably asymmetric, it is usually found that the corresponding solidus is also asymmetric, which means that the compound is actually a phase with a considerable width. (2) A relatively normal liquidus associated with a compound existing near a pure component may appear asymmetric at low temperatures because one side of it is lim-

ited by the edge of the phase diagram (see e.g., the Ba-Be phase diagram in [90Mas]).

4. An Abrupt Change of Slope (Point c in Fig. 2)

This is a more general situation of the case already considered in section 2. An abrupt change of slope in the liquidus is caused either by an abrupt change in the thermodynamic properties of the liquid phase or an abrupt change in the thermodynamic properties of the solid phase (in this case a compound) in equilibrium with the liquid [91Oka2]. In the previous section, it was shown that the slope of a liquidus does not change substantially even when the thermodynamic behavior of the liquid phase changes substantially. We now examine the influence of the change in the thermodynamic behavior of the compound on the slope of the liquidus.

Table 4 Relationship Between the Gibbs Energy and the Melting Point of an Equiatomic Compound (Liquid is an Ideal Solution)

Melting point, °C	Gibbs energy, J/mol	Comment
1600	$-4\,572 - 3.322T$...
1300	$-6\,144 - 1.857T$...
1100	$-8\,938 + 0.746T$...
1000	$-12\,430 + 4.000T$	Reference curve
950	$-15\,923 + 7.256T$...
900	$-22\,909 + 13.765T$...

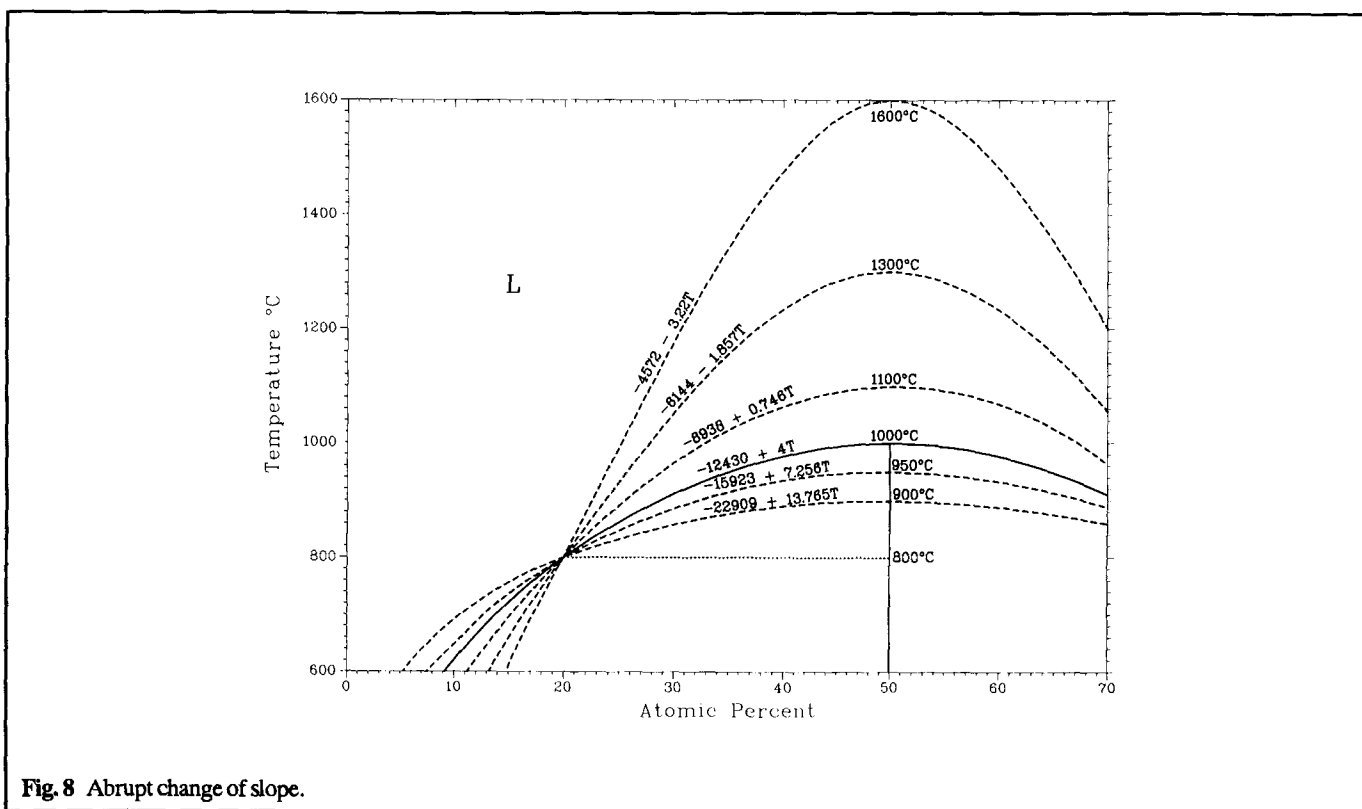


Fig. 8 Abrupt change of slope.

Table 4 lists various Gibbs energy functions of an equiatomic compound AB. The one melting at 1000 °C is used as the reference state, which was selected from the situation b2 in section 2. The corresponding liquidus is shown with a solid line in Fig. 8. The liquid in this case is an ideal solution. Other curves in Fig. 8 were drawn assuming that the thermodynamic behavior of the equiatomic compound changes discontinuously at 800 °C as the temperature is lowered. It is then possible to project metastable extensions of the low-temperature segments of the different liquidus forms. In Fig. 8, these are drawn to correspond to apparent melting points arbitrarily set at 1600, 1300, 1100, 900, and 850 °C. As may be seen, the required temperature coefficient of the Gibbs energy associated with these curves (Table 4) varies from -3.322 to 13.765 J/mol · K. In spite of this drastic change in the temperature coefficient (see section 6), the change of slope of the different liquidii at 800 °C is relatively small. Since no phase transformation is assumed to occur in the compound, the change in the temperature coefficient near 800 °C would have to derive from $\int \Delta C_p dT$, where ΔC_p is the difference in the specific heats of the compound and the average C_p for the liquid elements at that composition (reference state). The integration would be over the temperature range where the change of slope is indicated. Even if there existed a true phase transformation at 800 °C* (see section 11), it would be extremely difficult to explain an abrupt change of slope (concave or convex) of a liquidus boundary in terms of an abrupt change in the thermodynamic behavior of the compound. As a rough measure, the abruptness of the slope change may be judged by the apparent congruent melting points corresponding to the liquidus portions above and below the temperature at which the slope change occurs. In the present example, a change of only $\pm 10\%$ in the apparent melting point (in K) already seems to require too much change in the thermodynamic behavior of the compound (as judged by the temperature coefficients modeled in Table 4).

A phase boundary with an abrupt change as shown at point *c* in Fig. 2 is rarely found in the equilibrium portions of phase diagrams. However, numerous examples can be found where such an abrupt change is projected to occur (by extrapolation) in the metastable regions of existing phase diagrams. Sometimes such phase boundaries are drawn to avoid other phase rule violations [91Oka2], but they then introduce a projected liquidus abruptness that may be unacceptable.

5. Shape of a Miscibility Gap (Point *d* in Fig. 2)

Miscibility gaps are found in both the liquid and solid states. Usually, the shape of the gap near its critical point is uniformly round. We attempt here to find possible limits of the curvature of a miscibility gap near its critical point. For a reference miscibility gap, the excess Gibbs energy of a phase (it does not matter whether it is a liquid or a solid) was taken to be of the form $G^{ex} = 20\,000X(1 - X)$ J/mol, which means that the inter-

action parameter $\Omega = 20\,000$ J/mol. This yields a critical point at 50 at. % B (of the A-B system) and 930 °C. The shape of the calculated gap is quite round, as shown in Fig. 9. In order to make the form of this gap sharper, a temperature dependence and composition dependence were introduced to Ω , up to the feasible maximum limit, keeping the critical point at the same location. When the temperature dependence αT is added to Ω , the miscibility gap becomes sharper as α is increased (because the critical temperature is fixed, the constant term must be reduced accordingly). Because the usual limit of α is approximately 10 J/mol · K (see section 15), a miscibility gap for $\Omega = 7972 + 10T$ J/mol is shown in Fig. 9 as one of the examples. When a composition dependence is also added to Ω in the form of $\alpha X(1 - X)$, the miscibility gap becomes sharper as the value of α becomes larger. The constant term in Ω must be reduced as α is increased to maintain the critical temperature unaltered. The maximum possible value of α is then 40 000 J/mol to keep Ω positive for all X . When α exceeds 40 000, a negative constant term must be introduced in Ω , and Ω then becomes negative near $X = 0$ and 1. Under these modeling assumptions, the interaction between the two starting elements becomes too artificial. From this brief analysis, the miscibility gap cannot be structured to have a pointed peak in either case.

It is equally difficult to make a very flat miscibility gap. Even when a temperature dependence amounting to as much as $-10T$ is introduced in Ω , the form of the miscibility gap does not change markedly (Fig. 9). On the other hand, when the composition term is modified excessively, two peaks appear [93Oka1].

6. Relationship Between the Sharpness of the Liquidus of a Compound-Like Phase and the Corresponding Gibbs Energy Function (Point *e* in Fig. 2)

A useful notion here is that the “sharpness” of a liquidus of a compound is strongly related to the “stability” of this compound at low temperatures. To illustrate this point, Fig. 10 shows various forms of the liquidus of an equiatomic compound melting at 1000 °C. As before, the liquid phase is again assumed for simplicity to be an ideal solution. The Gibbs energy function of the compound is assumed to be of the form $G = a + bT$, where the reference states are the liquid elements. It is clear from Fig. 10 that the liquidus becomes increasingly more flat as the constant term a is made smaller, or the coefficient b is made larger. As understood from the fact that a is the value of G at 0 K, a reflects the relative stability of the compound at low temperatures. Because the stability of a compound increases when its Gibbs energy is lowered, a compound with a flat liquidus must be more stable than one with a sharp liquidus. Hence, when more than one compound exists in a system, a compound with a higher (less negative) Gibbs energy compared with the neighboring compounds cannot “survive” to low temperatures, because at low temperatures the Gibbs energy of a two-phase mixture composed of the neighboring compounds becomes even lower (Fig. 11). Therefore, a compound with a

*Then the abrupt change of slope becomes concave, rather than convex as shown at point *c* in Fig. 2. The slope change may be caused by a second-order transformation in the solid phase.

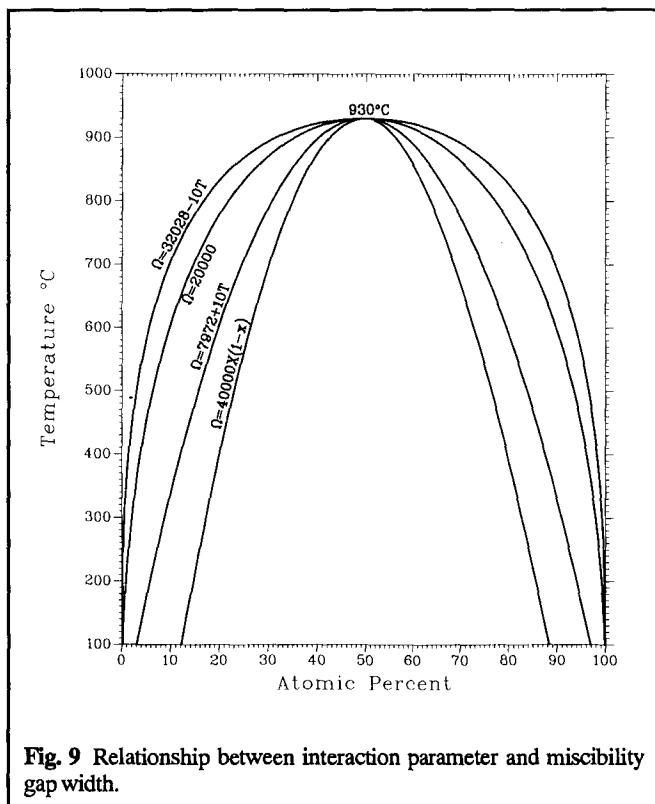


Fig. 9 Relationship between interaction parameter and miscibility gap width.

sharp liquidus is destined to decompose eutectoidally into two neighboring phases. This simple guide can save much time when realistic phase diagram calculations are being attempted.

The smallest possible value of b is limited by the fact that a solid phase at sufficiently low temperatures must become more stable than the liquid phase of the same composition. In the case of an ideal liquid, for example, the Gibbs energy of the liquid phase at equiatomic composition varies with temperature at a rate of $-5.763 \text{ J/mol} \cdot \text{K}$ —i.e., the value of $R[X \ln X + (1 - X) \ln(1 - X)]^*$ at $X = 0.5$. Thus, this is the minimum possible value of b in the expression of $G = a + bT$ for the equiatomic compound (if b is less than -5.763 , G would become more negative at high temperatures than the Gibbs energy of the liquid phase, causing an inverse melting). For a compound existing at an off-equiatomic composition ($X \neq 0.5$), the limit of b will be even less negative than -5.763 . If the compound is moved to positions where $X = 0$ or 1 (i.e., the terminal elements), b becomes equivalent to the entropy of fusion of the

*The ideal entropy of mixing term, $R[X \ln X + (1 - X) \ln(1 - X)]$, exists even in a hypothetical binary system consisting of the same two elements (extreme situation of ideal mixing). However, because this binary system is actually a pure substance, the entropy of mixing must be zero. This contradiction originates from the same cause as the Gibbs paradox (explained in most standard textbooks on thermodynamics). Due to this term, even when the entropy of fusion of an intermetallic compound is very similar to that of constituent elements, as expected from the Richard rule, the b term in the Gibbs energy function of the form $G = a + bT$ will appear to have a different value depending on the composition of the compound.

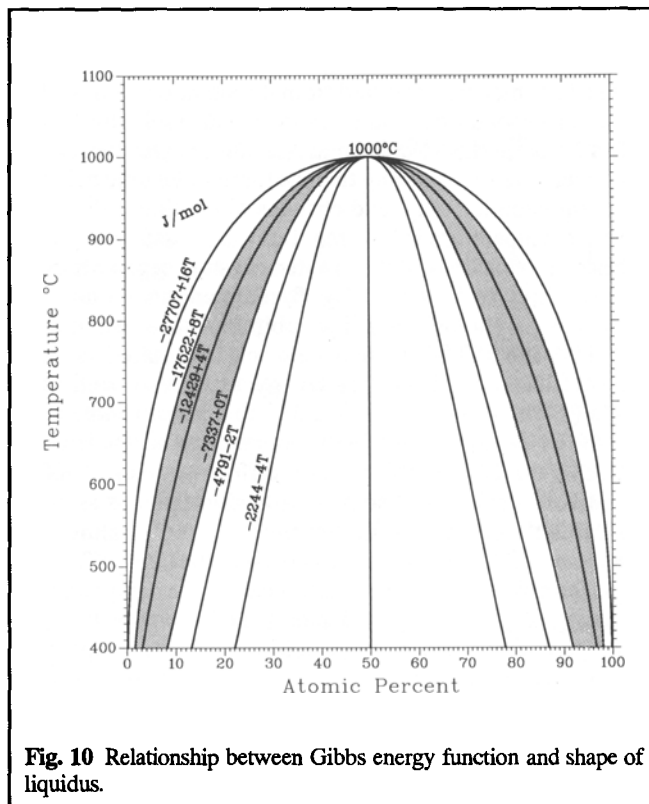


Fig. 10 Relationship between Gibbs energy function and shape of liquidus.

elements. Empirically, it is known that the values of b of most elements are approximately constant (the Richard rule) in the range of $\sim 10 (\pm 2)^{**} \text{ J/mol} \cdot \text{K}$, with only a few exceptions for nonmetallic elements such as Si and Ge ($>30 \text{ J/mol} \cdot \text{K}$). Because the entropy of fusion of a compound does not differ markedly from the entropies of the terminal elements [81 Goo], the value of b of a compound must be approximately $10 - R[X \ln X + (1 - X) \ln(1 - X)] \text{ J/mol} \cdot \text{K}$. The b values for various compounds in the same system therefore include a superficial contribution from the $-R[X \ln X + (1 - X) \ln(1 - X)] \text{ J/mol} \cdot \text{K}$ term. Thus, the value of b of most equiatomic compounds will be $\sim 4 (=10 - 5.763) \text{ J/mol} \cdot \text{K}$ (note that the melting point is not involved), and hence the resulting liquidus of a most normal compound will fall in the shaded range in Fig. 10 within a tolerable margin.

The discussion above was based on the assumption that the liquid is an ideal solution. When the excess entropy of mixing of the liquid phase, $\Delta_{\text{mix}} S^{\text{ex}}(\text{L})$, is not zero, the “sharpness” of the liquidus will change even for the same b value. However, the magnitude of $\Delta_{\text{mix}} S^{\text{ex}}(\text{L})$ is usually small (often assumed to be zero), and its influence is also small. When the enthalpy of mixing cannot be neglected, the sharpness of the liquidus varies substantially (but systematically), as already discussed in section 3.

** 9.7 ± 1.8 for 56 metallic elements (Ag, Al, Am, Au, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Np, Pa, Pb, Pd, Pr, Pt, Rb, Rh, Sc, Sn, Sr, Ta, Tb, Tc, Th, Ti, Tl, Tm, V, Y, Yb, Zn, Zr). Data were taken from [90Din]. Entropy of allotropic transformation is added.

7. Displaced Miscibility Gap (Point *f* in Fig. 2)

As mentioned in [91Oka2], the composition of the critical point of a liquid miscibility gap is usually found to occur in the center range of a phase diagram. A binary phase diagram having a liquid miscibility gap that is significantly displaced towards either end of the diagram may be considered to be rather suspect. The question then arises as to how much displacement from a near-central position is tolerable.

To establish the magnitude of the displacement of the critical point, the excess Gibbs energy for the liquid phase of a hypothetical system A-B may be expressed as a function of the B-component concentration *X* in the usual form

$$\Delta_{\text{mix}}G^{\text{ex}} = \Omega(X)X(1 - X)$$

where $\Omega(X)$ is the interaction parameter, and the excess entropy term is assumed to be negligible. When $\Omega(X)$ is constant

(and positive), the composition of the critical point of a miscibility gap (X_c) is, of course, at 50 at.%. Table 5 shows the calculated displacement of X_c for various asymmetric forms of $\Omega(X)$. The magnitude of $\Omega(1)$ has been set arbitrarily at 40 kJ/mol to permit also the calculation of the critical temperature (T_c) corresponding to X_c . However, the value of X_c is not related to $\Omega(1)$.

The selected composition-dependence expressions for $\Omega(X)$ are shown graphically in Fig. 12.

In the first-approximation “quasichemical” model, the solubility of A in B, or vice versa, in the liquid state is considered to be determined mostly by the relative magnitudes of the nearest-neighbor bonds between A and A, B and B, and A and B (Bragg-Williams approximation). Here, the deviation from the relationship $\Omega(X) = \text{const.}$ (Case 1 in Table 5) is expected to be small because the relative strengths of the bonds are expected not to vary significantly with composition. Case 2 corresponds to a limit of a normal situation where A is mostly indifferent to the introduction of B, but B strongly repels A in its own environment. Considering the omission of the entropy term and the

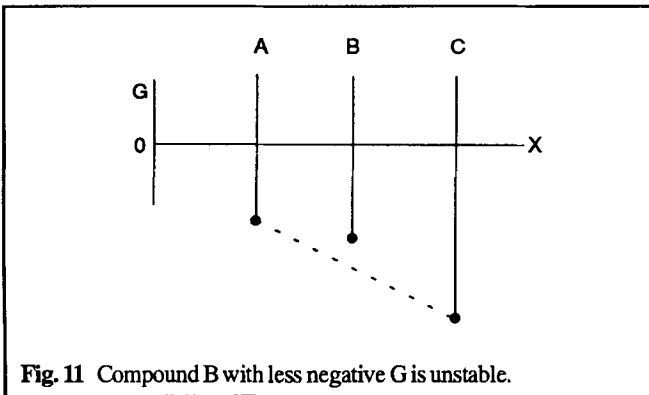


Fig. 11 Compound B with less negative G is unstable.

Table 5 Effect of Asymmetry of the Interaction Parameter on the Critical Composition of a Miscibility Gap

Case	$\Omega(X)$, kJ/mol	X_c , at. %	T_c , °C
1	40	50	2132
2	$40X$	74	1986
3	$40X^2$	82	1963
4	$40X^3$	86	1955
5	$40X^4$	89	1952
6	$40(-1 + 2X)$	79	2505

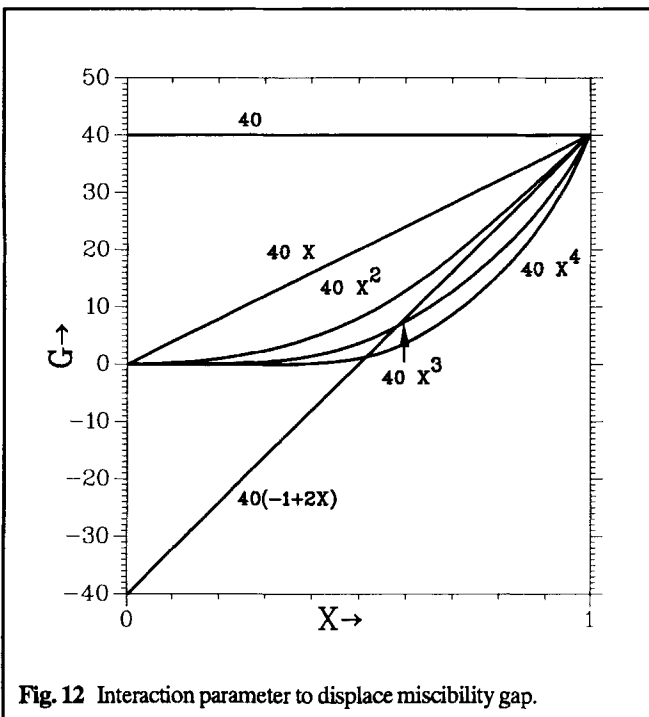


Fig. 12 Interaction parameter to displace miscibility gap.

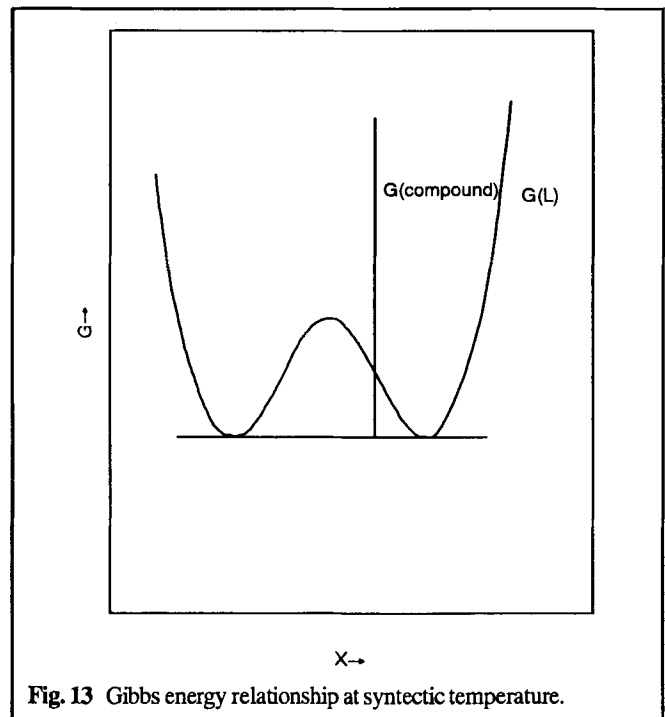


Fig. 13 Gibbs energy relationship at syntectic temperature.

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rather crude nearest neighbor approximation in the present estimate, it may be said that the location of a miscibility gap in

the liquid phase could be viewed as normal if X_c occurred between approximately 25 and 75 at.% (Cases 1 and 2).

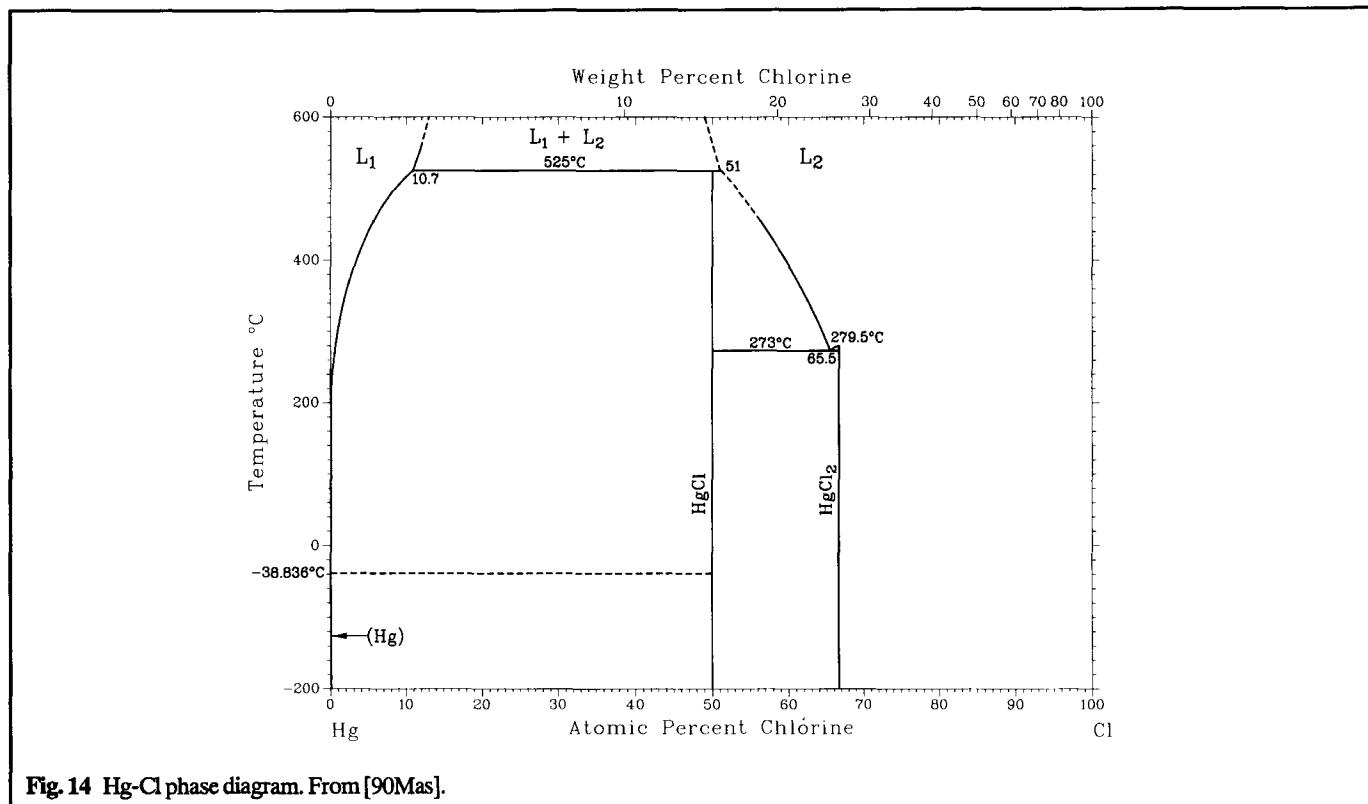


Fig. 14 Hg-Cl phase diagram. From [90Mas].

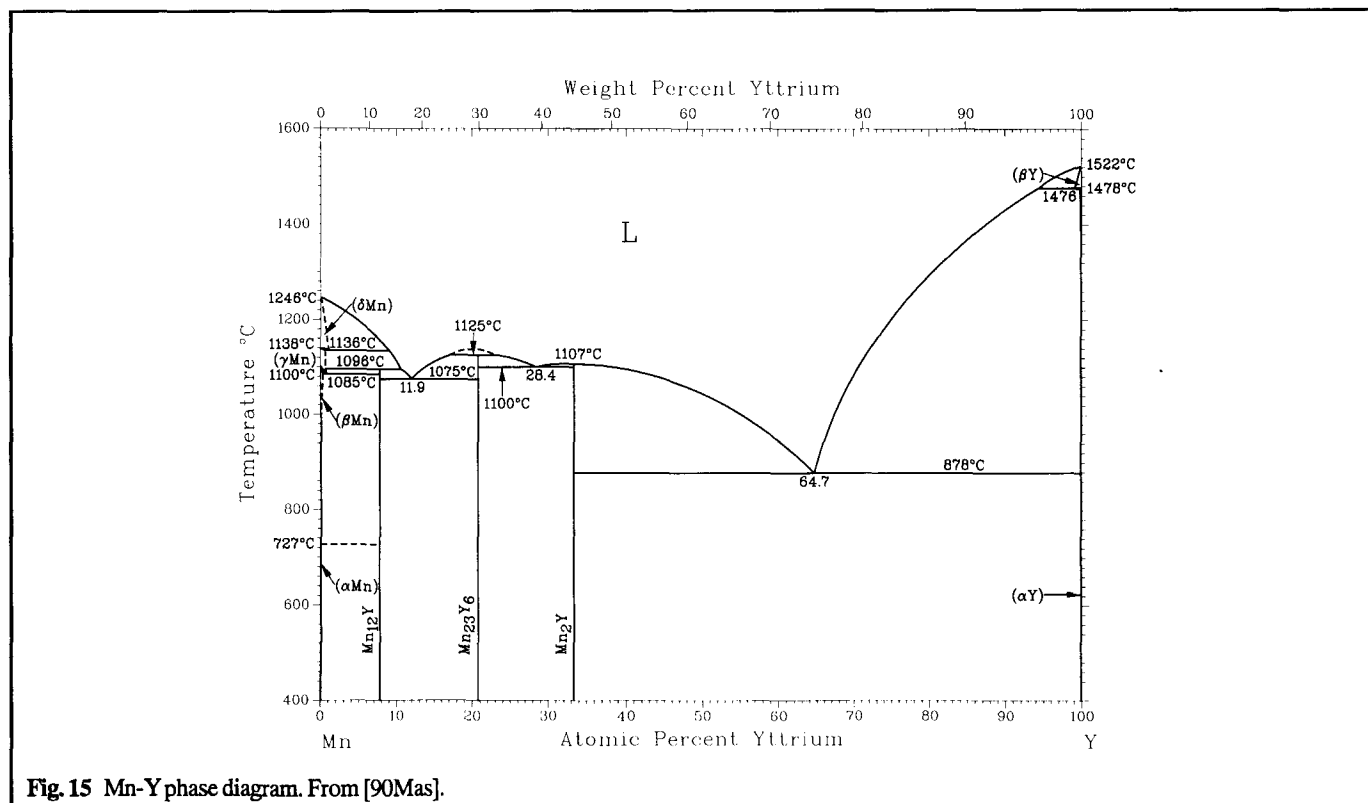


Fig. 15 Mn-Y phase diagram. From [90Mas].

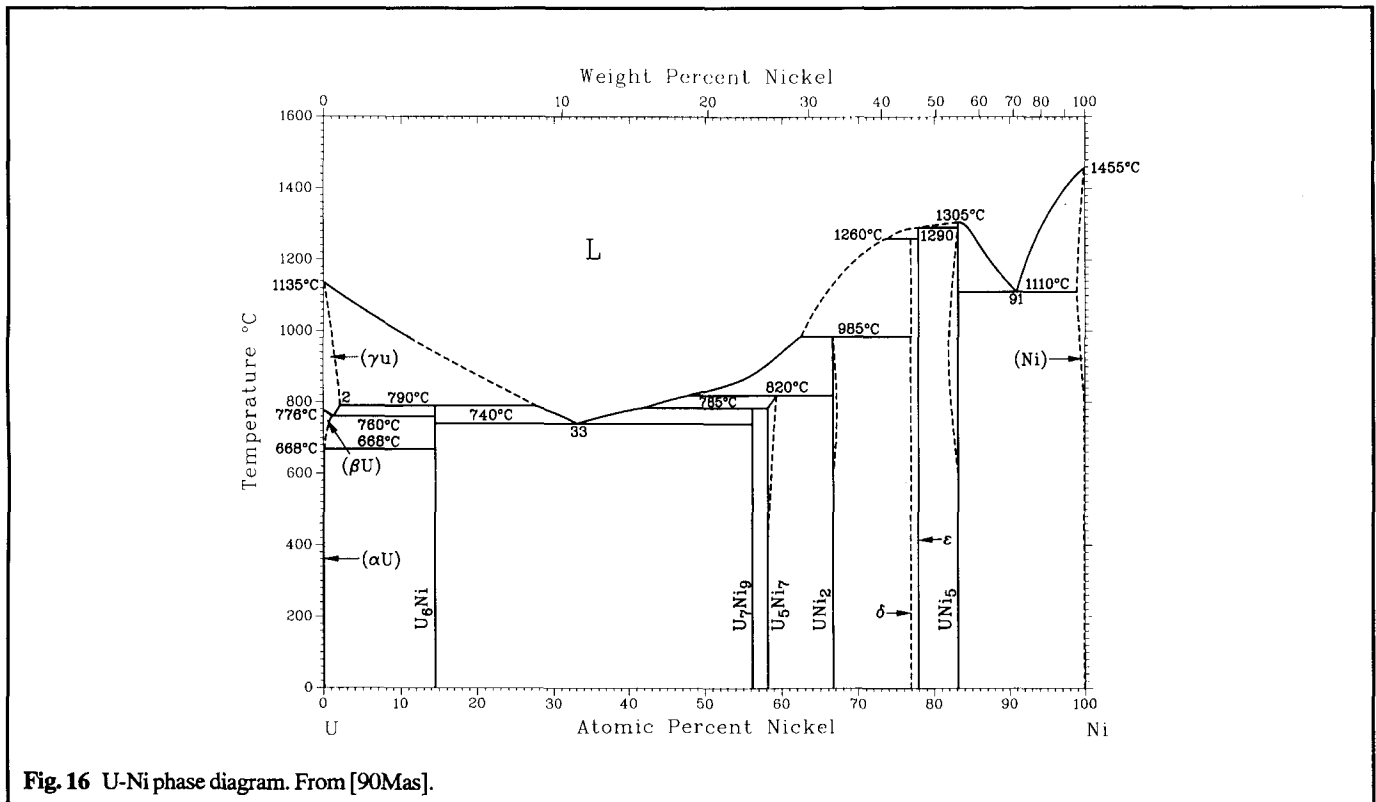


Fig. 16 U-Ni phase diagram. From [90Mas].

Table 6 Systems Including a Syntectic Reaction

Bi-Br	Bi-Cl	Bi-U	Cd-P	Cd-Rb	Cl-Hg
Cl-In	Cs-In	Ga-I	Ga-K	Ga-Rb	I-Tl
In-Rb	Mn-Y	Ni-S	Sn-P	Pb-U	Pd-Se

From [90Mas].

As the form of $\Omega(X)$ is made to become more distorted (Cases 3, 4, and 5), X_c moves away from the center of the phase diagram toward the B side. However, even when $\Omega(X)$ is assumed to have a 4th power dependence on X (Case 5), $X_c = 89$ at.%. Case 6 corresponds to an unusual situation whereby A favorably dissolves B (negative heat of formation), but B rejects A (positive heat of formation). This is of course an unlikely situation because the interaction between A and B should not be in general so drastically affected by the environment even when the next-nearest-neighbor, or higher-order effects, are taken into account. (Note: We are considering a liquid phase situation. If water does not dissolve oil, oil does not dissolve water either.) Based mainly on these propositions, a liquid miscibility gap having its critical composition outside the range of 20 to 80 at.% is very unlikely. If a liquid miscibility gap did actually occur near a pure element, this would signal a most unusual (and unique) situation, and it would be most challenging to determine some existing special reason for it (see [93Oka1]).

Note: (1) If the liquid phase develops associations (existence of molecules in the liquid state), the molecules behave like atoms. The "center range" for the purpose of considering the

phase diagram situations should then be taken as falling between the molecular composition and the pure element. The Hg-S system provides an example of this behavior. (2) A miscibility gap in the solid phase can of course occur near a pure element side (e.g., ϵ and (Cd) in the Ag-Cd phase diagram) because there may be strong crystal lattice effects.

8. Syntectic Reaction (Point *g* in Fig. 2)

In [90Mas], syntectic reactions ($L_1 + L_2 \rightarrow s$) are found in only relatively few binary systems, as listed in Table 6. Figure 13 shows a typical schematic Gibbs energy functions situation for the liquid and solid phases at the syntectic temperature; immiscibility in the liquid phase and compound formation in a solid phase occur at the same time. This is an unlikely situation unless the nature of the interactions between the elements constituting the binary system is very different in the liquid when compared with the solid state (elements A and B show affinity in the solid state, but they repel each other in the liquid state).* Thus, for a syntectic reaction to occur, involvement of two different types of interaction appears to be necessary. Not surprisingly, most systems in Table 6 involve a strongly ionic element (alkali, halogen, chalcogen). Moreover, the critical composition of the miscibility gap and the composition at which com-

*Similarly, associations in the liquid state are found only at compositions at which a compound exists below. Note that the opposite conclusion (when there is a solid compound, there is a liquid association) is not true.

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compound formation occurs are usually substantially different, as for example, in the Hg-Cl system (Fig. 14). Apparently, the tendency of separation into two liquids at one composition is overcome by an even stronger (and opposite) interaction for compound formation at another composition.

It follows from the above observation that the syntectic reaction in the Mn-Y system (Fig. 15) would have to be an exceptional situation of a simultaneous occurrence of two coincidences: the coincidence corresponding to a critical temperature of a miscibility gap and the syntectic temperature, and the coincidence of the composition of a critical point and the proposed stoichiometry of a compound. Accordingly, there is a strong possibility that this syntectic reaction is not real. If Mn-Y is excluded, Bi-U and Pb-U are the only systems in Table 6 not involving strongly ionic elements. This may be an interesting situation whereby the affinities between Bi and U or Pb and U are very high in the solid state, but very low in the liquid state.

Following the same reasoning, a situation shown in the U-Ni system (Fig. 16) is also rather unlikely because the liquidus just above the peritectic decomposition of U_7Ni_9 (and also U_5Ni_7) is concave. The form of the liquidus suggests that the enthalpy of mixing in the liquid phase is positive, but not high enough to develop a miscibility gap. In contradiction to this situation, the formation of compounds at lower temperatures implies a negative enthalpy of mixing between U and Ni in the same composition range. Other systems with similar features as U-Ni also should be considered in this light.

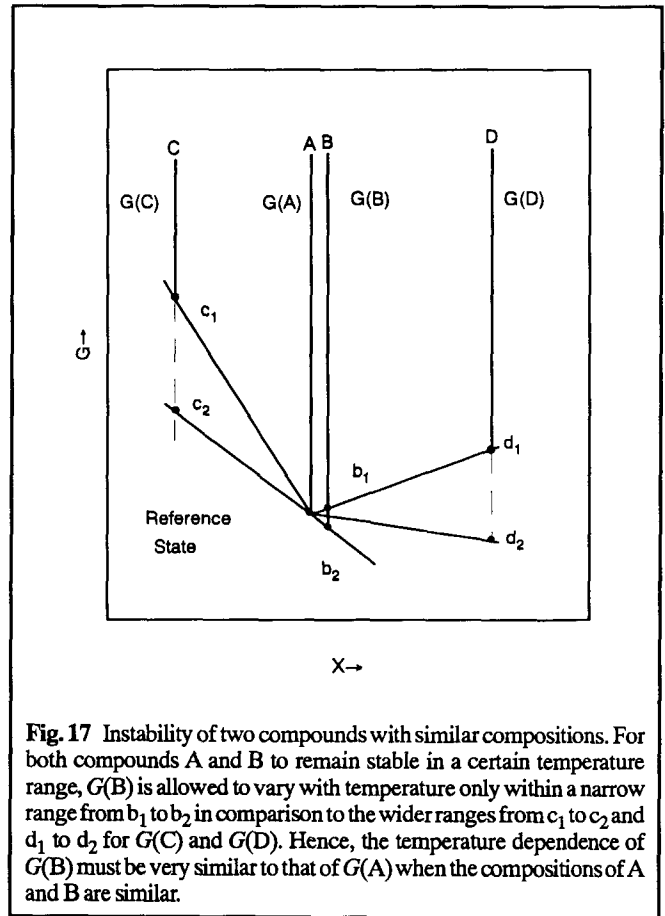


Fig. 17 Instability of two compounds with similar compositions. For both compounds A and B to remain stable in a certain temperature range, $G(B)$ is allowed to vary with temperature only within a narrow range from b_1 to b_2 in comparison to the wider ranges from c_1 to c_2 and d_1 to d_2 for $G(C)$ and $G(D)$. Hence, the temperature dependence of $G(B)$ must be very similar to that of $G(A)$ when the compositions of A and B are similar.

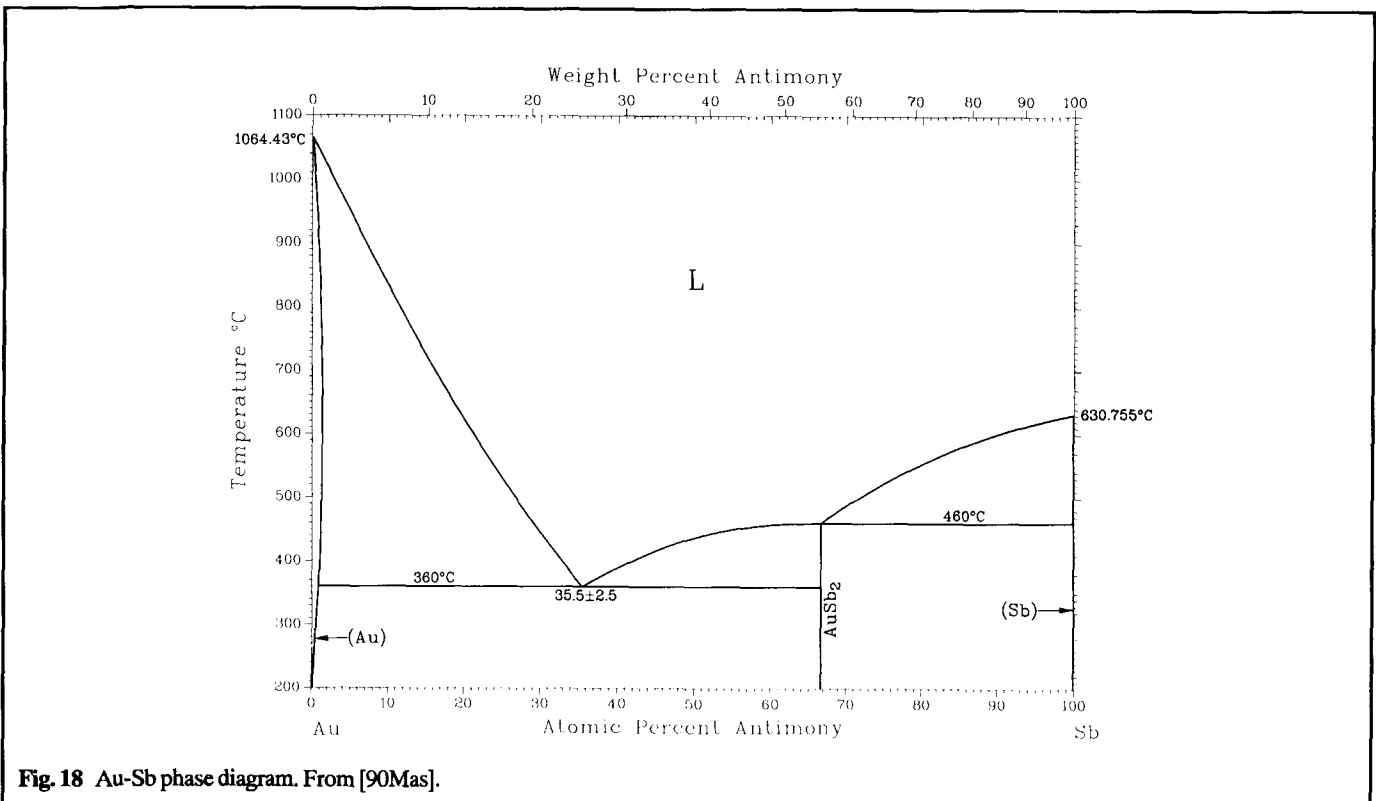


Fig. 18 Au-Sb phase diagram. From [90Mas].

9. Two Compounds with Very Similar Compositions Are Unlikely to Coexist in a Wide Temperature Range (Situation *h* in Fig. 2)

It is very unlikely that two compounds with very similar compositions should be able to coexist over a wide temperature range, as shown in a schematic phase diagram in Fig. 2. The relationship of Gibbs energies of compounds A and B existing near one another is shown in Fig. 17. In order for A and B to re-

main stable in a wide temperature range, the Gibbs energies, G , of both compounds must vary with temperature in almost exactly the same way because even a very small difference in G makes one of the compounds unstable (Fig. 17). This is especially true when the (stable or metastable) melting temperatures of the two compounds are not similar. The compound with a lower melting temperature will be in general more stable at lower temperatures (this is because, in such a situation, the temperature dependencies of G for the two compounds are dissimilar). Accordingly, the high-melting compound will become unstable with respect to its neighbor on cooling sooner or later, and only one compound will remain stable at low temperatures.

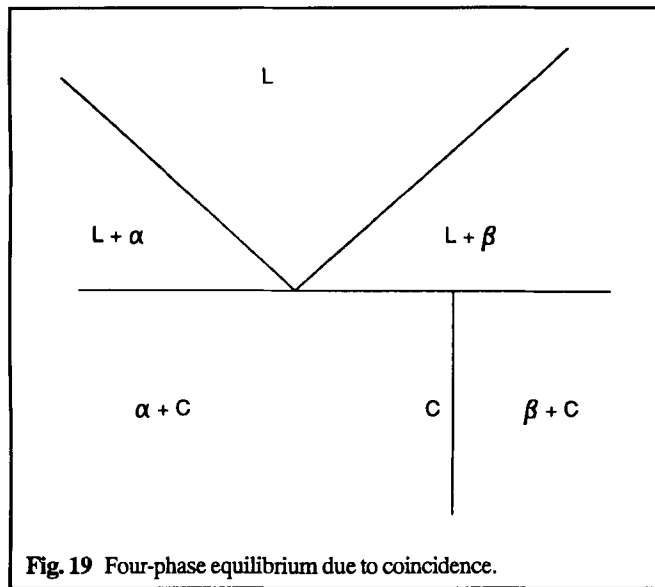


Fig. 19 Four-phase equilibrium due to coincidence.

10. Too Much Coincidence (Point *i* in Fig. 2)

As in any other phenomena or systems, unusual coincidence can happen in phase diagrams, causing an apparent violation of phase rules. For example, in the Au-Sb phase diagram (Fig. 18), the composition of the (Sb) liquidus at the $L + (Sb) \rightarrow AuSb_2$ peritectic reaction temperature (it could also be eutectic) is shown to be very close to the composition of $AuSb_2$. Here, the apparent difficulty regarding the reaction type at the melting point of $AuSb_2$ could be resolved by careful detailed experimentation. However, if a proposed phase diagram requires such two or more coincidences, a reexamination of a specific region may uncover some errors. For example, the apparent four-phase equilibrium shown by point *i* in Fig. 2 is possible only if the two independent reactions occur at the same temperature and composition. If the coincidence is in the "tem-

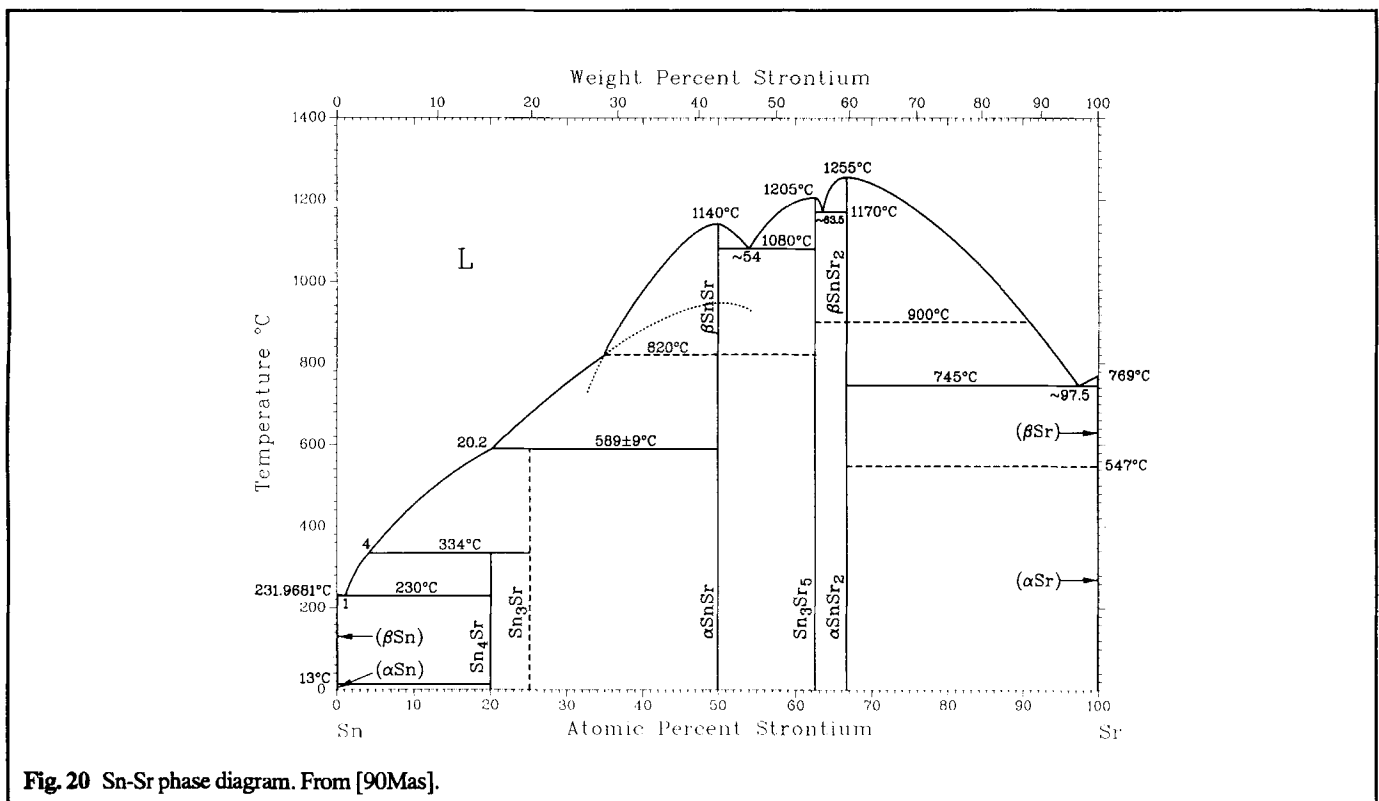


Fig. 20 Sn-Sr phase diagram. From [90Mas].

perature" only, the four-phase equilibrium is actually as shown in Fig. 19. Since even this type of coincidence is rare, the type *i* situation is either a matter of graphic scale, or is likely to be in error.

11. An Excessive Slope Change Associated with a Polymorphic Transformation (Point *j* in Fig. 2)

As already shown in section 4, a substantial change in the Gibbs energy function of a compound does not seem to cause much change in the slope of the liquid (or solid) phase boundary in equilibrium with the compound. Similarly, a phase diagram with a marked change in the slope associated with a polymorphic (or allotropic in the case of a terminal phase) transformation calls for careful handling because the change in the temperature coefficient of the Gibbs energy function accompanying a polymorphic transformation would be only of the order of $\sim 1 \text{ J/mol} \cdot \text{K}$. The slope change of the liquidii of β and αSnSr in the Sn-Sr system (Fig. 20) is a case in point.

12. Should There Be No Solid Solubility Range at 0 K? (Point *k* in Fig. 2)

Some phase diagrams show all the intermediate phases present within the diagram as having vanishing solubility at 0 K (for example, Ta-H in Fig. 21). The reasoning for this is that, according to the third law of thermodynamics, the entropy term is zero at 0 K and only perfectly ordered states are permissible. However, a perfectly ordered state with a specific composition

is not the only permissible state for alloy systems. As long as the enthalpy of mixing of a phase is negative in at least some composition range, the Gibbs energy of mixing always becomes negative in the same range as the temperature approaches 0 K because the contribution to the Gibbs energy from the entropy term also approaches 0. Hence, a continuous phase field can exist to 0 K.

The unlikely occurrence of a zero-width phase field at 0 K may be considered with reference to Fig. 21. The composition of the Ta-rich boundary of the η phase is determined by the Gibbs energy relationship between the η and β phases. The composition of the H-rich boundary of η is determined by the Gibbs energy relationship between the η and ζ phases. There is no reason why the boundaries should intersect at 0 K. The same applies of course to the other phases in Fig. 21. Hence an automatic attempt to draw boundaries of phases toward convergence of zero-width at 0 K (as shown by point *k* in Fig. 2) does not seem to be justified.

13. The Relationship Between Two Boundaries of a Two-Phase Field When Extrapolated Toward Higher Temperatures (Situation *l* in Fig. 2)

When the high-temperature ends of two boundaries delineating a two-phase field in a given phase diagram are terminated by an invariant reaction or experimental data to guide the form of the boundaries are scarce, extrapolation of these boundaries to higher temperatures may give a clue as to how they should be drawn to satisfy thermodynamic conditions.

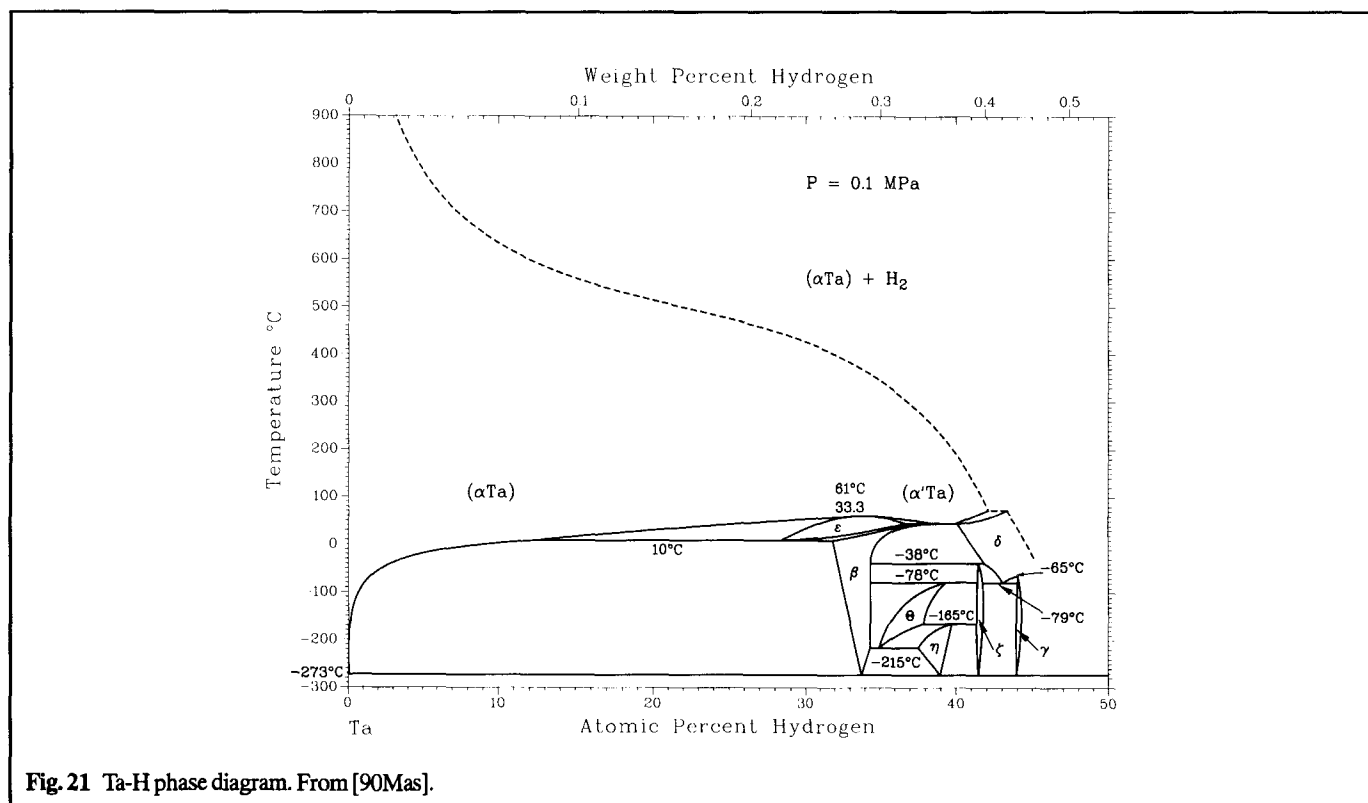


Fig. 21 Ta-H phase diagram. From [90Mas].

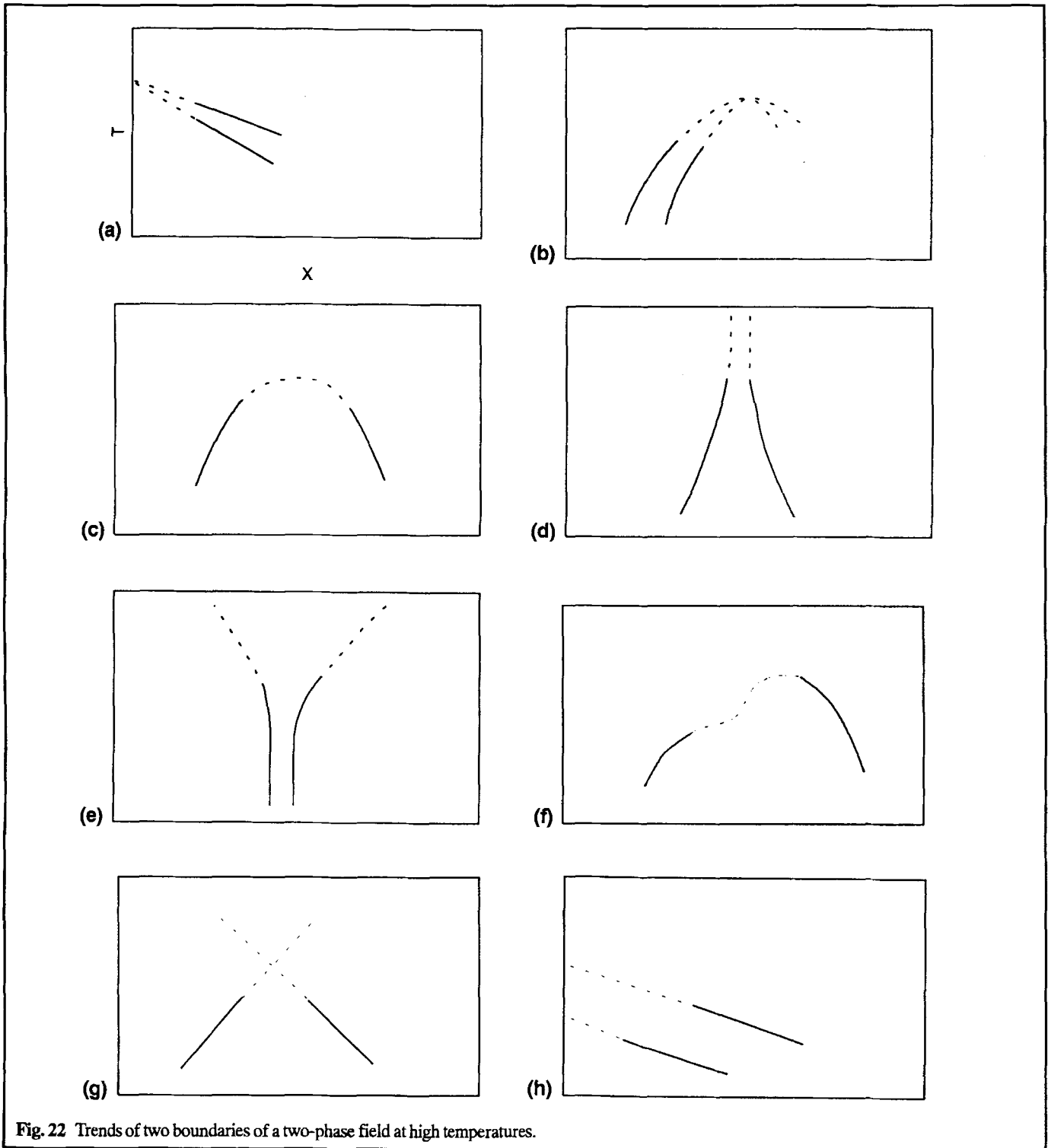


Fig. 22 Trends of two boundaries of a two-phase field at high temperatures.

Figure 22 shows possible relationships between two such boundaries of a two-phase field (in absence of other phases). Obviously, Fig. 22a, 22b, and 22c are the most common situations and are not considered here. When at least one of the two phases involved is a liquid, one of these situations is inevitable because a solid must eventually melt. Figures 22d and 22e are possible when the two phases are solids. In both situations, the

two boundaries may remain separated to infinitely high temperatures. This is possible when one type of crystal structure is always more stable when rich in A and the other type when rich in B. Figure 23 shows a possible schematic relationship of the Gibbs energies of the two phases. A question may be asked: Which of the two situations, Fig. 22d or 22e, is more plausible? When the temperature is increased, the solid solution of any

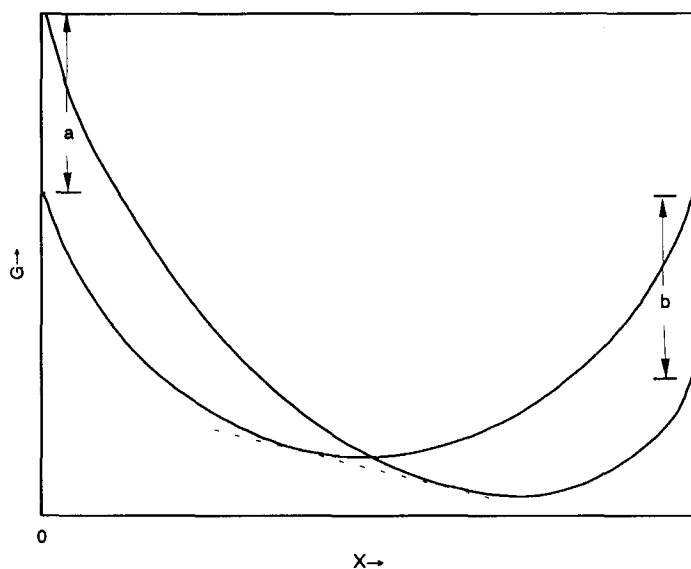


Fig. 23 Gibbs energy functions of two completely miscible phases.

Table 7 Thermodynamic Parameters of a Hypothetical Ag-Au System

Lattice stability parameter and Gibbs energy of formation, J/mol

$G^0(\text{Ag,L})$	= 0
$G^0(\text{Au,L})$	= 0
$G^0(\text{Ag,fcc})$	= -11 300 + 9.149T
$G^0(\text{Au,fcc})$	= -13 000 + 9.719T
$G^0(\text{AgAu})$	= -10 000 + 1.5T

Excess Gibbs energy of mixing, J/mol

$\Delta_{\text{mix}}G^{\text{ex}}(\text{L})$	= 0
$\Delta_{\text{mix}}G^{\text{ex}}(\text{fcc})$	= 0

crystal structure will behave more like an ideal mixture. The contribution of ideal mixing to the Gibbs energy is of the form $RT[X\ln X + (1-X)\ln(1-X)]$. This term decreases the Gibbs energy at a rate of $-5.76T$ J/mol at $X = 0.5$. On the other hand, the entropy of a possible transformation between two solid phases with different crystal structures is generally much smaller than 5.76 J/mol · K. Accordingly, if the magnitude of the Gibbs energy were drawn with the same scale on a graph, the lattice stability terms (a and b in Fig. 23) will tend to become smaller as the temperature increases, i.e., the two Gibbs energy curves will approach one another. Accordingly, the two boundaries of a two-phase field should tend to converge. Hence, Fig. 22d is more likely to occur than Fig. 22e. When the crystal structures of two phases are the same, the boundary must converge smoothly as shown in Fig. 22c. Therefore, Fig. 22f with an abrupt change of slope is unlikely to occur. Figures 22g and 22h are obviously wrong. It follows that if a two-phase region is drawn as if it were widening at higher temperatures, or the two boundaries appear to cross one another when extended, or if the two boundaries appear to cross the pure ele-

ment line at different temperatures, further experimental work may be needed to check the projected trend.

As is well known, the bcc phase always “wins” at high temperatures due to the large vibrational entropy contribution in the $-TS$ term (Zener-effect [61Mas, 66Zen]). As a result, the phase relationships between a bcc phase and phases with other structures tend to be of the Fig. 22a-type at the high-temperature end of the two-phase field (when the liquid phase is not considered).

14. Congruent Transformation of a Compound on Cooling (Point m in Fig. 2)

If metastable melting is included (i.e., no other solid phases are considered), any compound phase eventually melts congruently. Similarly, any compound phase will congruently transform to a continuous solid solution phase on heating if a transformation ever occurs (it may not occur, as shown in Fig. 22d). On the other hand, no compound has been reported to transform congruently on cooling. (Even if extended solid solution phases are also considered, a congruent transformation on cooling is not common. A rare exception is the transformation of the (γFe) in the Cr-Fe system into (αFe) on cooling.) However, it is very easy to construct a hypothetical phase diagram with a compound transforming to a continuous solid solution phase on cooling. For example, Fig. 24 shows a hypothetical Ag-Au phase diagram with an equiatomic compound “AgAu,” where, for simplicity, the liquid and solid phases are assumed to be ideal solutions. The relationship between the liquidus and solidus as calculated for this situation is essentially identical to that of the published assessed phase diagram. Table 7 shows all thermodynamic parameters assumed in this calculation. According to the criterion in section

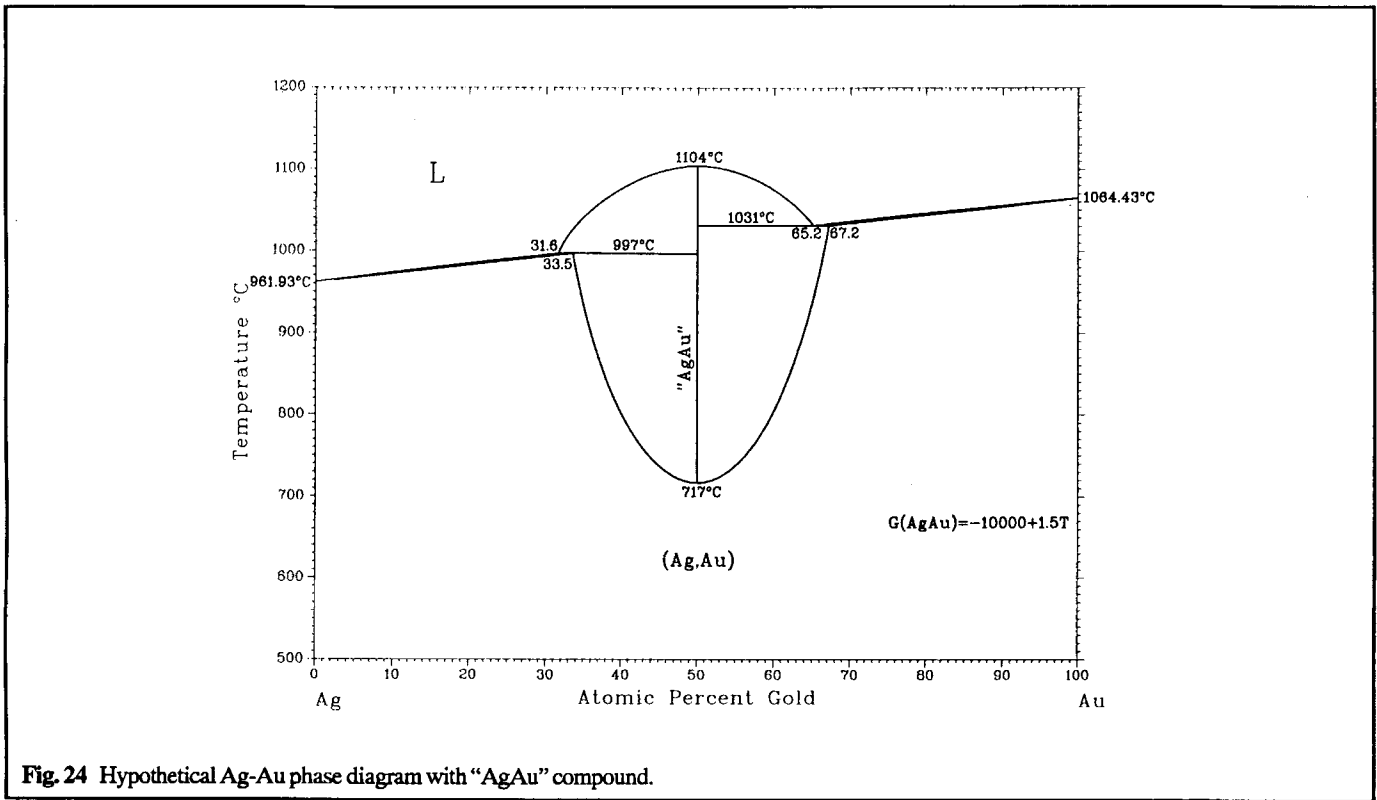


Fig. 24 Hypothetical Ag-Au phase diagram with "AgAu" compound.

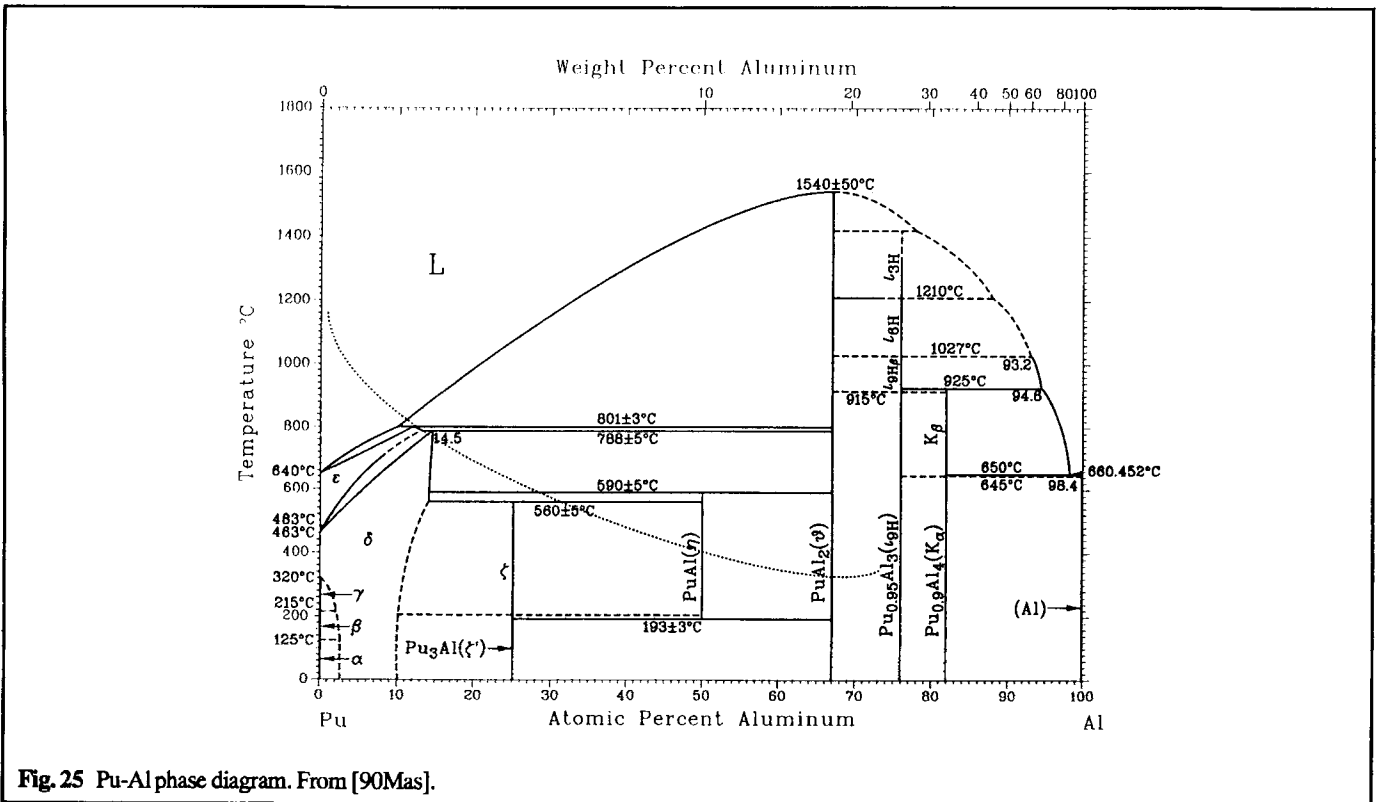


Fig. 25 Pu-Al phase diagram. From [90Mas].

6, the magnitude of the Gibbs energy of AgAu is quite normal. Then, why don't we see the congruent transformation on cool-

ing? The answer is in the entropy term. The entropy of an ordered phase is smaller than that of a disordered phase making

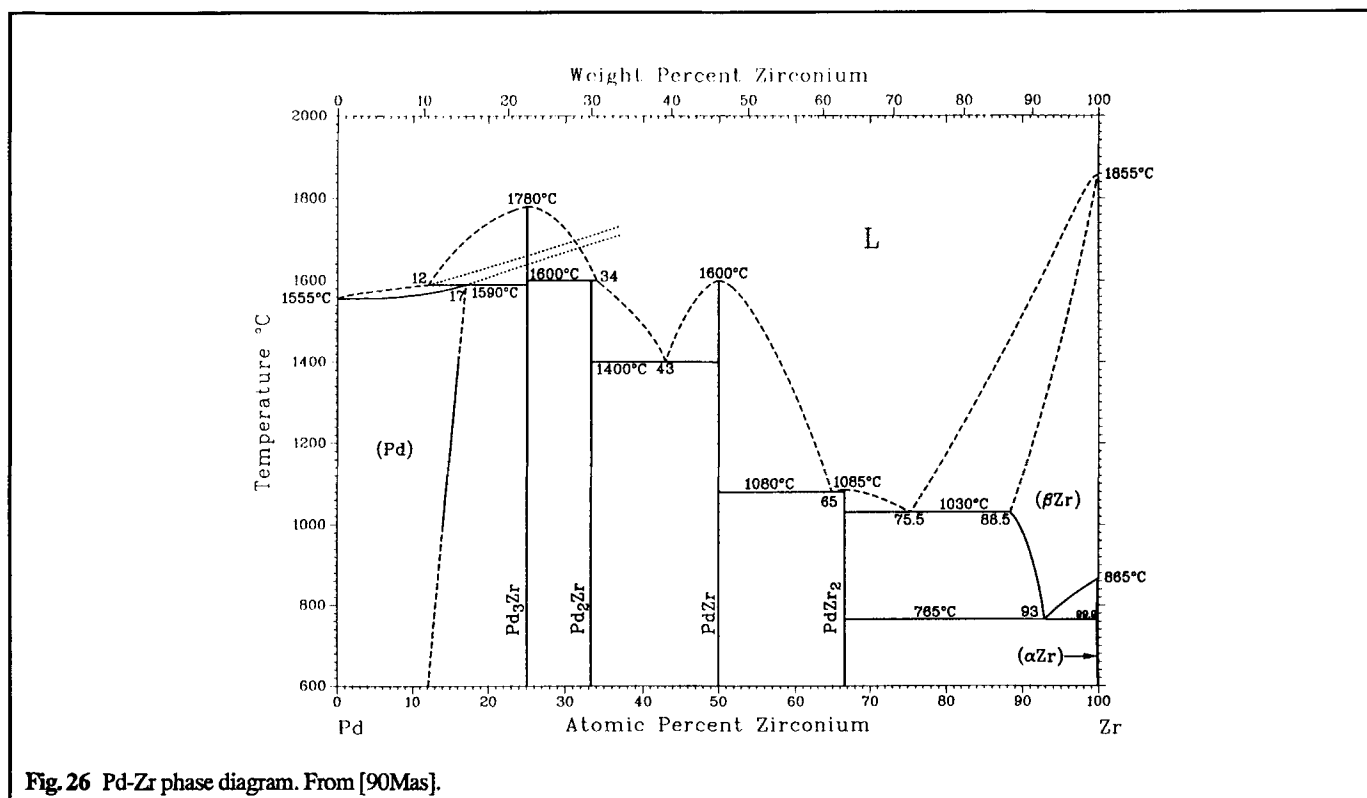


Fig. 26 Pd-Zr phase diagram. From [90Mas].

the $-TS$ term of the disordered phase overwhelm that of the ordered phase at high temperatures. Therefore, the disordered phase is always more stable at higher temperatures.

In the present model, the structure of "AgAu" was not considered. The transformation as shown in Fig. 24 could occur when the compound has a simple structure while that of the solid solution phase is relatively complex, e.g., in organic systems. However, it may be safe to conclude that a congruent transformation of a compound phase to a solid solution will not occur on cooling, especially when the structure of the solid solution phase is relatively simple, as in metallic systems.

The above conclusion may be restated by saying that a two-phase field between a compound phase and a solid solution phase must become, as a rule, narrower at higher temperatures. Otherwise, an unlikely transformation becomes inevitable. This obvious situation is sometimes forgotten when the bottom part of a two-phase field is masked by other reactions. The $\epsilon/\epsilon + \text{PuAl}_2$ boundary in the Pu-Al phase diagram (Fig. 25) provides a typical example of this unlikely situation.

15. An Inverse Miscibility Gap (Point n in Fig. 2)

A thermodynamic model that might result in the development of an inverse miscibility gap with a minimum-temperature critical point (as shown by point n in Fig. 2) is certainly conceivable. However, the existence of such a miscibility gap in a real system would be certainly unusual* because any solution in nature is expected to behave more ideally as the temperature

is increased. Hence, a thermodynamic model demanding an inverse miscibility gap may be considered to be unrealistic by its own nature, at least in simple metallic systems. An inverse miscibility gap will occur when the contribution from the excess entropy of mixing term overcomes the contribution from the ideal entropy of mixing term (maximum $-5.763 \text{ J/mol} \cdot \text{K}$); i.e., an inverse miscibility gap develops if the magnitude of the excess entropy is greater than $\sim 23X(1-X) \text{ J/mol}$. A situation corresponding to this large value of 23 ($=5.763 \times 4$) may already be too unnatural. A factor of 10 was assumed to be the limit in section 5.

A thermodynamic model proposed by [92Sto] for the Pd-Zr system may serve as a typical example of the present considerations. In order to reproduce the Pd-Zr phase diagram in [90Mas] (Fig. 26), [92Sto] obtained an expression for the excess Gibbs energy of mixing of the liquid phase in the form:

$$\Delta_{\text{mix}} G^{\text{ex}}(\text{L}) = X(1-X)[-476\,537 + 241\,068X + 292\,144X^2 + (123.89 + 16.22X - 310.32X^2)T] \text{ J/mol}$$

where X is the atomic fraction of Zr. The entropy term here is positive and large on the Pd-rich side, and an inverse miscibility gap (overlooked by [92Sto]) does develop with the critical point at $X = 0.387$ and $2428 \text{ }^\circ\text{C}$. Apparently, the model was inappropriate. (As a matter of fact, the (Pd) liquidus and solidus in the original phase diagram [90Mas] used for the modeling is

*Although no inverse miscibility gap is found in [90Mas], such gaps may occur in organic liquids (e.g., water-triethyl amine system) or under high pressures.

itself rather unlikely. The problem to be discussed in [93Oka2] is shown with dotted lines.)

16. A Narrow Gas+Liquid Two-Phase Field is Unlikely (Point o in Fig. 2)

The initial opening angle* of a G + L two-phase field as determined experimentally, or if calculated by using a thermodynamic model, is generally wide in comparison with a L + s opening in a similar situation. This is because the enthalpy of vaporization of any element is several times larger than the enthalpy of fusion of the same element. The opening angle can be small only when both boundaries are nearly horizontal, as expected from the well known van't Hoff relationships [91Oka2]. However, it is very unlikely that a narrow two-phase field G + L extends substantially away from a pure component line in a binary phase diagram, as will be considered below. This may be a helpful hint in drawing a schematic phase diagram.

Horizontal boundaries can occur only when the Gibbs energy of the liquid phase is very similar to that of the gas phase. In an ordinary situation, the gas phase can be regarded as an ideal mixture. At the boiling point of element A in an A-B system, the Gibbs energies of the gas and the liquid phase are

$$G(G) = RT[X \log X + (1 - X) \log(1 - X)] + aX$$

$$G(L) = RT[X \log X + (1 - X) \log(1 - X)] + \Omega X(1 - X)$$

where standard states are the liquid elements, and $a = S(B)_{\text{boil}} \Delta T_{\text{boil}}$ (constant). It follows that the interaction parameter Ω of the liquid phase must be equal to $a/(1 - X)$, i.e., the magnitude of Ω must be very close to a at $X = 0$. In addition to this coincidence, the composition dependence of Ω must be of the $(1 - X)^{-1}$ form (approximately $1 + X$ form when $X \ll 1$), whereas a typical Ω shows a $1 + kX$ form composition dependence (naturally $k \neq 1$).

In summary, a narrow G + L two-phase field is much less likely to occur than a narrow L + s two-phase field because the enthalpy of vaporization is typically large and the behavior of the gas phase is usually nearly ideal.

17. Conclusions

The present work was undertaken to provide a few more guidelines and examples for examining the validity of various phase boundaries in binary phase diagrams. The results of this work, together with those of our earlier papers [91Oka1, 91Oka2], have been applied in [93Oka2] as a basis for commenting on the reported features of the over 2000 phase diagram graphics published in [90Mas].

Admittedly, it is as well to keep in mind that the various guidelines discussed above are not rigid rules. Situations undoubt-

*The van't Hoff relationship is related to the horizontal width of the two-phase field (formed by the initial slopes) rather than the opening angle between the two phase boundaries. Because the horizontal width varies with temperature, the opening angle or slope difference is a more convenient measure for examining the validity of a phase diagram.

edly exist where some of the above guidelines do not apply. On the other hand, it is encouraging to see how many of the old phase diagrams that were not in compliance with the present guidelines are being constantly and consistently revised to more reasonable forms. The present authors believe that this trend will continue in the future and trust that their present effort will contribute to this trend.

Acknowledgment

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