Construction of Pressure-Temperature Diagrams for Multicomponent Systems After the Method of Schreinemakers—A Geometric Approach

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Construction of Pressure-Temperature Diagrams for Multicomponent Systems After the Method of Schreinemakers—A Geometric Approach

By E-AN ZEN

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A discussion of the topological relations between the compositions of phases and the p–T representation of the invariant, univariant, and divariant equilibria in which these phases participate

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CONSTRUCTION OF PRESSURE-TEMPERATURE DIAGRAMS FOR MULTICOMPONENT SYSTEMS AFTER THE METHOD OF SCHREINEMAKERS—A GEOMETRIC APPROACH

By E-an Zen

ABSTRACT

For an n-component system at chemical equilibrium, an assemblage of $n+2$ phases is thermodynamically invariant, an assemblage of $n+1$ phases is univariant, and an assemblage of n phases is divariant. On a pressure-temperature diagram, an invariant point could occur only at some specific temperature and pressure; from this point there radiate $n+2$ univariant curves, and from each curve there emanate $n+1$ divariant regions. How these univariant curves and divariant regions are related to one another and how these relations reflect the relative compositions of the $n+2$ phases are the subjects of this paper; the treatment is based largely on the method discovered by F. A. H. Schreinemakers.

Because each univariant reaction involves $n+1$ phases, one of the $n+2$ phases that occur at the invariant point is missing along this reaction line. The univariant line, therefore, can be uniquely identified by the missing phase; by convention this missing phase label is given in parentheses. This paper demonstrates that for any given univariant reaction, there exists a corresponding set of relations among the univariant curves. Thus, if in a ternary system the heterogeneous reaction

$$A+B=C+D \text{ (phase E missing)}$$

is univariant, then on the $p-T$ diagram the univariant curves bearing the labels (A) and (B) must occur on one side of the curve bearing the label (E), whereas the curves bearing the labels (C) and (D) must occur on the other side of curve (E). Because each univariant curve contains $n+1$ phases, any two univariant curves contain all the $n+2$ phases, barring compositional degeneracy. Knowledge of two nondegenerate univariant reactions in the system thus suffices to determine all the other univariant reactions and therefore the succession of univariant curves around the invariant point. When the succession of univariant curves is known, it is a simple matter to determine next the relative locations of the divariant assemblages on the $p-T$ (pressure-temperature) diagram.

The Schreinemakers method can be applied to systems containing any number of components. For both unary and binary systems, there is but one corresponding topological arrangement of the univariant curves; for ternary systems, there are three possible topological arrangements. The number of possible arrangements increases rapidly for systems beyond the ternary; however, all the possibilities can be readily enumerated by means of the "pencil theorem" of Schreinemakers, which is discussed in detail.

An n-component system is degenerate if one or more of the associated univariant curves can be described by fewer than n components. Chemographically, this corresponds to the coincidence of phases ($n=2,3,4, \ldots$), colinearity of phases ($n=3,4,5, \ldots$), coplanarity of phases ($n=4,5,6, \ldots$) and so on. The phases participating in degenerate univariant reactions are the singular phases; those which do not participate are the indifferent phases. In a degenerate system, two or more univariant lines assume the same value of slope at the invariant point. If the indifferent phases are chemographically on opposite sides of the singular phases, the degenerate curves coincide stable to stable (so that fewer than $n+2$ univariant lines obtain); if the indifferent phases are on the same side of the singular phases, the degenerate curves coincide stable to metastable. All the possible cases of degeneracy for binary and ternary systems are described in this paper.

The method of Schreinemakers is useful in analyzing petrologic problems. Thus, for a given mineralogical system, if only some of the $n+2$ univariant curves about an invariant point have been determined experimentally or by calculation from available thermodynamic data, the application of the method enables one to compute approximately the remaining curves. Because the chemographic relations of the phases determine the sequence of univariant curves about the invariant point, the method is useful in evaluating the consistency of existing thermochemical data on minerals of known compositions. Even when no experimental or thermochemical data are available, knowledge of the chemical compositions of the phases alone often allows one to calculate and predict the relative p–T dispositions of mineral assemblages in specified chemical and mineralogical systems; such knowledge is frequently helpful in the study of mineral paragenesis. Examples of the application of the Schreinemakers method to mineralogical systems are given.

INTRODUCTION

The methods of representation of heterogeneous phase equilibria on p–T (pressure-temperature) diagrams have been developed along two complementary lines. One of these is mathematical representation, perhaps most notably known through the work of Morey and Williamson (1918) and Morey (1936). The second main line of analysis is geometric, the study being based on graphical analysis. One of the classics in this latter method is a series of 29 articles by Schreinemakers (1915–25), remarkable for its originality. This graphical approach to phase diagrams has been adopted by most modern texts on the phase rule, for instance those by Ricci (1951) and Zernike (1955); it is especially familiar to petrologists through such works as those of Niggli (1930, 1954) and Korzhinskiy (1959).

No satisfactory summary of the method of Schreinemakers is readily available in the literature; the summary by Niggli (1954) is so succinct that many logical steps are omitted or obscured. The present paper is intended to fill this gap and is addressed primarily to students. The approach is largely that of Schreinemakers and is axiomatic. Emphasis, however, is placed on the direct relation between p–T diagrams and the Gibbs free-energy surfaces of phases that participate in the equilibria. A mathematical background will be helpful but hardly necessary; the degeneracy of phase equilibria, for example, can be represented with equal validity either by the linear dependence of algebraic equations or by the linear, planar, or hyperplanar coincidence of phase compositions in diagrams.

The present study considers only phases of fixed compositions; this procedure is justified because, even for phases of variable compositions, these compositions are constant at an invariant point. As conditions depart from those of the invariant point, of course, effects due to compositional variability may become manifest; however, these effects do not concern us here. Some of these effects have been studied by Schreinemakers (1915–25).

A knowledge of the theory of graphical representation of invariant, univariant, and divariant equilibria in n-component, $n+2$ phase systems is useful in many mineralogical and petrological problems; a few illustrations must suffice here. In recent years many univariant equilibrium curves on mineralogical systems have been determined experimentally. Seldom, however, have all the $n+2$ possible univariant curves about a given invariant point been determined, so it may be necessary to calculate relative locations of the remaining curves from those available. The Schreinemakers method is eminently suited for this purpose.

Even if no experimental data exist for a mineralogical system, data on the entropies and volumes of the phases allow one to calculate the slopes of the univariant curves by means of the Clapeyron equation. Information on these slopes, in turn, permits one to calculate the relative dispositions of the curves about the invariant point. However, the available thermodynamic data are not always mutually consistent, although these inconsistencies may be difficult to discover, inasmuch as they involve small numerical differences. Because the sequence of univariant curves must obey the restrictions imposed by the relative compositions of the phases, failure of the computed curves to obey these restrictions immediately reveals that the thermodynamic data are mutually inconsistent.

Many mineralogical systems have not been studied experimentally, and the thermodynamic data on them are absent or incomplete. Knowledge of the relative dispositions of the univariant curves, however, allows one to gain insight into the possible conditions of formation of the corresponding mineral assemblages. This situation is particularly true for reactions that involve devolatilization, because such reactions are in general favored by rising temperature. Similarly, because density data are available for most minerals, good estimates of the probable locations of mineral assemblages relative to the pressure axis often can be made with the aid of the density data and of a knowledge of the sequence of succession of the univariant curves. The estimate of the p–T relations of the three polymorphs of aluminum silicate, andalusite, kyanite, and sillimanite, based on incomplete thermodynamic data (Miyashiro, 1949), exemplifies such an application and an early triumph of the use of theoretical analysis of plausible p–T diagrams to geologically important systems.

Eight examples of the application of the Schreinemakers method to the construction of p–T diagrams for systems of geologic interest are given on page 41. These examples are designed to illustrate the construction of geometrically distinct types of diagrams in ternary and quaternary systems, for which the selected phases have known compositions as well as partial or complete thermodynamic data.

The extension of the so-called "Ostwald's step rule" to binary systems is discussed on page 52. The extension is a direct outcome of the concept of the relative heights of Gibbs free-energy surfaces in G–p–T space, and predicts the possible sequences of binary, two-phase equilibrium assemblages for given values of p, T, and the bulk composition of the system.

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GENERAL DISCUSSION

NOMENCLATURE

In this study, the term "component" will be used to mean independent chemical component, that is, one that is distinct and cannot be formed by combinations of other components in the set. The component, thus defined, need not be physically real and may even be a negative quantity. For instance, the components CO_3 and $-CO$ could be used to describe all compositions in the binary system C–O, because

$$C = -\tfrac{1}{2}(CO_3 + 3(-CO))$$

$$O = \tfrac{1}{2}(CO_3 + (-CO))$$

In practice, we are mainly interested in the number of components needed to describe a given system and only incidentally in their precise identity, because components have physical meaning only in reference to phases, which are part of the physical world. Special significance can be attached to components which coincide with compositions of real phases; such components have been called "composants" by Schreinemakers (1923, 24, p. 719)[1] and "inactive components" by Thompson (1959, p. 451), who discussed the subject in careful detail.

The letter n, without subscript, will be used to designate the number of components in a system. The labels n_1, n_2, . . . , will be used to indicate individual components. All symbols for components are in italics except for the chemical formulas which are in roman type.

The term "phase" refers to a physical entity. The symbol φ will be used to denote the number of phases in a system; the symbols 1, 2, 3, . . . , will denote specific phases in the system. All phase symbols are in roman type.

The symbol ω will be used to denote the variance or number of thermodynamic degrees of freedom as given by the Gibbs phase rule,

$$\omega=n+2-\varphi$$

A system is invariant, univariant, divariant, and so forth, according to the situations where $\omega=0$, 1, 2, and so forth.

Schreinemakers (1915, 1, p. 118) first introduced the useful notation whereby a univariant or divariant equilibrium is designated by the phase or phases that do not participate in the reaction; the absent phases are given in parentheses. The number of phase labels appearing in given parentheses immediately indicates the variance of the equilibrium: thus (3, 5) is a divariant equilibrium which does not include the phases 3 and 5.

THE COMBINATORIAL FORMULA

The phase rule is a formula that relates the number of phases, the number of components, and the variance; only indirectly does it identify these quantities with entities of the physical world. Thus it is a formula for reckoning, equally applicable to stable, metastable, or unstable assemblages of real or imaginary phases. The reckoning process is facilitated by the use of the combinatorial formula, which gives the number of ways, C, of combining k objects, taken m at a time, provided that the m chosen objects and the $(k-m)$ residual objects are not distinguished within each subgroup. The formula states that

$$\begin{aligned} C(k,\, m) &= k!/m!(k-m)! \\ &= \frac{k(k-1)(k-2)\ldots 2\times 1}{m(m-1)(m-2)\ldots 2\times 1\times (k-m)(k-m-1)\ldots 2\times 1} \end{aligned}$$

---

[1] Reference to Schreinemakers (1915–25) will be given hereafter by the serial number of the article and the page number of the journal.

In terms of the phase-rule notation, the combinatorial formula may be written as

$$C(n+2,\varphi)=(n+2)!/\varphi!(n+2-\varphi)!$$
$$=(n+2)!/\varphi!\omega!$$

Figure 1 shows the number of $C(k, m)=C(n+2, \varphi)$ for integer values of k between 1 and 10, although only those rows with $k \geq 3 (n \geq 1)$ have physical meaning. The diagonal rows group systems with the same variance.

	$m=\phi$										
$k=n+2$	1	2	3	4	5	6	7	8	9	10	n
1	1										
2	2	1									
3	3	3	1								1
4	4	6	4	1							2
5	5	10	10	5	1						3
6	6	15	20	15	6	1					4
7	7	21	35	35	21	7	1				5
8	8	28	56	70	56	28	8	1			6
9	9	36	84	126	126	84	36	9	1		7
10	10	45	120	210	252	210	120	45	10	1	8
$\omega=k-m$	9	8	7	6	5	4	3	2	1	0	

FIGURE 1.—Coefficients of binomial expansion,

$$\frac{k!}{m!(k-m)!}=\frac{(n+2)!}{\varphi!\omega!}, \text{ where } \omega=n+2-\varphi.$$

From the combinatorial formula, it is easy to compute the number of possible assemblages of any given variance ($\omega=0, 1, 2, \ldots$) for a system of any given number of components. Thus, for example, in an equilibrium ternary five-phase system there is (5, 0) = 1 invariant point, C(5, 1) = 5 distinct univariant lines, C(5, 2) = 10 distinct divariant assemblages.

INTERSECTION OF FREE-ENERGY SURFACES

The change of the molar Gibbs free energy, $\bar{G}$, of any phase of fixed composition, whether stable or metastable, can be written as

$$d\bar{G}=-\bar{S}dT+\bar{V}dp$$

so that

$$\left(\frac{\partial\bar{G}}{\partial p}\right)_T=\bar{V}>0$$

$$\left(\frac{\partial\bar{G}}{\partial T}\right)_p=-\bar{S}<0$$

where $\bar{V}$ and $\bar{S}$ are the molar volume and entropy of the phase. Moreover, because the inequalities express intrinsic properties of phases, they are true also for any assemblage of phases in arbitrary but positive proportions. Inasmuch as $\bar{V}$ and $\bar{S}$ are always finite and positive quantities, and for any given phase assume unique values at any specified T and p, in a plot expressing $\bar{G}$ as functions of T and p, for any specified assemblage of phases, $\bar{G}$ is a single-valued continuous surface having positive and finite slopes in G–p sections and negative and finite slopes in G–T sections. These slopes are never parallel to the T, p, or G axes, though sharp changes in the slopes (fig. 2*B*), corresponding to the occurrence of higher order phase transitions, are not precluded.

The phase assemblages of particular interest to us are those which constitute divariant equilibrium assemblages. Consider two divariant assemblages that are derived from the same invariant assemblage in a system of n components, and that share $n-1$ phases in common. We further assume that the quantities of the two assemblages are such as to contain the same number of moles of the components. Inasmuch as all the phases are fixed in composition, each assemblage may be described by a single surface in G–p–T space; these two surfaces will meet along a line, the univariant line of reaction. The orthographic projection of this line onto the p–T plane is the familiar univariant curve of p–T diagrams; because the G-surfaces are never parallel to the G-axis, the procedure of projection never reduces the line to a point.

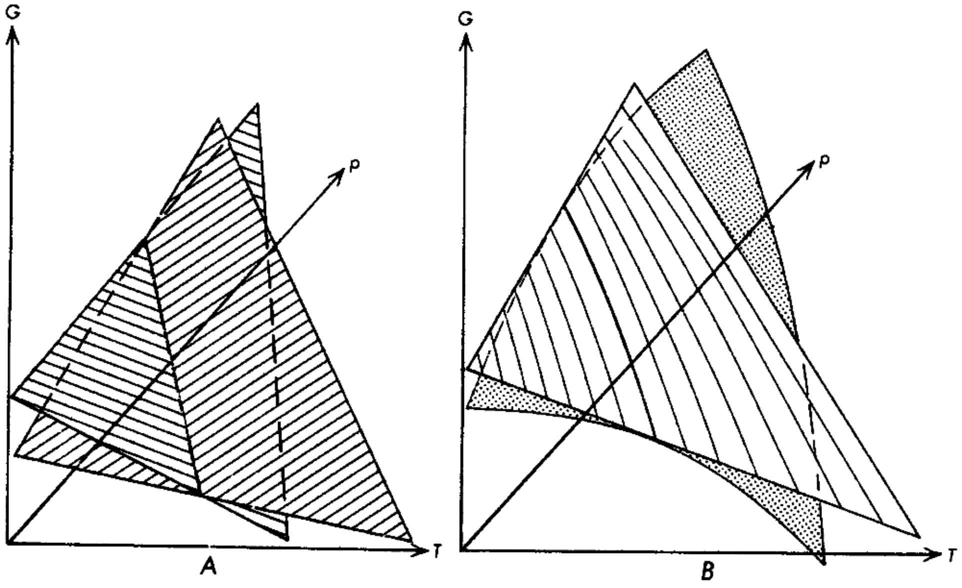

FIGURE 2.—The meeting of two Gibbs free-energy surfaces, $G=G(p, T)$. (*A*) By interpenetration: On one side of the line of intersection, one of the surfaces is higher than the other; on the other side of the line, it is lower. The two surfaces are differently ruled. For clarity, both surfaces are shown as planar. (*B*) By common tangency. The same surface is higher on both sides of the line of intersection. One surface is dotted and the other is ruled.

Most probably, two *G*-surfaces meeting in space will interpenetrate (fig. 2*A*). This, however, is not the only possibility. Under special circumstances, the two surfaces could meet along a common tangent (fig. 2*B*). Such a meeting of two surfaces is most likely when one of the surfaces, in the neighborhood of the meeting, happens to be undergoing strong changes in curvature consequent upon, for example, a high-order phase transformation with resultant discontinuities in the isothermal incompressibility and in the isobaric heat capacity. Univariant lines that arise from the tangential meeting of two surfaces, one of which is strongly curved, are instances of univariant lines which may be isolated in space and not related to any invariant point.[2]

Because *G*-surfaces for divariant assemblages are never parallel to the coordinate axes, when two *G*-surfaces meet in space one surface can always be described as higher than the other, that is, at the same *p* and *T*, the Gibbs free-energy content of one divariant assemblage is greater, and this assemblage is therefore less stable than the other. A univariant curve that results from the common tangency

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[2] Point-contact of two surfaces may be considered as a limiting case of the intersection of two *G*-surfaces where the line of intersection forms a closed loop. In this general case, one divariant assemblage is completely surrounded by another, and the univariant line is not associated with any invariant point. It is clear that such a relation between the two *G*-surfaces could reduce either directly into tangency at a point or indirectly through tangency along a line.

of two *G*-surfaces has the same surface occupying the lower position on both sides of the curve, so the divariant assemblage represented by the surface is relatively more stable on both sides on the univariant curve. If the curve is isolated in space and is not associated with some invariant point, then one divariant assemblage completely surrounds the univariant curve.

In contrast, when two divariant *G*-surfaces intersect by penetration, then one surface will be lower on one side of the univariant line of intersection, and vice versa. The univariant line, in this instance, separates distinct divariant assemblages, each of which occupies a part of the *p*–*T* plane. The univariant line continues until it is terminated at an invariant point.

Meeting of divariant *G*-surfaces by tangency is very unlikely. The fact that such an occurrence is probably associated with higher order phase transformations makes it progressively more improbable as the phase assemblage becomes more complex, for the effect of anomalies in the higher order derivatives of the free energy of a single phase becomes less pronounced as more and more free-energy functions are summed together. Meeting of *G*-surfaces by common tangency is not known empirically. For these reasons, we will hereafter disregard this remote possibility, and consider only the situation of intersection of *G*-surfaces.

THE FUNDAMENTAL AXIOM

A *G*-surface that represents a given divariant-phase assemblage cannot possess singularities because all the constituent *G*-functions of individual phases are continuous functions of *T* and *p*. The univariant curve that results from the intersection of two *G*-surfaces, therefore, must also be smooth and continuous. This fact enables us to speak unambiguously about "one side" and "the other side" of a univariant curve at each and every point along the curve.

We then arrive at the following obvious, but extremely powerful, conclusion (first pointed out in a slightly different form by Schreinemakers, 1915, 1, p. 119): When two divariant assemblages, each of *n* phases, meet along a univariant curve of $n+1$ phases, then on one side of the univariant curve the divariant assemblage I is relatively less metastable than assemblage II, whereas on the other side of the curve assemblage II is relatively less metastable than assemblage I.

Much of the following discussion depends on the verity of this statement. The statement is true so long as only univariant curves resulting from intersection of *G*-surfaces are considered. We will refer to the statement as the "fundamental axiom."

THE MOREY-SCHREINEMAKERS RULE

Consider an n-component system which at equilibrium consists of $n+2$ phases, which we designate as 1, 2, 3, . . ., n+1, n+2. These phases can coexist only at an invariant point. From this invariant point, $n+2$ univariant lines emanate, bearing the labels (1), (2), (3), . . ., (n+1), (n+2); each of these lines represents equilibrium among $n+1$ phases and the absent phase is identified by the phase-label in parentheses. Now consider the equilibrium divariant assemblage (n+1, n+2)[3] which consists of phases 1, 2, 3, . . ., n; phases n+1 and n+2 are missing. If to this assemblage the phase n+2 is added, we recover the univariant assemblage (n+1) of $n+1$ phases. By the fundamental axiom, the stable divariant assemblage (n+1, n+2) can extend only to this univariant curve; beyond this curve some other divariant assemblage, for example (n, n+2), will be relatively more stable. Thus the stable part of assemblage (n+1, n+2) is bound by the univariant curve (n+1); likewise, it is bound by the curve (n+2). The two curves that bound the divariant assemblage bear phase labels that are precisely those that identify the divariant assemblage itself.[4]

The two curves (n+1) and (n+2) divide the p–T plane into two sectors. Because in general these two curves do not possess the same slope value at the invariant point, one sector will subtend an angle greater than 180°, whereas the other sector will subtend the explementary angle less than 180° (fig. 3). In which sector does the assemblage (n+1, n+2) occur? The answer follows directly from the fundamental axiom.

Because in general the two curves have distinct slopes at the invariant point, the metastable extension of, let us say, (n+1) beyond the invariant point will be within the larger sector defined by the two curves (fig. 3). Suppose this is the sector in which the assemblage (n+1, n+2) occurs stably throughout. By the fundamental axiom, the curve (n+1), whether stable or metastable, necessarily separates that part of the sector in which (n+1, n+2) is stable from the part in which it is metastable. Thus in the region denoted by θ in figure 3,

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[3] We will assume that the equilibrium relations discussed above pertain to stable relations; however, the arguments are the same for metastable equilibrium relations. What is significant is the relative stabilities of two competing divariant assemblages at given values of p and T; the absolute stabilities of the phase assemblages are less significant properties in the present context and commonly cannot be defined by the Schreinemakers method.

[4] Because the two univariant reaction equations that bound a given divariant assemblage are different, they involve different amounts of the phases of this divariant assemblage. Consequently, the Gibbs free-energy surface of this assemblage at the two boundaries cannot be directly compared. This apparent inconsistency can be resolved by the following consideration: As long as all the phases of the given divariant assemblage are present at either boundary curve regardless of their proportions, these phases will always tend to react to form the alternative assemblage that is more stable beyond the boundary curve, with a net decrease in the free-energy content of the total system. Therefore, regardless of the proportions of the phases present, the Gibbs free-energy surface of the given divariant assemblage is always higher across the boundary curves relative to another divariant assemblage of phases having the same bulk composition.

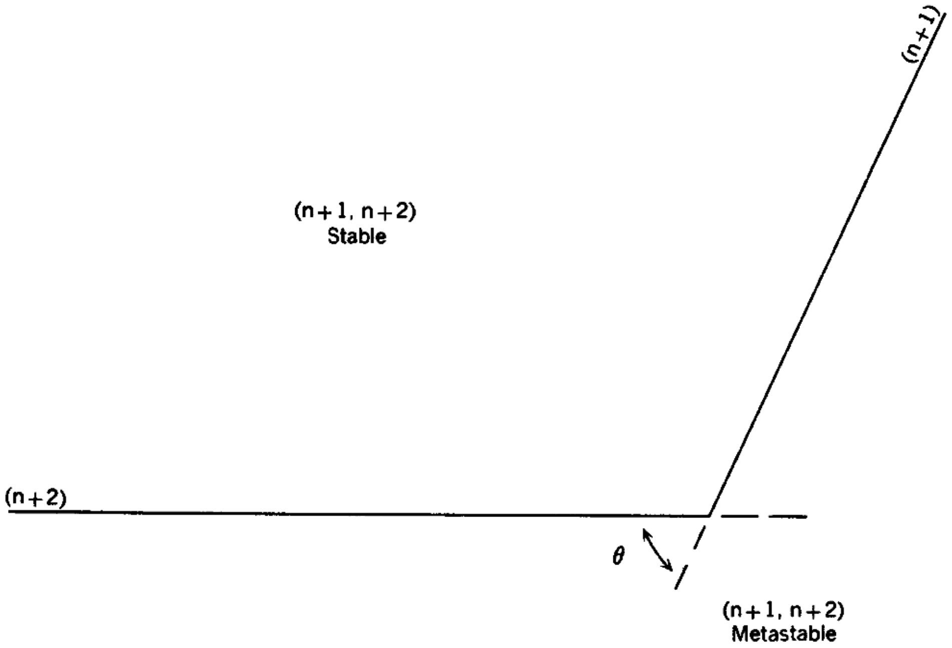

FIGURE 3.—The Morey-Schreinemakers rule. The assemblage (n+1, n+2) must be stable in the smaller sector, for otherwise in the sector marked by the angle θ this assemblage must be simultaneously stable and metastable.

the assemblage (n+1, n+2) must be both stable and metastable, and we arrive at a contradiction.

We therefore conclude: a divariant assemblage (n+1, n+2) always occurs in a sector which makes an angle about the invariant point no greater than 180°. The limiting value of 180° may be assumed when there is compositional coincidence or compositional degeneracy (see p. 30); it is clearly still compatible with the fundamental axiom.

This statement is the Morey-Schreinemakers rule, deduced geometrically by Schreinemakers (1915, 1, p. 121) and analytically by Morey and Williamson (1918, p. 66). It is the cornerstone of the method of geometric construction of *p–T* diagrams.

A direct consequence of the Morey-Schreinemakers rule is the following: The *p–T* region in the neighborhood of each invariant point is divided by univariant curves into $n+2$ sectors ($n \geq 1$), each of which is $\leq 180°$ in angular extent and is occupied by one or more divariant assemblages, one of which is unique for the sector.

The above statement is true for the stable univariant and divariant assemblages as well as for their metastable reflections about the invariant point.

Except for one-component systems, more than two divariant equilibria can be generated by a given univariant equilibrium. Therefore, in general at least on one side of the univariant curve there could simultaneously exist two or more distinct divariant assemblages under identical values of p and T; which assemblages in fact prevail in a particular sector depends on the bulk composition of the system. The different divariant assemblages on the same side of the univariant curve will, of course, extend to different univariant curves.

The following statement (Schreinemakers, 1915, 1, p. 121) governs the mutual relations of these divariant assemblages that overlap in the p–T field: Each divariant assemblage that extends across the univariant line (j) (stable or metastable) contains the phase j.

The truth of this statement is easy to see. Consider, for example, the divariant assemblage (j, j+1). This assemblage extends to, but does not cross, the stable part of the line (j). Because the assemblage (j, j+1) occupies a sector in the p–T field that is $\leq 180°$ in angle, the assemblage can at most extend to, but not beyond, the metastable part of (j). Because the assemblage (j, j+1) is arbitrary, any assemblage that does not contain phase j cannot extend over (j); only those assemblages that do contain j can do so.

We shall refer to this statement as the "overlap rule." Notice, however, that the converse of the statement is incorrect; not all assemblages that contain j extend over (j).

The overlap rule will be useful in confirming the consistency of arrangements of assemblages in the construction of phase diagrams. There are, however, other potent chemographic (Niggli, 1954, p. 380) canons which can be used for this purpose.

ARRANGEMENT OF UNIVARIANT CURVES

One elegant achievement of the Schreinemakers method is that correct arrangements of univariant curves on a p–T diagram can be constructed with minimum information on the chemography of the phases. The method may be explained best by an example.

Consider a univariant reaction involving $n+1$ phases; we label this curve and the univariant assemblage (n+2). Suppose the reaction is

$$1 + 2 + \ldots + k = k+1 + k+2 + \ldots + n + n+1$$

where the stoichiometric coefficients of the phases, though not specified, are all positive. The divariant assemblages associated with the reaction (n+1) bear the labels (1, n+1), (2, n+1), (3, n+1), . . . (n, n+1) and (n+2, n+1); each of these assemblages can be obtained by depleting the appropriate phase as a result of the univariant reaction. As a specific example, consider the divariant assemblage (n+1, n+2). This assemblage is bounded by the stable parts of the curves (n+1) and (n+2), and the stable part of the assemblage occupies the angular sector that is $\leq 180°$. Therefore, if we start out with the stable part of (n+2), and traverse in such a direction (let us suppose this direction to be clockwise) as to cross the stable part of the assemblage (n+1, n+2), we will meet the stable part of (n+1) before we meet the metastable extension of (n+2) at 180°. We say, then, that in relation to curve (n+2), curve (n+1) lies in the clockwise direction. Conversely, in relation to curve (n+1), curve (n+2) is in the counterclockwise direction.

Divariant assemblages that include all the phases 1, 2, . . ., k−1, k must occur stably only on one and the same side of the curve (n+2) because of the fundamental axiom. Therefore, it follows that the divariant assemblages (k+1, n+2), (k+2, n+2), . . ., (n, n+2), (n+1, n+2) must all occur on the same side of the curve (n+2), which we have stipulated to be in the clockwise direction in relation to (n+2). By the same token, all the assemblages (1, n+2), (2, n+2), (3, n+2), . . ., (k−1, n+2) and (k, n+2) must lie in the counterclockwise direction from (n+2). The curve (n+2) divides the *p–T* plane into two half planes, in each of which a distinct group of divariant assemblages is located. The only overlap is the divariant field into which the curve (n+2) extends metastably.

Therefore, the curve (n+2) divides the univariant curves into two groups. One group, (1), (2), (3), . . ., (k−1), (k), lies on the counterclockwise side of the curve (n+2), whereas the other group, (k+1), (k+2), (k+3), . . ., (n), (n+1), lies on the clockwise side of (n+2). Schematically, we can represent the relations in the form (1)(2)(3) . . . (k−1)(k)|(n+2)|(k+1)(k+2)(k+3) . . . (n)(n+1) where the univariant curve enclosed between the vertical bars is the reference curve about which the grouping is effected. We will refer to representations such as this, relating the geometry of univariant curves, as the "univariant scheme."

Comparison of the univariant scheme with the original univariant reaction equation shows a remarkable similarity. Thus

$$1 + 2 + 3 + \ldots + k-1 + k \overset{(n+2)}{=} k+1 + k+2 + k+3 + \ldots + n + n+1$$

and

$$(1)(2)(3)\ \ldots\ (k)|(n+2)|(k+1)(k+2)(k+3)\ \ldots\ (n+1)$$

The parallelism of course is no accident; it results from the fact that both expressions depict the same physical process. The reaction equation portrays the relations in terms of chemography; the univariant scheme portrays them in terms of the corresponding pressure and temperature coordinates. The formal one-to-one correspondence of the two representations is generally true. Any symmetry relation that exists among the compositions of the phases is reflected in the symmetry of arrangement of the univariant curves about the invariant point. As soon as a reaction is written, with positive values for the stoichiometric coefficients (that is, no phase is placed on the "wrong" side of the equation), the grouping of the corresponding univariant curves is determined. Clearly, if enough reactions can be specified to this extent, the relative arrangements of all the univariant curves about the invariant point can be determined.

The present method, however, can carry the solution no farther. Three other categories of information about the univariant curves and their generative invariant points, important in the physical interpretation of phase diagrams, cannot be derived by the method; these are: the location of the invariant point in the p–T diagram, the numerical values of the slopes of the univariant curves in the neighborhood of the invariant point, and the choice between a given sequence of the univariant curves (with specified sense of progression) and its mirror image ("enantiomorphic form") (see fig. 4; also Niggli, 1954, p. 408). The determination of these properties in general requires subsidiary data, either through determination of the thermodynamic properties of the phases, or through direct experimental determination of univariant equilibrium curves.[5] Only for activity-activity diagrams can the choice of the enantiomorphic form and the numerical values of the slopes be determined directly through the values of the stoichiometric coefficients of the univariant reaction equations (Korzhinskiy, 1959, p. 96; Zen, 1961a).

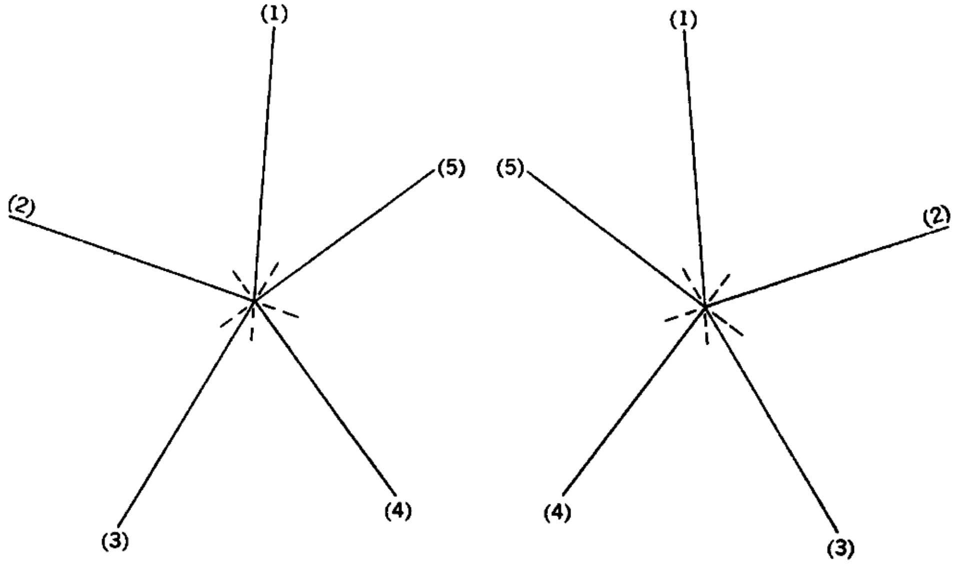

FIGURE 4.—Two enantiomorphic forms of succession of univariant lines consistent with a given univariant scheme. The correct choice from the two forms for a given p–T diagram cannot be determined by the chemographic relations alone.

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[5] Actually, only $n+1$ slope values at the invariant point are independent; the $(n+2)th$ slope is determined by the other $n+1$ values because, for a given bulk composition, the net change in ΔS and ΔV are both zero for the system after it undergoes a complete p–T circuit around the invariant point.

SYSTEMATIC DISCUSSION

ONE-COMPONENT SYSTEM

An invariant assemblage for a one-component system consists of three phases; the invariant point is surrounded by three univariant curves of two phases each. These curves separate three divariant fields of one phase each. The invariant point is a triple point.

The three reaction curves and their corresponding univariant schemes are:

1=2
(1)|(3)|(2)
1=3
(1)|(2)|(3)

and

2=3
(2)|(1)|(3)

The only arrangements of the curves consistent with the requirements of the univariant schemes are given by the two possibilities of figure 5. The result is geometrically reasonable: because there are only three curves while two are needed to define a sector, no more than one metastable extension can be found within a sector subtended by ≤180°, defined by two stable curves. Therefore, no fewer than one metastable extension must exist within this sector. The stable-metastable succession around the invariant point results.

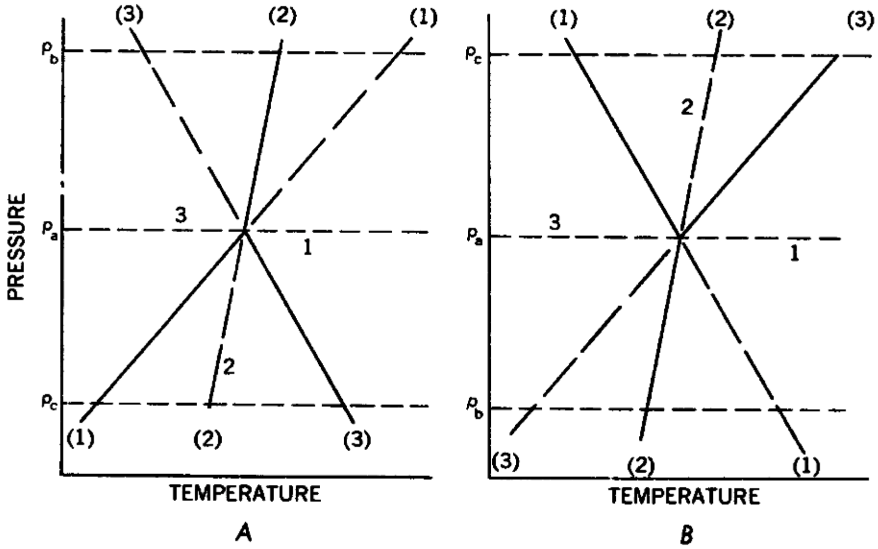

Figure 5.—The general geometric relations of the three univariant lines about the triple point in a one-component system. Two enantiomorphic forms are shown; both are consistent with the relations depicted in figure 6.

Figure 5 may also be instructively derived by considering the Gibbs free-energy surfaces for the three phases (see Darken and Gurry, 1953, p. 311). At the pressure of the invariant point, p_a, the *G–T* section of the surfaces for the three phases will be as given in figure 6*A*. (The lines for phases 1, 2, and 3 may be thought of as for steam, water, and ice, respectively, in the system H_2O; the slopes are all negative and the steepest curve represents the phase of greatest molal entropy content.) At slightly higher (or lower) pressures the three curves cease to meet at a single point; the relations will be as given in figure 6*B*. Correspondingly, at a lower (or higher) pressure than p_a the relations will be as given in figure 6*C*.

At a given pressure, the sequence of stable phase-assemblages with increasing temperature is traced by the lowest set of free-energy curves in the system. Thus for figure 6*B*, the sequence with rising temperature is 3 and 1; 2 is metastable. At the pressure p_b, the only stable univariant line (appearing as a piercing point in the figure) that is intersected with rising temperature is (2); the metastable univariant lines intersected are (3) at a temperature below the stable intersection with (2), and (1) at a temperature above the stable intersection with (2). Correspondingly, at p_c the stable sequence of phases is 3–2–1; the intersections with stable univariant lines are (1) and (3), in that order with rising temperature. The intersection with (2) is metastable and at a temperature between the two stable intersections.

Figure 6*A* shows that at the pressure of the invariant point, p_a, 2 is metastable throughout except at the point itself. This fact is expressed in figure 5; clearly two and only two divariant fields could straddle the isobaric line p_a in the neighborhood of the invariant point.

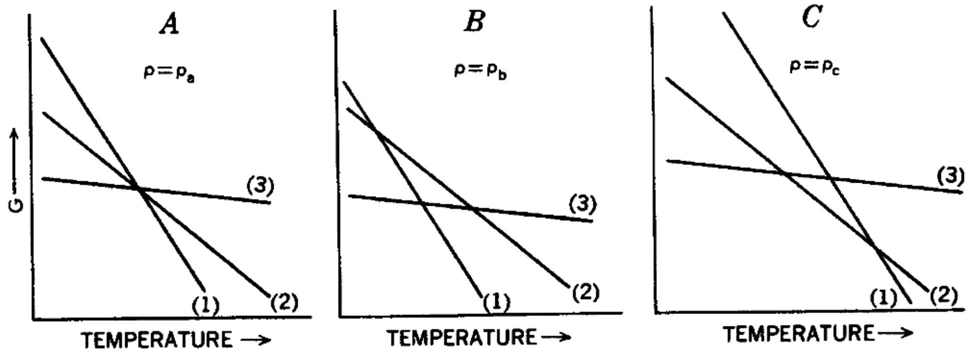

FIGURE 6.—Three isobaric *G–T* sections (lines) of the *G–p–T* surfaces of three polymorphs. *A*, At $p=p_a$, the pressure of the triple point, the three lines intersect at a single point. *B*, At $p=p_b$, slightly higher (or lower) than p_a. *C*, At $p=p_c$, slightly lower (or higher) than p_a. In each diagram, the sequence of stable univariant and divariant assemblages with rising temperature is given by the lowest set of free-energy lines. Note labels refer to phases, not phases absent.

Moreover, in both figures 5*A* and 5*B*, 1 is the high-temperature phase, 3 the low-temperature phase, and 2 the intermediate phase, being more stable than 3 but less stable than 1 at higher temperatures. This relation reflects the assumption that the entropies of the phases are such that $S_1 > S_2 > S_3$.

However, to choose between the two mirror images of figure 5, we need information on the molal volumes of the phases: geometric considerations alone do not suffice. Let us suppose that $V_1 > V_3 > V_2$, so that at a given temperature rising pressure favors 2 relative to both 1 and 3, and 3 relative to 1. These conditions cannot be fulfilled by figure 5*A*, but are compatible with figure 5*B*. The diagram thus might look like figure 7. The numerical values of the slopes can be determined by the Clapeyron equation,

$$dP/dT = \Delta S / \Delta V;$$

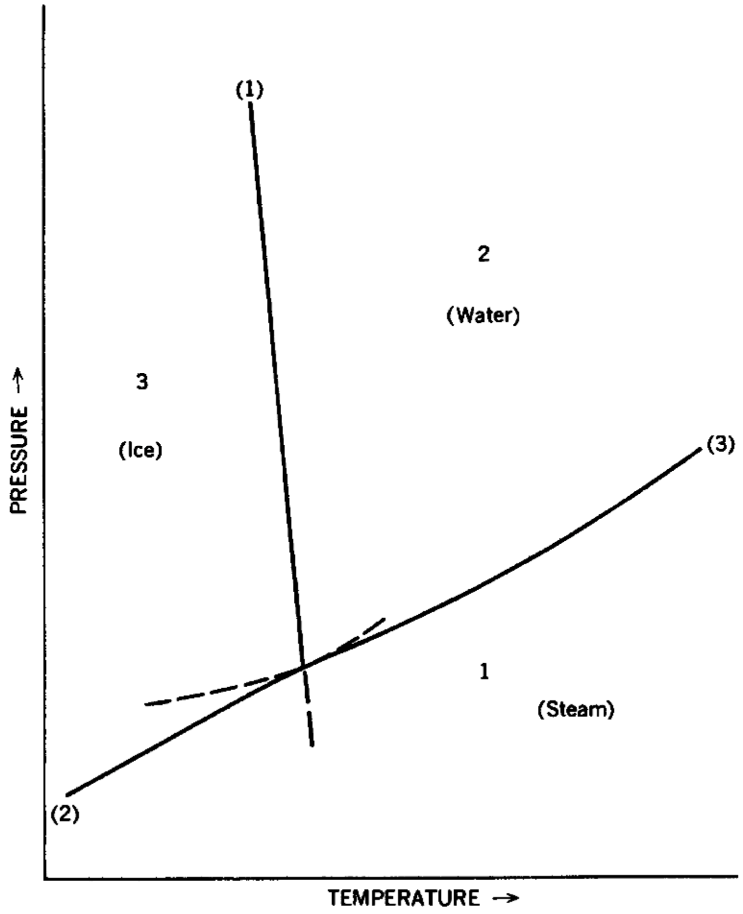

FIGURE 7.—The p–T diagram for the phases ice, water, and steam in the unary system H_2O; the diagram is consistent with figure 5*B*.

however, to locate the curves and the triple point, additional thermodynamic data (for example, enthalpies of the phases) are needed.

TWO-COMPONENT SYSTEM

Chemographically, all phases in a binary system can be represented along a straight line. The invariant point is a quadruple point, involving four phases. Four univariant curves emanate from the invariant point, and, according to the combinatorial formula, there are $4!/2!2!=6$ distinct divariant assemblages consisting of two phases each.

We consider here only the situation where the compositions of all four phases are distinct and fixed; the situation where two or more phases have the same composition is treated in the section on degenerate systems. The chemography of the phases, therefore, may be represented by figure 8. Phases 1 and 4 are related by the symmetry of their chemographic locations, as are phases 2 and 3.

The four univariant reactions and their corresponding univariant schemes are:

$$(1):\quad 2+4=3$$

$$(2)(4)|(1)|(3)$$

$$(2):\quad 1+4=3$$

$$(1)(4)|(2)|(3)$$

$$(3):\quad 1+4=2$$

$$(1)(4)|(3)|(2)$$

$$(4):\quad 1+3=2$$

$$(1)(3)|(4)|(2),$$

With (1) as the reference line, (2) and (4) are on one side and (3) is on the other. However, the diagram is not yet determined because the mutual relation of (2) and (4) and their relation to the metastable part of (3) are not known. The third univariant scheme, however, shows that, relative to (3), (1) and (4) are on the same side whereas (2) is on the opposite side; (4) must therefore lie between (1) and (2),

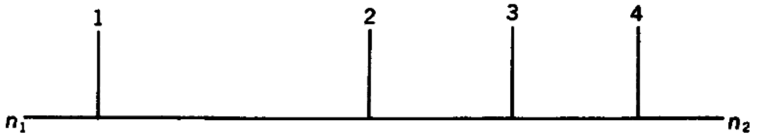

FIGURE 8.—The designation of the four phases in a binary system.

and the metastable extension of (3) must lie between the stable parts of (2) and (4). These considerations uniquely fix the diagram, as in figure 9; it is readily established that the arrangement agrees with the second and fourth univariant schemes.

The four sectors of the p–T surface are occupied by the assemblages 1+4, 1+3, 2+3, and 2+4. These four assemblages completely define the possible relations, for the two remaining divariant assemblages, 1+2 and 3+4, are thereby implied.

The assemblage 1+2 lies between (3) and (4) and straddles (1); the assemblage 3+4 lies between (1) and (2) and straddles (4). Similarly, the assemblage 1+4 straddles the metastable extensions of (1) and (4), the assemblage 2+4 straddles the metastable extension of (2), and so forth, so that the overlap rule is obeyed. Notice, however, that the converse of the overlap rule is emphatically invalid: for example the assemblage 2+3 does not straddle the curves (2) or (3), either stably or metastably.

The chemographic symmetry between 1 and 4, and also between 2 and 3, are reflected in the mirror symmetry of the disposition of the univariant curves.

Note that in the sector (2, 3) (assemblage 1+4), there exist two metastable extensions; this sector is flanked by two sectors each with

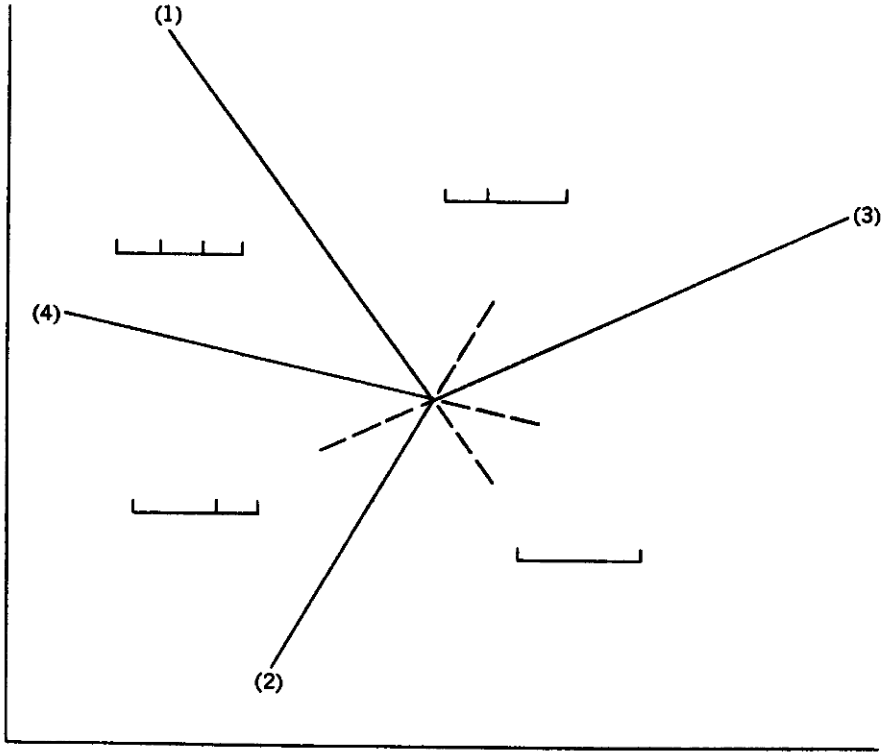

FIGURE 9.—The unique geometric relation of the four univariant lines about a given invariant (quadruple) point in a binary system.

one metastable extension, and finally the sector (1, 4) contains no metastable extension. This arrangement is unique in a binary system.

As the phase reactions are traced around the invariant point, only one event occurs each time a univariant curve is crossed; for example, 3 appears between 1 and 4 across (2). This is as it should be, for each event represents a distinct reaction; simultaneous occurrence of two or more events requires a most unlikely coincidence of two or more independent slopes of univariant equilibria.

On a purely geometric basis, the sequence of stable and metastable curves around an invariant point in a binary system can be derived from the corresponding diagram for the unary system. In a unary system, there is a stable curve between two adjacent metastable curves, and vice versa. Let these be labeled *aa′*, *bb′*, and *cc′* (fig. 10). When the invariant point generates four univariant curves, as in a binary system, one more curve, *dd′*, must be added. This added curve inevitably divides one of the three stable sectors into two parts, one of which can contain no metastable extension (sector *cod* in fig. 10),

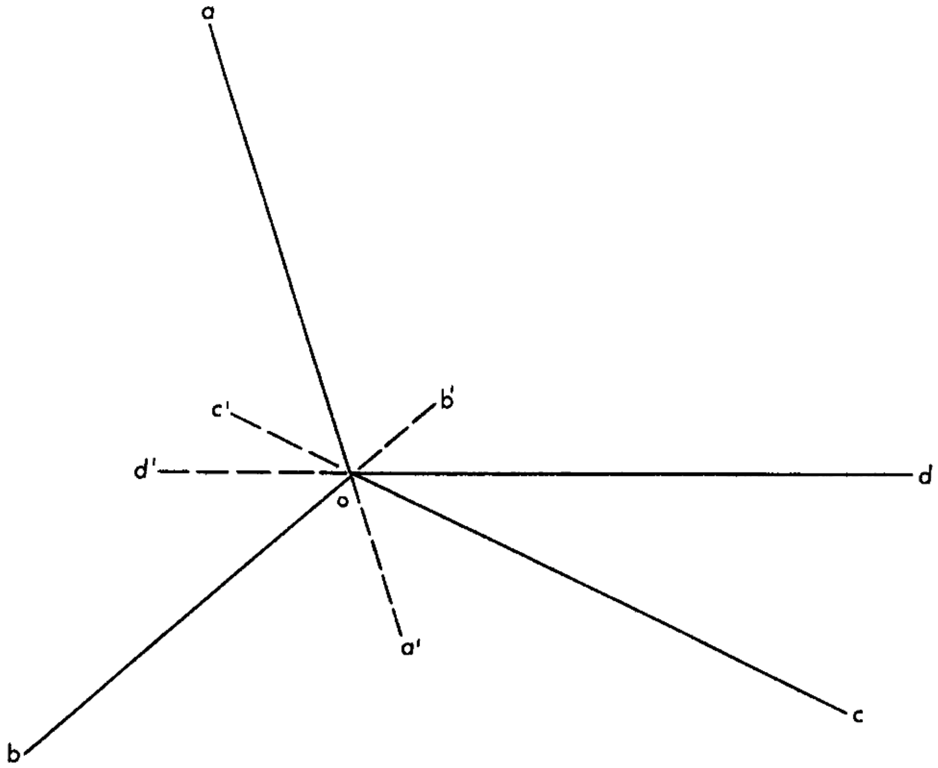

FIGURE 10.—Derivation of the geometric relations of a binary system from that of a unary system. If *aa′*, *bb′*, and *cc′* are the three univariant lines of a unary system, the addition of a fourth line, *dd′*, required by a binary system, necessarily results in one sector having no metastable extension and its opposite sector having two metastable extensions. Each of the two flanking sectors has one metastable extension.

and the other of which must contain one metastable extension (sector *doa*). The metastable part of the added curve, *od'*, extends into one of the adjacent stable sectors which initially contains one metastable extension. By the Morey-Schreinemakers rule, both sectors *bod* and *aod* are $\leq 180°$, therefore the sector that now contains two metastable extensions cannot be adjacent to the sector that now contains none.

THREE-COMPONENT SYSTEM

A system of three components can be depicted chemographically by a plane triangle. The invariant point in a three-component system consists of five phases; it is a quintuple point. From the invariant point, five univariant lines of four phases each emanate; from these curves, 10 divariant regions of three phases each develop.

Barring accidents of colinearity in compositions, which will be discussed in the section on degenerate systems, the compositions of the five phases that occur at the quintuple point are related to one another in one of three ways: (a) the five phase compositions can be used to define a pentagon without reentrant angles (fig. 11*A*); (b) four of the five phase compositions can be used to define a quadrilateral without reentrant angles, whereas the fifth phase composition falls within the limits of the quadrilateral (fig. 12*A*); and (c) three of the five phase compositions can be used to define a triangle, whereas the remaining two phase compositions fall within the limits of the triangle (fig. 13*A*). These three different chemographic relations will be separately analyzed.

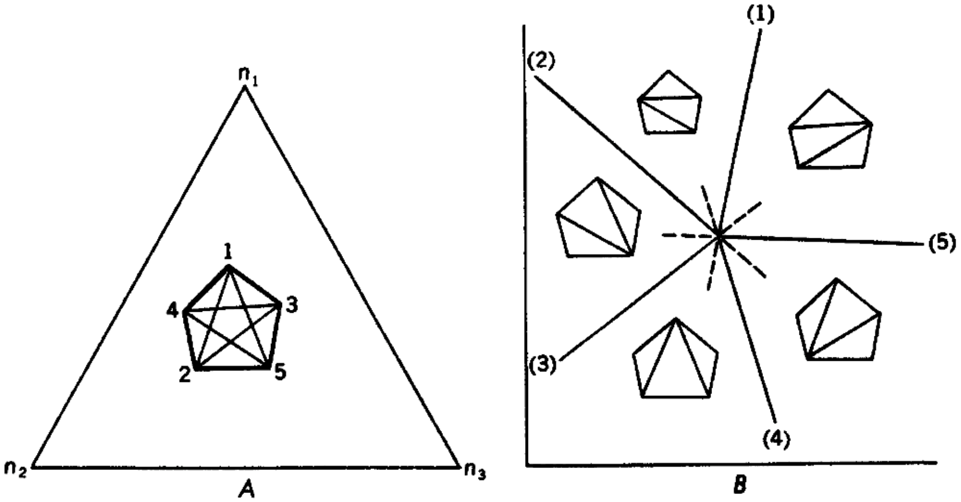

FIGURE 11.—The p–T diagram in a ternary system where the five phases form a convex pentagon. *A*, The chemographic relations; *B*, the corresponding p–T diagram. Notice that the univariant curves follow in numerical sequence when the phases are labeled in diagonal sequence.

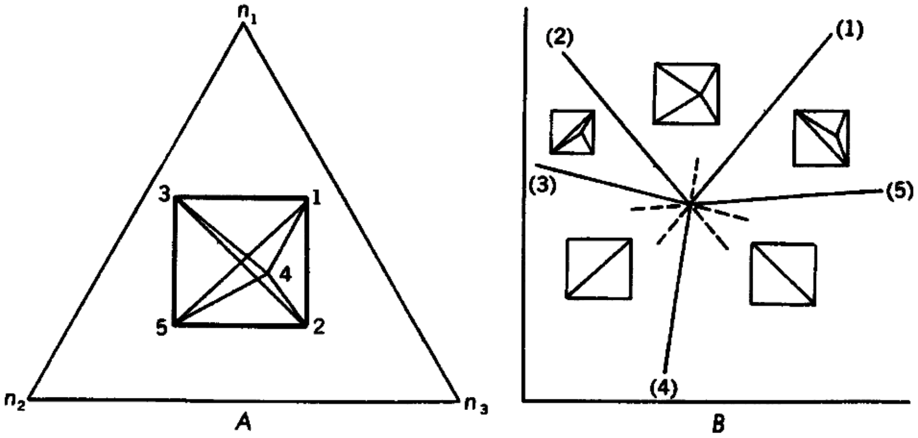

FIGURE 12.—The p–T diagram in a ternary system where four of the five phases form a quadrilateral and the fifth phase is an interior point. See also caption for figure 11.

Case (a) Five phase compositions define a pentagon.—For reasons shown below, the phases are labeled in the diagonal order shown in figure 11*A*. The five univariant reactions and their univariant schemes are:

(1): $2+3=4+5$
$(2)(3)|(1)|(4)(5)$
(2): $1+5=3+4$
$(1)(5)|(2)|(3)(4)$
(3): $1+2=4+5$
$(1)(2)|(3)|(4)(5)$
(4): $1+5=2+3$
$(1)(5)|(4)|(2)(3)$
(5): $1+2=3+4$
$(1)(2)|(5)|(3)(4)$

Relative to curve (1), (2) and (3) lie on one side and (4) and (5) on the opposite side. Relative to (2), (1) and (5) must be on one side and (3) and (4) on the opposite side. The sequence of curves therefore must be (1), (2), (3), (4), and (5) around the invariant point. Because the chemographic relations of the five phases are entirely symmetrical, so that upon cyclic rotation of the phase indices the mutual relations of the phases are topologically indistinguishable from the original, the five univariant lines also must be symmetrically disposed with respect to one another, and there must be one metastable extension between each pair of adjacent stable curves. The diagram must be as shown in figure 11*B*. The univariant curves succeed one another in numerical order when the phases are labeled diagonally in the chemographic representation.

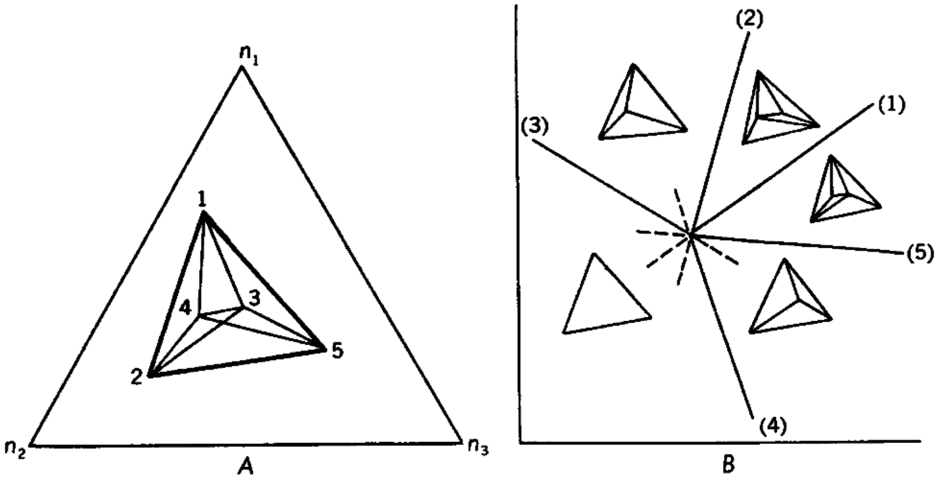

FIGURE 13.—The p–T diagram in a ternary system where three of the five phases form a triangle and the remaining two points fall inside the triangle. See also caption for figure 11.

The chemography in the five sectors of the p–T diagram can be readily ascertained. For instance, between (1) and (2) lies the assemblage $(1,2)=3+4+5$, which defines the chemography of the sector. Each such divariant assemblage is indicated by a triangle of three-phase coexistence. Clearly, a triangle indicating an assemblage such as (1,2) gives rise to two other triangles which complete the five-phase chemography. In the example used, these are $(1,3)=2+4+5$ and $(2,5)=1+3+4$. These three divariant assemblages could exist under the same set of physical conditions for different bulk compositions. The chemography of the five sectors is indicated in figure 11*B*; notice that in crossing each univariant curve only one pair of tie lines is switched. To switch more than one pair of tie lines under a given set of p and T values requires coincidence, provided only at the invariant point; extension of such a coincidence over a continuous set of p–T conditions, as along a univariant curve, is extremely improbable.

Although in figure 11*B* each sector has three possible divariant assemblages, depending on the bulk composition, the total number of divariant assemblages is only 10 because each of the 5 nondefining assemblages (all of which have two "outside" edges of the pentagonal figure) occurs in two sectors. Thus we have $(1,3)=2+4+5$ between (1) and (3) and straddling (2). The overlap rule is obeyed.

The succession of univariant reaction curves in figure 11*B* can be deduced also by symmetry considerations. As has been discussed (p. 22), the five phases of figure 11*A* are symmetrically disposed to one another, so between each adjacent pair of stable univariant curves there must be one metastable extension, and vice versa. Next, we note that each defining divariant assemblage must possess two inside diagonals as its boundary, for only such triangles unequivocally delimit the entire five-phase region. There are just five such triangles, one for each sector. One of these defining triangles, for example, is $3+4+5 = (1, 2)$; for this assemblage the stable parts of (1) and (2) must be adjacent univariant curves. Similarly, (2) and (3) must be adjacent. By symmetry, (1) and (5) must be adjacent on the side away from (2), and (4) must be next to (5) on the side away from (1).

Case (b) Four phase compositions define a quadrilateral and the fifth composition point is inside the quadrilateral.—The phases can be labeled in the following manner:

Construct the two diagonals in the quadrilateral. The fifth phase, barring degeneracy, will fall within one of the four sectors. The resulting figure can be made into the pentagonal figure of figure 11*A* if the "inside" phase is "pulled" outside through the adjacent leg of the quadrilateral, that is, without crossing more than one line. Next, designate the five phases in the same way as before, using the diagonal rule; then restore the "inside" phase to the original position within the quadrilateral. We can then complete all the diagonals for the five-sided figure; the result is shown in figure 12*A*.

The five univariant reactions and the univariant schemes are:

(1): $2+3=4+5$
$(2)(3)|(1)|(4)(5)$
(2): $1+5=3+4$
$(1)(5)|(2)|(3)(4)$
(3): $1+2+5=4$
$(1)(2)(5)|(3)|(4)$
(4): $1+5=2+3$
$(1)(5)|(4)|(2)(3)$
(5): $1+2+3=4$
$(1)(2)(3)|(5)|(4)$

The curves (1), (2), and (4) are formally identical with the corresponding curves for the example in case (a). The schemes (1), (3), and (5), on the other hand, are formally identical with case (c) in the next section. Neither of these triplets of lines can be used to define the p–T diagram. However, if the curves (2), (3), and (4) are selected, for example, the unique result of figure 12*B* is obtained, in which the progression of the labels for the univariant curves is again sequential.

We observe again that each univariant curve brings about one shift of tie lines, or a single disappearance of a phase that results from the intrinsic instability of this phase relative to a divariant assemblage of the same bulk composition. Where 4 appears or disappears, thus, it does so in or into a field of three phases so that the divariancy of the assemblage is not violated: 4 does not disappear across (1) or (2).

There are again 10 divariant assemblages altogether, but the distribution of the 5 nondefining assemblages is different from that of case (a). Three of the sectors have four assemblages each, and two sectors have only two assemblages each. This distribution reflects the fact that 4 is intrinsically not stable in these two latter sectors which share the boundary (4). The situation is different from case (a), in which no phase is intrinsically unstable. We notice that the overlap rule and also the Morey-Schreinemakers rule are observed.

The arrangement of the stable and metastable segments of the univariant curves reflects the bilateral symmetry of the chemography: 2 and 5 have their symmetry counterparts in 1 and 3, and 4 occupies a special position.

Case (c) Three phase compositions define a triangle, and the two remaining composition points fall inside the triangle.—The relation corresponds to that of figure 13*A*. In order to number the phases according to the diagonal rule, all the possible connecting lines are drawn among the phases, and, as in case (b), each inside phase is mentally transferred to the outside in such a way as to cross only one line.

The univariant reaction curves and their univariant schemes are:

(1): 2+3=4+5
(2)(3)|(1)|(4)(5)
(2): 1+4+5=3
(1)(4)(5)|(2)|(3)
(3): 1+2+5=4
(1)(2)(5)|(3)|(4)
(4): 1+2+5=3
(1)(2)(5)|(4)|(3)
(5): 1+2+3=4
(1)(2)(3)|(5)|(4)

Because (1), (3), and (5) are formally identical with their counterparts in case (b), this triplet of univariant schemes cannot be used to define the succession of curves. We can use any other combination, however, as for example (2) and (5), and the Morey-Schreinemakers rule. The result is shown in figure 13*B*.

The succession of univariant curves follows in sequential order of their labels. Each sector contains one defining divariant assemblage as well as zero, two, or four additional divariant assemblages which lap over one or more univariant curves, so that, in all, 10 distinct divariant assemblages exist. The nondefining assemblages obey the overlap rule as well as the Morey-Schreinemakers rule.

Chemographically, phase 1 occupies a special symmetry position, where 3 and 4 as well as 2 and 5 are symmetrically disposed towards each other. These facts are fully expressed by the symmetry relations of the univariant curves in figure 13*B*, as well as by the symmetry of the chemography of the divariant assemblages in the sectors. The sectors having the fewest phases have the greatest number of metastable extensions, and vice versa.

The three types of succession of univariant curves in a ternary system can be appreciated also from a purely geometric point of view. We begin with the unique arrangement for a binary system (fig. 9). To change to a ternary system, one univariant curve must be added to the invariant point. As figure 14 shows, there are only three ways to do this, which lead to the distinct diagrams of cases (a), (b), and (c) above. Each case can be derived by adding a stable curve to the correspondingly labeled sector; for example, if a stable curve were added to the sector labeled (a), case (a) results. Thus the three types of ternary p–T relations, which were derived from the chemographic relations and the Morey-Schreinemakers rule, are also direct consequences of geometry.

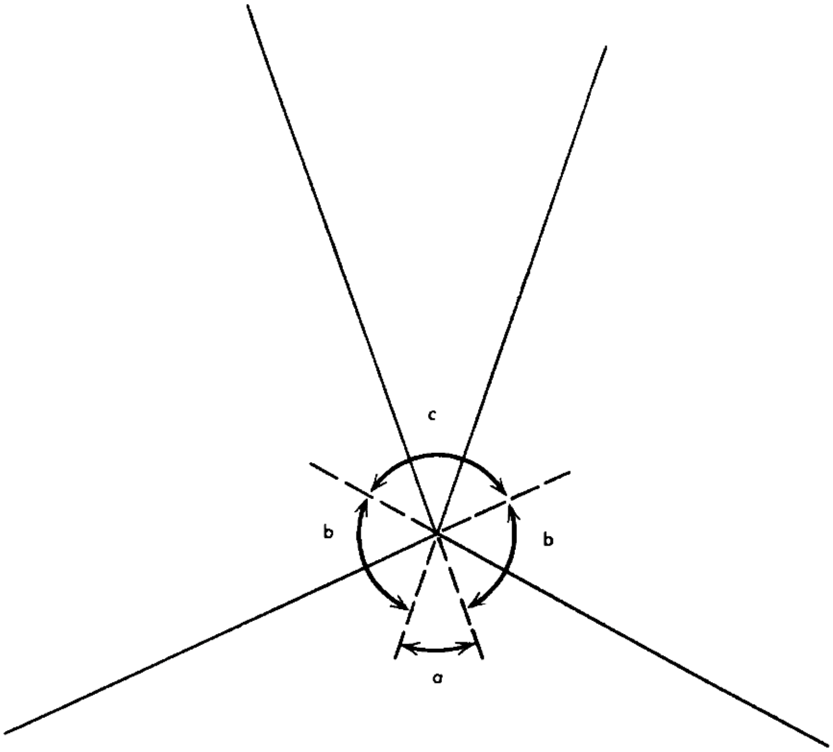

FIGURE 14.—Derivation of the three types of p–T diagrams for ternary systems from the unique configuration for a binary system. Addition of a fifth curve in the sectors labeled *a*, *b*, or *c* results in figures 11, 12, or 13, respectively, by geometric considerations alone.

SYSTEMS OF MORE THAN THREE COMPONENTS

Graphic portrayal of systems which have more than three components is difficult and will not be attempted. If the compositions of the phases are known, however, the appropriate balanced univariant reaction equations can be written, and these equations define the correct sequence of univariant curves about the invariant point. Two independent and nondegenerate univariant equations ultimately suffice, because all the other equations can be derived from linear combinations of these two equations.

The balancing of univariant reaction equations of a system of n components can be done by solving a set of simultaneous linear algebraic equations that relate $n+1$ unknowns with n equations. When n is a large number (in practice when $n \geq 4$), the use of determinants may be helpful. A simple illustration of the use of determinants is given on page 46; additional examples may be found in Korzhinskiy (1959, p. 103).

The pencil theorem, discussed below, predicts the total possible number and geometric arrangements of distinct univariant curves about an invariant point for any given number of n, so that for systems of more than three components, the construction of p–T diagrams can be readily accomplished.

THE PENCIL THEOREM

The p–T plane in the neighborhood of an invariant point is separated by adjacent pairs of stable univariant curves into a number of sectors. Within each sector, there may be zero, one, two, or more metastable extensions of univariant lines. The topological arrangement of the stable and metastable curves about an invariant point, thus, can be uniquely specified by giving the number of metastable extensions within each sector and by listing the sectors sequentially around the invariant point. For example, in a one-component system the succession of lines can be given as "1,1,1," which indicates that there is just one metastable extension in each sector and that there are three sectors altogether. Likewise, for a binary system the statement is "1,2,1,0," which indicates that there are four sectors, that one sector contains two metastable extensions, that this sector is flanked by two sectors each containing one metastable extension, and that the fourth and last sector contains no metastable extension.

In the three-component system, the three distinct types of relations may be similarly summarized. Thus case (a) corresponds to the statement "1,1,1,1,1"; case (b) corresponds to the statement "1,0,2,2,0"; and case (c) corresponds to the statement "1,3,1,0,0."

The notation, however, can be further simplified by means of the concept of a "pencil." Let us define a "pencil" of stable univariant curves in the following manner (the following statement will remain true if the terms "stable" and "metastable" are interchanged): A pencil of stable univariant curves about an invariant point consists of all those curves that are not separated from one another by metastable extensions of univariant curves.[6]

Thus a pencil is limited on both sides by metastable curves. A pencil may be designated by the number of stable univariant curves it contains; the sequence of pencils around an invariant point is preserved by the sequential listing of these numbers. Such a sequence of numbers, enclosed in brackets, completely specifies the topology of univariant lines about an invariant point.

Thus, the pencils about a unary invariant point may be designated [1,1,1]. The pencils about a binary invariant point are [2,1,1] because the sector previously designated as "0" does not constitute a separate pencil. A ternary invariant point may be in [1,1,1,1,1], [1,2,2], or [1,1,3] arrangement; the sum of the numbers in all the pencils is $n+2$.

We can now give the remarkable pencil theorem of Schreinemakers (1915, 5, p. 1027): The number of pencils about a given invariant point is always odd. The proof of the theorem is simple. In figure 15 let each solid line, $P_1, P_2, \ldots, P_k$, represent schematically a pencil of unspecified number of stable univariant lines. Similarly each dashed line represents the pencil of metastable extensions. There are k pencils in all. Let the metastable part of P_1 fall between the stable parts of P_{r+1} and P_{r+2} (by definition, there must be one and only one metastable pencil between any two adjacent stable pencils). In traversing from the stable part of P_1 to its metastable part clockwise around the invariant point, r stable pencils will be crossed. As between each adjacent pair of stable pencils there is a metastable one, the same number, r, of metastable pencils are crossed. However, each metastable pencil in the clockwise traverse implies a stable pencil in the counterclockwise traverse, so that the total number of stable pencils, including P_1 itself, is $k=(2r+1)$ where r is an integer ≥ 1 (by the Morey-Schreinemakers rule, the minimum number of pencils is 3).

With the aid of the pencil theorem, all the possible geometric arrangements of univariant curves about an invariant point in any polycomponent system can be listed; each arrangement corresponds to a unique set of chemographic relations. These are given in table 1 for n to 7. In a complex system, the sequence of numbers is im-

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[6] This definition is Schreinemakers' (1915, 5, p. 1026). Schreinemakers called these pencils "bundles." Korzhinskiy, however, used the term "Schreinemakers' bundles" (1959, p. 96) to designate the totality of univariant curves about a given invariant point. To avoid possible confusion, therefore, the term "pencil," introduced by Palatnik and Landau (1964, p. 12), is used for the "bundle" in the original sense of Schreinemakers.

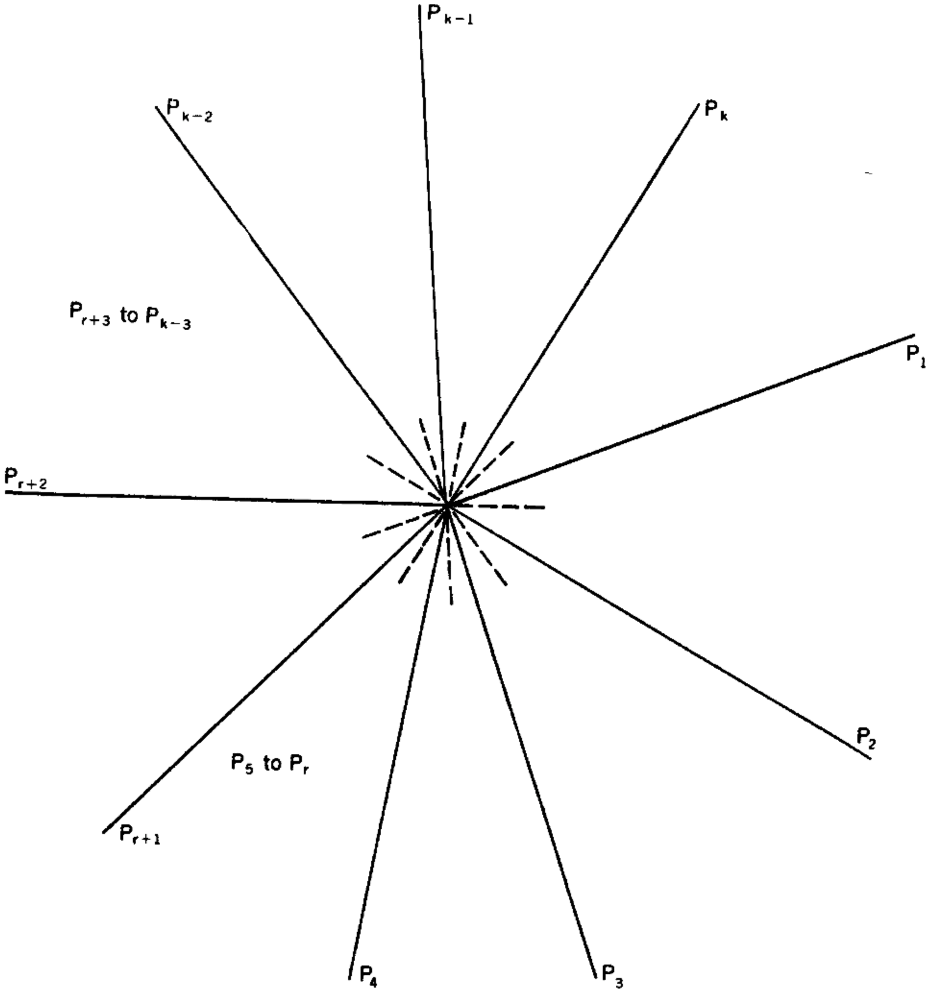

Figure 15.—Demonstration of the pencil theorem. Each stable line labeled P_1, P_2, . . ., represents a pencil of stable univariant lines which are not separated from one another by metastable extensions of other univariant lines. The total number of pencils is always odd.

portant; thus the sequence of pencils [1,2,1,2,1] in a quinary system is different from the sequence [1,2,2,1,1], but the latter is identical with [1,1,1,2,2] or [2,1,1,1,2].

By analogy with the Morey-Schreinemakers rule, we can state: the angle subtended by a pencil about the invariant point is no greater than 180°. This rule is useful in the construction of p–T grids that consist of many invariant points in the same chemical system (Zen, 1966).

Knowledge of the pencil theorem clearly aids in the construction of invariant points and associated univariant curves in systems of many components.

TABLE 1.—*Possible pencils for $n \leq 7$*

Number of components, n	Number of pencils	Topological arrangement of the pencils
1	3	[1,1,1]
2	3	[1,1,2]
3	5	[1,1,1,1,1]
	3	[1,2,2], [1,1,3]
4	5	[1,1,1,1,2]
	3	[1,1,4], [1,2,3], [2,2,2]
5	7	[1,1,1,1,1,1,1]
	5	[1,1,1,1,3], [1,1,1,2,2], [1,1,2,1,2]
	3	[1,1,5], [1,2,4], [1,3,3], [2,2,3]
6	7	[1,1,1,1,1,1,2]
	5	[1,1,1,1,4], [1,1,1,2,3], [1,1,2,1,3], [1,1,2,2,2], [1,2,1,2,2]
	3	[1,1,6], [1,2,5], [1,3,4], [2,2,4], [2,3,3]
7	9	[1,1,1,1,1,1,1,1,1]
	7	[1,1,1,1,1,1,3], [1,1,1,1,1,2,2], [1,1,1,1,2,1,2], [1,1,1,2,1,1,2]
	5	[1,1,1,1,5], [1,1,1,2,4], [1,1,2,1,4], [1,1,1,3,3], [1,1,3,1,3], [1,1,2,2,3], [1,1,2,3,2], [1,2,1,2,3], [1,2,2,1,3], [1,2,2,2,2]
	3	[1,1,7], [1,2,6], [1,3,5], [1,4,4], [2,2,5], [2,3,4], [3,3,3]

DEGENERATE SYSTEMS

A system is said to be degenerate if either of the following coincidences exists among the phases participating at a given invariant point:

(a) Two or more phases have the same composition, that is, are polymorphs of one another.

(b) In a n-component system, three or more phases are compositionally colinear (for $n=3, 4, 5, \ldots$); four or more phases are compositionally coplanar (for $n=4, 5, 6, \ldots$), and so forth.

In both instances, certain assemblages of phases, because of compositional coincidences, participate in univariant equilibria which can be described by fewer than n components.

ONE-COMPONENT SYSTEM

All phases in an one-component system are degenerate in a trivial sense.

TWO-COMPONENT SYSTEM

Four chemographically distinct types of degeneracy are possible in a binary system as shown in figure 16, where a heavy dot is used to denote degenerate compositions. Clearly, compositional colinearity can play no part in binary degeneracy.

Those phases which are related to one another by fewer than n components (and therefore fewer than $n+1$ phases in the corresponding univariant equilibria) are called the "singular phases;" the remaining phases are called the "indifferent phases" (Schreinemakers, 1916, 10, p. 515). These compositional coincidences lead to special-

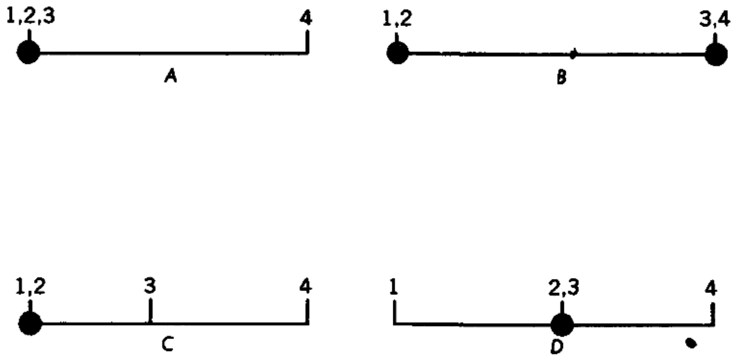

FIGURE 16.—Four possible sets of degenerate relations in a binary, four-phase system. A heavy dot indicates that the composition point is shared by two or more phases.

ized arrangements of the univariant curves around the invariant point (see Niggli, 1930) as is discussed below.

Two kinds of indifferent phases can be distinguished: (1) those which are absolutely indifferent and participate in none of the univariant equilibria of the system and (2) those which are relatively indifferent and participate in some of the univariant equilibria (Sobel'man, 1964, p. 545). Relative indifference leads to the coincidence of two or more univariant curves about the invariant point. Absolute indifference leads to the coincidence of the curves bearing the labels of these phases with all other univariant curves in the system.

Figure 16*A* depicts a situation of unary invariant and univariant equilibria involving phases 1, 2, and 3; 4 cannot participate in any of the reactions. The p–T diagram therefore is figure 17*A*; 4 may be present throughout the region. 4 is an absolutely indifferent phase; 1, 2, and 3 are the singular phases.

In figure 16*B*, reactions between 1 and 2 and also between 3 and 4 describe unary univariant equilibria; there can be no participation of 1 or 2 in reactions involving 3 and 4, and vice versa. The p–T diagram must correspond to figure 17*B*.

In contrast, figures 16*C* and *D* lead to univariant equilibria which involve both the singular and the relatively indifferent phases. In figure 16*C*, the four univariant equilibria and their univariant schemes are:

(1): $2+4=3$
$(2)(4)|(1)|(3)$
(2): $1+4=3$
$(1)(4)|(2)|(3)$
(3): $1=2$
$(1)|(3)|(2)$
(4): $1=2$
$(1)|(4)|(2)$

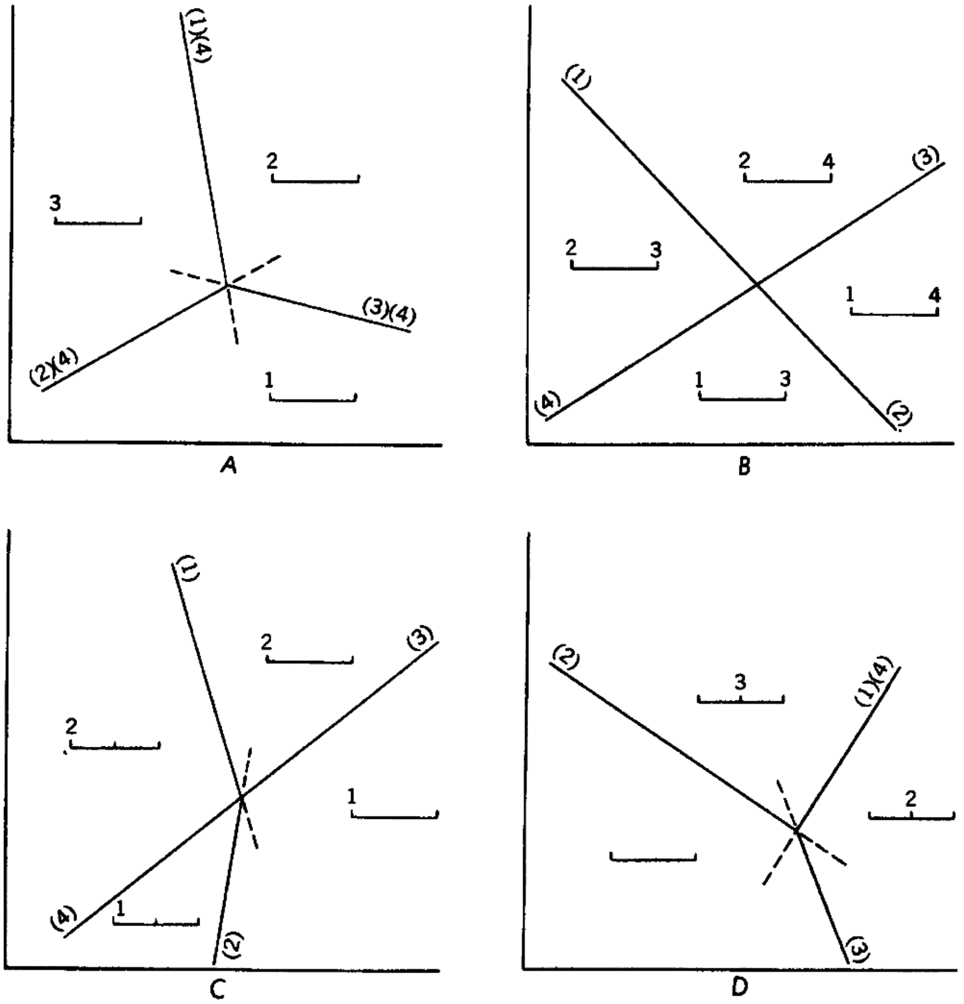

Figure 17.—The *p–T* diagrams corresponding to the four sets of degenerate relations of figure 16; *A* refers to figure 16*A* and so forth. Lines with multilabels are degenerate, that is, each of them represents the coincidence of two univariant lines. The coincidence may be stable to stable (*A* and *D*) or stable to metastable (*B* and *C*), depending on whether the indifferent phases are on opposite sides or the same side, respectively, of the singular phases. In all cases, however, three distinct slope values obtain at the invariant point.

Curves (3) and (4) refer to the same reaction, so the two curves must coincide; curves (1) and (2) lie on opposite sides of this combined curve. As (2) and (4) lie on the same side of (1), the disposition of curves must conform to figure 17*C*. Note that although the combined curve (3)(4) courses through the quadruple point continuously, the curve does change its label; the metastable part of one curve coincides with the stable part of the other.

The above example illustrates a general rule, the "coincidence rule," which states that when the two indifferent phases chemographically lie on the same side (about a point in a binary system, about a line in a ternary system, about a plane in a quaternary system, and so forth) of the singular phases, then the univariant curves bearing the labels of the indifferent phases coincide stable to metastable; when the two indifferent phases lie on opposite sides of the singular phases, then the univariant curves bearing the labels of the indifferent phases coincide stable to stable (Schreinemakers, 1916, 10, p. 522; Morey and Williamson, 1918, p. 69).

In figure 16*D* the univariant equilibria are:

(1): 2=3
(2)|(1)|(3)
(2): 1+4=3
(1)(4)|(2)|(3)
(3): 1+4=2
(1)(4)|(3)|(2)
(4): 2=3
(2)|(4)|(3)

Curves (1) and (4) refer to the same reaction and they must coincide; curves (2) and (3) lie on opposite sides of this combined curve. (1) and (4), however, must be on the same side of (2) or (3), so that the curves (1) and (4) must coincide stable to stable and metastable to metastable, the stable part terminating at the invariant point. The coincident curve possesses the double label (1)(4). According to (2), the metastable part of (2) must lie between the stable parts of (3) and (1)(4); the disposition of the univariant curves and the divariant chemographic relations therefore must be as given in figure 17*D*. The relations obey the second part of the coincidence rule.

In figure 17*C* four curves radiate from the invariant point, in figure 17*D* three curves do so; however, only three distinct slope values are associated with the curves at each invariant point. In a nondegenerate system, as we have seen, there are $n+2$ curves having $n+2$ distinct slope values at each invariant point. Figures 17*C* and *D* are examples of singly degenerate systems, each showing $n+2-1=n+1$ distinct slope values.

THREE-COMPONENT SYSTEM

Different sets of degenerate relations are possible in a ternary system because degeneracy could result both from polymorphism and from compositional colinearity, and because for five phases as many as two independent sets of degenerate relations could occur simultaneously. In all, 16 possibilities exist, as given in figures 18–24.

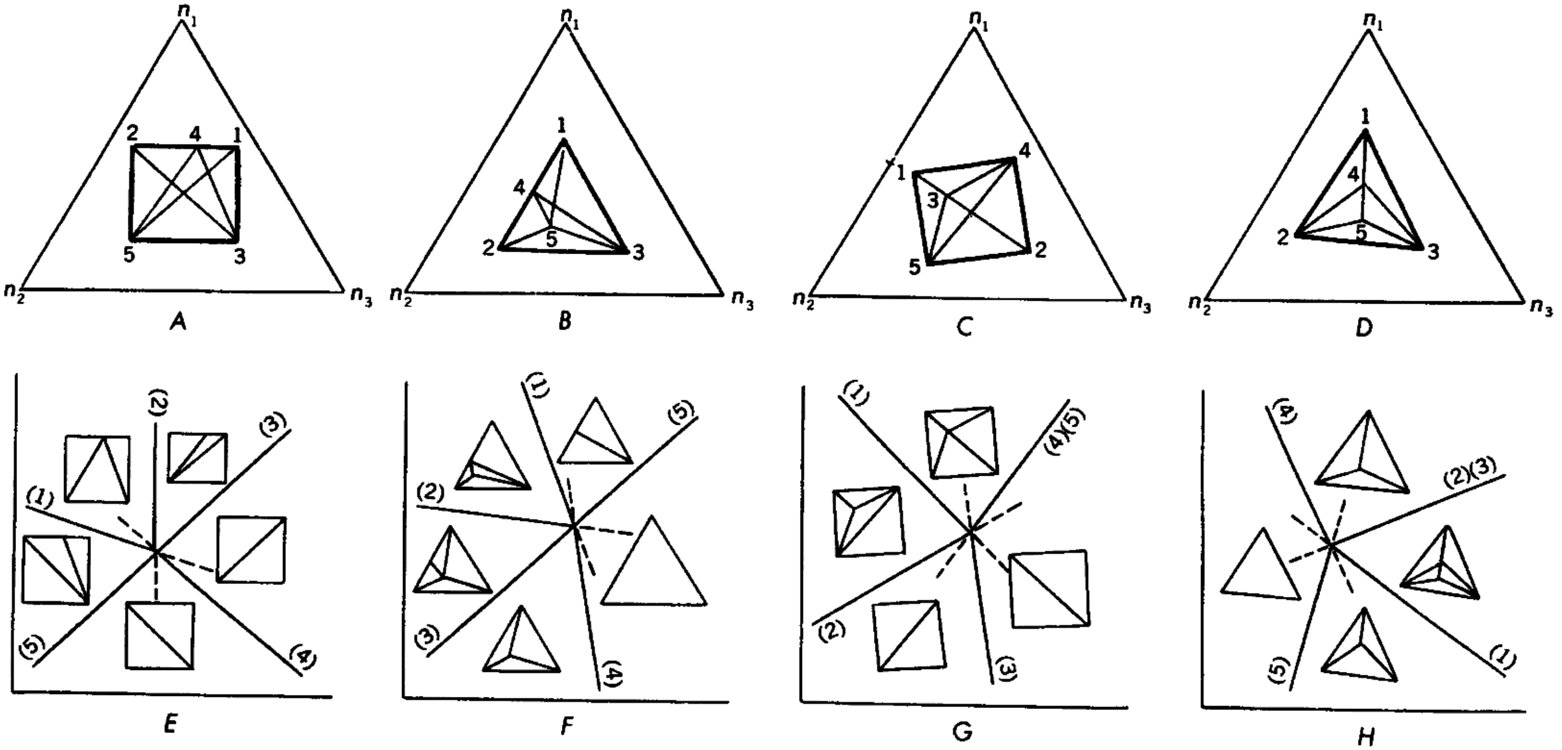

Figure 18.—The four possible sets of degenerate relations among the compositions of five phases in a ternary system (*A–D*) effected by the colinearity of three phases and their corresponding *p–T* diagram types (*E–H*). Note that five stable univariant lines obtain when the indifferent phases lie on the same side of the singular phases; four stable univariant lines obtain when the indifferent phases lie on opposite sides of the singular phases. In all events, four distinct slope values obtain at the invariant point.

One compositional colinearity of three phases (fig. 18).—We give illustrations below. The reactions corresponding to figure 18*A* are:

(1): $2+3=4+5$
(2): $1+5=3+4$
(3): $1+2=4$
(4): $1+5=2+3$
(5): $1+2=4$

These relations show that curves (3) and (5) are identical but for the label; 3 and 5 are the indifferent phases for the singular reactions depicted by these two curves. Inasmuch as (3) and (5) occur on opposite sides of (1), (2), and (4), the univariant curves must be disposed as shown in figure 18*E*, which verifies the coincidence rule: the two indifferent phases occur on the same side of the singular phases, and the curves (3) and (5) coincide stable to metastable. Five curves radiate from the invariant point, but they have only four distinct slope values. The symmetry of the chemographic relations is carried over, as it should be, into the p–T diagram.

The five univariant reactions corresponding to figure 18*D* are:

(1): $2+3+4=5$
(2): $1+5=4$
(3): $1+5=4$
(4): $1+2+3=5$
(5): $1+2+3=4$

The indifferent phases are 2 and 3, and curves (2) and (3) describe the same reaction and are coincident. Because (2) and (3) occur on the same side of the other three reactions, the combined curve terminates at the invariant point. The p–T diagram must be as given in figure 18*H*, having only four distinct curves and four slope values.

The p–T diagrams corresponding to figures 18*B* and *C* are figures 18*F* and *G*, the derivation of which is straightforward.

The coincidence rule can be given a simple physical explanation. If the two indifferent phases chemographically lie on the same side of the singular phases (for example, fig. 18*A*), any univariant reaction that involves these two phases must have them on opposite sides of the reaction as a direct consequence of the compositional degeneracy of the singular phases, together with the fact that the bulk composition must be the same for the two sides of the univariant equation. In the set of univariant schemes, the two corresponding curves must lie on opposite sides of the three curves whose labels are those of the singular phases. These indifferent curves, therefore, must occur on both sides of the invariant point, and the coincidence is stable to metastable.

Conversely, if the two indifferent phases chemographically lie on opposite sides of the three singular phases (for example, fig. 18*C*), they must be on the same side of the reaction equation because of the compositional degeneracy of the singular phases, combined with the fact that the bulk compositions for the two sides of the reaction must be equal. Hence, the curves that bear the labels of these indifferent phases lie on the same side of the three curves bearing the labels of the singular phases, and the two indifferent curves must terminate at the invariant point. The coincidence must be stable to stable.

One compositional coincidence of two phases (fig. 19).—Figure 19*A* will illustrate the relations. The five univariant reactions are:

(1): $4+5=2+3$
(2): $1=4$
(3): $1=4$
(4): $1+5=2+3$
(5): $1=4$

Here we have three indifferent and two singular phases. Accordingly, curves (2), (3), and (5) coincide. Because (2) and (3) lie on the

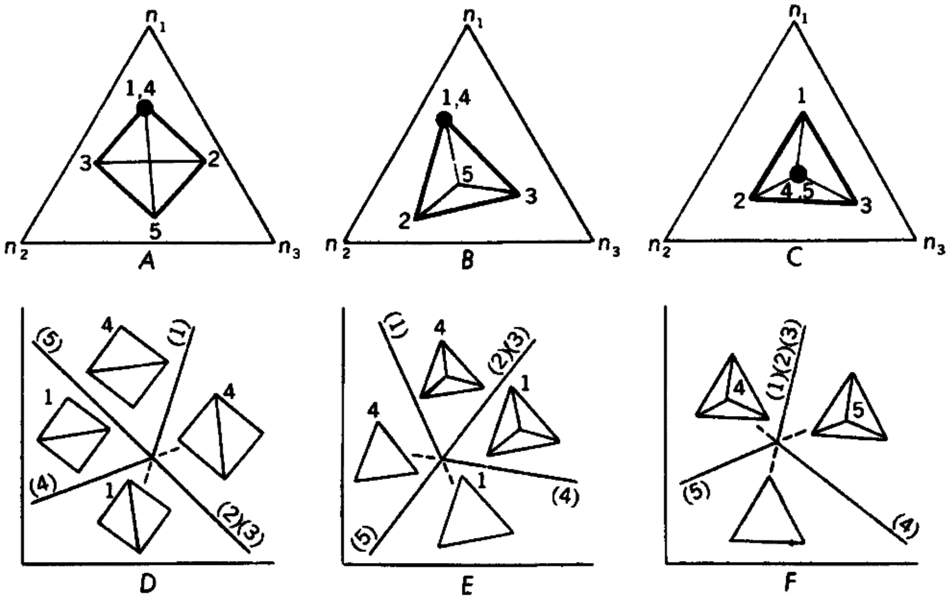

Figure 19.—The three possible sets of compositionally degenerate relations in ternary, five-phase systems effected by a single compositional coincidence (dimorphism) of two phases (*A–C*) and their corresponding *p–T* diagram types (*D–F*). Note that four stable lines obtain when the indifferent phases are on the same side of the singular phases; three stable lines obtain when the indifferent phases are on opposite sides of the singular phases. In all cases, three distinct slopes values obtain at the invariant point. On the *p–T* diagrams, only those phases are labeled whose identities, because of compositional coincidences, would otherwise be ambiguous. Heavy dots indicate phases with coincident compositions.

same side of (1) or (4) and (5) on the other side, (2) and (3) coincide stable to stable but (5) coincides with (2) and (3) stable to metastable. The disposition of the curves and their metastable extensions must be as shown in figure 18*D*; four curves radiate from the invariant point, but these have only three distinct slopes.

The *p–T* diagrams corresponding to figures 19*B* and *C* are, respectively, figures 19*E* and *F*. In both instances, there exist three distinct slope values, and one of the curves bears a triple label. For figure 19*F*, the three indifferent curves all coincide stable to stable, reflecting the chemographic symmetry of phases 1, 2, and 3 in their mutual relations and in their relations to 4 and 5. In figure 19*E*, (2) and (3) coincide stable to stable, but (5) coincides stable to metastable, again reflecting the chemographic symmetry.

Figures 19*D* and *E* are similar. In figure 19*D*, the smaller angle between (1) and (4) is on the side of (5), but the converse is true in figure 19*E*. This difference reflects the fact that in figure 19*A*, 5 is outside the compositional triangle of phases 1–4–2–3, but it is inside the same triangle in figure 19*B*.

Two compositional colinearities of three phases each (fig. 20).—Corresponding to figure 20*A*, we have

(1): $2+3=4+5$
(2): $1+5=3$
(3): $1+2=4$
(4): $1+5=3$
(5): $1+2=4$

Curves (2) and (4) are coincident; according to (1) the coincidence is stable to metastable. Similarly for curves (3) and (5). Moreover, relative to (1), the pair of curves (4) and (5) is on one side but the pair of curves (2) and (3) is on the other side; relative to (3), (1) and (2) are on the same side but (4) is on the opposite side. The *p–T* diagram must be as given in figure 20*D*. The five curves emanating from the invariant point possess three distinct slope values, agreeing with the existence of two independent single degeneracies. Figure 20*D* may be regarded as a special case of figure 11 where 3 becomes colinear with 1 and 5, and 4 with 1 and 2, so that curves (3) and (5) coincide and curves (2) and (4) coincide. It is clear that the relations can also be derived from figure 13 by analogous reasoning. The coincidences are all stable to metastable because the indifferent phases, in both instances, are on the same side of the respective singular phases.

The *p–T* diagrams corresponding to figures 20*B* and *C* are derived likewise; they are given, respectively, in figures 20*E* and *F*. In each case there are three slope values at the invariant point. In figure 20*E* one coincidence is stable to stable and the other is stable to meta-

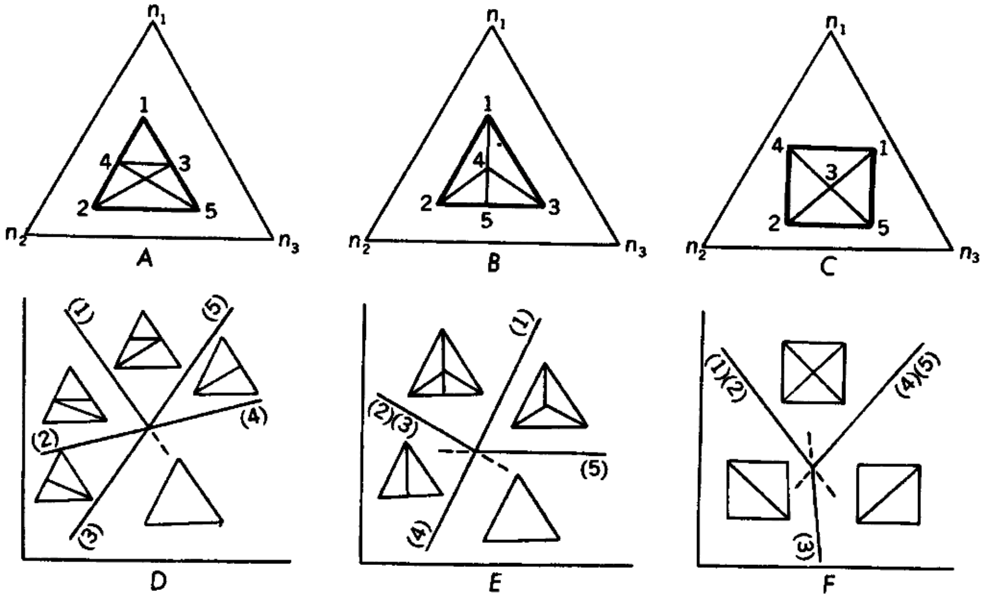

FIGURE 20.—The three possible sets of compositionally degenerate relations in ternary, five-phase systems each effected by two independent sets of three colinear phases (*A–C*), and their corresponding *p–T* diagram types (*D–F*). Depending on the chemographic relations of the indifferent and singular phases, five, four, or three stable univariant lines may obtain, but in all cases only three distinct slope values obtain at the invariant point.

stable, so that four curves exist. In figure 20*E*, both coincidences are stable to stable, so that only three curves obtain. These relations fully reflect the chemographic arrangements.

One compositional coincidence of two phases (*dimorphism*) *and one colinearity of three phases* (*fig. 21*).—Two situations may be distinguished: either these two degeneracies are coupled, that is, share one phase in common (fig. 21*A* and *B*), or not coupled (fig. 21*C*).

The chemographic relations to figure 21*A* or *B* are directly related to binary degeneracies depicted in figures 16*C* and *D*, with a fifth phase, 5, now added, which, however, is absolutely indifferent to all the binary univariant equilibria. The *p–T* relations are therefore given in figures 21*D* and *E*, strictly similar to figures 17*C* and *D*. Both figures display three distinct slope values.

For the chemographic relation of figure 21*C*, two entirely independent univariant equilibria, one unary and one binary, are obtained; the *p–T* diagram is given by figure 21*F*.

One compositional coincidence of three phases.—The chemographic relations, figure 22*A*, are analogous to the binary degeneracy of figure 16*A*, with a fifth phase added which is absolutely indifferent to the equilibria in the system. The *p–T* diagram is given in figure 22*B*, displaying three distinct slope values.

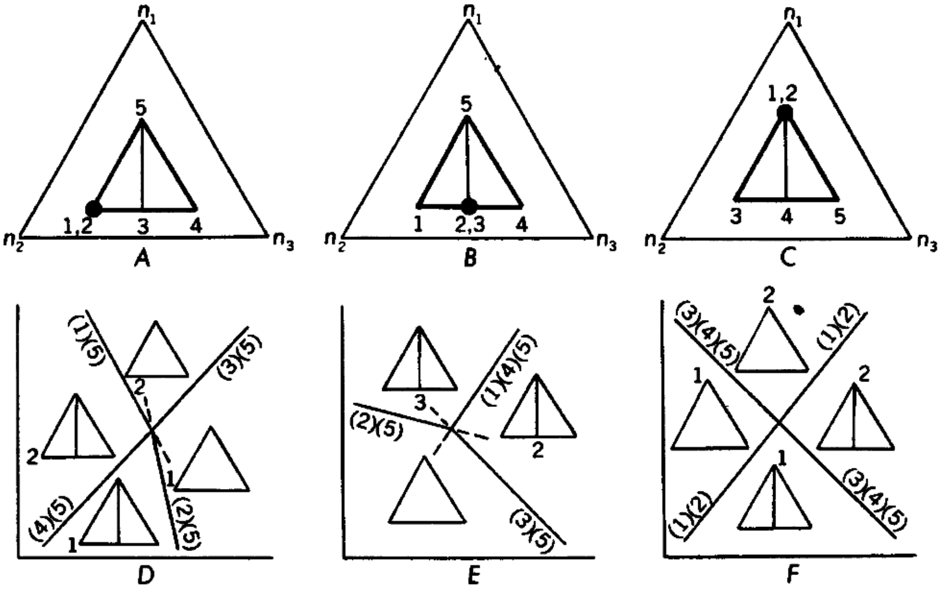

FIGURE 21.—The three possible sets of compositionally degenerate relations in ternary, five-phase systems effected by the colinearity of three phases and a compositional coincidence of two phases (*A–C*), and their corresponding *p–T* diagram types (*D–F*). If the two degeneracies are coupled (*A*, *B*), three distinct slope values exist at the invariant point; if the two degeneracies are not coupled (*C*), only two distinct slope values exist at the invariant point. 20*A* and *B* correspond to the binary degeneracies of figures 17*C* and *D*, with an absolutely indifferent fifth phase added. On the *p–T* diagrams, only those phases are labeled whose identities, because of compositional coincidences, would otherwise be equivocal. Heavy dots indicate phases having coincident compositions.

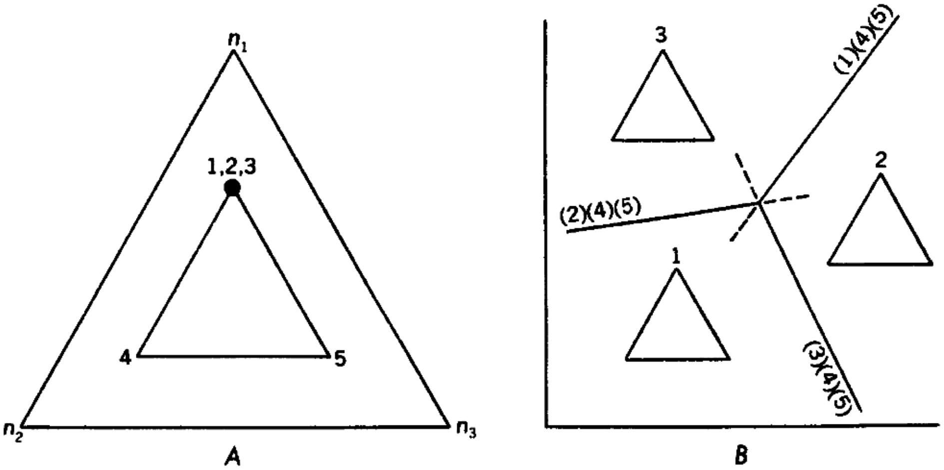

FIGURE 22.—The single possible set of compositionally degenerate relations in ternary, five-phase systems effected by one compositional coincidence of three phases, and its corresponding *p–T* diagram type. Phases 4 and 5 are absolutely indifferent phases. On the *p–T* diagrams, only those phases are labeled whose identities, because of compositional coincidences, would otherwise be ambiguous. Heavy dots indicate phases with coincident compositions.

Two compositional coincidences of two phases each.—The chemographic relations (fig. 23*A*) are analogous to binary degeneracies depicted in figure 16*B*, with a fifth phase added which is absolutely indifferent to the equilibria in the system. The p–T diagrams therefore must correspond to figure 23*B*, displaying two distinct slope values.

One compositional colinearity of four phases (fig. 24). —The relations correspond to a binary four-phase system with an absolutely indifferent fifth phase added; the p–T diagram is given by figure 24 *B*.

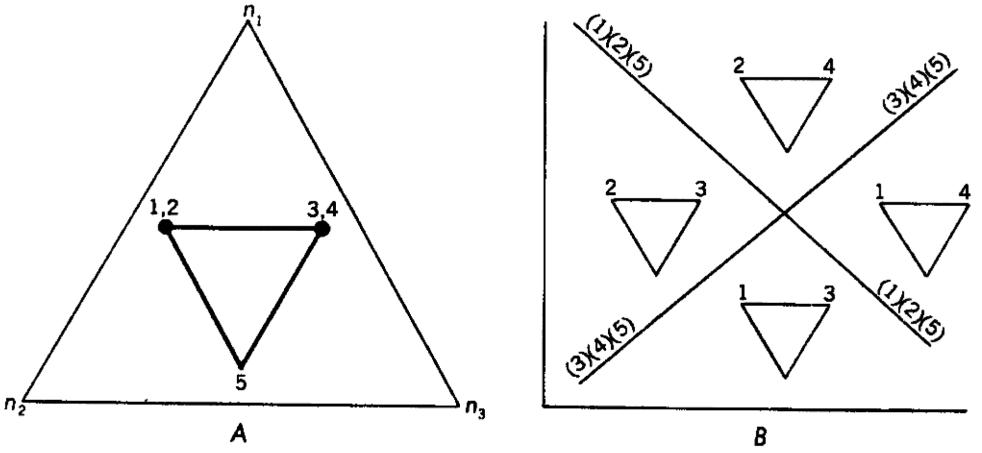

FIGURE 23.—The single possible set of compositionally degenerate relations in ternary, five-phase systems effected by two compositional coincidences of two phases each, and its corresponding p–T diagram type. Phase 5 is an absolutely indifferent phase. On the p–T diagram only those phases are labeled whose identities, because of compositional coincidences, would otherwise be equivocal. Heavy dots indicate phases with coincident compositions.

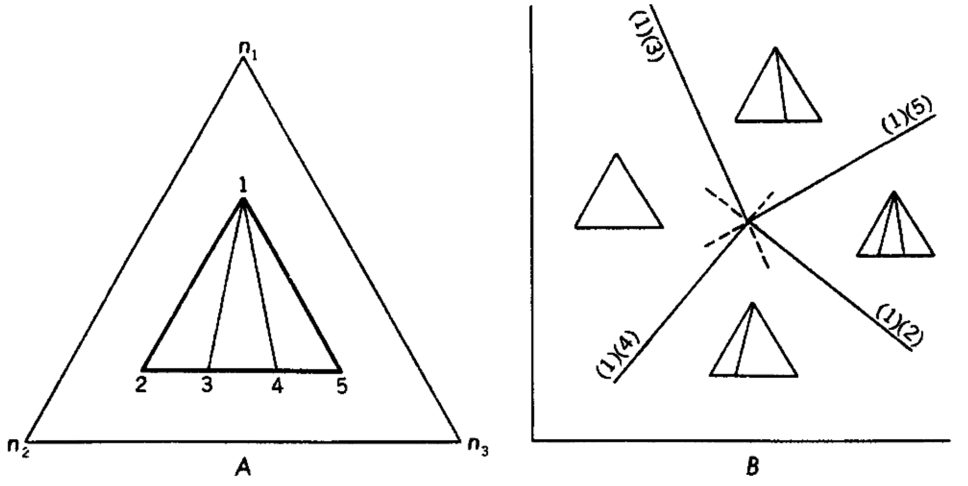

FIGURE 24.—The single possible set of compositionally degenerate relations in ternary, five-phase systems effected by the colinearity of four phases, and its corresponding p–T diagram type. The diagram is that of a binary four-phase system, with an absolutely indifferent fifth phase added.

APPLICATION OF SCHREINEMAKERS' METHOD

EXAMPLES AS APPLIED TO MINERAL ASSEMBLAGES

The following examples of the actual application of the results of the preceding discussions to rock-forming minerals illustrate the different chemographic relations and show how even an incomplete set of thermodynamic data on the phases can be useful in delimiting the arrangement of the p–T diagrams. Although the mineral assemblages may not all be physically realistic, Schreinemakers' method is not limited in its use to systems in stable equilibrium. The phases are presumed to have fixed compositions specified in each example.

Example 1.—The five-phase assemblage andalusite (A; Al_2SiO_5), pyrophyllite (P; $Al_2Si_4O_{10}(OH)_2$), kaolinite (K; $Al_2Si_2O_5(OH)_4$), quartz (Q; SiO_2), and water (W; assumed to be pure H_2O) belongs to a ternary system whose components may be chosen as Al_2O_3, SiO_2, H_2O. The chemographic relations are given in figure 25*A*; they correspond to the triangular configuration with two interior points given by figure 13. The five univariant lines that emanate from the quintuple point therefore must have the relative dispositions shown in figure 25*B*.

The determination of the numerical values for the slopes of the univariant lines, by means of the Clapeyron equation, requires both entropy and volume data for all the phases; unfortunately the molar

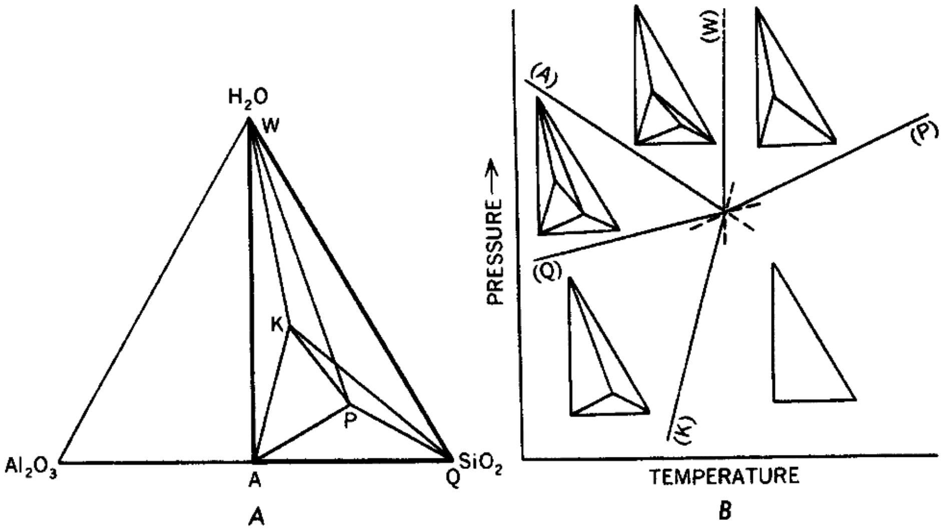

FIGURE 25.—The ternary system Al_2O_3–SiO_2–H_2O, with the five phases water (W; H_2O), andalusite (A; Al_2SiO_5), quartz (Q; SiO_2), kaolinite (K; $Al_2Si_2O_5(OH)_4$), and pyrophyllite (P; $Al_2Si_4O_{10}(OH)_2$). *A*, The chemographic relations in gram-formula proportions of the oxide components; *B*, the p–T diagram. The diagram is properly oriented with respect to the pressure axis, but not to the temperature axis. In this and the succeeding figures, an arrow following the label "temperature" or "pressure" shows that the diagram is properly oriented with respect to that coordinate axis.

entropies for many minerals are not known. However, molar volume data are commonly available for minerals and can be used to orient the univariant curves properly with respect to the pressure axis.

To orient the univariant curves with respect to the pressure axis, the balanced univariant reaction equations must first be derived. Figure 25*A* shows that both pyrophyllite and kaolinite break down into water, andalusite, and quartz; the properly balanced equations are:

$$(\mathrm{K}):\quad \mathrm{A+3Q+W=P}$$

$$(\mathrm{P}):\quad \mathrm{A+Q+2W=K}$$

By eliminating in turn A, Q, and W from the two equations, we obtain:

$$(\mathrm{A}):\quad \mathrm{2Q+K=W+P}$$

$$(\mathrm{Q}):\quad \mathrm{3K=P+5W+2A}$$

$$(\mathrm{W}):\quad \mathrm{A+5Q+K=2P}$$

The molar volumes are given in table 2; ΔV for the reactions (right minus left) are, respectively, −11.1cc (cubic centimeters), −11.1cc, −0.2cc, +22.1cc, and −11.1cc.[7] The assemblage on the right-hand side of each reaction is favored by high pressure if ΔV is negative, and vice versa. Moreover, the reaction that produces liquid water probably leads to an entropy increase, and therefore is favored by rising temperature. Figure 25*B* is constructed with these restrictions in mind; with the exception of (W), the slopes of the univariant curves probably have correct signs; reaction (W) involves only solids, and its entropy change, hence the sign of the slope, cannot be predicted.

Example 2.—The five-phase assemblage enstatite (E; $MgSiO_3$), forsterite (F; Mg_2SiO_4), kyanite (K; Al_2SiO_5), spinel (Sp; $MgAl_2O_4$), and sapphirine (S; $Mg_4Al_{10}Si_2O_{23}$), having the specified compositions, belongs to the ternary system $MgO–Al_2O_3–SiO_2$. The chemography of the phases is given in figure 26*A*. This is an example of a quadrilateral configuration with one interior point; the *p–T* diagram therefore must correspond to figure 12 and is given by figure 26*A*. The diagram is not oriented with respect to the temperature or pressure axis.

The compositions of both enstatite and sapphirine are variable even within this ternary system. Enstatite can dissolve significant amounts of Al_2O_3 (Boyd and England, 1964, p. 157) under high

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[7] Although these values refer to 25° C and 1 bar pressure, for reactions involving only condensed phases the error caused by this approximation is likely negligible.

TABLE 2.—*Entropy and volume data at 25°C and 1 bar pressure for selected minerals*

[Data are from Robie (1962) except as indicated]

Mineral	Composition	Entropy (decijoule per deg per mole)	Volume (cc per mole)
Åkermanite	$Ca_2MgSi_2O_7$	[1]2,903	92.82
Anatase	TiO_2	499	20.49
Andalusite	Al_2SiO_5	932	51.54
Calcite	$CaCO_3$	928	36.94
Clinoenstatite	$MgSiO_3$	679	31.47
Cordierite	$Mg_2Al_4Si_5O_{18}$	[1]4,072	[2] 233.50
Corundum	Al_2O_3	510	25.57
Diaspore	$HAlO_2$	352	17.76
Diopside	$CaMgSi_2O_6$	1,430	66.10
Dolomite	$CaMg(CO_3)_2$	1,551	64.35
Forsterite	Mg_2SiO_4	952	43.67
Gibbsite	$Al(OH)_3$	700	31.96
Kaolinite	$Al_2Si_2O_5(OH)_4$	2,031	[3] 99.31
Kyanite	Al_2SiO_5	838	44.11
Merwinite	$Ca_3MgSi_2O_8$	[1]2,532	[4] 98,22
Monticellite	$CaMgSiO_4$		51.37
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$		[2] 126.6
Quartz	SiO_2	414	22.69
Rutile	TiO_2	503	18.80
Sillimanite	Al_2SiO_5	960	49.91
Sphene	$CaTiSiO_5$	1,291	55.70
Spinel	$MgAl_2O_4$	806	39.72
Water	H_2O	700	18.07
Wollastonite	$CaSiO_3$	819	39.94

[1] Weller and Kelley (1963).

[2] Robie and Bethke (1963).

[3] Volume data for dickite.

[4] American Society for Testing Materials (1963).

pressure, and the composition of sapphirine may depart from the oxide ratios of 4:5:2 (Keith and Schairer, 1952), apparently reaching 2:2:1(Deer and others, 1962, p. 176–177). These variations must be considered when one analyses the p–T behavior of univariant curves pertaining to actual mineral assemblages.

Example 3.—The five phases clinoenstatite (E), forsterite (F), sillimanite (S), cordierite (C), and spinel (Sp), having the specified compositions of table 2, belong to the ternary system $MgO–Al_2O_3–SiO_2$. Figure 27*A* shows the chemographic relations; the configuration is pentagonal, and thus the five univariant curves are disposed as given in figure 27*B* corresponding to the type of figure 11.

For the five phases given, entropy and volume data are available (table 2) so that the actual slopes of the univariant lines can be calculated. Two of the five reactions are:

$$\text{(E)}: \quad 5F+10S=3C+4Sp$$

$$\text{(F)}: \quad 5E+5S=2C+Sp$$

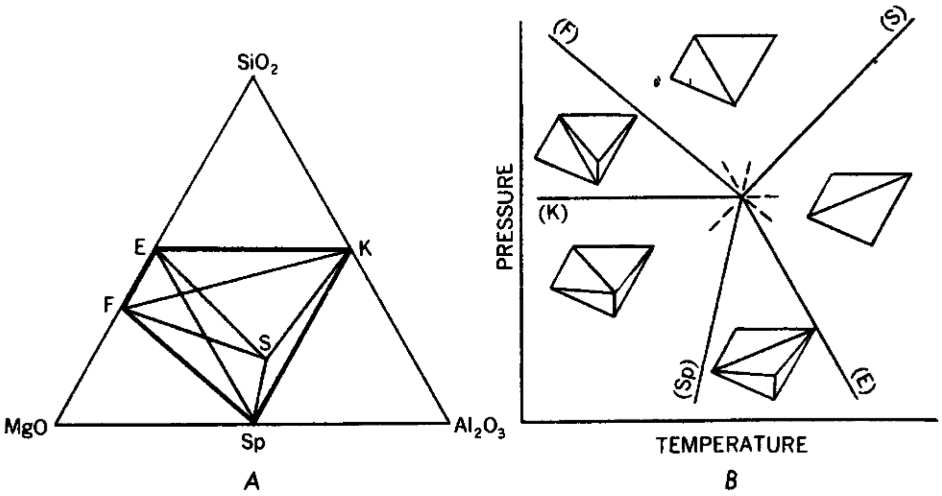

Figure 26.—The ternary system $MgO–Al_2O_3–SiO_2$, with the five phases enstatite (E; $MgSiO_3$), forsterite (F; Mg_2SiO_4), spinel (Sp; $MgAl_2O_4$), kyanite (K; Al_2SiO_5), and sapphirine, S, whose composition is taken to be $Mg_4Al_{10}Si_2O_{23}$. *A*, The chemographic relations in gram formula proportions of the oxides; *B*, the *p–T* diagram. The *p–T* diagram is not properly oriented with respect to either the temperature or the pressure axis.

These equations suffice to determine all the others:

$$(S)(=(E)-2(F)):\quad 10E+2Sp=5F+C$$

$$(C)(=(E)-3(F)):\quad 3E+Sp=S+2F$$

$$(Sp)(=(E)-4(F)):\quad 2S+4E=F+C$$

The univariant slopes are given by the Clapeyron equation,

$$dP/dT=\Delta S/\Delta V$$

and have the values, for (E), (F), (S), (C), and (Sp), of +7.6, +7.5, +7.5, +6.7, and +7.5, respectively, in bars per degree. As the reactions are written above, the assemblages on the right-hand sides are relatively more stable at higher temperatures and lower pressures.

The slope values are so similar that the differences are well within the uncertainties of the data. Thermodynamic data, in this instance, cannot be used to verify the qualitative results of the Schreinemakers method, although they are not contradictory. Figure 27*B* therefore was constructed mainly on the basis of the results of the qualitative analysis, where the signs of the slopes were taken from the numerical data.

In general, disagreements between the qualitative and quantitative considerations can stem from one of three sources: (1) erroneous thermodynamic values are used; (2) the approximation introduced

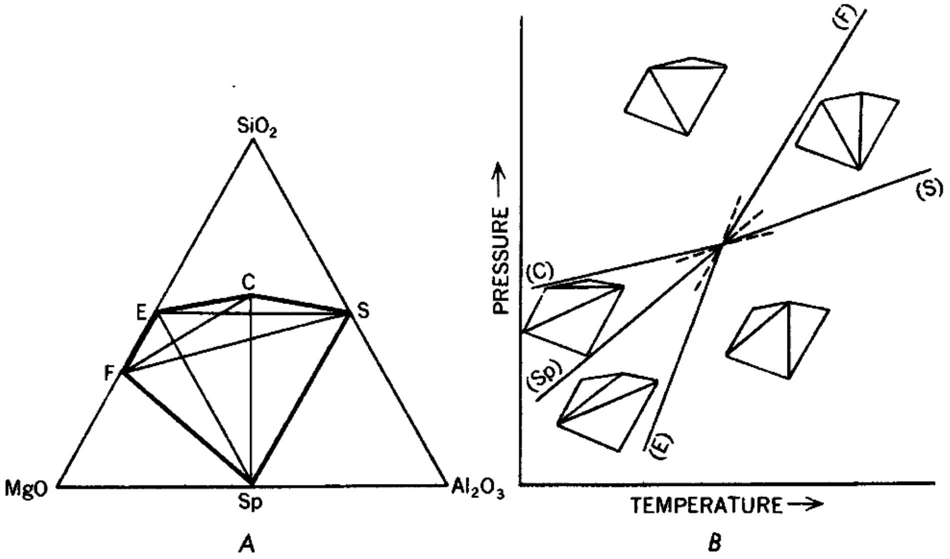

FIGURE 27.—The ternary system $MgO-Al_2O_3-SiO_2$, with the five phases clinoenstatite (E; $MgSiO_3$), forsterite (F; Mg_2SiO_4), cordierite (C; $Mg_2Al_4Si_5O_{18}$), sillimanite (S; Al_2SiO_5), and spinel (Sp; $MgAl_2O_4$). *A*, The chemographic relation in gram formula proportions of the oxides; *B*, the *p–T* diagram. The univariant curves are properly oriented with respect to both the temperature and the pressure axis.

by using the entropy and volume data for 25°C is invalid, or (3) the phases for which the values were measured do not have the compositions stipulated by the chemographic diagrams.

Example 4.—The five phases andalusite (A), kyanite (Ky), kaolinite (K), pyrophyllite (P), and quartz (Q), constitute assemblages found in some North Carolina pyrophyllite deposits (Zen, 1961b). The chemography is given in figure 28*A*. A single degeneracy occurs between kyanite and andalusite; the other phases are relatively indifferent. The *p–T* relations are shown in figure 28*B*, corresponding to the type of figure 19*B*. The entropy of pyrophyllite is unknown; however, the diagram is correctly oriented with respect to the pressure axis, and the volume data are given in table 2. The balanced reactions are:

$$(A): \quad Ky+5Q+K=2P$$

$$(Ky): \quad A+5Q+K=2P$$

$$(Q)=(K)=(P): \quad A=Ky$$

Example 5.—The five phases merwinite (Me), monticellite (Mo), wollastonite (W), diopside (Dp), and åkermanite (Å) belong to the ternary system $CaO-MgO-SiO_2$. The chemography is given in figure 29*A*; there are two separate sets of compositional colinearities. The *p–T* diagram must have the relative dispositions of figure 29*B*, cor-

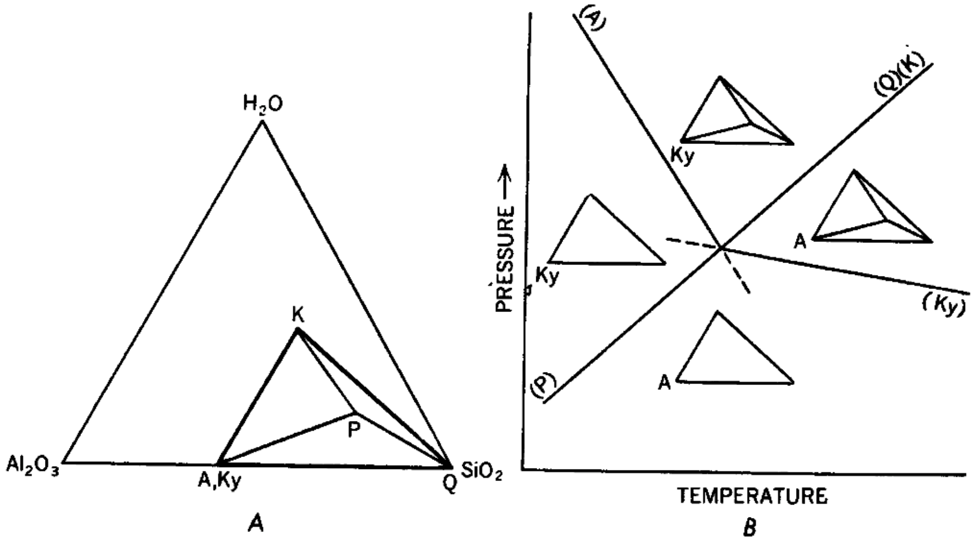

FIGURE 28.—The ternary system Al_2O_3–SiO_2–H_2O, with the five phases kaolinite (Ky; $Al_2Si_2O_5(OH)_4$), pyrophyllite (P; $Al_2Si_4O_{10}(OH)_2$), andalusite (A; Al_2SiO_5), kyanite(Ky; Al_2SiO_5), and quartz (Q; SiO_2). *A*, The chemographic relations in gram formula proportions of the oxides; *B*, the *p–T* diagram which is properly oriented with respect to the pressure axis. An instance of compositional degeneracy is introduced by the polymorphism of andalusite and kyanite. The indifferent phases lie on the same side of these two singular phases; as a result the curve bearing the labels of the indifferent phases courses through in invariant point, and there are only three distinct slope values at the invariant point.

responding to figure 20*C*. The molar volume data for the phases are given in table 2; the diagram has been properly oriented with respect to the pressure axis.

Although the univariant reaction equations can be easily balanced by inspection, we will use this system to illustrate the use of determinants. Korzhinskiy (1959) discussed many aspects of the procedure as applied to univariant reactions; a particularly lucid presentation of the mathematical theory has been given by Aitken (1951).

A univariant reaction involves $n+1$ phases in an n-component system. Therefore, the determinant can be formulated in the following way: Each phase is assigned to one of the $n+1$ rows of the determinant, and each component is assigned to one of the $n+1$ columns. The number of gram-formulas of component i, as it appears in the formula of phase j, is entered in position ij of the determinant. However, there is one more row than column, so that in the position $1j$ we write the label of phase j. The $(n+1)$ by $(n+1)$ determinant can

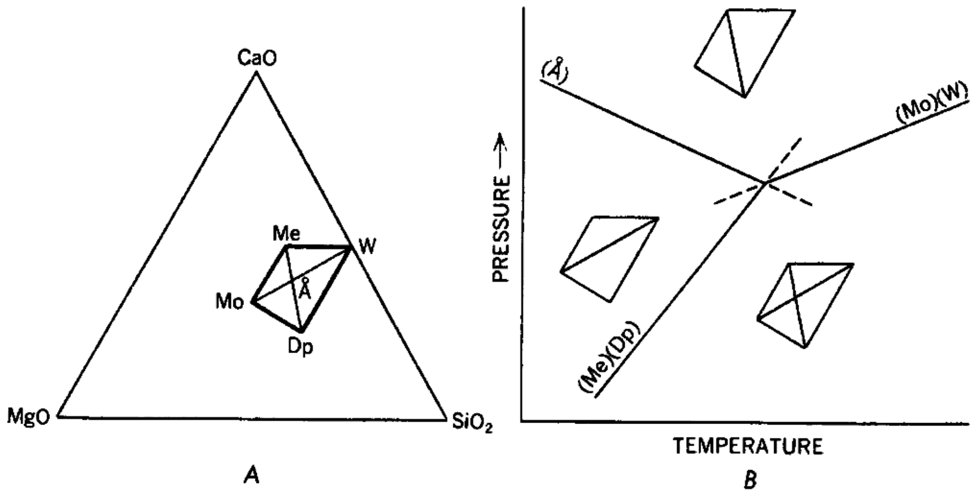

FIGURE 29.—The ternary system $CaO-MgO-SiO_2$, with the five phases merwinite (Me; $Ca_3MgSi_2O_8$), diopside (Dp; $CaMgSi_2O_6$), monticellite (Mo; $CaMgSiO_4$), wollastonite (W; $CaSiO_3$), and åkermanite (Å; $Ca_2MgSi_2O_7$). *A*, The chemographic relations in gram formula proportions of the oxides; *B*, the $p-T$ diagram which is properly oriented with respect to the pressure axis. Two distinct cases of compositional colinearity exist; they are reflected in the fact that only three distinct univariant curves emanate from the invariant point. The univariant curves all terminate at the invariant point, because for both cases of degeneracy the indifferent phases lie on opposite sides of the singular phases.

now be expanded in terms of the minors and the stoichiometric coefficients of the phases in the univariant reaction calculated directly.

Applying this procedure and listing the components in the order $CaO-MgO-SiO_2$ from the left-hand column to the right-hand column, we have

$$(\text{Å}): \quad \left|\begin{array}{llll} \text{Me} & 3 & 1 & 2 \\ \text{Mo} & 1 & 1 & 1 \\ \text{W} & 1 & 0 & 1 \\ \text{Dp} & 1 & 1 & 2 \end{array}\right| = 0$$

Expanding by minors, and recalling that each odd permutation of the row (or column) introduces a minus sign in front of the determinant, we have

$$\text{Me}\begin{vmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 2 \end{vmatrix} - \text{Mo}\begin{vmatrix} 3 & 1 & 2 \\ 1 & 0 & 1 \\ 1 & 1 & 2 \end{vmatrix} + \text{W}\begin{vmatrix} 3 & 1 & 2 \\ 1 & 1 & 1 \\ 1 & 1 & 2 \end{vmatrix} - \text{Dp}\begin{vmatrix} 3 & 1 & 2 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \end{vmatrix} = 0$$

$$2\text{Mo}+2\text{W}=\text{Dp}+\text{Me}$$

Similarly, we can calculate

$$(\mathrm{Me}):\ \left|\begin{array}{llll} \mathrm{Mo} & 1 & 1 & 1 \\ \mathrm{W} & 1 & 0 & 1 \\ \mathrm{Dp} & 1 & 1 & 2 \\ \text{Å} & 2 & 1 & 2 \end{array}\right| = 0$$

$$\mathrm{Mo}\begin{vmatrix} 1 & 0 & 1 \\ 1 & 1 & 2 \\ 2 & 1 & 2 \end{vmatrix} - \mathrm{W}\begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 2 \\ 2 & 1 & 2 \end{vmatrix} + \mathrm{Dp}\begin{vmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 2 & 1 & 2 \end{vmatrix} - \text{Å}\begin{vmatrix} 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 2 \end{vmatrix} = 0$$

$$\text{Å} = \mathrm{Mo} + \mathrm{W}$$

In this example, the coefficient of Dp is zero, and diopside does not appear in the reaction equation. This fact immediately signifies that (Me) = (Dp) and that the system is degenerate.

Finally, we have

$$(\mathrm{W}):\ \left|\begin{array}{llll} \mathrm{Me} & 3 & 1 & 2 \\ \mathrm{Mo} & 1 & 1 & 1 \\ \mathrm{Dp} & 1 & 1 & 2 \\ \text{Å} & 2 & 1 & 2 \end{array}\right| = 0;$$

$$\mathrm{Me}\begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & 2 \\ 2 & 1 & 2 \end{vmatrix} - \mathrm{Mo}\begin{vmatrix} 3 & 1 & 2 \\ 1 & 1 & 2 \\ 2 & 1 & 2 \end{vmatrix} + \mathrm{Dp}\begin{vmatrix} 3 & 1 & 2 \\ 1 & 1 & 1 \\ 2 & 1 & 2 \end{vmatrix} - \text{Å}\begin{vmatrix} 3 & 1 & 2 \\ 1 & 1 & 1 \\ 1 & 1 & 2 \end{vmatrix} = 0$$

$$\mathrm{Me} + \mathrm{Dp} = 2\text{Å}$$

This result shows that (W) and (Mo) must refer to the same reaction and that there is a second degeneracy involving the colinearity of three phases. Because (Me) and (Dp) appear on the same side of the univariant scheme (Mo) = (W), the curves (Me) and (Dp) coincide stable to stable; similar consideration indicates that (W) and (Mo) also coincide stable to stable.

Example 6. —The five phases diaspore (D; $HAlO_2$), gibbsite (G; $Al(OH)_3$), corundum (C; Al_2O_3), pyrophyllite (P; $Al_2Si_4O_{10}(OH)_2$), and vapor (V; H_2O) belong to the ternary system Al_2O_3–SiO_2–H_2O. The chemography is given by figure 30*A*. The four phases, corundum-diaspore-gibbsite-vapor are colinear in composition, and pyrophyllite is, therefore, an absolutely indifferent phase. The *p–T* diagram is that for a binary four-phase system, with a fifth phase present throughout; the situation corresponds to figure 24. Because, however, a vapor high in entropy and low in density is present along three of the univariant equilibria, the divariant assemblage that includes the vapor must be on the high-temperature and low-pressure side of each associated univariant curve; such curves also have positive slopes.

The fourth reaction, C+G=3D, involves only solids, and the *p–T* slope can be calculated from thermodynamic data (table 2); the value is +36 bars per degree, and diaspore is the low-temperature

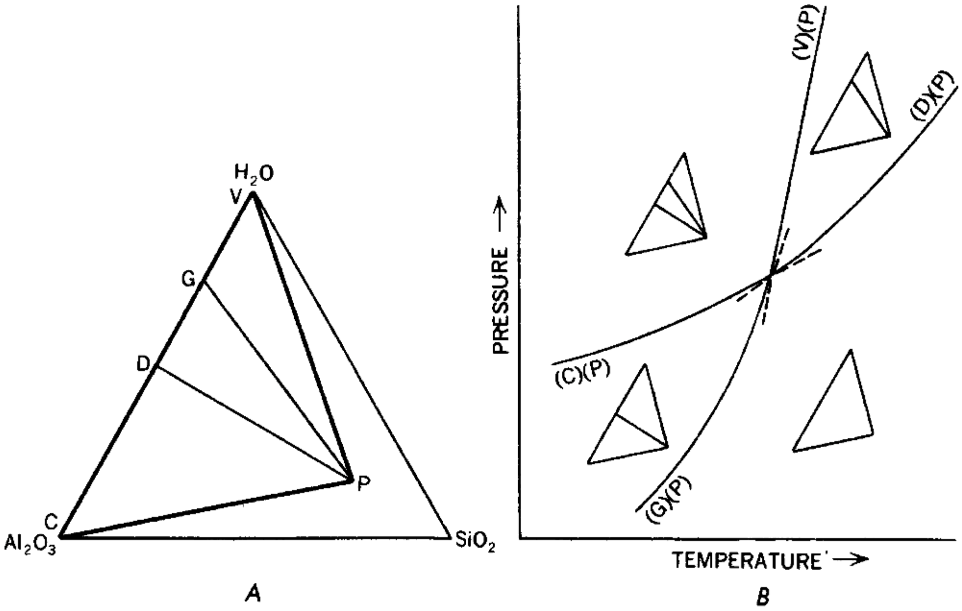

FIGURE 30.—The ternary system Al_2O_3–SiO_2–H_2O, with the five phases corundum (C; Al_2O_3), diaspore (D; $HAlO_2$), gibbsite (G; $Al(OH)_3$), vapor (V; H_2O), and pyrophyllite (P; $Al_2Si_4O_{10}(OH)_2$). *A*, The chemographic relations in gram formula proportions of the oxides; *B*, the *p–T* diagram which is properly oriented with respect to both the temperature and the pressure axes. Because pyrophyllite is an absolutely indifferent phase, the diagram corresponds to that of a binary four-phase system with a fifth phase present throughout.

and high-pressure assemblage. The *p–T* diagram must look something like figure 30*B*.

Example 7.—The five-phase assemblage wollastonite (W), sphene (S), quartz (Q), rutile (R), and anatase (A) belong to the ternary system CaO–TiO_2–SiO_2. The chemography is given in figure 31*A*. Quartz is an absolutely indifferent phase, whereas sphene and wollastonite are relatively indifferent with respect to the transition between rutile and anatase. The situation thus corresponds to figure 21*A*, and only three distinct univariant lines exist. The univariant reactions are:

$$(A)=(Q):\quad R+W=S$$

$$(R)=(Q):\quad W+A=S$$

$$(W)=(S)=(Q):\quad R=A$$

The slopes of the univariant curves are calculated from the data of table 2; these slope values are, respectively, +10.5, +5.8, and −2.7, in bars per degree; the assemblage on the right-hand side of each reaction is the low entropy and therefore low-temperature assemblage. The quantitatively correct *p–T* diagram is given in figure 31*B*.

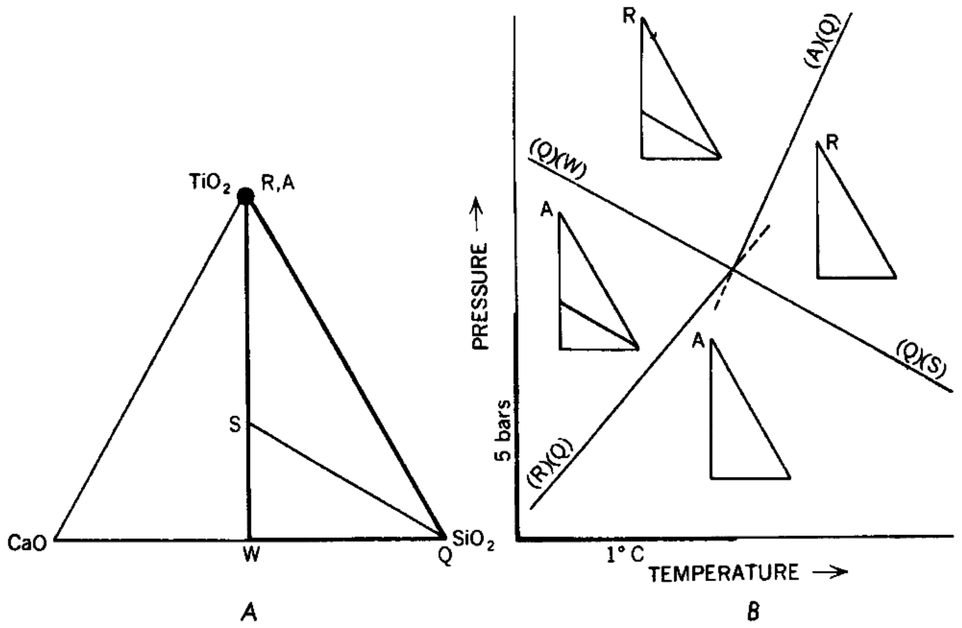

Figure 31.—The ternary system $CaO–TiO_2–SiO_2$, with the five phases wollastonite (W; $CaSiO_3$), quartz (Q; SiO_2), sphene (S; $CaTiSiO_5$), rutile (R; TiO_2), and anatase (A; TiO_2). *A,* The chemographic relations in gram formula proportions of the oxides; *B,* the $p–T$ diagram which is properly oriented with respect to both the temperature and the pressure axes and for which the numerical values of the univariant slopes, calculated from thermodynamic data, are indicated by the scale. Two separate cases of compositional degeneracy exist: the polymorphism of rutile and anatase, and the colinearity of either of these phases with wollastonite and sphene. Quartz is an absolutely indifferent phase and sphene and wollastonite are relatively indifferent phases. Only three distinct slope values exist at the invariant point, while four univariant curves emanate therefrom. The curve marked (Q)(S)(W) courses through the invariant point because the three phases bearing these labels lie on the same side of the singular phases A and R.

Example 8.—The six phases clinoenstatite (E), diopside (Dp), dolomite (D), calcite (C), quartz (Q), and vapor (V), all presumed to be stoichiometric and to have the compositions given in table 2, belong to a quaternary system whose components may be taken to be CaO, MgO, SiO_2, and CO_2. The chemographic relations are given in perspective in figure 32*A*. From the phase compositions two univariant reactions are immediately obvious:

$$(Q)=(V):\quad 2C+2E=D+Dp$$
$$(C)=(E):\quad D+2Q=Dp+2V$$

By linear combinations of these we can eliminate Dp and D in turn to get, respectively,

$$(Dp):\quad D+Q=C+E+V$$

and

$$(D):\quad C+Q+E=Dp+V$$

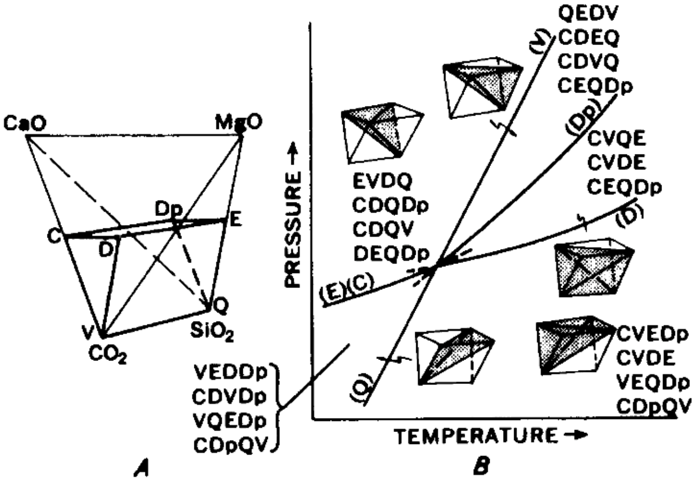

FIGURE 32.—The quaternary system CaO–MgO–SiO$_2$–CO$_2$, with the six phases calcite (C; CaCO$_3$), dolomite (D; CaMg(CO$_3$)$_2$), diopside (Dp; CaMgSi$_2$O$_6$), enstatite (E; MgSiO$_3$), quartz (Q; SiO$_2$), and vapor (V, CO$_2$). *A*, The chemographic relations drawn in perspective, in gram formula proportions of the oxides; *B*, the *p–T* diagram, which is properly oriented with respect to both the temperature and the pressure axes. Two separate cases of compositional degeneracy (coplanarity) exist: In one, Q and V lie on the same side of the singular phases, and the curve (Q) (V) courses through the invariant point; in the other, E and C lie on opposite sides of the singular phases, and the curve (E)(C) ends at the invariant point. As a result, five distinct curves emanate from the invariant point having but four distinct slope values. Within each sector of the *p–T* diagram, the compositional wedge defined by the six phases are divided into three adjoining tetrahedra, one of which characterizes and defines the phase assemblages of the sector. This defining assemblage is shaded and is given at the top of the list of assemblages for that sector.

Because there are two sets of degeneracies in the system, only four distinct univariant schemes exist. We note that (C) and (E) always occur on the same side of the other four schemes, but (Q) and (V) always occur on opposite sides; these relations reflect the facts that C and E occur on opposite sides, but Q and V on the same side, of the respective singular phases. The curve (C)=(E) therefore must terminate at the univariant point (a sextuple point), but the curve (Q)=(V) must course through the point.

On the basis of the thermodynamic data of table 2, the *p–T* slope of the vapor-free reaction (Q)=(V) can be computed to be 36 bars per degree; diopside and dolomite are favored by low temperature and high pressure. The numerical values of the slopes for the other univariant equilibria cannot be determined because in these equations the entropy and volume values of CO_2 gas dominate, and these values depend sensitively on the location of the curves on the p–T diagram. However, the reactions leading to the evolution of gas are favored by high temperatures and low pressures, and so tend to have positive slopes on the p–T plot, thus the curves must be qualitatively describable by figure 32*B*.

EXTENSION OF OSTWALD'S RULE TO BINARY SYSTEMS

There are many different versions of the so-called "Ostwald's step rule" in the geochemical literature. One original statement by Ostwald (1902, p. 447) is as follows:

> In allgemeiner Weise findet sich der Satz, dass beim Verlassen eines unbeständigen Zustandes ein gegebenes chemisches Gebilde nicht den beständigsten Zustand aufsucht, sondern den nächstliegenden, d.h. den (Vorübergehend oder dauernd) beständigen, welcher von dem augenblicklichen aus mit dem geringsten Verlust von freier Energie erreicht werden kann. [Freely translated: In general, one finds the rule that, by the breakdown of an unstable state [=phase], a given chemical composition will form not the most stable state, but rather the adjacent, that is, a transitory state, which can be reached directly from the existing one with the least loss of free energy.]

Ostwald's rule was originally proposed for the polymorphic transition in one-component systems. The stepwise progression from phase assemblages of relatively higher free energy to those of lower free energy, however, can be applied equally well to systems of more than one component. The application to binary systems is immediate, and the results allow the prediction of possible relative sequences of formation of metastable assemblages.

As explained in an early section of this paper, the invariant point, univariant curves, and divariant fields of a p–T diagram are the projections of points, curves, and areas of Gibbs free-energy surfaces of phase assemblages from the G–p–T space onto the p–T plane. It is therefore possible to construct a qualitatively correct G–X (X= composition) diagram for each divariant field, univariant curve, and invariant point, depicting the free-energy relations among the phases, directly from the p–T diagrams. For divariant fields, no more than two phases (represented as points in the G–X plot) are colinear; for univariant curves, the three phases in equilibrium are colinear; for invariant points, all four points are colinear. These colinearity relations are valid regardless of whether an assemblage is stable or metastable; the stable set of assemblages is given by the geometrically lowest set of straight lines connecting phase points in the G–X plot.

On the *G–X* plot, therefore, the three colinear points occur on the lowest set of straight lines along the stable part of a univariant curve, but they lie above the lowest set of lines along the metastable part of the same univariant curve. The lowest set of straight lines remains the same between any two adjacent stable univariant curves; the phase points, however, move relatively up and down at different *p–T* values between these univariant curves in such a way that the higher sets of straight lines, which apply to the metastable assemblages, change their relations as successive metastable extensions of univariant curves are crossed.

By using these criteria, the straight lines connecting the free-energy values of phases are constructed for every part of the *p–T* diagram around an invariant point; these are shown in figure 33. This diagram immediately allows one to predict the possible sequence of metastable assemblages according to the step rule. The sequence of assemblages depends not only on the location of a given *p–T* point relative to the univariant curves, but also on the precise bulk composition of the system. Thus, for instance, for some specific bulk composition lying between phases 2 and 3 and in the *p–T* sector between the stable parts of (1) and (4), one possible set of successively more stable divariant assemblages is: 1+4, 2+4, 1+3, and finally 2+3, which is the stable assemblage. In this example, it is interesting that phase 2, which is stable, may initially form in equilibrium with the metastable phase 4, but may then disappear as 2+4 is replaced by 1+3; this latter assemblage may in turn be replaced by the stable assemblage, in which phase 2 reappears. The mere appearance of a stable phase in an equilibrium assemblage, thus, does not guarantee that the assemblage is stable. Conversely, the disappearance of a phase is no assurance that the phase is not intrinsically stable under the prevailing *p–T–X* conditions.

At particular values of temperature and pressure, certain bulk compositions, X', could lead to two alternative metastable divariant assemblages that have the same total Gibbs free energy and therefore the same degree of metastability; for example, between lines (1) and (4) in figure 33 where the composition X' is indicated by the crossing of the two lines that connect the phases of the divariant assemblages. At the bulk composition X', the chemical potential of each component is the same in both phases of a given assemblage, however, it is not equal in the two assemblages. The two alternative assemblages, therefore, are not in true chemical equilibrium, nevertheless they do not tend to interreact because ΔG of reaction is zero. As the *p–T* values sweep the sector, the bulk composition X' also shifts, spanning the entire range of compositions between phases 2 and 3.

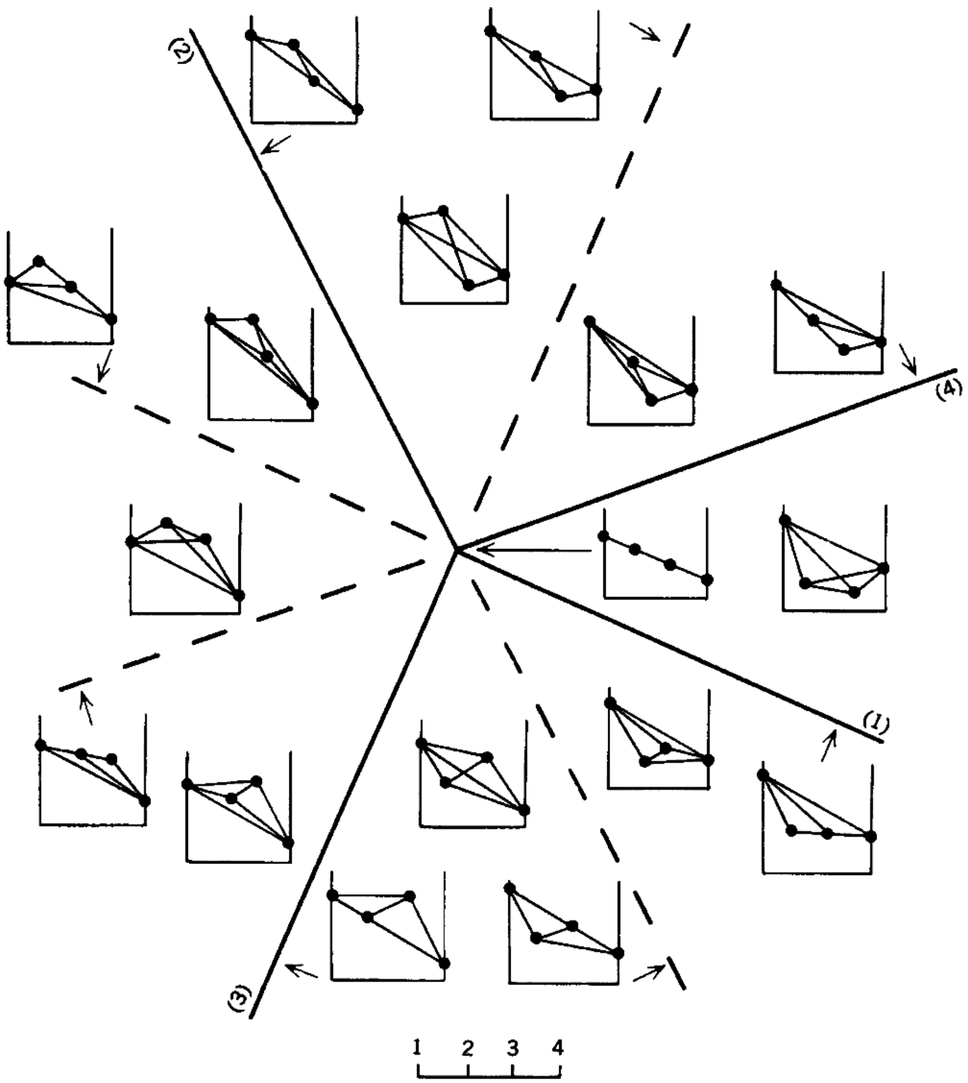

FIGURE 33.—Schematic representation of Gibbs free-energy relations of the phases around an invariant point in a binary four-phase system. The metastable univariant lines are extended in full, but are shown as dashed lines. Each G–X plot is topologically correct for the entire sector as shown; the Gibbs free-energy values increase upward so that the straight lines connecting the lowest set of points depict the stable univariant or divariant assemblages. In each G–X plot, the successively higher lines connect univariant or divariant assemblages which are successively more metastable. Where two such lines cross, for instance between univariant curves (1) and (4), a metastable four-phase assemblage could form fortuitously; such an assemblage, however, is not invariant.

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