

SINGULAR POINT ANALYSIS: CONSTRUCTION OF SCHREINEMAKERS PROJECTIONS FOR SYSTEMS WITH A BINARY SOLUTION

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ABSTRACT. Variation in the composition of a solution phase in a univariant equilibrium can lead to a condition such that the reaction coefficient of one phase in the equilibrium vanishes. This condition is known as a *singular point*, and at such points the univariant equilibrium becomes degenerate with a singular univariant equilibrium. In general, in a $(c + 2)$ -phase system that contains a single binary solution any two univariant equilibria will share a common singular equilibrium. The number of ways two univariant equilibria can be related by a singular equilibrium is constrained by Schreinemakers principles. These constraints are summarized by seven rules that limit the number of ways in which singular points can be arranged about an invariant point in a Schreinemakers projection. The resulting projection is a singular-point net, and for each singular-point net the direction of compositional variation in the solution phase is uniquely determined along every univariant curve. This has the interesting consequence that if the direction of compositional variation along one univariant curve around an invariant point is known, then the directions of compositional variation along the remaining curves can be determined solely from topologic constraints. The same constraints can be applied to systems containing simple mineral solutions or melts in order to predict compositional variations.

INTRODUCTION

The principles governing the invariant point topologies of phase diagram projections for systems in which all phases have fixed composition have been widely applied to geologic problems since their introduction by Niggli and Johnston (1914), Korzhinskii (1959), and Zen (1966). These principles are also valid for invariant points at which one, or more, of the phases has variable composition, but until recently (Connolly and Trommsdorff, 1991) it does not appear to have been recognized that these principles can also be used to predict compositional variations along univariant curves. The object of this paper is to present a more general and systematic treatment of these principles. The treatment is useful not only in a predictive capacity but also permits the recovery of essential information on the compositional variations of phases.

Several new features appear in phase-diagram projections if compositional degrees of freedom are associated with the phases of a system. These features are the traces of *singular equilibria* that arise from compositional variations of phases that lead to degeneracies in composition space. Singular equilibria project as curves in P-T projection which coincide with univariant curves at *singular points*. The basis of the treatment

presented here is that the arrangement of the singular points that occur along univariant curves emanating from an invariant point is subject to topologic constraints that can be deduced from chemographic relationships. The first section of this paper details the topology of the singular points and curves along an individual univariant curve for an equilibrium involving a binary solution. When two such curves, involving the same binary solution, intersect at an invariant point the resulting arrangement of singular points and curves form a network designated here as a *singular-point net*. An analytic method for constructing singular-point nets is developed in the second section. The complications caused by compositional degeneracies are discussed in the subsequent section. The final section gives an example of application of singular-point analysis to a geologic problem.

FREQUENTLY USED SYMBOLS

c	number of thermodynamic components
d	dimension of a phase-diagram element
G_i	Gibbs free energy of phase i
P	pressure
T	temperature
n_j	number of moles of component j
S_i	composition of a solution phase at an invariant condition
S_n	singular point, n indexes the singular composition
$S_{(x,y)}$	singular point, x and y are phases absent from the equilibrium
X_j^i	composition of phase i with respect to component j
α_i	reaction coefficient of phase i
ϕ_i	composition vector of phase i
β_k	coefficients of a plane in composition space
δ_x	displacement of composition x with respect to a $(c - 2)$ -dimensional plane in composition space
$\Gamma_{x,y}$	δ_x/δ_y

TOPOLOGY OF SINGULAR POINTS AND CURVES ALONG A UNIVARIANT CURVE

To illustrate the principles governing the arrangement of singular points it will be useful to begin by considering a univariant equilibrium in a hypothetical ternary system consisting of 3 compounds, that is stoichio-

metric phases, and a binary solution. The P-T loci of the equilibrium will define a univariant curve in P-T space that satisfies the condition

$$\sum_{i=1}^{c+1} \alpha_i G_i = 0, \quad (1)$$

where the α_i are reaction coefficients obtained from the mass balance constraint:

$$\sum_{i=1}^{c+1} \alpha_i \phi_i = 0, \quad (2)$$

where i indices the phases in equilibrium, and c is the number of thermodynamic components for the system, ϕ_i is a vector describing the composition of the i^{th} phase, and α_i is the reaction coefficient of that phase. At any arbitrary condition for this equilibrium the P, T, and composition of the solution phase ϕ_s will be fixed, and if any one of these parameters is varied then all the remaining parameters will vary as a function of this parameter. This implies that ϕ_s and the reaction coefficients ($\alpha_1, \dots, \alpha_{c+1}$) will vary along the univariant curve as it is traced through P-T space. In the course of such variation it is possible that a reaction coefficient changes sign and therefore that at a point in P-T space one coefficient vanishes, such a point is called a *singular point*. At a singular point the univariant equilibrium is still among $c + 1$ phases, but the reaction involves only c phases that can be described by a subset of $c - 1$ components. As it is possible to constitute a system consisting of only these $c - 1$ components, it must also be possible to obtain an equilibrium with the same reaction equation among only c phases. Therefore, at a singular point, two univariant equilibria are realized, one consisting of all $c + 1$ phases, and another consisting of a subset of c phases. Both equilibria have the same reaction equation at the singular point; however, in contrast to the reaction equation of the $(c + 1)$ -phase equilibrium, the reaction coefficients of the c -phase equilibrium cannot vary as a function of P or T, because the solution composition is fixed. Thus, the P-T loci of the two equilibria are the same only at the singular point and must diverge away from it. This is illustrated in figure 1 which shows a three-component system. For this system if the composition of the solution S is S_i , the reaction will be $1 + 3 = 2 + S_i$. If the composition of the solution shifts toward S_1 , the coefficient α_2 becomes smaller, reaching zero at S_1 . This condition is a singular point. Inspection of figure 1 reveals that there are three possible singular points, represented by [1], [2], and [3] which occur respectively at compositions S_1 , S_2 , and S_3 . Thus, in this case there are three c -phase univariant curves related to the $(c + 1)$ -phase univariant equilibrium. Such curves were first designated turning lines by Schreinemakers (1916), but Schreinemakers more general term *singular curve* is preferred and used in this restricted sense.

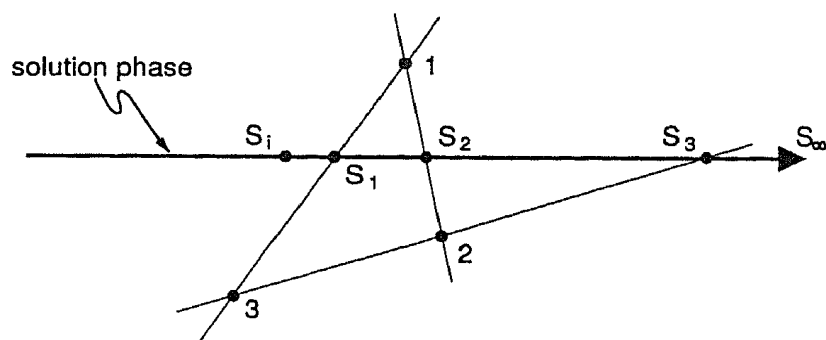


Fig. 1. Chemography of three compound phases (1–3) and a binary solution S in the three component system discussed in the text. The composition of the solution phase at the invariant point is S_i . Compositions S_1 , S_2 and S_3 represent singular compositions of the solution phase that arise through linear compositional degeneracies between the solution and two compound phases, as shown by thin lines (hinges). The arrowhead points in direction of the solution composition S_∞ , this composition is used arbitrarily to indicate the direction of solution-composition variation in a univariant equilibrium.

Enumeration of Singular Points

Singular equilibria involve only a subset of the phases involved in the univariant equilibrium. For purposes of introduction, consideration will first be restricted to phase chemographies in which the compounds are nondegenerate and in which none of the compounds lies within the composition space of the solution. In this case, the singular reactions can be enumerated by taking all possible permutations of $c - 1$ compound phases. The compositional coordinates of such a $(c - 1)$ -phase permutation are spanned by a $(c - 2)$ -dimensional geometrical element which will be shown to be of importance in determining phase diagram topologies and will be referred to as a *hinge*. If a hinge intersects the solution-composition space, then the equilibrium of the phases that define the hinge together with the solution comprise a singular equilibrium, where the singular solution composition is given by the intersection of the hinge with the solution-composition space.

The singular points that occur along a $(c + 1)$ -phase univariant curve can be enumerated through linear algebra. To accomplish this it is useful to choose the endmember compositions of the solution phase as components. These will be designated here as the $c - 1^{\text{th}}$ and c^{th} components. The intersection of a hinge with the composition space of the binary solution is then determined by solving the equation:

$$\begin{pmatrix} X_1^1 & X_1^2 & \cdots & X_1^{c-2} \\ X_2^1 & X_2^2 & \cdots & X_2^{c-2} \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ X_{c-2}^1 & X_{c-2}^2 & \cdots & X_{c-2}^{c-2} \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \cdot \\ \cdot \\ \alpha_{c-2} \end{pmatrix} = \begin{pmatrix} X_1^{c-1} \\ X_2^{c-1} \\ \cdot \\ \cdot \\ X_{c-2}^{c-1} \end{pmatrix} \quad (3)$$

where the leftmost matrix contains the composition vectors of the $c - 2$ compound phases in the subcomposition defined by the first $c - 2$ components. The solution composition vector is then

$$\sum_{i=1}^{c-1} \alpha_i \phi_i = \phi_s, \quad (4)$$

and the composition of the solution with respect to component c , X_c^s is given by $n_c/(n_c + n_{c-1})$. If $0 \leq X_c^s \leq 1$ the intersection lies between the solution endmembers, and the assemblage is a potential singular equilibrium for which the singular reaction equation is:

$$\begin{pmatrix} X_1^1 & X_1^2 & \cdots & X_1^c \\ X_2^1 & X_2^2 & \cdots & X_2^c \\ \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdots & \cdot \\ X_c^1 & X_c^2 & \cdots & X_c^c \end{pmatrix} \begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \cdot \\ \cdot \\ \alpha_c \end{pmatrix} = 0. \quad (5)$$

Otherwise the hinge does not correspond to a real singular equilibrium.

SINGULAR POINT TOPOLOGY

Given the existence of singular points along a $(c + 1)$ -phase univariant curve the question arises as to the nature of the connections between this curve and its conjugate¹ singular curves. The topology of these connections is dictated by the rules presented below:

1. *The stability of a $(c + 1)$ -phase univariant curve cannot change at a singular point.*—This rule can be justified given that in order for the stability of the univariant curve to be affected, the representative G-X coordinates of an additional phase must pass through the G-X plane containing the coordinates of the phases in equilibrium. As the singular equilibrium involves only a subset of the phases of the conjugate univariant equilibrium, there is no additional phase present to affect the stability of the univariant curve.

2. *The stability of a singular curve may change through a singular point.*—This is due to the fact that the singular equilibrium involves only a subset of the phases of the univariant equilibrium. Therefore it may become metastable with respect to the additional phase present in the univariant equilibrium.

3. *A singular curve cannot cross a conjugate univariant curve.*—There are two scenarios in which such crossings can be envisioned. In one case the solution phase in both conjugate curves has the same composition,

¹The term conjugate is used here to describe any equilibria, or representative phase-diagram elements, that include a common c -phase assemblage; in the present context this implies that any curves connected by a singular curve are conjugate to each other and to the singular curve.

that is, the intersection would be a singular point. This in itself is extremely improbable as it would require the coincidence of an inflection in one of the curves and the singular point. However, even if this should occur, such a crossing would affect the stability of the univariant curve in violation of rule (1), as the singular curve always must limit the stability of a subset of the phases present in the conjugate univariant equilibrium. In the alternative scenario the solution would have a different composition in the conjugate singular and univariant curves. In this case, which implies immiscibility of the solution, there would be $c + 2$ phases in equilibrium at the crossing, which would therefore be an invariant point. This scenario would require the coincidence of the singular solution composition and a limb of the solvus together with the conditions for the univariant equilibrium, which is extremely unlikely.

4. *The singular curve divides P-T space into regions in which a divariant assemblage exclusive of the solution is more and less stable than at least one other c-phase permutation of the univariant assemblage* (for example, assemblage $1 + 2 + 3$ in fig. 2).—As the univariant reaction is identical with the singular reaction at the singular point this assemblage must lie on the same side of both conjugate curves. Without this restriction there are

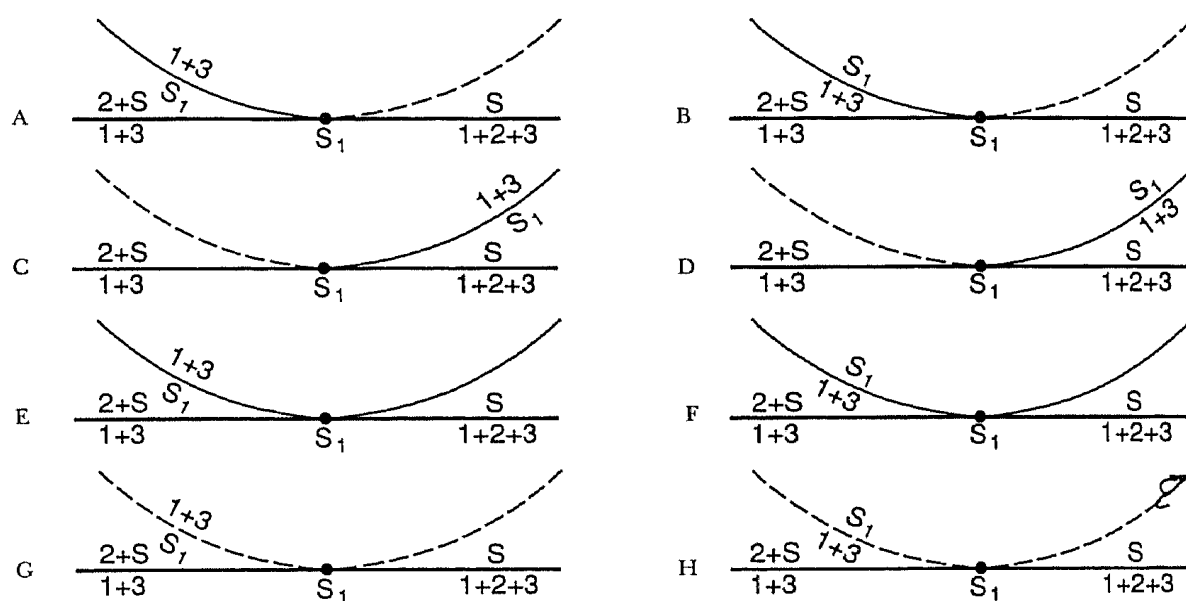


Fig. 2. Eight topologically distinct ways of arranging a singular and a univariant curve around a conjugate singular point, shown for the example of singular point S_1 in figure 1. Singular points are labeled by the composition of the solution phase. Stable and metastable singular curves are shown by thin solid and dashed curves, respectively. Nondegenerate univariant curves are drawn with thick lines. Of these topologies only D represents a thermodynamically valid topology. Topologies E to H violate rule 2 and consequently rule 5, according to which stability of a singular curve changes as it passes through a conjugate singular point and thus are not valid topologies. Likewise topologies A, C, E, and G are invalid because the solution-absent assemblage is stable on opposite sides of the conjugate univariant and singular curves in violation of rule 4. Lastly topology B is invalid according to rule 5, because the assemblage $1 + 3$ cannot be stable on both sides of the extension of the univariant curve that limits the stability field of $1 + 3$. Note that on either side of a singular point the reaction coefficient of the phase present in the univariant equilibrium, but absent from the singular equilibrium, changes sign.

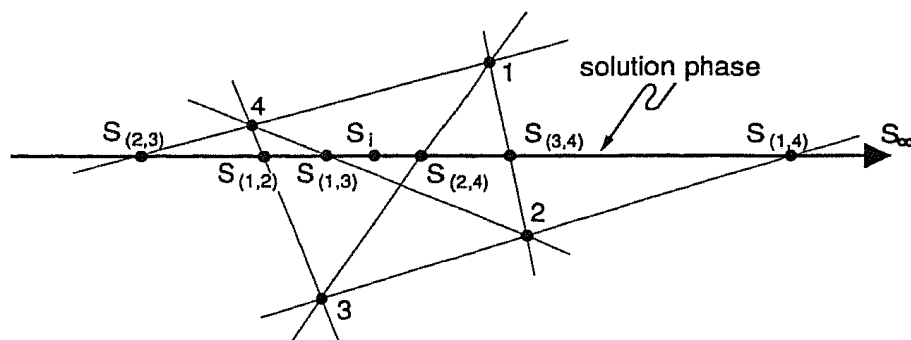


Fig. 3. Chemographic relations among the compound phases 1 to 4 and a binary solution S in a three-component system. The invariant solution composition is S_i , and $S_{(1,2)}$ to $S_{(3,4)}$ represent singular solution compositions which are labeled by the phases absent from the corresponding hinges. Hinges are shown by thin lines.

eight ways in which a singular and univariant curve can be arranged around a singular point as illustrated in figure 2. It can be seen in this figure that this rule excludes the choices A, C, E, and G.

5. *The segments of the curves that limit the stability of the assemblage or phase referred to in rule (4) cannot have the same stability on the same side of the singular point.*—This rule can be argued by observing that if these sections of the conjugate singular and univariant curves lie on the same side of the singular point they necessarily affect each others stability. This leads to the conclusion that of the topologies B, D, F, and H shown in figure 2 only D is thermodynamically valid. It should be noted that, in the general case, this requires that the stability of a singular curve always changes through a singular point.²

CONNECTION OF UNIVARIANT CURVES THROUGH SINGULAR CURVES

In a $(c + 2)$ -phase system (fig. 3) any two univariant curves may be connected by a common singular curve. The nature of such connections is constrained by the topology of the singular curves around each singular point as dictated by the rules detailed in the foregoing section. By considering a $c + 2^{\text{th}}$ phase it is then possible to distinguish two kinds of chemographic relationships between univariant assemblages related by a conjugate singular equilibrium. Either the $(c - 2)$ -dimensional hinge spanning the compositions of the c phases of the singular equilibrium separates the compositions of the two phases not present in the singular equilibrium, as illustrated in figure 4B or both these phases lie on the same side of the hinge (fig. 4A). This distinction is manifest in the singular-point topologies of both curves. Thus, relative changes in stabilities of the singular curves emanating from conjugate singular points on univariant curves labeled by phases that lie on the same side of a hinge are the same with respect to the direction of compositional variation of the solution along each univariant curve. This must be true because the

² An exception to this rule occurs if a hinge contains an extremal composition of the solution. This will be dealt with in a later section.

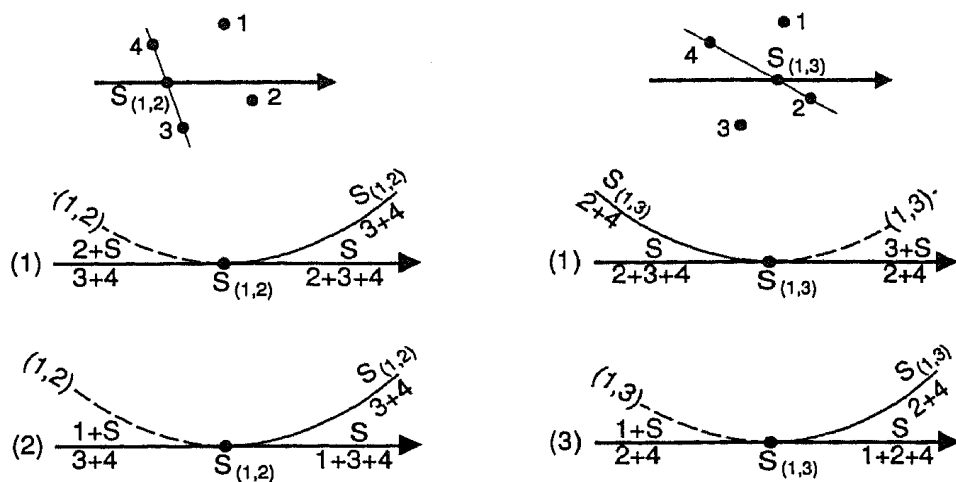


Fig. 4. Possible topologies of a singular curve and its conjugate univariant curve around conjugate singular points. On singular curve (1, 2) (left chemography and topologies) the stability sequence with respect to the solution compositional variation along the univariant curve is the same around $S_{(1,2)}$ on univariant curves (1) and (2), but the stability sequence on singular curve (1, 3) (right chemography and topologies) is different around $S_{(1,3)}$ on (1) and (3) with respect to the direction of solution compositional variation along (1) and (3). This difference reflects the chemographic relationships in that phases 1 and 2 lie on one side of the hinge corresponding to $S_{(1,2)}$, whereas phases 1 and 3 lie on opposite sides of the $S_{(1,3)}$ hinge. Arrowheads indicate the direction in which the solution composition approaches C_∞ (figure 1).

two univariant chemographies differ geometrically but are topologically identical relative to the hinge. In contrast, if the phases absent from the singular equilibrium lie on either side of the hinge then the relative stability sequences around the singular points on the univariant curves labeled by these phases are opposite with respect to the compositional variation of the solution along the univariant curves.

To illustrate this point it is useful to define the direction of compositional variation relative to an arbitrarily chosen extremal composition of the solution phase, S_∞ . Referring to figure 4, consider the two univariant curves (1) and (2)³ which share the hinge and singular curve defined by the phases 3, 4, and $S_{(1,2)}$. Both phases absent from the singular equilibrium (1, 2) lie on one side of the hinge. If the singular point $S_{(1,2)}$ on both univariant curves is drawn such that the solution composition shifts toward S_∞ to the right, then the relatively more stable segment of the singular curve (1, 2) about each singular point must lie to the right of the singular point as shown in figure 4C. If instead, univariant curves (1) and (3), labeled by phases that lie on either side of the (1, 3) hinge, are drawn such that the solution composition along the univariant curves shifts toward S_∞ to the right, then the relative more stable segment of (1, 3) must lie to the left of the singular point on univariant curve (1) and to the right of the singular point on (3) (fig. 4D).

³ Univariant curves and equilibria are designated by the phases absent from the equilibria in parentheses.

The foregoing consideration dictates the manner in which any two univariant curves are connected by a conjugate singular curve; in this respect there are two general cases: either both univariant curves have the same levels of stability, or their stabilities differ by one level. Given that a singular curve cannot cross itself then it is evident that two subparallel univariant curves (x) and (y) which share a hinge (x,y) that separates x and y can only be connected if either the directions of compositional change of the solution phase are opposite, and they are equally stable; or the directions of compositional change are the same along both univariant curves, and they have different stability levels. Likewise if x and y lie on the same side of the hinge (x,y) then (x) and (y) can only be connected if either the directions of compositional change of the solution are the same, and the stability levels are identical; or the directions of compositional variation are opposite, and the curves have different stabilities. This leads to a total of eight topological types of connection among two univariant curves (x) and (y) and their conjugate singular curve, four of which are illustrated in figure 5, the remaining four topologic types are obtained by inverting the stabilities of the univariant curves in figure 5.

For topologies in which the directions of solution compositional change along the univariant curves are the same (fig. 5D and E), it is possible that the univariant curves could intersect at a P-T condition at which they have the same solution composition generating an invariant point. However this intersection can only occur at a solution composition on one side of the singular composition. If both phases absent from the univariant curves lie on one side of the hinge, then the solution composition at the invariant point must be on the same side of the hinge as the phases absent from the hinge if both univariant curves are stable (fig. 5D) and must lie on the opposite side of the hinge if both univariant curves are metastable. A violation of these conditions would require an assemblage to be stable over a sector of more than 180° around the invariant point, or that a univariant curve crosses its conjugate singular curve. Likewise, if the hinge separates the phases absent from the univariant curves, then the solution composition at the invariant point must be on the opposite side of the hinge from the phase absent from the metastable univariant curve, and it must be on the same side of the hinge as the phase absent from a stable univariant curve (fig. 5E). A violation of this would require connection of a singular curve with different levels of stability which is impermissible.

For topologies in which the directions of change in solution composition along the univariant curves are not the same (fig. 5C and F), it is evident that the first crossing of the univariant curves must be indifferent, because the solution composition in both equilibria must be different. However, if the univariant curves are traced from their conjugate singular points in the same direction through the indifferent crossing it is possible that they may then intersect at an invariant point. In this case the invariant solution composition may lie on either side of the hinge.

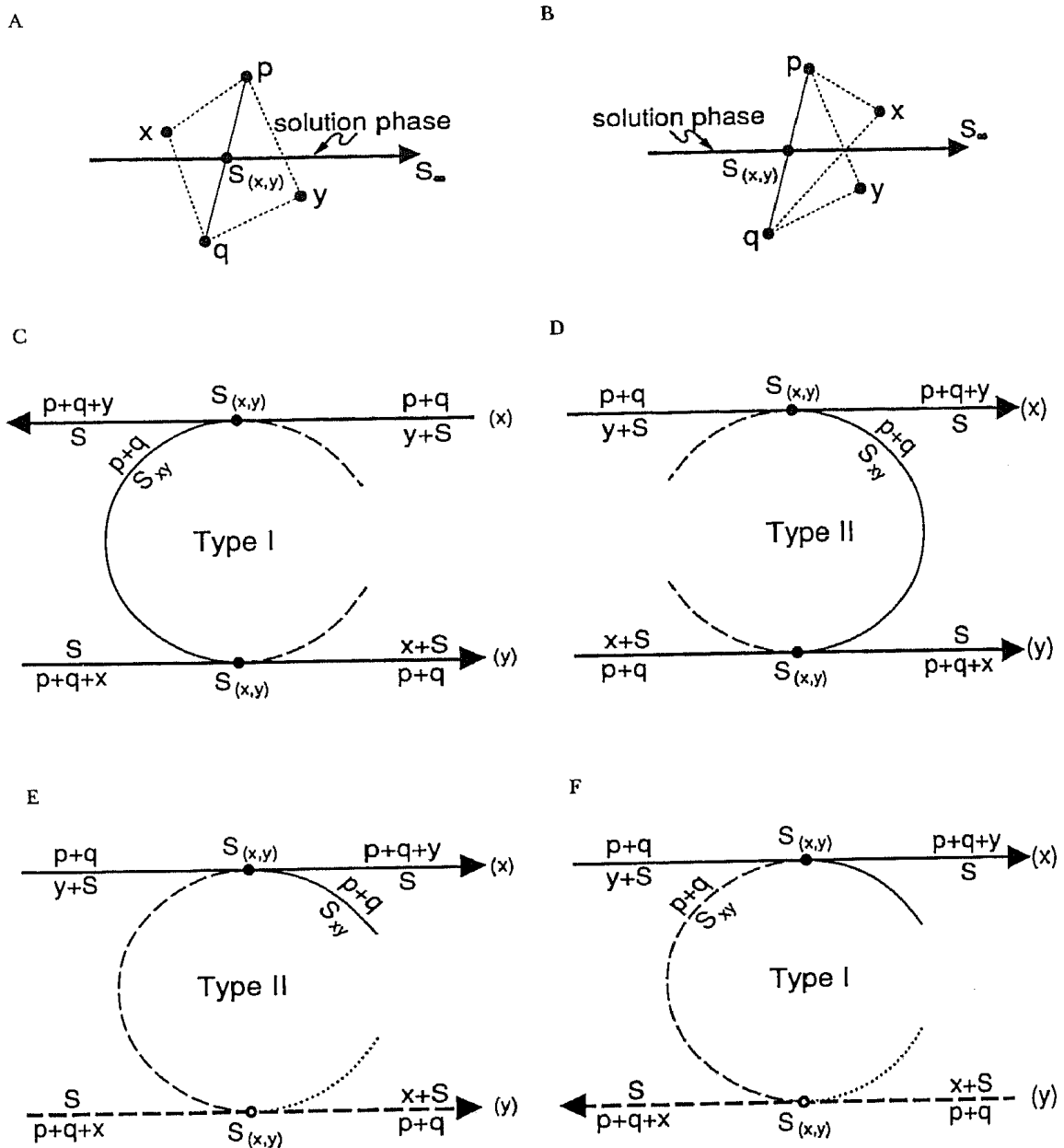


Fig. 5. In general in a $c + 2$ phase system there are two phases, x and y , the compositions of which are not spanned by the hinge (x,y) . Phases x and y may lie on either side of the (x,y) -hinge as in (A) or on the same side as in (B). This distinction, in combination with the stability levels of univariant curves (x) and (y) , determines the manner in which (x) and (y) can be connected by a singular curve. For chemographies (A) and (B), if both univariant curves are of the same stability they must be connected as in topologies (C) and (D), respectively, but if the univariant curves are of different stabilities they must be connected as in topologies (E) and (F), respectively. Arrowheads indicate the direction in which the solution composition approaches S_∞ (fig. 1). Doubly metastable singular curves are dotted, other notation as in figure 2.

This distinction permits classification of topologic connections into two broad categories designated herein as type I and type II connections. Univariant curves that connect by a type I connection must cross at an indifferent crossing before an invariant point is possible, whereas univariant curves connected by a type II connection can intersect at an invariant point with no intervening indifferent crossing.

Based on the foregoing discussion a rule can be formulated on the stability of singular points along univariant curves intersecting at an invariant point connected by a type II connection:

6. *If the phase absent from the univariant curve is separated from the invariant solution composition by a hinge, then the singular point on the univariant curve corresponding to this hinge will be metastable. Likewise if the absent phase and the invariant solution composition are on the same side of the hinge, then the singular point will be stable.*

The foregoing considerations allow a total of eight topologically distinct ways of connecting two univariant curves with a common singular equilibrium. The problem addressed in the next section is to determine the additional constraints imposed by the presence of more than one singular equilibrium.

SINGULAR-POINT NETS

The complete topology of a singular point net about an invariant point can only be determined if the invariant-point chemography is known, that is, the solution composition at the invariant point is known with respect to the singular-point compositions. This composition determines the topology of the univariant curves in the immediate vicinity of the invariant point. Given such a topology then the specification of the stability of a singular point along a univariant curve determines the stability of all the other singular points along that univariant curve, assuming monotonic compositional variation of the solution along the univariant curve. For the chemography illustrated in figure 3, if an invariant point occurs with the composition S_i then the invariant point topology can be deduced from Schreinemaker's method to be that shown in figure 6. Beginning with one univariant curve the stability of one singular point can be arbitrarily specified as there are as yet no topologic arguments against this. For example, $S_{(1,4)}$ can be placed on the metasta-

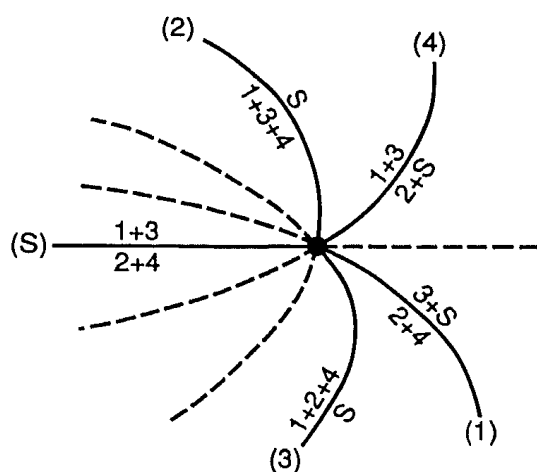


Fig. 6. Schreinemaker's projection of univariant curves around the invariant P-T conditions of the three component system of figure 3.

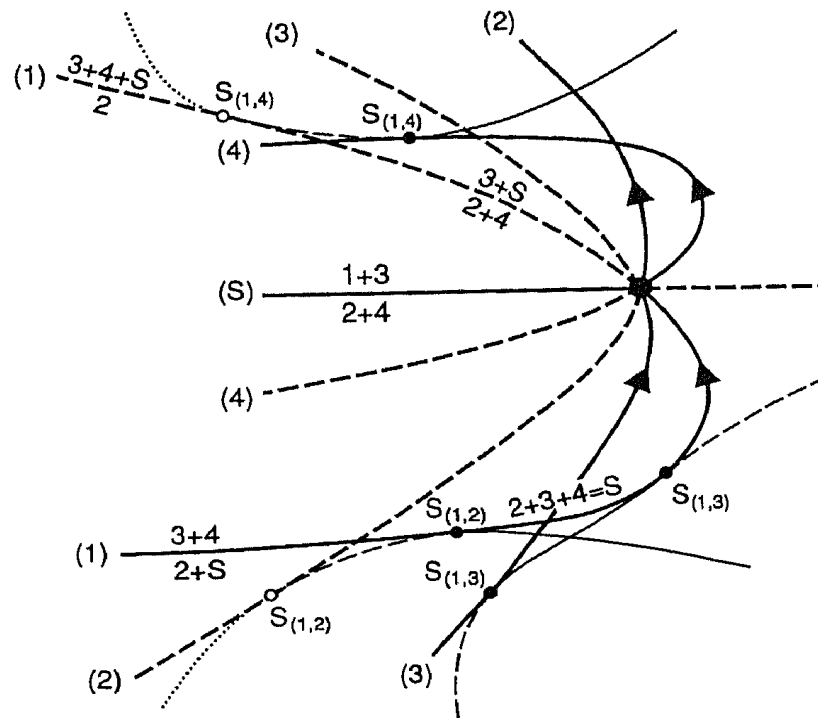


Fig. 7. Schreinemaker's projection showing singular equilibria around the invariant P-T conditions of the ternary system illustrated in figure 3. Only the singular points on univariant curve (1) and its conjugate singular points and curves are shown. $S_{(1,4)}$ was arbitrarily placed on the metastable extension of (1), and $S_{(1,2)}$ and $S_{(1,3)}$ were placed on (1) so as to be consistent with monotonic compositional variation of the solution along (1). Singular points on (1) were then connected to the conjugate singular points on (2), (3), and (4) through type I connections. Arrows on univariant curves point toward S_{∞} .

ble extension of (1) as done in figure 7. The arrangement of the singular points along the remaining univariant curves can then be determined by considering the topologic connections with the singular points on the first univariant curve. In this regard the distinction between type I and type II topologic connections is important; for it is always possible to connect two univariant curves on either side of an invariant point with a type I connection, whereas type II connections are confined to one side of the invariant point. Thus it can be anticipated that type II connections will not, in general, be possible given an arbitrarily specified stability for one singular point. This is demonstrated by the case of $S_{(1,4)}$ which occurs on both (1) and (4). Consideration of the possible type II connection for this case reveals that there is no way to connect these curves such that $S_{(1,4)}$ is metastable on (1) for an invariant point composition of $X_{S_i} < X_{S_{(1,4)}}$.

As type I connections allow singular points to lie on either side of an invariant point it will always be possible to construct singular-point nets involving only type I connections. Therefore the approach taken here will be to first construct singular-point nets with all possible type I connections and subsequently to consider the possibility of type II connections.

Construction of Singular-Point Nets of Type I Connections

In a $(c + 2)$ -phase system, the same invariant phase assemblage may be stable at more than one invariant condition. This would require that all the univariant curves emanating from one invariant point intersect the fluid-absent univariant curve at each additional invariant point. For present purposes this possibility will be excluded. This suggests a rule concerning type I connections, which will later be shown to be also true in systems where the same invariant assemblage is stable at more than one condition:

7. *Only those extensions of univariant curves that lie on the same side of the solution-absent reaction (S) about an invariant point may be connected through a type I connection.*—A requirement of rule (7) is that two singular points related by a type I connection will have equal stability levels if they occur on univariant curves labeled by phases that have the same sign in the reaction equation of (S); otherwise they will have different levels of stability. This rule can be justified in the present context because univariant curve extensions emanating from an invariant point and connected by type I connections must cross indifferently. However, if the singular points to be connected lie on univariant curve extensions on opposite sides of (S) it would be impossible to generate an indifferent crossing without creating a second invariant point. The construction of a type I singular-point net about a single invariant point may be accomplished through the following procedure:

A. The stability of one singular point along a univariant curve is specified, and the remaining singular points along this curve are located to be consistent with this specification (that is consistent with the direction of compositional variation of the solution implicit from the relative positions of the singular point and the invariant point).

B. Each univariant curve that shares a conjugate singular equilibrium with the first curve specified in (A) is connected to the original curve through a type I connection so as to satisfy rule (7). Each connection requires an indifferent crossing of the conjugate univariant curves such that the singular curve lies on the same side of both univariant curves.

The foregoing procedure can be demonstrated for the invariant point and phase chemography of figure 3. Given the assumption that the $S_{(1,4)}$ singular point is metastable on (1), the type I connections with curves (2), (3), and (4) can be drawn with the result shown in figure 7. These connections constrain the locations of all the remaining singular points, and if these singular points are also connected by type I connections the topology of figure 8 is obtained. Given such a topology it is always possible to derive three additional type I topologies. The second topology can be derived by inverting the stabilities of the singular points of the first (that is, by placing $S_{(1,4)}$ on the stable extension of (1) in fig. 8). The other two topologies are enantiomorphs of the first two. In such constructions the order of the univariant curves immediately about the invariant point is determined by Schreinemakers analysis, and the shape of the curves is topologically irrelevant.

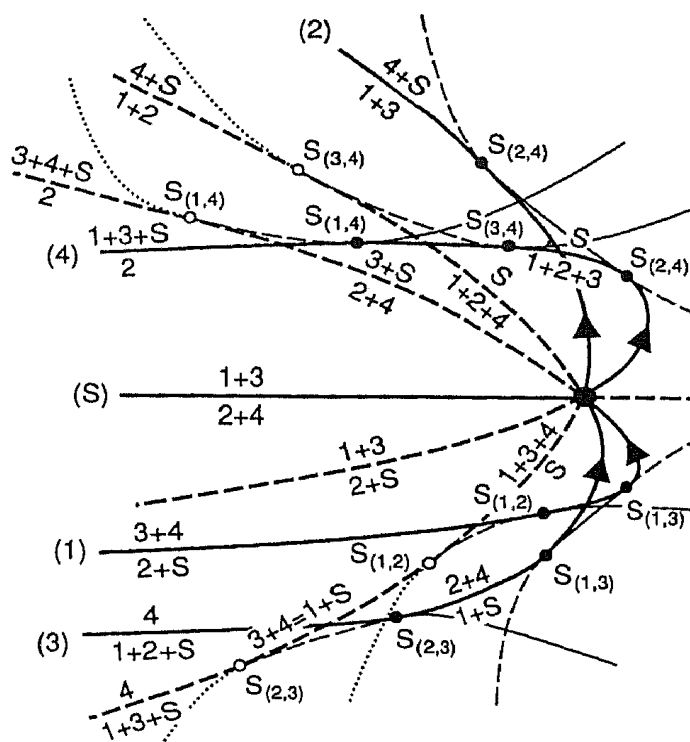


Fig. 8. Complete Schreinemakers projection around the invariant P-T condition of the ternary system of figure 3. This topology involves only type I connections and thus represents one of the four type I singular-point nets that can be drawn for the system. Note that the direction of solution compositional variation across (S) is the same in all solution present univariant curves and that every type I connection requires an indifferent crossing.

The topology of figure 8 demonstrates a feature common to all topologies of type I connections which is that the direction of compositional variation across the invariant point with respect to the solution-absent reaction is the same along all univariant curves (arrows in fig. 8). This implies that in a P-T phase diagram if (S) were parallel to either axis, the compositional variation of the solution phase is constrained to be the same in all univariant equilibria in a direction perpendicular to that axis.

The characteristics of type I singular-point nets can be summarized by a table such as that shown in table 1A for the system of figure 8. The rows of such tables give the stabilities and sequence of singular points along each univariant curve, and the columns locate and represent the stabilities of conjugate singular points. It is useful to note that such tables can be constructed without actually drawing the topology, because the stability of all the singular points is determined once the invariant point composition and the stability of one singular point is specified. For example the effect of changing the invariant point composition for the system illustrated in figure 8 to a composition between $S_{(2,3)}$ and $S_{(1,2)}$ and specifying that $S_{(1,4)}$ is on the stable extension of (1) can be derived from table 1A. First the stabilities of all singular points in table 1A are inverted to obtain table 1B which gives the inverted singular-point net of figure 8. The effect of changing the invariant point composition from a value

TABLE 1

Descriptive tables for the singular-point nets around invariant points for the phase chemography illustrated in figure 3. The rows of each table indicate stability levels (s-stable, m-metastable) and sequence of singular points along the designated univariant curve. (A) Pure type I singular-point net with an invariant solution composition between $S_{(1,3)}$ and $S_{(2,4)}$. (B) Inverse stability singular-point net of (A). (C) Singular point net as (A), but with the invariant point composition of the solution between $S_{(2,3)}$ and $S_{(1,2)}$. (D) Pure type II singular-point net for an invariant point comparison between $S_{(1,3)}$ and $S_{(2,4)}$. Table (D) was constructed by applying rule 6 for each entry independently; as the rows contain inconsistencies the singular-point net is not valid (for example, on (3), singular points $S_{(2,3)}$ and $S_{(1,3)}$ have different stabilities but lie on the same side of the invariant point). (E) Mixed-type singular-point net, obtained by inverting the stability levels along (1) in (A). This inversion requires that all connections with (1) are of type II and leads to inconsistencies; for example, a type II connection between the $S_{(1,2)}$ singular points on (1) and (2) is only possible if the singular points are stable on both curves (as indicated by (D)). Thus, singular-point net (E) is not valid. (F) and (G) Valid mixed-type singular-point nets derived from (A) by inverting stabilities of singular points along (2) for (F), and both (2) and (3) for (G). (H) and (I) Valid mixed-type singular-point nets derived from (B) by inverting stabilities of singular points along (4) for (H), and both (1) and (4) for (I). Together, tables (A, B, F–I) define all the valid singular-point nets for an invariant solution phase composition between $S_{(1,3)}$ and $S_{(2,4)}$.

A.							B.						
	$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$		$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$
(1)		s	s			m	(1)		m	m			s
(2)	m	m		s			(2)	s	s		m		
(3)			s		m		(3)	m		m		s	
(4)				s	s	s	(4)				m	m	m
C.							D.						
	$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$		$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$
(1)		s	s			s	(1)		s	s			s
(2)	s	m		m			(2)	s	s		m		
(3)	m		s		s		(3)	s		m		s	
(4)				m	m	m	(4)				s	s	s
E.							F.						
	$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$		$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$
(1)		m	m			s	(1)		s	s			m
(2)	m	m		s			(2)	s	s		m		
(3)			s		m		(3)	s		s		m	
(4)				s	s	s	(4)				s	s	s
G.							H.						
	$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$		$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$
(1)		s	s			m	(1)		m	m			s
(2)	s	s		m			(2)	s	s		m		
(3)	m		m		s		(3)	m		m		s	
(4)				s	s	s	(4)				s	s	s
I.													
	$S_{(2,3)}$	$S_{(1,2)}$	$S_{(1,3)}$	$S_{(2,4)}$	$S_{(3,4)}$	$S_{(1,4)}$							
(1)		s	s			m							
(2)	s	s		m									
(3)	m		m		s								
(4)				s	s	s							

between $S_{(1,3)}$ and $S_{(2,4)}$ to a composition between $S_{(2,3)}$ and $S_{(1,2)}$ is simply to invert the stabilities of all the singular points in the columns between the old and new invariant point compositions with the result given in table 1C. It may be noted that although four different type I singular-point nets can be drawn around an invariant point, the tables for the enantiomorphic nets are identical. Thus there are only two tables for all four type I topologies, and these two are related to each other by inverting the stabilities of the singular points.

Repeated Invariant Points in a Type I Singular-Point Net

In the foregoing section, the possibility of two univariant curves intersecting to generate an additional invariant point was excluded. However there is no fundamental reason to reject this possibility. The number of invariant points for a $(c + 2)$ -phase system is unlimited in that any two univariant curves may intersect any number of times. As long as the compositional variation along both univariant curves does not cross a singular composition, each successive invariant point topology will be enantiomorphic. As there is no topological constraint on the nature and number of these invariant points, this type of invariant point repetition will not be considered further. The alternative is that the intersections of the univariant curves occur at solution compositions separated by a singular composition. In this case the phase chemography at each invariant point will be different.⁴ Each change in chemography is reflected by a change in relative order of two univariant curves (exclusive of (S)) about the invariant point. Such a change in relative order of two univariant curves occurs on either side of an indifferent crossing. Figure 9 illustrates the interrelation of the invariant point topologies and the singular-point net that results if an invariant point occurs after every indifferent crossing. This case relates every possible nonenantiomorphic invariant point topology for the system given in figure 3. It is, of course, possible to draw a similar diagram with fewer invariant points and a greater number of intervening indifferent crossings. With regard to the general application of rule (7) (p. 790), it may be noted that if two singular points of the same composition lie on two univariant curve extensions that emanate on opposite sides of (S) from one invariant point, then the two singular points will always be separated by (S) even if the invariant point is repeated. This follows from the consideration that it would be impossible to cross one univariant curve extension over (S) without crossing the second at the same point.

TYPE II SINGULAR-POINT NETS

The feasibility of topologies consisting entirely of type II connections can be tested through the use of tables similar to those presented in table 1 for type I connections. However in contrast to type I topologies the

⁴ A change in chemography is considered here to occur when the number of phases on either side of any hinge changes. This is a phase-region deformation in the sense of Schreinemakers (1916).

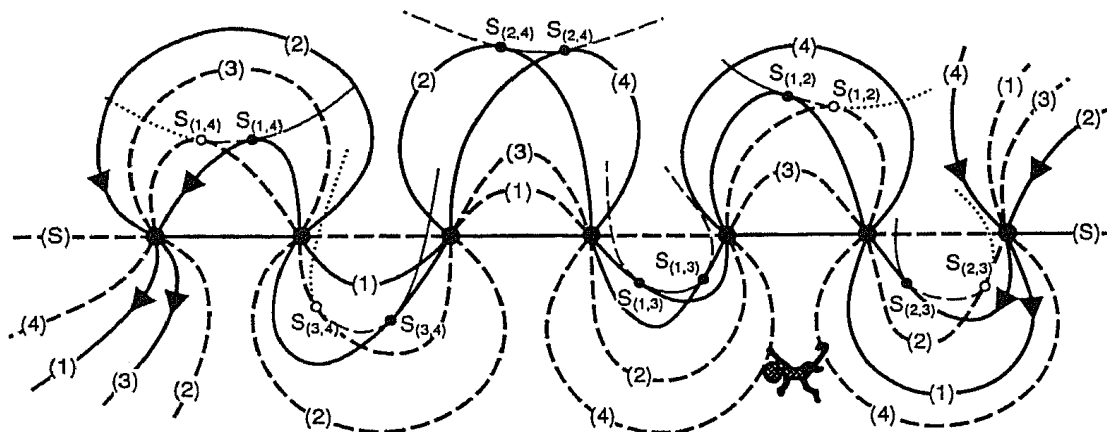


Fig. 9. Multiple-invariant point type I singular-point net for the phase chemography of figure 3, invariant P-T conditions occur at solution compositions between each singular composition. The arrangement of univariant curves around two adjacent invariant points differs in that the order of two of the univariant curves is changed. Such changes are effected by indifferent crossing of the univariant curves. This sequence of invariant points represents all possible, nonenantiomorphic invariant point topologies for the given system.

specification of an invariant point composition determines the stabilities of all the singular points in type II topologies. These stabilities are determined by rule 6 (p. 788). This is best demonstrated by the example of figure 8. For curve (1), rule 6 requires that $S_{(1,2)}$, $S_{(1,3)}$, and $S_{(1,4)}$ are stable. These stabilities can be entered in a table, which can be completed by applying rule 6 to each singular point on the remaining univariant curves with the result given in table 1D. Examination of table 1D reveals conflicts for curves (1) and (3) in that $S_{(1,2)}$, $S_{(1,3)}$, and $S_{(1,4)}$ are equally stable on (1) although the invariant solution composition lies between $S_{(1,3)}$ and $S_{(1,4)}$, and on (3), $S_{(2,3)}$ and $S_{(1,3)}$, which both lie on one side of the invariant point, have different stabilities. Thus it may be concluded that a singular-point net consisting only of type II connections is not possible for the system with invariant point composition between $S_{(1,3)}$ and $S_{(2,4)}$. It can be shown that in systems where the number of hinges is the combinatorial limit $\binom{c+1}{c-1}$, it is never possible to construct a type II singular-point net (app.). However, for systems in which the number of singular points is less than $\binom{c+1}{c-1} - c$, type II topologies may be possible (app.). An example of such a system was used by Connolly and Trommsdorff (1991, fig. 4).

MIXED-TYPE TOPOLOGIES

Although it is generally not possible to construct type II nets, consistent nets can be drawn by mixing type I and type II connections. Mixed topologies can be derived from type I nets by inverting the stabilities of singular points along one or more univariant curves. Such inversions can be envisioned as the result of flipping of the singular points on the effected univariant curve across the invariant point and are represented by inversion of the stabilities in the corresponding rows of

the descriptive tables. Such inversions yield consistent topologies only if the columns of the resulting table occur either in the table for type II connections or in one of the two possible tables for type I connections. The maximum number of inversions is modulus $[(c + 1), 2]$, as inversion of a greater number of rows would be equivalent to inversion of the remaining curves in the alternate type I table.

The derivation of all possible topologies by the use of descriptive tables for the ternary chemography illustrated in figure 3, with the invariant solution composition between $S_{(1,3)}$ and $S_{(2,4)}$, is demonstrated here. As a first step, one of the two type I tables is constructed by arbitrarily specifying the stability of a singular point and completing the table according to rule 7 (p. 790) with the result given in table 1A. This table is then inverted⁵ to yield the second type I table shown in table 1B. The type II table (table 1D) is then constructed by determining the singular point stabilities by rule 6 (p. 788). The tables for mixed-type topologies can then be derived by inverting the singular-point stabilities in one or more of the rows of the type I tables. Such descriptive tables represent valid singular-point nets if, and only if, every column of the table is identical with the corresponding column of either the type II table or one of the type I tables. If, for example, in table 1A the singular-point stabilities along (1) are inverted, table 1E results, which contains inconsistencies and thus does not represent a valid topology. If instead the singular-point stabilities on (2) are inverted in table 1A, a valid singular-point net is obtained (table 1F). Topologically valid singular-point nets also result from inverting the singular-point stabilities along (2) and (3) simultaneously (table 1G), starting from table 1A, and from inverting singular-point stabilities in table 1B along (4) (table 1H) or along (1) and (4) simultaneously (table 1I). There are no other mixed-type topologies possible. Without taking into account the constraints from singular-point analysis, each solution-present univariant curve around an invariant point can be independently oriented with respect to the direction of compositional change in the solution phase. As there are $c + 1$ solution-present univariant curves, there are a total of 2^{c+1} nonenantiomorphic topologies⁶ possible. According to the foregoing analysis there are only 6 nonenantiomorphic singular-point nets possible for the given invariant-point chemography; thus in this case singular-point analysis eliminates more than half the number of ways in which univariant curves can be oriented around an invariant point entirely from topologic considerations.

⁵ In this context, inversion refers to the change of stabilities of only the singular points, whereas the univariant curves are not affected.

⁶ In conventional Schreinemaker analysis univariant equilibria are represented by lines with no associated direction attribute. Here the association of a direction with each univariant line is equivalent to considering the topologic arrangement of arrows, rather than lines, about a point.

COMPOSITIONAL DEGENERACIES

The preceding discussion has been restricted to general chemographic phase relations among $c + 1$ compounds and a binary solution and the compositional degeneracies that give rise to singular equilibria. However in many cases, particularly in geologic systems additional compositional degeneracies arise. In such cases the rules derived in the previous sections always apply, but several new features may appear. In regard to singular-point analysis there are two categories of degeneracy: (1) Coincidence of a singular composition with a compositional limit of the solution phase; and (2) compositional degeneracy among the compounds of the system, or a degeneracy of compounds with the solution. Systems of $c + 2$ phases, in which more than one solution-absent reaction are possible, are excluded from consideration here.

*Coincidence of a Singular Composition with a Compositional Limit
of the Solution*

Examples of this are common in systems including H_2O-CO_2 fluids in which many of the singular reactions involve only one volatile component or in AFM projections for which all the important solutions have endmember compositions that lie in the AF or AM joins.

Four considerations dictate the phase relations about a singular point defined by a singular reaction that involves a phenomenological endmember of a solution: (1) the phase relations in a true thermodynamic subsystem (Connolly and Kerrick, 1987) cannot be affected by phases outside the subsystem, therefore the stability of the singular equilibrium does not change at the singular point; (2) as the singular equilibrium consists of a subset of the phases of the univariant equilibrium it cannot be less stable than the univariant equilibrium; (3) as the composition of the solution becomes extremal at the singular point the univariant and singular equilibria must coincide on one side of the singular point although they are not identical; (4) the singular curves divide P-T space into regions in which an assemblage involving the solution is relatively more and less stable, and the univariant curves must lie in the region in which this assemblage is less stable in order to avoid violating Schreinemakers principles. Aside from the changes in singular-point topology this degeneracy has only one significant implication which is that it eliminates the indifferent crossings that arise from type I connections (see fig. 7 of Connolly and Trommsdorff, 1991).

*Compositional Degeneracies Among Compounds or Among Compounds
and a Solution*

Compositional degeneracies that occur in a $(c + 2)$ -phase system can be classified by the number of phases involved in the solution-absent reaction (S). Degeneracy purely among the compounds of the system results in a solution-absent reaction with fewer than $c + 1$ phases. This in turn requires the coincidence of hinges such that $d + 3$ phase compositions (including the solution phase) lie along a d -dimensional geometrical

element that spans the compositional coordinates of the phases of (S). All $d + 3$ of these phases can only coexist at another invariant point along (S) which is defined by the intersection of (S) and the singular reactions corresponding to each of the coinciding hinges. The number of such invariant points generated along (S) will depend on the chemography of the system. The effect of a degenerate solution-absent reaction is illustrated in figure 10 in which the coincidence of phases 3 and 4 results in the overlapping of two pairs of hinges. An interesting feature of such systems is that the solution-absent reaction may occur in the presence of the solution phase. However, the composition of the solution phase in equilibrium with the solution-absent reaction is uniquely determined at any point along (S). The direction of compositional variation of the solution phase along the solution-absent reaction can be determined from the location of the $(d + 3)$ -phase invariant point which is located so as to satisfy the constraints imposed by singular-point analysis. Thus from the topology of figure 10, it can be deduced that the metastable phase assemblage $1 + 3 + 4$ buffers the solution composition in a direction away from S_1 toward S_2 as the metastable extension of curve (S,1,2) is traced

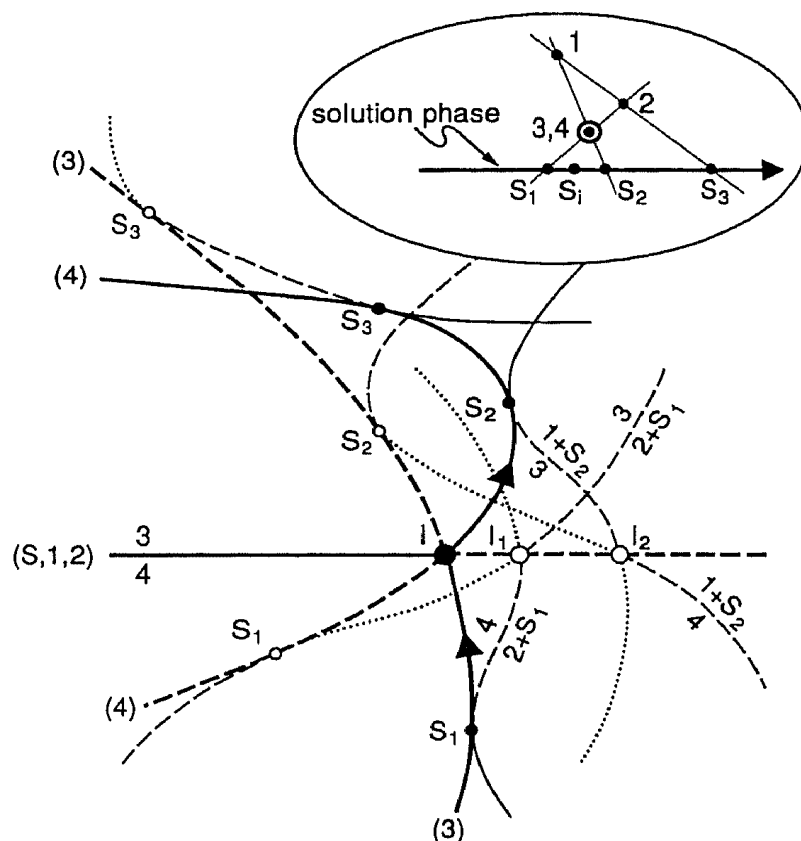


Fig. 10. Singular point net for a degenerate ternary system (phase chemography shown as inset). The degeneracy is such that two pairs of hinges overlap producing $(c - 2)$ -dimensional geometrical elements containing the compositional coordinates of $c + 1$ phases. The $(c + 1)$ -phase assemblages $2 + 3 + 4 + S_1$ and $1 + 3 + 4 + S_2$ occur metastably at invariant points I_1 and I_2 , at the intersection of the singular curves involving S_1 and S_2 with (S). This requires that these assemblages buffer the composition of S along (S) in opposite directions.

away from the invariant point, and likewise that the assemblage 2 + 3 + 4 buffers the solution composition toward S_1 along the same portion of (S,1,2).

A second type of degeneracy occurs when a hinge has dimension $d < (c - 2)$. This is manifest from the corresponding singular reaction that involves $(d + 2) < c$ phases. For systems in which this type of degeneracy occurs the degenerate singular curves will connect $c-d$ univariant curves.

AN APPLICATION OF SINGULAR POINT ANALYSIS

To demonstrate the application of singular-point analysis to geologic problems the antigorite(At)–calcite(Cc)–tremolite(Tr)–dolomite(Do)–diopside(Di)–forsterite(Fo)–fluid(F) invariant point in the CaO–MgO–SiO₂–H₂O–CO₂ system will be considered here. In this system, the minerals have essentially fixed compositions, and the fluid is a binary solution between H₂O and CO₂. In contrast to the problems presented earlier for ternary systems, the chemographic relations in the CaO–MgO–SiO₂–H₂O–CO₂ system cannot be visualized graphically because its composition space is four-dimensional. Consequently, it is necessary to determine valid hinges and the relative displacement of phases with respect to hinges by linear algebra (Connolly and Kerrick, 1987). The equation of a $(c - 2)$ -dimensional plane spanning the composition of $c - 1$ phases is obtained by solving the equation⁷:

$$\begin{pmatrix} 1 & X_1^1 & \dots & X_{c-2}^1 \\ 1 & X_1^2 & \dots & X_{c-2}^2 \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ 1 & X_1^{c-1} & \dots & X_{c-2}^{c-1} \end{pmatrix} \begin{pmatrix} \beta_0 \\ \beta_1 \\ \dots \\ \dots \\ \beta_{c-2} \end{pmatrix} = \begin{pmatrix} X_{c-1}^1 \\ X_{c-1}^2 \\ \dots \\ \dots \\ X_{c-1}^{c-1} \end{pmatrix} \quad (6)$$

If an assemblage of $c - 1$ phases defines a hinge, then the plane spanning the compositions of these phases determined from eq 6 must also span a possible composition of the solution. Provided the $c - 1^{\text{th}}$ and c^{th} components are taken as the endmember compositions of the solution, the intersection of a plane defined by eq 6 with the compositional range of the solution is:

$$X^S = \beta_0. \quad (7)$$

If the intersection is at a valid composition for the solution, then the composition is a singular composition, and the $(c - 1)$ -phase assemblage defines a valid hinge. To apply rule 6 (p. 788) with respect to a hinge (x,y) , it is necessary to determine the relative displacements of the invariant point composition S_i and the compositions of phases x and y relative to the hinge. Given the parameters $\beta_0, \dots, \beta_{c-2}$ of the hinge, the

⁷ A fortran program for this purpose can be obtained from the authors.

displacement of a composition x is given by:

$$\delta_x = \beta_0 + \sum_{i=1}^{c-2} X_i^x \beta_i - X_{c-1}^x \quad (8)$$

If two compositions x and y lie on the same side of a hinge then the displacements of both compositions calculated from eq 8 will have the same sign and the ratio

$$\Gamma_{x,y} = \frac{\delta_x}{\delta_y} \quad (9)$$

will be positive, and if the compositions x and y lie on opposite sides of the hinge, $\Gamma_{x,y}$ will be negative. Returning to the Fo-At-Tr-Do-Di-Cc-F example, table 2 summarizes the foregoing algebra for the fifteen combinatorially possible $(c - 1)$ -phase assemblages. From this table it can be seen that assemblages (Cc, Fo), (Di, Fo), and (Fo, Tr) do not define valid singular equilibria, because the corresponding hinges do not intersect the fluid composition (that is, $B_0 > 1$ or $B_0 < 0$, eqs 6 and 7). The equation of the fluid-absent reaction (F) is of the form $Do + Di + At =$

TABLE 2

Equations for the $c-2$ dimensional hinges defined by the fifteen $c-1$ phase permutations of the compounds Tr-Fo-Cc-At-Do-Di which coexist with an H_2O-CO_2 fluid at an invariant point. Permutations are identified by the phases x and y which are absent from the hinge. The parameter β_0 (eq 6) is the point ($X_{CO_2}^F$) at which a hinge intersects the fluid composition space, only those hinges that intersect within the real composition space of the fluid ($0 \leq \beta_0 \leq 1$) correspond to possible singular equilibria. The parameters Γ_{x,S_i} and Γ_{y,S_i} (eq 9) indicate the displacements of the phases x and y , with respect to both the hinge (x, y) and the invariant point fluid composition ($X_{CO_2}^F = 0.01$ mol CO_2). Positive values of Γ_{x,S_i} indicate the composition of the phase x lies on the same side of the hinge as the invariant point composition S_i .

x	y	β_0	β_1	β_2	β_3	Γ_{x,S_i}	Γ_{y,S_i}
At	Cc	0.714	-0.285	-0.571	-1	0.242	0.101
At	Di	0.900	-0.800	-0.800	-1.100	0.257	-0.056
At	Do	0.625	-0.250	-0.500	-0.875	0.243	-0.102
At	Fo	0.500	0	0	-1	0.406	0.340
At	Tr	1	-1	-1	-1	0.277	0.063
Cc	Di	0.173	1.214	0.095	-0.708	1.718	0.896
Cc	Do	0	0	0	0	50.00	50.00
Cc	Fo	2	-2	-4	-1	0.251	-0.502
Cc	Tr	0.244	0.890	0.134	-1	0.808	-0.440
Di	Do	0.111	0.778	0.061	-0.454	0.927	-1.779
Di	Fo	-2.147	5.294	5.294	-0.338	-0.153	-0.589
Di	Tr	0.392	0.216	0.216	-1.608	-0.795	-0.831
Do	Fo	1	-1	-2	-0.500	-0.252	-0.505
Do	Tr	0.177	0.646	0.097	-0.726	-0.821	-0.447
Fo	Tr	-0.823	2.647	2.647	-1	-0.729	0.198

Fo + Tr + Cc, and if the invariant point composition S_i is between $S_{(Cc,Do)}$ and $S_{(Di,Do)}$, then the descriptive tables for type I singular-point nets can be constructed by applying rule 7 (p. 000) for the remaining singular equilibria (table 3A). With reference to the application of rule 6 (p. 000), the stabilities of any two conjugate singular points connected by a type II connection can be determined from the values of Γ (eq 9) in columns 7 and 8 of table 2. For example, for the singular equilibrium (Di, Do), Γ_{Di,S_i} is positive, and Γ_{Do,S_i} is negative. Thus, Di and Do lie on opposite sides of the hinge (Di, Do), and Di lies on the same side of the hinge as S_i ; by rule 6 this requires that if (Di) and (Do) are to be connected with a type II connection then the (Di, Do) singular point is stable on (Di) and metastable on (Do). If rule 6 is applied for every singular equilibrium then the descriptive table for a type II singular-point net (table 3B) results. Inspection of this table reveals conflicts in the stabilities of the singular points along (Fo), (Tr), (Cc), and (Di); thus the pure type II singular-point net is not possible for this system. The singular reactions (Cc, Do), (Do, Fo), and (At, Tr) are degenerate in the sense that the corresponding singular compositions coincide with the phenomenological extremes of the fluid. Thus, all these singular equilibria are always stable, and rules 6 and 7 only determine the location of the singular points. This implies that the stabilities of the (Cc, Do), (Do, Fo), and (At, Tr) singular points are irrelevant in mixed-type topologies and that corresponding columns in the pure type I and II tables do not provide any constraints on mixed-type topologies. Valid mixed-type topologies can be generated by inverting stabilities of the remaining singular points along one or more univariant curves in table 3A. Omitting the (Cc, Do), (Do, Fo), and (At, Tr) columns in table 3, a total of 12 topologically valid mixed-type singular-point nets can be derived. For a five component system there are a total of

TABLE 3

Descriptive tables for singular-point nets around the Fo-At-Tr-Do-Di-Cc-F invariant point in the CaO-MgO-SiO₂-H₂O-CO₂ system for an invariant fluid composition between $S_{(Cc,Do)}$ and $S_{(Di,Do)}$

A. Pure type I singular-point net												
	$S_{(Cc,Do)}$	$S_{(Di,Do)}$	$S_{(Cc,Di)}$	$S_{(Do,Tr)}$	$S_{(Cc,Tr)}$	$S_{(Di,Tr)}$	$S_{(At,Fo)}$	$S_{(At,Do)}$	$S_{(At,Cc)}$	$S_{(At,Di)}$	$S_{(At,Tr)}$	$S_{(Do,Fo)}$
(Fo)							m					m
(Tr)				m	m	m					m	
(Cc)	s		m		m				m			
(At)							s	s	s	s		
(Di)		s	s			s				s		
(Do)	m	s		s				s				s
B. Pure type II table; this table does not represent a valid singular-point net, as conflicts occur in the stability levels along univariant curves (Tr), (Cc), and (Di)												
	$S_{(Cc,Do)}$	$S_{(Di,Do)}$	$S_{(Cc,Di)}$	$S_{(Do,Tr)}$	$S_{(Cc,Tr)}$	$S_{(Di,Tr)}$	$S_{(At,Fo)}$	$S_{(At,Do)}$	$S_{(At,Cc)}$	$S_{(At,Di)}$	$S_{(At,Tr)}$	$S_{(Do,Fo)}$
(Fo)							s					m
(Tr)				m	m	m					s	
(Cc)	s		s		s				s			
(At)							s	s	s	s		
(Di)		s	s			m				m		
(Do)	s	m		m				m				m

64 (2^{c+1}) nonenantiomorphic singular-point nets, but in this example it is possible to eliminate 50 nets through singular-point analysis even though only 12 of the 15 combinatorially possible singular equilibria occur, and of these only 9 provide constraints in singular-point analysis.

Both thermodynamic calculations and field evidence suggest that the singular-point net about the Fo–At–Tr–Do–Di–Cc–F invariant point is that of table 3A (Connolly and Trommsdorff, 1991; Carmichael, 1991). Indeed, it is interesting to note that in topologies calculated from thermodynamic data only type I connections have been observed by the authors. More generally, it has been observed in calculated phase diagrams of degenerate invariant points (for example, the zoisite–aluminosilicate–Cc–quartz–anorthite–F invariant point in the CaO–Al₂O₃–SiO₂–H₂O–CO₂ system (Connolly and Trommsdorff, 1991) that univariant curves may have opposite orientations on the same side of the solution-absent reaction if the curves are not connected by a singular curve.

SUMMARY AND CONCLUSIONS

Any two univariant curves that represent equilibria involving the same solution phase may be connected by a singular curve. If these curves emanate from a common invariant point then there are only two possible types of topologic connections between them by the singular curve. These kinds of connections are distinguished in that one of the types, designated type I, requires an indifferent crossing of the interconnected univariant curves, whereas the second type, designated type II, does not require such an indifferent crossing. Both types of topologic connections constrain the direction of compositional change of the solution along the interconnected univariant curves. For a set of univariant curves emanating from an invariant point these constraints limit the possible arrangements of singular points and curves around the invariant point, that is the singular-point nets. For each such net the direction of compositional variation in the solution phase along every univariant curve is uniquely determined. Seven rules based on Schreinemakers' principles have been formulated to facilitate the construction of singular-point nets. About any invariant point it is always possible to construct four topologically valid singular-point nets consisting entirely of type I connections. These four topologies are related to each other by inversion of the singular-point stabilities and by mirror symmetry. The characteristics of type I singular-point nets are that singular points of the same composition always lie on the same side of the solution-absent curve. The singular points have equal stabilities if they occur on univariant curves labeled by phases that have the same sign in the solution-absent reaction equation, and they have different stabilities if the phases labeling the interconnected univariant curves have different signs in the solution-absent reaction equation. This implies that all univariant curves have the same direction of solution compositional change across (S). These characteristics can be summarized in tables consisting of rows giving the stabilities and sequence of singular points along individual univariant curves and

columns giving stability relations between singular points of the same composition. Such tables can also be drawn for singular-point nets consisting entirely of type II connections. There is a degree of freedom in the construction of type I singular-point nets in that the stability of one singular point can be arbitrarily specified. In contrast, the stability of any singular point connected through a type II connection is uniquely determined by topologic principles (rule 6, p. 788). Descriptive tables for type II singular-point nets can thus be constructed by determining the stability of every singular point according to rule 6. In the general case, the stabilities of the singular points along the univariant curves indicated by the rows of such a table are inconsistent with the stabilities of the univariant curves; thus it is generally not possible to draw type II singular-point nets. Although type II singular-point nets are generally not possible, consistent topologies can always be drawn by mixing type I and type II connections. These topologies can be derived from pure type I singular-point nets by inverting the stabilities of singular points along one or more univariant curves, which in terms of the "table description" means the inversion of the stabilities of the singular points in the relevant rows. Such operations yield consistent topologies if each of the resulting columns is identical with a corresponding column in either the type II table or one of the type I tables.

Without taking into account the constraints from singular-point analysis, each solution-present univariant curve around an invariant point can be independently oriented with respect to the direction of compositional change in the solution phase; that is, if the compositional variable of the solution is X^S , X^S may increase or decrease toward the invariant point along the stable extension of the curve. As there are $c + 1$ solution-present univariant curves, in the general case, there are 2^{c+1} nonenantiomorphic singular-point nets or a total of 2^{c+2} singular-point nets possible. Although there does not seem to be any simple way of counting the number of topologically consistent singular-point nets, singular-point analysis can eliminate a large fraction of the topologies. This fraction increases with the number of univariant curves around the invariant point; in the two examples considered here singular-point analysis of a ternary invariant point eliminates 10 out of 16 possible nets, whereas the analysis of a quinary invariant point eliminates 50 out of 64 nonenantiomorphic singular-point nets. Type II connections have not been observed in calculated phase-diagram projections, but type I topologies are commonplace. In this regard, two general features of type I topologies are important (1) for a given invariant point composition, in a system involving a binary solution, there are only four singular-point nets possible; and (2) regardless of the invariant point composition, the direction of compositional change of the solution phase across the solution-absent reaction is the same in every univariant curve through a nondegenerate invariant point.

The reason for the importance of Schreinemakers' principles is that they enable theoretically rigorous integration and extension of knowl-

edge from a variety of sources, which include thermodynamic data and field and experimental observations. This work contributes to the tools available to petrologists. Recent advances in computational methods (Connolly, 1990; Powell and Holland, 1990) have enabled the calculation of phase diagrams for systems involving solution phases. The principles enumerated here are useful for both understanding and testing the validity of such diagrams. Although not explicitly discussed here, an understanding of phase-diagram projections is also an aid in interpreting phase-diagram sections with the compositional variable of a solution phase on one axis of the section coordinate frame (Connolly and Trommsdorff, 1991).

Only systems containing a single binary solution have been treated here, but the rules concerning singular-point topology are completely general. However, in more complex systems the interconnections of univariant curves can be considerably more complex or entirely absent.

APPENDIX

The topologies and relative stability levels around singular points connected by type II connections are determined by rule 6 (p. 788). For ternary systems involving a single binary solution it can be shown geometrically that, in the general case, it is impossible to draw consistent type II topologies that match the stability requirements for singular points along an individual univariant curve imposed by the assumption of monotonic solution composition change. According to rule 6 the stabilities of singular points along an univariant curve (x), which are connected to the conjugate singular points by type II connections, are determined by the relative position of the compound x and S_i with respect to the hinges

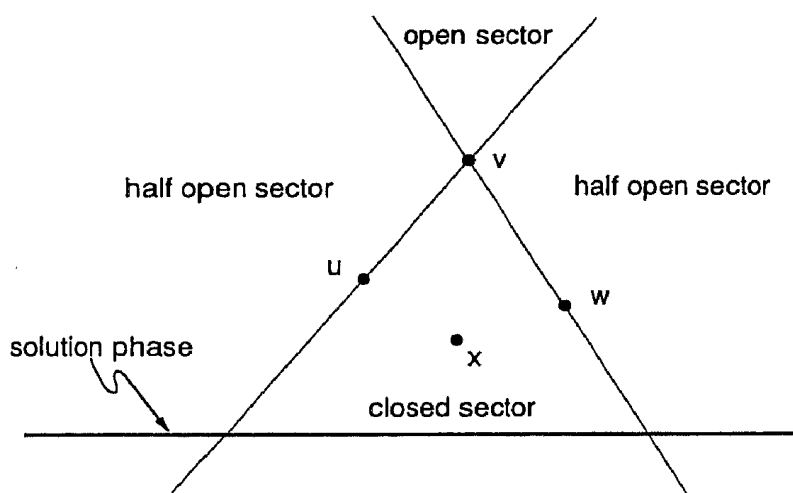


Fig. 11. Phase chemography of four compounds u , v , w , and x and a binary solution in a three-component system. If singular points $S_{(u,x)}$ and $S_{(w,x)}$ on univariant curve (x) are to be connected with their conjugate singular points through type II connections, their stabilities can be deduced by application of rule 6. The stabilities are not compatible with the stability sequence of singular points required by monotonic solution compositional variation along (x). If the invariant solution composition lies between $S_{(u,x)}$ and $S_{(w,x)}$ both singular points $S_{(u,x)}$ and $S_{(w,x)}$ would have same stabilities according to rule 6, which is incompatible with their occurrence on different sides of the invariant point. Similar arguments can be used to show that inconsistencies occur also if S_i does not lie between the two singular compositions.

under consideration. Any two non-parallel hinges relevant for an individual univariant curve intersect and thus divide composition space into four sectors: two of which will contain half-infinite portions of the solution compositional range, designated *half-open sectors*, one will contain a finite portion of the solution compositional range, designated a *closed sector*, and the fourth sector will not span any portion of the solution compositional range and is referred to as an *open sector*.

From figure 11 it can be seen that if a compound phase lies within a closed or open sector the stabilities of the singular points along the univariant curve labeled by this phase, determined by rule 6, are incompatible with the required stability sequence along an individual univariant curve regardless of the invariant solution composition. If the compound phase labeling a univariant curve lies in a half open sector, then the stabilities of the singular points on this univariant curve that correspond to the hinges defining the half

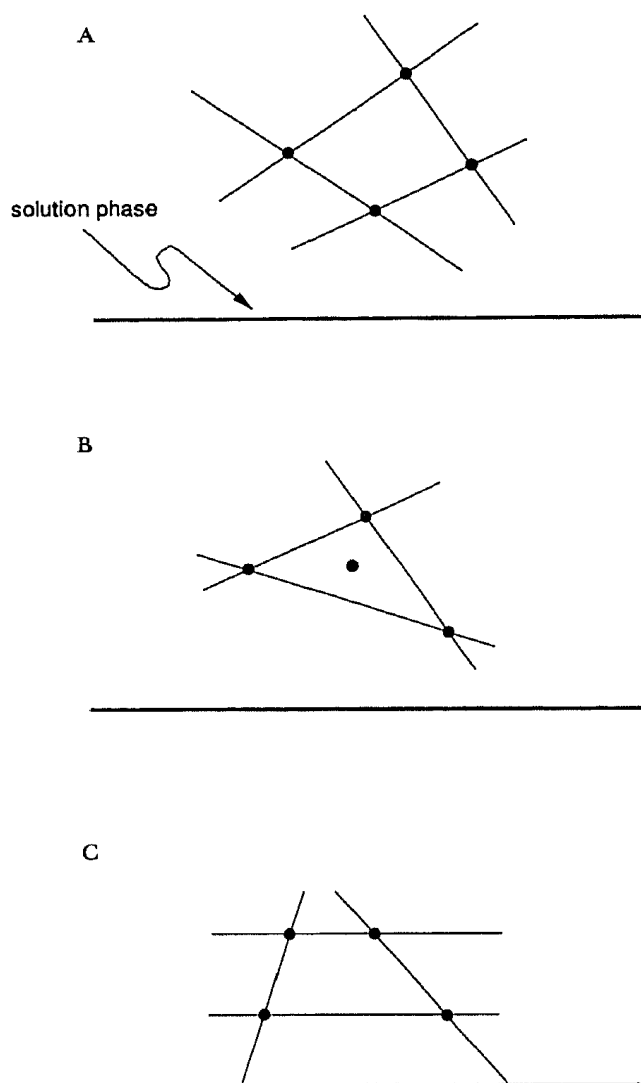


Fig. 12. Phase chemography of four compounds and a binary solution in a three-component system. In the general case (A and B), there is always a phase that lies in a closed or open sector, and it is impossible to draw consistent singular-point nets involving only type II connections. The only case where no compound phase is positioned in either an open or closed sector is shown in (C) where two hinges are parallel to the solution compositional range. For this chemography, a consistent singular-point net consisting of only type II connections can be drawn (see Connolly and Trommsdorff, 1991).

open sector will be compatible with monotonic solution compositional variation along the univariant curve.

From these observations it follows that inconsistencies in stability levels arise as soon as a compound phase lies in a closed or open sector with respect to one pair of hinges. A pure type II singular-point net is only possible if none of the compound phases lies in a closed or open sector with respect to all hinges. From figure 12A and B it can be seen, that in the general case at least one compound phase will be positioned in open or closed sectors. The only way to avoid this case in a ternary system is to orient two of the hinges parallel to the solution compositional range, as shown in the chemography of figure 12C, for which Connolly and Trommsdorff (1991) have presented a pure type II singular-point net.

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