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PHASE DIAGRAM TOPOLOGY AND THE INTRINSIC STABILITY RULE

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ABSTRACT. **An analysis of the ways in which n + 3 invariant points may be interconnected in phase diagrams reveals a fundamental relationship between the chemography of any system of n + 3 phases and the relative stabilities of those invariant points. The intrinsic stability rule as formulated here states that only those straight line nets (potential solutions) are possible for which the composition space defined by the missing phases at the stable invariant points overlaps the space defined by the missing phases at the metastable invariant points. In the absence of such overlap, the missing phases in each space are intrinsically stable (or metastable), because there are no chemical reactions among the phases in the one space that can affect the stabilities of phases in the other space. In the special case proven by Zharikov (1961) where only one of n + 3 invariant points is metastable, we show that this invariant point must be chemographically interior; that is, the phase that is missing at this invariant point is inside the space defined by the remaining phases.**

Application of the intrinsic stability rule results in 14 and 22 straight line nets for unary 4-phase and binary 5-phase systems, respectively. Each of the 16 nondegenerate chemographies in ternary systems with 6 phases yields exactly 32 straight line nets, although the number of combinatorial possibilities is far greater. These results are in accordance with the number given by the Mohr and Stout (1980) formulation of (n + 2)(n + 3) + 2. The intrinsic stability rule allows the identity and correct numbers of straight line nets for any system of n + 3 phases to be determined simply by visual inspection of the chemography alone or from an appropriate set of mass balance equations. These procedures are useful for evaluating whether the topology of a proposed phase diagram is a valid one and for analyzing more complex systems with greater numbers of phases.

INTRODUCTION

A remarkable feature of phase diagrams is the extent to which their most complex phase relationships depend on the simplest aspects of the chemical system used to describe them, namely the number of components (n), the number of phases, and the arrangement of those phases in composition space. The Gibbs phase rule, of course, relates the number of components and phases in a manner familiar to every petrologist. The specific arrangement of those phases with respect to each other, hereafter referred to as the phase chemography, goes a step further to define uniquely several important relationships fundamental to the understand-

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ing of phase diagrams. A well-known example is the configuration of univariant reactions around invariant points. This fact was shown by Schreinemakers (1915–1925) long ago to depend only on the chemography of the n + 2 phases involved in the equilibria. Unary and binary systems of n + 2 phases have a topologically unique triple point and quadruple point, respectively. There are also unique invariant point configurations for each of the 3 nondegenerate ternary chemographies as well as unique configurations for each of the nondegenerate quaternary chemographies involving 6 phases. The concepts of stability and metastability are embodied in each of these examples and are implemented in practice by the application of Schreinemakers rule (Zen, 1966a).

Other fundamental relationships have emerged as petrologists and geochemists have turned their attentions to systems that consist of more than n + 2 phases and that necessarily consist of more than a single invariant point. If the chemography has n + 3 phases, there will be n + 3 invariant points. The permissible linkages among the n + 3 invariant points and the univariant reactions that connect them were embodied in the concept of the closed net introduced by Zen (1966b). The closed net serves as a topological generating function from which all other nets can in principle be derived. The important point here is that there exists only one closed net for each chemography in any system of n + 3 phases. There is a single closed net for unary systems with 4 phases and a single closed net for non-degenerate binary systems of 5 phases, because there is only one way 4 phases can be arranged at a point, and only one way 5 nondegenerate phases can be arranged on a line, respectively. Similarly, there exists a single closed net for each of the 16 unique nondegenerate chemographies in ternary systems of 6 phases (Zen and Roseboom, 1972).

Although closed nets in of themselves are not reasonable topologic analogs for real phase diagrams, any of the straight line nets derived from them is. Straight line nets are equivalent in every way to the potential solutions of Mohr and Stout (1980). It has been shown by Mohr and Stout (1980) that the true phase diagram of any system of n + 3 phases can be deformed into a straight line net in which all univariant curves are straight lines providing that each of the invariant points predicted by combinatorics exists exactly once, either stably or metastably, in any given net. That assumption alone enables the n + 3 invariant points in any such net to be connected by straight reaction curves. That net, or any like it, can then be rotated and deformed as if on a rubber sheet until the positions of the invariant points and the curvature of the reactions match those determined by experiment or calculation.

The usefulness of straight line nets is that once their number and identities are known for any particular problem, the topologic form of the real (and often unknown) phase diagram must be included among these nets. Fortunately, the number of such nets is relatively small and depends only on the number of components, n, necessary to describe the, chemical system. This number for any combination of n + 3 nondegenerate phases is given by Mohr and Stout (1980) as (n + 2)(n + 3) + 2. For unary and non-degenerate binary systems, that there exists a unique number (14 and 22, respectively) does not seem particularly notable in view of the fact that there is only one chemography in each case. But in the ternary system with 16 topologically different arrangements of 6 phases, the fact that each one of them yields the same number (32) of straight line nets is remarkable.

A starting point in these analyses of n + 3 multisystems is the number of invariant, univariant, and divariant equilibria as given by the combinatorial rule. These are the elements that must connect as a coherent entity by the rules of chemographic analysis (Korzhinskii, 1959). In general, n + 3 invariant points are connected by (n + 2)(n + 3)/2 univariant lines. This relationship requires that every line pass through just 2 invariant points. Moreover, every univariant line must change its stability level upon passing through an invariant point. Given these constraints, it would seem a relatively simple matter to generate all possible combinations of invariant points and reaction curves and thus directly determine the total number of straight line nets. One quickly reaches the point by this reasoning where the number of combinatorial possibilities far exceeds the actual number of straight line nets as predicted by the Mohr and Stout formulation. The problem we address in this paper is to identify the fundamental relationships responsible for this observation and ultimately to relate the resulting phase relationships to the simplest aspect of the chemical system, namely the chemography of the phases.

THE COMBINATORIAL POSSIBILITIES

A simple combinatorial approach for analyzing a multisystem with n + 3 phases is to represent each of the n + 3 invariant points in each of its possible forms and then connect them in the allowable ways until all combinations are found. Each invariant point will appear only once in any straight line net, in 1 of 4 ways. It may be stable or metastable, and it may be right-handed or left-handed at each of those stability levels. Figure 1 illustrates the 4 ways a triple point, labelled [B], can appear in any particular straight line net. The assignment of handedness is arbitrary, but if the right-handed form corresponds to, say, a clockwise sequence of reactions about an invariant point, the counterclockwise sequence would then be referred to as left-handed. The terms right- and left-handed parity (Mohr and Stout, 1980) are also used in this context. We designate invariant points in the usual way by placing the name of the phase that is not involved in the invariant equilibrium in square brackets, with superscripts and subscripts denoting the stability (S is stable, M is metastable) and handedness (R is right-handed, and L is left-handed). In figure 1, the invariant point designated as $[B]_L^S$, for example, signifies the stable equilibrium between phases A, C, and D with an arbitrarily assigned left hand parity.

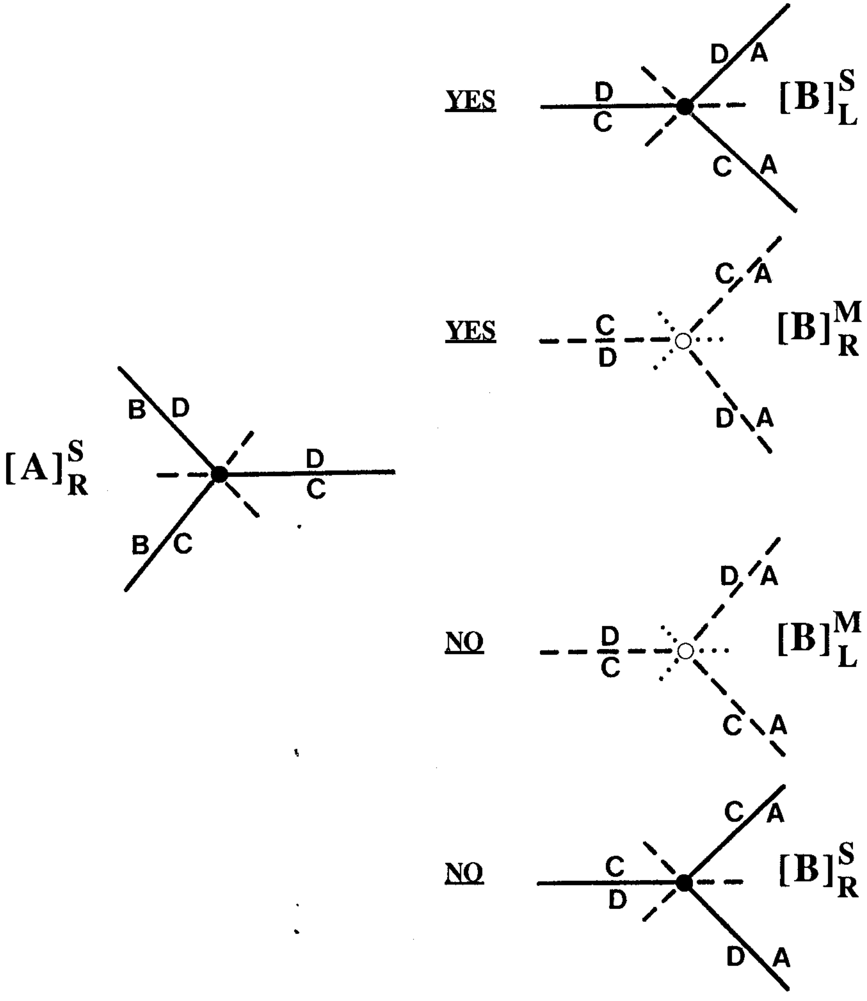


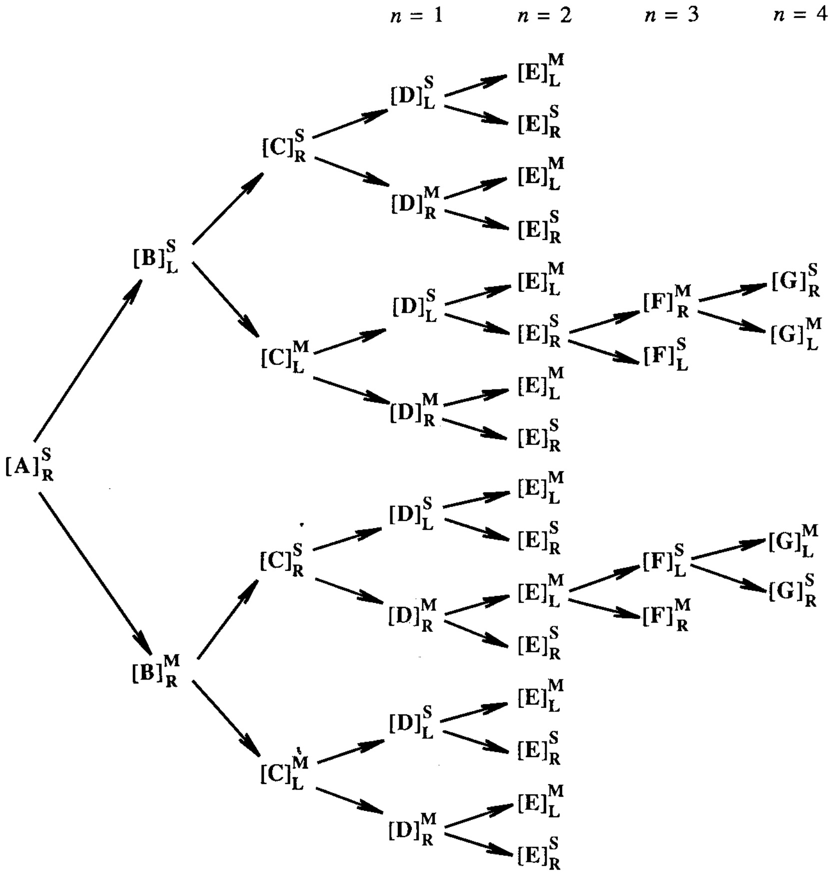
Fig. 1. The 2 ways an invariant point [A] with arbitrary stability and parity can connect by a common univariant line (D = C) to the 4 possible forms of a second invariant point [B].

There are important symmetry relationships between each of the forms of a single invariant point. For example, invarant points [B]$^{S}_{L}$ and [B]$^{M}_{R}$ in figure 1 are related to each other by transposition, an operation defined by Mohr and Stout (1980) by which the parity and stability level of one invariant point in a straight line net for nondegenerate chemographies are changed. When an invariant point is transposed from one valid straight line net, another valid straight line net is generated. When every invariant point has been transposed from any initial straight line net, the resulting straight line net is referred to as a trivial conjugate (Mohr and Stout, 1980, p. 153). Invariant points $[B]_L^M$ and $[B]_R^S$ in figure 1 are related to each other by transposition and these forms are mirror images of $[B]_R^M$ and $[B]_L^S$, respectively.

Unary systems.—If we now focus on just one of these forms, $[A]_R^S$, for example in figure 1, we can determine the possible pairings it may have with invariant point [B]. We could have focussed on any of the other 3 forms of [A], but the results would be related to those in figure 1 by symmetry. Note in figure 1 that $[A]_R^S$ combines with $[B]_L^S$ and $[B]_R^M$ but not with $[B]_L^M$ and $[B]_R^S$. The criterion for combination is that the connecting reaction (C = D) has the same stability and that the reactant (C) side and the product (D) side of the reaction match up. Invariant point $[A]_R^S$ connects directly by the stable reaction with $[B]_L^S$ in figure 1. If one rotates $[A]_R^S$ clockwise by 180 degrees, the reaction C = D connects metastably with $[B]_R^M$, and the 2 invariant points are validly joined. Had we had chosen to focus initially on $[A]_L^S$, the mirror image of $[A]_R^S$, then connections with $[B]_L^M$ and $[B]_R^S$ at the bottom of figure 1 would have been valid. The reason is because once the parity and stability level of [A] is defined such as in figure 1, only the parity or the stability of [B] can also be arbitrary. Invariant point $[A]_R^S$ can thus connect stably with stable $[B]_L^S$ but not with stable $[B]_R^S$. Had we chosen to focus initially on $[A]_L^M$, the transposed form of $[A]_R^S$, the same connections with $[B]_L^M$ and $[B]_R^S$ would be possible.

The arrows in figure 2 illustrate how $[A]_R^S$ can combine with 2 forms of [B] and how each of these forms can connect with 2 forms each of invariant points [C], [D], and [E]. The combination $[A]_R^S[B]_L^S[C]_R^S[D]_L^S$ following the arrows across the top of figure 2 is a valid combinatorial collection of 4 invariant points for a unary system of n + 3 phases. The addition of either of the [E] invariant points in figure 2 provides the fifth invariant point for binary systems. The 2 forms of each of these invariant points not shown in figure 2 would be appropriate were we to begin instead with either $[A]_L^S$ or $[A]_L^M$. Because all of the $[A]_L^S$ combinations are mirror images of those derived from figure 1, they are not considered further here nor are they included in the $(n + 2)(n + 3) + 2$ formulation of Mohr and Stout (1980). All of the $[A]_L^M$ combinations, however, yield the trivial conjugates of those derived from figure 2, and these are counted in the Mohr and Stout (1980) formulation.

Counting both $[A]_R^S$ and $[A]_L^M$ and the combinatorial connections that follow up to the "D" column (n = 1) in figure 2, there are 16 combinations (only 8 shown in first entry of row a) of 4 invariant points for unary systems. The formulation of Mohr and Stout (1980) yields 14 valid straight line nets. A comparison of the combinations that lead up to column "D" in figure 2 and the 14 actual straight line nets for the unary system of 4 phases shown in figure 3 reveals the 2 combinations that are physically impossible. They are $[A]_R^S[B]_L^S[C]_R^S[D]_L^S$ (the top sequence in fig. 2) and its trivial conjugate (not shown), namely $[A]_L^M[B]_R^M[C]_L^M[D]_R^M$. Note



a.	8	16	32	64
b.	16	32	64	128
c.	2	10	32	84
d.	14	22	32	44

Fig. 2. The combinatorial possibilities for the connectivity of invariant points beyond that given in figure 1. Column 4, labelled n = 1, is appropriate for unary systems with 4 phases; column 5, labelled n = 2, is appropriate for binary systems with 5 phases. Row (a) sums the combinatorial possibilities for each of the columns. Row (b) gives the total number of combinatorial possibilities for n + 3 phases which is twice the number given in row (A). Row (c) gives the number in (b) which cannot be valid straight line nets. Row (D) is the number of straight line nets from the formula (n + 2)(n + 3) + 2.

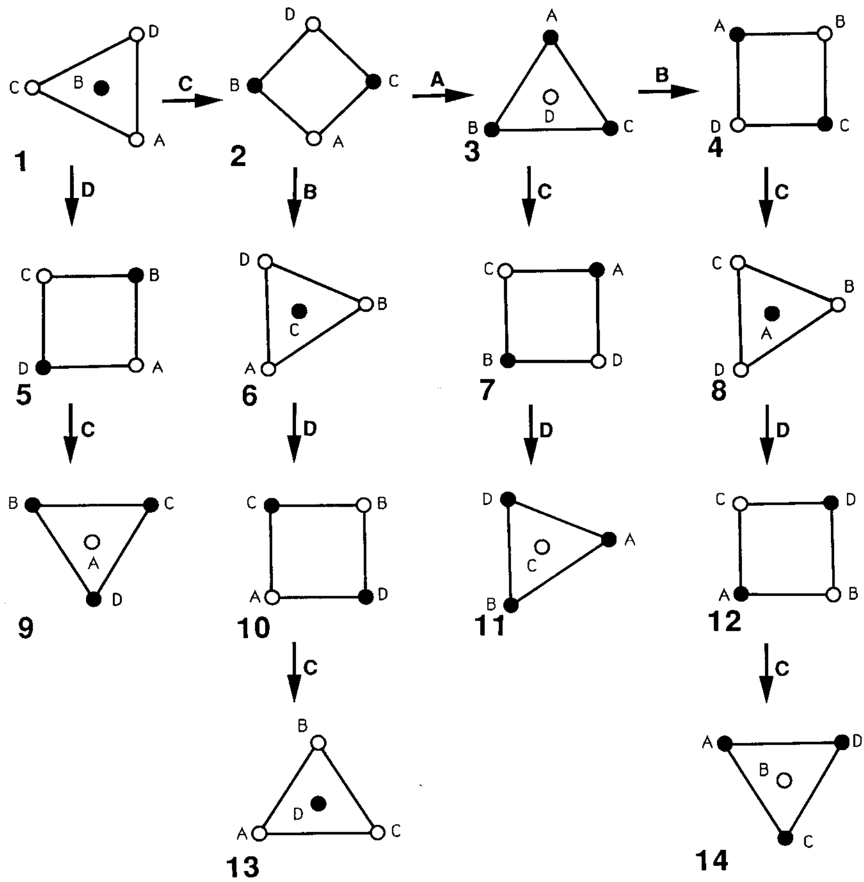


Fig. 3. The 14 straight line nets for unary systems with 4 phases (from Mohr and Stout, 1980, fig. 9). In this and subsequent diagrams stable invariant points are shown as solid circles and metastable points by open circles.

that each of these combinations is characterized by having the same stability level for each of the 4 invariant points.

The explanation for this observation is provided by Zharikov (1960) who proved in general that in any system of n + 3 nondegenerate phases, not all of the n + 3 invariant points can be stable in the same straight line net. At least one of the invariant points must be metastable. Zharikov's rule applies in an equally general way to straight line nets in which all but one of the invariant points is metastable. All valid straight line nets in unary (fig. 3), binary (fig. 4), and ternary systems were derived by Mohr and Stout (1980) by independent means, and there are no nets in which all invariant points have the same stability level.

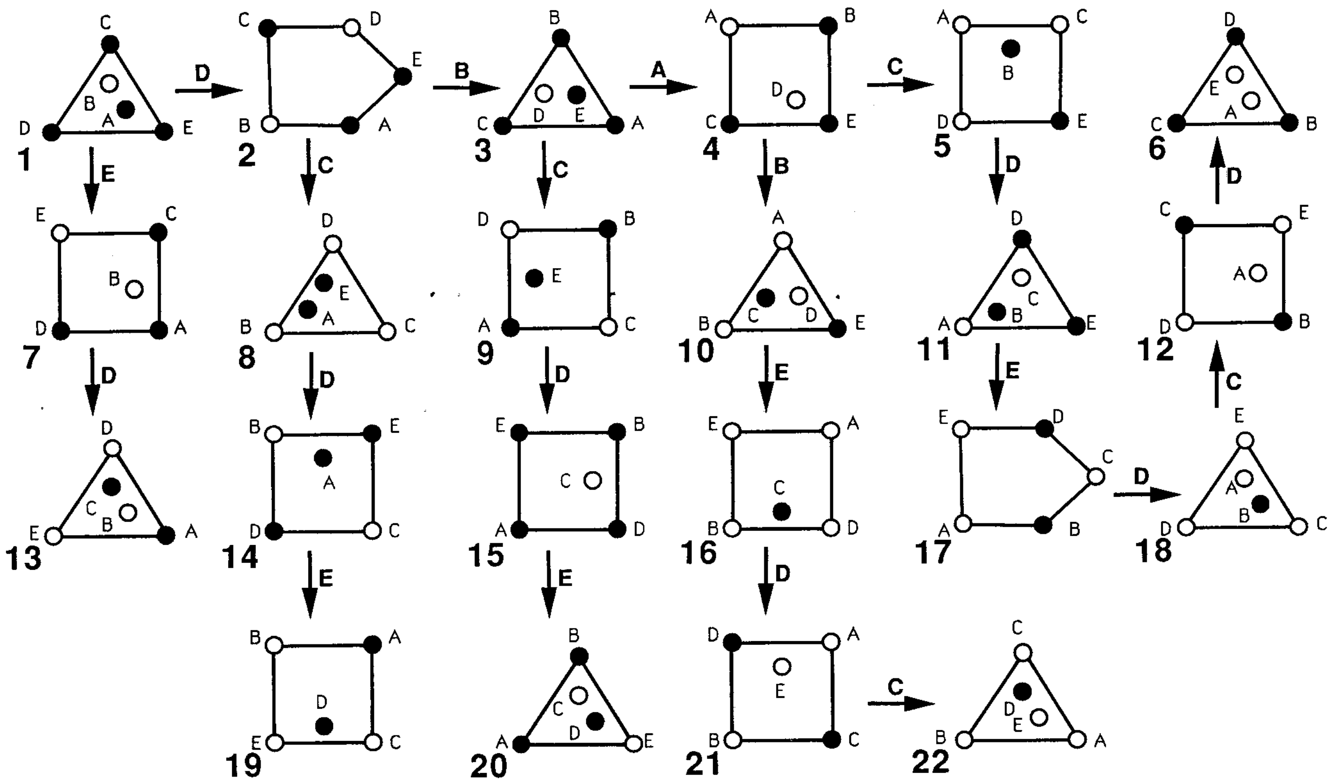


Fig. 4. The 22 straight line nets for binary systems with 5 phases. Phases (letters) which are encircled are those transposed to yield the next-numbered straight line net.

Binary systems.—Column "E" in figure 2 shows the combinatorial possibilities for binary systems with 5 phases. Because the binary system has 5 invariant points, the additional invariant point [E] is added to the unary results. An example of one valid straight line net among these possibilities is given in figure 5, taken from net 3 in figure 4, and expanded to show the specific reactions and divariant fields. This valid net is $[A]^S_R[B]^S_L[C]^S_R[D]^M_R[E]^S_R$, and it can be traced from $[A]^S_R$ to $[E]^S_R$ in figure 2. There are 5 combinations in figure 2 that cannot be valid straight line nets, and they can be identified as such by comparison with the 22 actual straight line nets for the binary system of 5 phases shown in figure 4. They are as follows:

1. $[A]^S_R[B]^S_L[C]^S_R[D]^S_L[E]^S_R$
2. $[A]^S_R[B]^S_L[C]^S_R[D]^S_L[E]^M_L$
3. $[A]^S_R[B]^S_L[C]^S_R[D]^M_R[E]^M_L$
4. $[A]^S_R[B]^S_L[C]^M_L[D]^M_R[E]^M_L$
5. $[A]^S_R[B]^M_R[C]^M_L[D]^M_R[E]^M_L$

As in the unary case, the reason the first of these combinations is an invalid straight line net is because the stability levels of each invariant point are the same. The trivial conjugate (not shown) is also invalid. The remaining 4 possibilities above and their trivial conjugates (not shown)

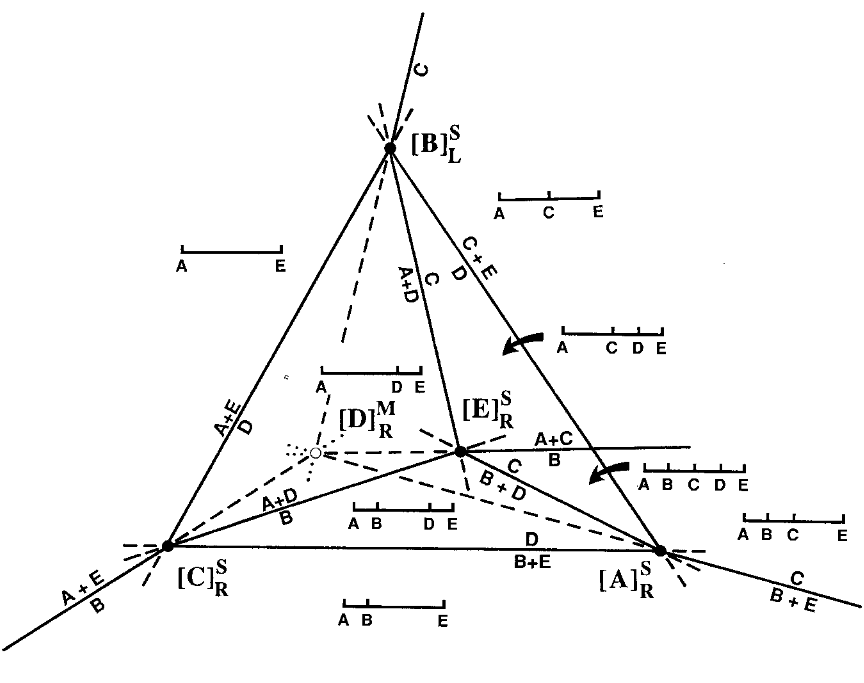


Fig. 5. Straight line net 3 from figure 4 expanded to show all connecting reactions and associated divariant fields.

are also impossible but for a different reason. Thus of the 32 total combinatorial possibilities, 10 are impossible straight line nets.

Ternary and higher dimensional systems.—The extension of figure 2 to include a sixth invariant point yields the 64 combinatorial possibilities for ternary systems of 6 phases. Only 4 of the 64 possibilities are shown in the "F" column in figure 2. The Mohr and Stout (1980) formulation predicts only half (32) of that number as valid straight line nets. Still only two of the 64 possibilities can be excluded by Zharikov's rule. The remaining 30 combinations for ternary systems and the remaining 82 (total of 84) combinations in the case of quaternary systems of 7 phases are impossible straight line nets for a different reason which we now address.

INTRINSIC STABILITY

The reason why the remaining number of combinatorial possibilities of invariant points cannot be valid straight line nets is because of an important relationship between phase chemography and the relative thermodynamic stability of those phases. We define here a chemographically exterior phase in non-degenerate chemographies as one whose chemistry is outside the composition space defined by the remaining phases. For example, the 2 phases at opposite ends of a chemographic bar in binary systems are chemographically exterior as are phases that occupy the apices of triangles, quadrilaterals, pentagons, and hexagons in ternary systems. A chemographically interior phase is positioned inside the space. The latter are always recognizeable, because their composition can be written in a terminal reaction involving 2 or more phases on the opposite side of the reaction. Chemographically exterior phases can only be involved with nonterminal reactions in which at least one other phase, either interior or exterior, is on the same side of the reaction as the original phase. As such, chemographically exterior phases and their exterior connecting tielines are intrinsically stable for all pressures and temperatures, because in these nondegenerate systems there is no other phase or combination of phases of equivalent composition that could possess a lower Gibbs energy. Such phases and tielines must be stable for all P-T conditions. On the other hand, chemographically interior phases can be metastable with respect to combinations of the other phases that surround them in composition space. This relationship was recognized explicitly by Day (1972, p. 719) but was not fully developed to the point where it could be generalized.

Another definition we clarify here is in reference to the "phase missing" designation for invariant points. Henceforth we designate a chemographically exterior or interior invariant point as one in which a chemographically exterior or interior phase does not participate in the equilibrium. There is an important distinction between the energetic interpretation of these 2 types of invariant points. Figure 6a illustrates the case in the binary system where an interior phase (B) is missing from the stable invariant equilibrium, labelled [B]. In this case, phase B is not involved, because as an interior phase it is energetically metastable with

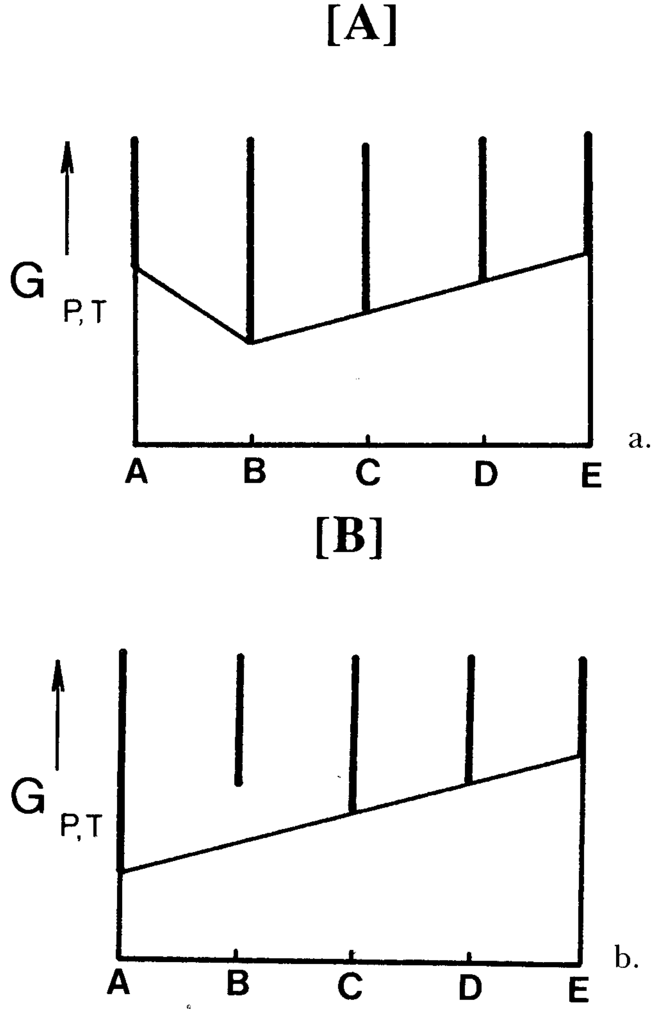


Fig. 6(a) Gibbs energy-composition relationships for a chemographically interior invariant point [B] in a binary system with 5 phases. (b) Similar relationships for a chemographically exterior invariant point [A].

respect to the other phases. Figure 6b illustrates the case where an exterior phase (A) is missing from the stable invariant point designated as [A]. In this case, however, phase A is stable as it must be as a chemographically exterior phase. Phase A is not involved in the stable invariant equilibria, because it is positioned outside the composition space defined by the reacting phases. The compositional reach is defined here as that part of composition space that lies interior to the actual phases involved in the equilibrium. Assemblages that lie outside of this compositional reach are unaffected by the equilibrium in question. The compositional reach of chemographically interior invariant points extends over the entirety of composition space defined by the n + 3 phases in the system, whereas that of chemographically exterior invariant points extends only over the space interior to the phases involved in that invariant point.

Invariant points will also be either topologically internal or external depending on whether the location of the point is inside or outside the areas defined by the other invariant points in the particular net. In the net labelled 3 in figure 4, [A], [B], and [C] are topologically external whereas [D] and [E] are topologically internal. The significance of this distinction is that only topologically external invariant points in a straight line net can be transposed to generate another valid straight line net (Mohr and Stout, 1980, p. 156). Transposition of [A] (labels without square brackets in fig. 4) in net 3 yields net 4 in figure 4. Transposition of [B] in net 4 yields net 10 and so forth.

Although chemographically exterior phases are intrinsically stable, chemographically exterior invariant points may be either stable or metastable depending on the conditions of P, T, et cetera. The latter case can easily be envisioned in figure 6b if the P, T conditions were such that the Gibbs' energy of phase A was lower than the extension of the tangent line describing the invariant equilibrium.

STABILITY RELATIONS AMONG n + 3 INVARIANT POINTS

Although Zharikov's rule states that at least one of n + 3 invariant points must be metastable in a system of n + 3 phases, no constraint is provided on which one it must be. We now show in steps that if all but one of n + 3 invariant points are stable, the one that is metastable must be chemographically interior. The first step supposes that the single metastable invariant point is topologically external. If the resulting straight line net were valid, then it would be possible to change the stability of the single metastable invariant point by transposition, leaving the stabilities of the other invariant points unchanged. This operation would produce a straight line net in which all invariant points were stable and would be in violation of Zharikov's rule. Therefore the single metastable invariant point must be topologically internal.

The second step utilizes the fact that a metastable invariant point must appear in an area where the missing phase is stable. If the invariant point is topologically internal, then this area is bounded by at least 3 reactions (see also proposition 2 of Day, 1972, p. 719) that would change the stability of the missing phase. Chemographically exterior phases are intrinsically stable and cannot be the missing phase in such a case. The single metastable invariant point in Zharikov's Rule must therefore be chemographically interior.

Figure 7 is an example of a valid straight line net for the binary 5-phase system taken from figure 4 (net 4) in which the details of the

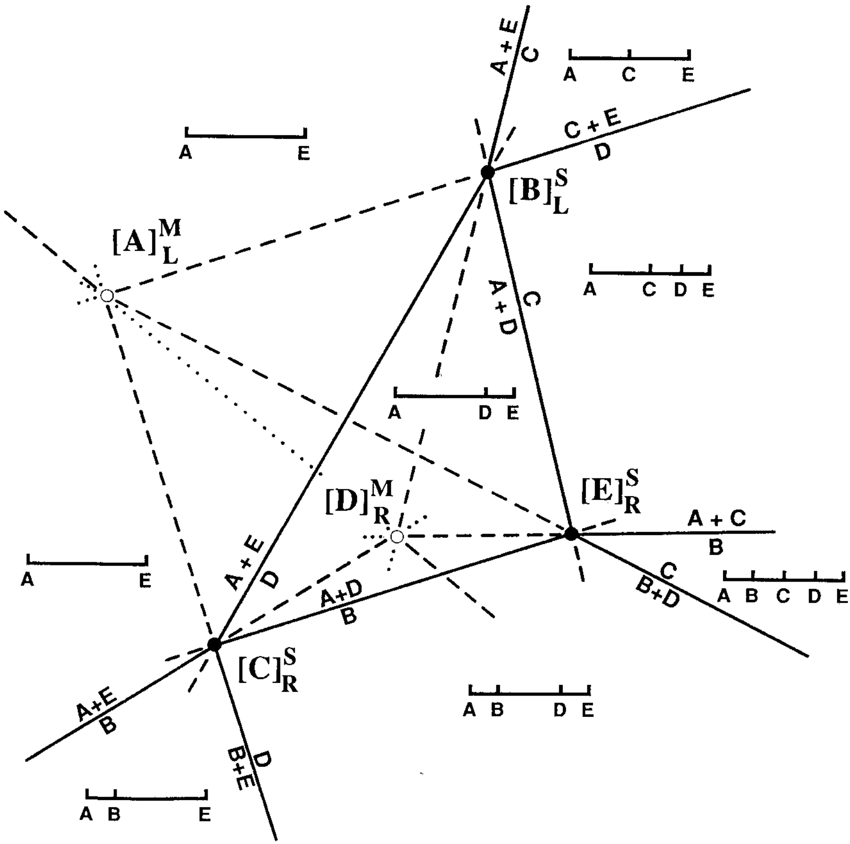


Fig. 7. Straight line net 4 from figure 4 derived by transposition of invariant point [A] from net 3. Note that both stability and parity of all other invariant points remain unchanged from net 3.

reaction lines and the divariant fields are shown. Note that $[A]^M_L$ is topologically external in this net and metastable within the divariant field A + E. Note also that there is only one other metastable invariant point in this net, namely $[D]^M_R$. The only way a valid straight line net can be generated in which $[A]^M_L$ is the only metastable invariant point is for $[D]^M_R$ to be transposed and thereby changing its stability. This operation cannot be accomplished, because $[D]^M_R$ is topologically internal (Mohr and Stout, 1980). On the other hand, in order for $[D]^M_R$ to be the only metastable invariant point, we need only transpose $[A]^M_L$ which is a perfectly valid operation in this case because it is a topologically external invariant point. The result is shown in figure 5 where $[D]^M_R$ is the only metastable invariant point.

An inspection of the 22 valid straight line nets for binary systems in figure 4 shows that there are no nets in which a chemographically exterior invariant point (either [A] or [E]) is uniquely metastable. In all cases, [A] or [E] can be metastable only if at least one other invariant point is also metastable.

In summary, the importance of our extension of Zharikov's rule is that a chemographically exterior invariant point can never be metastable in straight line nets in which all the remaining invariant points are stable. The single invariant point that must be metastable in Zharikov's rule must be a chemographically interior one. Consequently, combinatorial possibilities (2) and (5) listed earlier in the text for binary systems and their trivial conjugates are impossible straight line nets because each has a single metastable (or stable) invariant point that is chemographically exterior. An examination of the 22 straight line nets in figure 4 shows nets 1, 3, and 15 each with a single metastable invariant point. In each case the invariant point is chemographically interior.

THE INTRINSIC STABILITY RULE

The fact that chemographically exterior phases are intrinsically stable can be extended formally to include additional phases in the following way: If one or more adjoining phases in the chemography lie outside the composition space defined by the remaining phases, they cannot simultaneously be made metastable relative to any assemblage that could form among those remaining phases. This means that the set of adjoining phases is an intrinsicly stable phase assemblage. Stated another way, if each phase is assigned to just one set, then 2 sets of phases in the same chemography that do not overlap in composition space cannot interact in any way. As an example, the chemographic bar in figure 6 has 5 phases, labelled A through E. Let phases A and B be in one set and phases C, D, and E be in the other. The 2 sets do not overlap, and there are no reactions in the second set (for example, C + E = D) that could possibly affect the stability relationships in the first set.

These stability relationships in composition space have an important parallel with respect to invariant point stability. Let the phases in one of the sets above correspond to those missing in some selection of invariant points. In the previous example (fig. 6), the invariant points could be [A] and [B]. Let the remaining phases be in the other set and correspond to the phases missing at the remaining invariant points. In the example of figure 6, those invariant points would be [C], [D], and [E]. The intrinsic stability rule states that the only straight line nets possible for this chemography are those for which the composition space defined by the missing phases at the stable invariant points (set 1) overlaps the space defined by the missing phases at the metastable invariant points (set 2). As these 2 sets do not overlap in the example of figure 6, it is impossible for both [A] and [B] to be metastable when the remaining invariant points are all stable. It is also impossible for both [A] and [B] to be stable when the remaining invariant points are all metastable. The reason this must be so is that there can be no reactions among the phases of one set above that could affect the stability of the missing phases associated with invariant points in the other set.

The intrinsic stability rule explains why combinatorial possibilities (3) and (4) and their trivial conjugates discussed earlier for binary systems are impossible straight line nets. Combination (3) cannot be a valid straight line net, because the set of missing phases (A, B, and C) for the stable invariant points does not overlap with the set of missing phases (D and E) for the metastable invariant points. Combination (4) cannot be a valid straight line net because the set of missing phases (A and B) for the stable invariant points does not overlap the set of missing phases (C, D, and E) for the metastable invariant points.

K-POINT NETS

Because of Zharikov's rule, the maximum number of stable invariant points in any straight line net in an $n + 3$ multisystem is $n + 3 - 1 = n + 2$. This means, for example, that at most 4 of the 5 invariant points in binary systems can be stable in the same straight line net, or conversely, that at most 4 of the 5 invariant points can be metastable. Zen (1966b) defined the number of stable invariant points in any net by the letter k and proposed that the total possible number of k-point nets be determined (p. 408) by combinatorics as:

$$C(n + 3, k) = \frac{(n + 3)!}{k!(n + 3 - k)!} \tag{1}$$

This formulation correctly predicts the 16 possibilities for unary systems as indicated in figure 2 when one sums the results for $k = 0$ (1 possibility), $k = 1$ (4 possibilities), $k = 2$ (6 possibilities), $k = 3$ (4 possibilities), and $k = 4$ (1 possibility). We have already demonstrated why the 0-point net and its trivial conjugate (residual net of Zen, 1966b), the 4-point net, are not valid straight line nets. This brings the total down to 14 (table 1), the value predicted by the Mohr and Stout (1980) formulation. Zen (1966b) also eliminated $k = 0$ and $k = 4$ for the same reason given above.

For binary and higher dimensional systems, the number of possible k-point nets by the Zen (1966b) formulation far exceeds the actual number of valid straight line nets. The intrinsic stability rule presented earlier provides a simple and direct way to count the number of valid straight line nets for each value of k based solely on the phase chemography. For each chemography, first choose a value for k. If $k = 1$, there will be one stable invariant point and the remaining ones will be metastable. The phase missing at the stable invariant point defines a set (of one) which may or may not overlap with the set defined by the phases missing at the metastable invariant points. If the 2 sets overlap, the 1-point straight line net is a valid one. If the 2 sets do not overlap, that particular 1-point net is not a valid one. If $k = 2$, there will be 2 stable invariant points, and the remaining ones will be metastable. The 2 phases missing

TABLE 1

Tabulation of k-point nets for each of the chemographies shown in figure 8. Column 1 gives the number of components. Column 2 gives the number of invariant points among the n + 3 phases. Column 3 gives the value of k, namely the number of stable invariant points in each k-point net. Column 4 gives a simplified symbol without brackets to represent the missing phase at the appropriate invariant point. Only those symbols underlined are valid straight line nets. Column 5 gives the number of valid straight line nets for each value of k from the previous column. Column 6 gives the total number of straight line nets for each chemography shown in figure 8

n	I.P.	k	Possible k-point nets from eq (1)	Number of SLN (Underlined in Column 4)	Total Number of SLN
1	4	1	A B C D	4	
		2	AB AC AD BC BD CD	6	
		3	ABC ABD ACD BCD	4	14
2	5	1	A B C D E	3	
		2	AB AC AD AE BC BD BE CD CE DE	8	
		3	ABC ABD ABE ACD ACE ADE BCD BCE BDE CDE	8	
		4	ABCD ABCE ABDE ACDE BCDE	3	22
3	6	1	None	0	
H		2	AB AC AD AE AF BC BD BE BF CD CE CF DE DF EF	9	
		3	ABC ABD ABE ABF ACD ACE ACF ADE ADF AEF DEF CEF CDF CDE BEF BDF BDE BCF BCE BCD	14	
		4	ABCD ABCE ABCF ABDE ABDF ABEF ACDE ACDF ACEF ADEF BCDE BCDF BCEF BDEF CDEF	9	
		5	None	0	32
3	6	1	A B C D E F	1	
Pa		2	AB AC AD AE AF BC BD BE BF CD CE CF DE DF EF	9	
		3	ABC ABD ABE ABF ACD ACE ACF ADE ADF AEF DEF CEF CDF CDE BEF BDF BDE BCF BCE BCD	12	
		4	ABCD ABCE ABCF ABDE ABDF ABEF ACDE ACDF ACEF ADEF BCDE BCDF BCEF BDEF CDEF	9	
		5	ABCDE ABCDF ABCEF ABDEF ACDEF BCDEF	1	32
4	7	1	None	0	
El		2	AB AC AD AE AF AG BC BD BE BF BG CD CE CF CG DE DF DG EF EG FG	6	
		3	ABC ABD ABE ABF ABG ACD ACE ACF ACG ADE ADF ADG AEF AEG AFG BCD BCE BCF BCG BDE BDF BDG BEF BEG BFG CDE CDF CDG CEF CEG CFG DEF DEG DFG EFG	16	
		4	ABCD ABCE ABCF ABCG ABDE ABDF ABDG ABEF ABEG ABFG ACDE ACDF ACDG ACEF ACEG ACFG ADEF ADEG ADFG AEFG BCDE BCDF BCDG BCEF BCEG BCFG BDEF BDEG BDFG BEFG CDEF CDEG CDFG CEFG DEFG	16	
		5	ABCDE ABCDF ABCDG ABCEF ABCEG ABCFG ABDEF ABDEG ABDFG ABEFG ACDEF ACDEG ACDFG ACEFG ADEFG BCDEF BCDEG BCDFG BCEFG BDEFG CDEFG	6	
		6	None	0	44
3	6	1	None	0	
		2	AB AC AD AE AF BC BD BE BF CD CE CF DE DF EF	7	
		3	ABC ABD ABE ABF ACD ACE ACF ADE ADF AEF DEF CEF CDF CDE BEF BDF BDE BCF BCE BCD	12	
		4	ABCD ABCE ABCF ABDE ABDF ABEF ACDE ACDF ACEF ADEF BCDE BCDF BCEF BDEF CDEF	7	
		5	None	0	26

from the 2 stable invariant points define a set that must overlap with the set defined by the missing phases in the metastable invariant points if a valid straight line net is to result.

Binary systems.—The binary chemography (fig. 8b) is labelled such that phases A and E are chemographically exterior, and phases B, C, and D are chemographically interior. The combinatorial possibilities for k-point nets are tabulated in column 4 of table 1. The value of k ranges from zero in which case all the invariant points would be metastable to 5 in which case all the invariant points would be stable. Zharikov's rule assures us that neither of these possibilities is a valid straight line net. When k = 1, one of the 5 invariant points is stable. As each of the 5 phases can be missing, there are 5 combinatorial possibilities for 1-point nets but those two for which the missing phase is chemographically exterior cannot be valid straight line nets. Only the 1-point nets labelled and underlined B, C, and D are possible based on our extension of Zharikov's rule discussed earlier. Henceforth in our discussion of table 1, we eliminate the usual closed parentheses notations for nets (for example, ([A]) and ([A][B])) in order to conform with table 1.

For k = 2, two of the 5 invariant points are stable. Of the 10 combinatorial possibilities listed in table 1, those for which both a chemographically exterior invariant point and an immediately adjacent one are stable are impossible straight line nets. This must be true because of the intrinsic stability rule. Thus AB and DE are eliminated in table 1. The 8 valid 2-point straight line nets are underlined in table 1.

The numbers of straight line nets that result for k = 3 are identical to those for k = 2, because nets of one are trivial conjugates of the other. That is, a straight line net with 2 stable invariant points will have 3 metastable invariant points and vice versa. Similarly, there are as many 1-point straight line nets as there are 4-point straight line nets. In total, there are 22 valid straight line nets for this binary system of 5 phases. This is the same number predicted by the Mohr and Stout (1980) formulation.

Ternary systems.—For the ternary case with 6 phases, there are 16 nondegenerate chemographies (Day, 1972; Zen and Roseboom, 1972). Table 1 tabulates the combinatorial possibilities for just two of these and then shows which of those are possible straight line nets. The first example (fig. 8c) is ternary chemography H, a hexagon defined by 6 chemographically exterior phases. Zharikov's rule states that there are no zero-point and no 6-point nets. Moreover, the intrinsic stability rule requires that there are no 1-point and no 5-point straight line nets, because no chemographically exterior invariant point can be uniquely stable or metastable in any valid straight line net.

There are 15 combinatorial possibilities for 2-point nets, but of these only 9 are valid straight line nets (table 1, column 4). The only valid straight line nets are those for which the line defined in the chemography by the 2 missing phases at the 2 stable invariant points overlaps the area defined by the remaining phases. For example, the line connecting phases A and B in figure 8c overlaps the area defined by phases D, E, C,

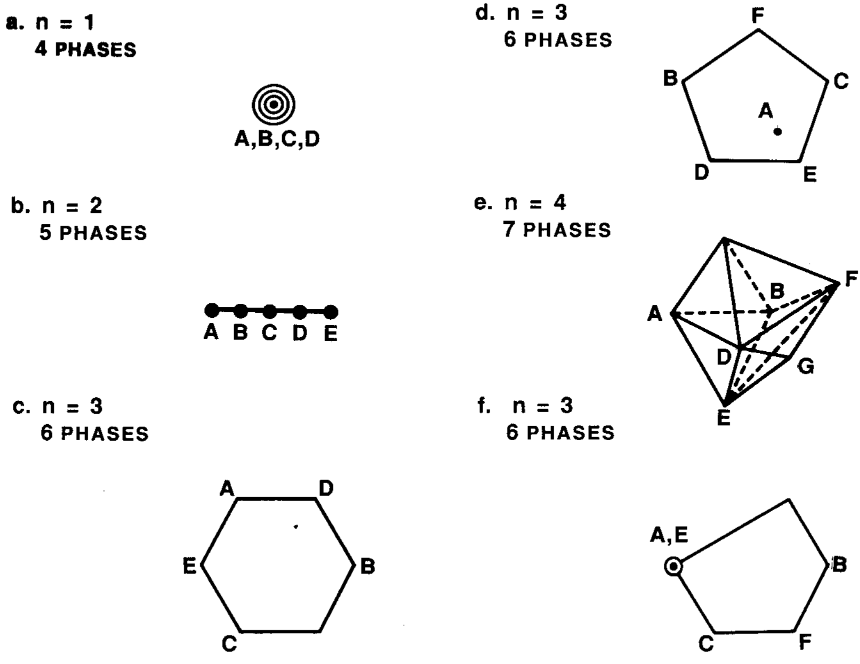


Fig. 8. Chemographies for various n + 3 phase systems. (a) unary system with 4 phases. (b) binary system with 5 phases. (c) Ternary system with 6 phases, specifically chemography H from Zen and Roseboom (1972). (d) Ternary chemography Pa from Zen and Roseboom (1972). (e) Quaternary chemography E1 from Stout (1990). (f) Degenerate ternary chemography with phases A and E coincident in composition (polymorphs).

and F. The 2-point net labelled AB (and its trivial conjugate, the 4-point net CDEF) in table 1 is thus a valid straight line net. By the same reasoning, the nets labelled AC, AF, BC, BE, CD, DE, DF, and EF in table 1 are all valid straight line nets. In contrast, the line connecting phases A and D is exterior in the chemography and therefore cannot overlap the area defined by the remainder of the phases. The combinatorial possibility labelled AD in table 1 is therefore not a valid 2-point straight line net.

There are 20 combinatorial possibilities for 3-point nets, but only 14 of them constitute valid straight line nets. The number of valid 3-point straight line nets can be determined by recognizing the intersecting triangles among the 6 phases. The 20 distinct triangles are represented in table 1, and as each must interact with just one other, there is a total of 10 pairs from which 7 overlapping pairs of triangles are found. An example is the overlap of triangle A + B + C with triangle D + E + F. If invariant points [A], [B], and [C] are considered metastable, then invariant points [D], [E], and [F] are stable and vice versa. Counting these trivial conjugates, there are 14 valid 3-point straight line nets for chemography H. The total of all k-point straight line nets for this chemography is 32.

The second example (fig. 8d) is ternary chemography Pa (Zen and Roseboom, 1972), a pentagon defined by 5 chemographically exterior phases with the sixth phase interior to the others. Zharikov's rule assures us that there are no zero-point and no 6-point nets. The only valid 1-point straight line net is $\underline{A}$ (column 4, table 1), because that invariant point unlike the others is chemographically interior and can be metastable by itself. The 5-point net, $\underline{BCDEF}$ is the trivial conjugate of the 1-point straight line net and is also valid.

There are 15 combinatorial possibilities for 2-point nets (and 4-point nets) in chemography Pa but only 9 of them constitute valid straight line nets. A glance at figure 8d shows, for example, that the line connecting phases A and B overlaps the area defined by phases F + C + E + D. Therefore invariant points [A] and [B] can both be stable, and invariant points [F], [C], [E] and [D] can all be metastable in a single 2-point straight line net which we label $\underline{AB}$ in table 1. Because phase A is chemographically interior, it can also define a tieline with each of the exterior phases C, D, and F which will overlap the areas defined by the remaining phases in each case. Thus $\underline{AC}$, $\underline{AD}$, and $\underline{AF}$ in table 1 are all valid straight line nets. Note that because phase A is positioned in the chemography to the phase E side of the line C + D, the tieline A + E does not overlap the area defined by phases C + D + B + F, and therefore AE is not a valid straight line net.

Similar reasoning applies to the remaining 2-point nets to give a total of 9 straight line nets. There are also 9 valid 4-point straight line nets, namely the trivial conjugates of the 2-point straight line nets.

As with the previous ternary chemography, the number of 3-point straight line nets can be determined by recognizing the intersecting triangles among the 6 phases. In this case, however, the 2 triangles A + C + F and B + D + E do not intersect whereas they did in the previous ternary example. The number of 3-point straight line nets thus reduces to 12 compared to 14 previously. The total number of valid k-point straight line nets for this ternary chemography is 32.

These procedures have been repeated for each of the remaining 14 nondegenerate chemographies in the ternary system. The results are summarized in table 2. Each of these chemographies has a different sequence of numbers of k-point straight line nets, but in every case the total is 32. Nets of maximum closure as defined by Day (1972) are those that have the maximum value of k for a given chemography. For ternary systems, these are the 5-point nets for all chemographies except the hexagonal arrangement (H, table 2). Each of the 3 pentagonal chemographies (Pa, Pb, Pc) has just one 5-point straight line net. Each of the 6 quadrilateral chemographies (Qa–Qf) has two 5-point straight line nets, and each of the 6 triangular chemographies (Ta–Tf) has three 5-point straight line nets for a total of 33 5-point straight line nets. Cheng and Greenwood (1990) omitted one of the 5-point straight line nets for chemography Tc in their incorrect total of 32 such nets.

TABLE 2

Summary of valid straight line nets for all unary, binary, and ternary nondegenerate chemographies for systems of n + 3 phases

Chemographic Type	k: 1	2	3	4	5	Total Number of SLN
H	0	9	14	9	0	32
Pa	1	9	12	9	1	32
Pb	1	8	14	8	1	32
Pc	1	10	10	10	1	32
Qa	2	7	14	7	2	32
Qb	2	8	12	8	2	32
Qc	2	7	14	7	2	32
Qd	2	9	10	9	2	32
Qe	2	9	10	9	2	32
Qf	2	8	12	8	2	32
Ta	3	9	8	9	3	32
Tb	3	8	10	8	3	32
Tc	3	8	10	8	3	32
Td	3	8	10	8	3	32
Te	3	7	12	7	3	32
Tf	3	6	14	6	3	32

The 4-point straight line net is the one of maximum closure for the hexagonal chemography (H). There is a total of 9 such nets rather than the 3 listed by Cheng and Greenwood (1990, p. 309). The latter are correct for the ([A][F]), ([C][D]), and ([B][E]) nets (((1)(4)), ((3)(6)), and ((2)(5)) nets of Cheng and Greenwood, 1990, p. 309) which are characterized topologically by a quadrilateral of 4 stable invariant points with 2 metastable interior invariant points. Application of the intrinsic stability rule reveals 6 additional nets as follows. Each of the 6 phases in the H chemography (fig. 8c) has 3 internal diagonals for a total of 18 diagonals. But because each diagonal is shared with 2 phases, there are only 9 unique diagonals each of which overlaps the composition space defined by the remaining phases. Each of the corresponding straight line nets has 2 metastable invariant points labelled with the phases that define the particular diagonal and 4 stable invariant points labelled with the 4 remaining phases. In terms of net topology, the 6 additional straight line nets have 3 stable invariant points that define a triangle with a single, stable interior invariant point. Altogether, the total number of distinct ternary nets of maximum closure is 42.

Quaternary systems.—Quaternary systems consisting of 7 phases define 3-dimensional volumes in composition space. The phases may all be chemographically exterior in which case there are exactly 5 topologically distinct chemographies (Stout, 1990). Up to 3 phases may be chemographically interior, but the total number of chemographies is as yet unknown. Figure 8e shows one of the 5 exterior types, labelled by Stout (1990) as E1. This chemography happens to correspond to an important

4-component system in granulite facies rocks involving the phases sillimanite (G), orthopyroxene (A), cordierite (D), saphirrine (C), garnet (E), spinel (B), and corundum (F) (Hensen, 1987).

The analysis of the total number of k-point straight line nets for this chemography is straightforward, if one recognizes the various geometric elements of the space defined by the 7 phases. Because all 7 phases are exterior there are 7 vertices, and because there are no degeneracies, the exterior surface of the volume consists entirely of triangles. There are 10 such triangles connected by 15 edges. There are C(7, 2) = 21 pairs of phases altogether so there must be 6(21-15) interior diagonals.

Table 1 summarizes the results for quaternary chemography E1. Zharikov's rule assures us that there are no 7-point and no 0-point nets. There are also no 6-point and no 1-point straight line nets because all the invariant points are chemographically exterior, and thus one cannot be uniquely stable or metastable when all the others are required to be stable in the same net. There are six 5-point straight line nets, determined by the number of 2-phase lines that pierce the interior of the space defined by all 7 phases. None of the 15 exterior lines can do this, leaving the 6 interior diagonals. Each of these pierces an interior volume, and therefore each of these 2-point (and 5-point) nets is a valid straight line net.

There are sixteen 4-point straight line nets and 16 trivial conjugates, the 3-point straight line nets. These are determined by the intersections of interior 3-phase triangles with 4-phase volumes. The 10 exterior triangles cannot overlap, leaving 25 triangles with at least one edge as an interior diagonal. Exactly 16 of these (fig. 8e and table 1) cut at least one face of an interior volume and thus constitute valid 4-point straight line nets. As there are 16 trivial conjugates, the sum of 3-point and 4-point straight line nets is 32. The addition of the twelve 2-point and 5-point straight line nets gives a grand total of 44. This is the same result given by the formula (n + 2)(n + 3) + 2 for n = 4. A similar analysis of the other 4 convex chemographies (E2, E3, E4, and E5; Stout, 1990) yields the same results for both the total of k-point straight line nets and the numbers of each.

It has been noted by Hensen and Harley (1990, p. 27) that a minimum of two and a maximum of 5 invariant points are stable in quaternary straight line nets. This is certainly true for the specific chemography (E1) considered here, because all phases are chemographically exterior. There are other quaternary chemographies, however, that have one or more interior phases in much the same way as ternary chemography Pa has an interior phase in figure 8d. In the latter case, both the 5-point net and the 1-point net are perfectly valid, and both are listed in table 1. In the quaternary case with one chemographically interior phase, the 6-point net and the 1-point net are equally valid and in fact are trivial conjugates of each other. A 1-point net is distinctive, because one of the n + 3 phases has no stable divariant field, and the stable portion of the straight line net consists only of an n + 2 equilibria. The metastable equilibria in this net, however, are unique and convey all the information typical of n + 3 multisystem nets. This fact is the basis by which Guo (1980) distinguishes between the 10 typical and 5 non-typical closed nets in unary systems with n + 4 phases.

DEGENERATE CHEMOGRAPHIES

The principles established for nondegenerate chemographies for any system of n + 3 phases can be readily extended to any degenerate chemography as well. The compositional degeneracies are coincidencies of composition (for example, polymorphs) within binary systems, coincidencies and colinearities in ternary systems, and each of these degeneracies with coplanarities in quaternary systems. A slight change in procedure for determining all k-point nets is required here, because now a phase and its polymorph could be chosen in separate sets which require that the sets share a common point in composition space. In all such degenerate cases, 2 sets of phases that share points, lines, areas, et cetera along the common boundary between the 2 sets are not considered to overlap.

As before, one begins with the chemography and then applies the intrinsic stability rule to determine the numbers of k-point straight line nets. In general, that number will be less than the total number of straight line nets given by the expression (n + 2)(n + 3) + 2. The application of the intrinsic stability rule to degenerate chemographies is best illustrated with the following example: Figure 8f shows a ternary chemography with 6 phases, where phases A and E coincide in composition. This chemography can be derived directly from figure 8c by collapsing the line between phases A and E to a point.

For k = 1 and k = 5, no straight line nets are possible because all phases are chemographically exterior. For k = 2, the line connecting the 2 missing phases in the 2 stable invariant points will overlap the remaining composition space providing that line is an interior diagonal in the chemography. There are only 7 such lines, and they define the valid 2-point straight line nets in the last example in table 1. There are also 7 valid 4-point straight line nets.

The number of 3-point straight line nets and their trivial conjugates is determined by intersecting triangles as was done for the nondegenerate cases. Here, however, some triangles degenerate to a line, because of the coincidence of phases A and E. The criterion for a valid 3-point straight line net in these cases is whether or not this line intersects any triangle. For example, the triangles A + B + C and D + E + F overlap in the nondegenerate example (H, table 1), but in the degenerate example here, the line (A, E) + B intersects the triangle D + E + F. Thus the 3-point net labelled $\underline{\text{ABE}}$ in column 4, table 1 is a valid straight line net as is the net labelled $\underline{\text{CDF}}$, its trivial conjugate.

The 4-point straight line nets are the trivial conjugates of the 2-point straight line nets, and together total 14. As there are twelve 3-point straight line nets and no 1-point or 5-point straight line nets, the total number of straight line nets is 26. This is the same number calculated by

Eq 12 in Mohr and Stout (1980, p. 165) for this degenerate chemography. In general, all degenerate chemographies yield fewer straight line nets than do nondegenerate ones.

SUMMARY AND CONCLUSIONS

We have shown here that there exists a fundamental relationship between the chemography of any system of n + 3 phases and the relative stabilities of the resulting n + 3 invariant points. Zharikov (1960) provided the first step in establishing this relationship by proving that at least one invariant point out of n + 3 such points in a straight line net must be metastable. We have extended Zharikov's rule in this paper to show that if only one invariant point is metastable, it must be chemographically interior; that is, the phase that is not involved in the actual invariant equilibrium must have a chemistry that is inside the composition space defined by the remaining phases in the system.

The reason for this relationship between chemography and phase diagram topology is formalized here as the intrinsic stability rule. Any chemographically exterior phase is intrinsically stable relative to other phases in an n + 3 multisystem, because there are no combinations of other phases in the system that can possess a lower Gibbs energy than the phase in question. It is also true that combinations of both chemographically exterior and interior phases are intrinsically stable providing the composition space defined by those phases does not overlap with the space defined by the remaining phases. The reason this is true is that there are no reactions among the phases of one set that can affect the stabilities of phases in the second set.

If the phases in one set as defined above are now identified as the missing phases at one or more stable invariant points and the missing phases at the remaining metastable invariant points are identified with the second set, that collection of stable and metastable invariant points will constitute a valid straight line net if and only if the 2 sets overlap in composition space. This relationship is the basis for enumerating all the valid straight line nets in any system of n + 3 phases. In all cases, the resulting numbers are in accordance with those derived by totally different means by Mohr and Stout (1980) and given by (n + 2)(n + 3) + 2.

These theoretical considerations apply to any system of n + 3 phases for which the phase diagram is either nonexistent, incomplete, or suspect of error. One can determine by inspection of the chemography alone whether a proposed phase diagram or any part of it is topologically permissible.

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