

**Schreinemakers Rule as Applied to
Non-Degenerate Ternary Systems**

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Abstract

In experimental studies of phase relations in chemical, ceramic, metallurgical, and mineralogical systems, it is fairly rare for pressure-temperature (P-T) diagrams to be fully mapped, i.e. with all the univariant lines directly determined. This typically requires an extraordinarily large number of experiments; in many cases this is impractical or, due to extreme temperature or pressure conditions, sluggish kinetics, or other considerations, effectively impossible. Even if the availability of thermodynamic data allows the slopes of such univariant curves to be calculated, there remains a possibility that such data are not always mutually consistent. Fortunately, in a series of classic monographs published in Dutch between 1915 and 1925, F.A.H Schreinemakers derived and demonstrated the usefulness of a set of rules which is aptly suited to overcoming this problem. When some subset of the $n+2$ univariant lines that meet at an invariant point in an n -component system are known, this set of topologically-governed principles, which later came to be known as Schreinemakers rules, not only allows the determination of the location of remaining univariant lines, it also provides insights into the stability of divariant assemblages around the invariant point at various temperatures and pressures. In this paper, we review the 180° rule, overlap rule and half-plane rule, all of which make up Schreinemakers rules, and show how they can be applied to a ternary non-degenerate system where five phases coexist at an invariant point.

Introduction

A ternary chemical system can be completely described and visualized only in a five-dimensional space, where intensive Gibbs free energy, G , can be plotted as a function of the four independent variables pressure (P), temperature (T), and two compositional variables such as the mass fractions of components 1 and 2. Of course, few people can easily imagine five-dimensional relations. It is therefore necessary to consider partial representations of the relations that can be shown as three-dimensional or, better, two-dimensional plots on a computer screen, blackboard, or paper. For example, we might hold pressure and temperature constant and make a map of minimum Gibbs energy assemblages in composition space, often represented as a triangle whose vertices are the three components of the ternary system. On the other hand, we might project reaction lines and points where various combinations of phases have equal Gibbs energy at particular compositions onto the P-T plane. However, it is important to remember that these two-dimensional plots are both reduced representations of the original five-dimensional relations, and as such they are not independent of one another. There are systematic rules governing how the distribution of phases in composition space (which we call the chemography) affects the layout of reaction curves in (P, T) space. The purpose of this review is to describe these rules, so that the discerning scientist may appreciate how to distinguish legal from illegal phase diagrams and to predict aspects of phase

diagrams that have not been (or cannot be) computed or measured experimentally.

Invariant, Univariant, and Divariant Assemblages

We need to begin with some remarks on what we mean by stable, metastable, and equilibrium. Elementary thermodynamics demonstrates that the stable state of a chemical system at prescribed pressure, temperature, and chemical composition is that with the minimum value of the intensive Gibbs free energy. Thermodynamics also shows that a necessary condition for a heterogeneous system (that is, one containing more than one coexisting phase) to achieve a state of minimum G is that the chemical potential (that is, the partial molar Gibbs free energy) of each component must be equal among all the phases, i.e. (Equation 1). This is because, if chemical potential of any

$$\mu_i^A = \mu_i^B = \dots = \mu_i$$

Equation #1

component differs between phases, then the overall G of the system can be lowered by transferring some mass of that component from the high chemical potential phase to the low chemical potential phase. Note, however, that equality of chemical potentials among phases is not sufficient to establish a minimum in G . These considerations require some care in terminology. When we say here that an assemblage of phases

is stable, we mean that at a given pressure, temperature, and composition it has lower G than any other assemblage of phases that could exist there. On the other hand, when we say two (or more) different phases are in equilibrium with one another at some pressure and temperature, we mean that the chemical potential of each component among all those phases is equal. If there are two (or more) phases in equilibrium and, furthermore, the value of G of the assemblage at some composition is also the lowest among all possible assemblages at that composition, then we say that this is a stable assemblage and the equilibrium is a stable equilibrium. The remaining possibility is also quite important in this review: when two or more phases are in equilibrium but there exists still another assemblage of phases that could constitute the given composition and whose value of G is lower, then we have a metastable assemblage and this equilibrium is a metastable equilibrium.

In a system consisting of n-components at chemical equilibrium, the Gibbs phase rule provides the variance, or number of degrees of freedom, f, as $n - \phi + 2 - (\text{other constraints})$, where ϕ is the number of phases that are in equilibrium with one another, while other constraints refers to the presence of coincidences, singular points, collinearities, critical phenomena or other forms of degeneracy which can lower the variance of the equilibrium assemblage. In the absence of degeneracies, the Gibbs phase rule is reduced to $f = n - \phi + 2$. Therefore, for an assemblage to be thermodynamically invariant, $f=0$, n+2 phases must be in equilibrium with each other. Similarly, an assemblage of n+1 phases at equilibrium is univariant, $f=1$, while an assemblage of n phases at equilibrium is divariant, $f=2$. Note that the Gibbs phase rule applies to assemblages of phases in equilibrium with each another; it does not depend on whether these assemblages are stable or metastable.

The number of different assemblages of a given variance is given by the number of combinations of the appropriate number of phases

$$\text{Number of assemblages} = \frac{(n+2)!}{\phi! n!}, \text{ where } \phi = n + 2, n + 1, \text{ and } n \text{ for } f = 0, 1, \text{ and } 2 \text{ respectively}$$

Equation #2

that can be drawn from the original n+2 phases (Equation 2).

Invariance

Consider an n-component system which consists of a total of n+2 phases, there can only be one possible combination of phases which can result in

invariance (as mentioned, n+2 phases are needed) according to the combinatorial formula, ${}^{n+2}C_{n+2}=1$.

Pressure and temperature are examples of intensive parameters that might be free to vary while keeping the same set of phases in the equilibrium assemblage. If the variance is zero, then, both pressure and temperature are determined, and cannot vary. As such, the invariant equilibrium can be presented on a P-T diagram as a single point, commonly known as the invariant point. The compositions of the phases (that is, the fraction of each of the n chemical components out of the total mass of each phase) are also intensive parameters that might vary while keeping the set of coexisting phases fixed but, again, at an invariant point they are all determined. Hence, there is a definite set of compositions characterizing each of the n+2 phases at equilibrium at the invariant point. We will take advantage of this property of fixed phase compositions at the invariant point below when we plot chemographic relations at and around the invariant point.

Univariance

Univariance, on the other hand, requires a total of n+1 phases, thereby giving a total of n+2 possible combinations of univariant assemblages of n+1

$${}^{n+2}C_{n+1} = \frac{(n+2)!}{(n+1)! [(n+2)-(n+1)]!} = \frac{(n+2)!}{(n+1)! 1!} = n + 2$$

Equation #3

phases, each derived from the invariant assemblage by subtracting one phase (Equation 3).

On the P-T diagram, these n+2 univariant conditions are presented as n+2 lines (or curves) passing through the invariant point. Now, assuming the invariant point itself is stable, each of these univariant assemblages changes from stable to metastable as it passes through the invariant point, such that there are n+2 stable univariant lines (represented by solid lines) emanating from the invariant point and, opposite these, n+2 metastable extensions (represented by dashed lines).

Divariance

Applying the combinatorial formula again for the divariant condition, a total of $(n+1)(n+2)/2$ combinations of divariant assemblages of n phases are possible, each derived from the invariant assemblage by deleting two phases (Equation 4).

Each divariant condition is stable on the P-

$${}^{n+2}C_n = \frac{(n+2)!}{(n)! [(n+2)-(n)]!} = \frac{(n+2)!}{n! 2!} = \frac{(n+2)(n+1)}{2}$$

Equation #4

T diagram in a sector of the circle surrounding the invariant point (again, assuming the invariant point itself is stable). These sectors are bounded by the stable parts of univariant lines. The conditions defining these sectors – how large an arc of the circle they can occupy, and which univariant lines they can cross – were laid out by F.A.H. Schreinemakers in a series of classic monographs published in Dutch around 1915. Our purpose here is to explain how these rules result from the topology of continuous surfaces intersecting in free energy space, to show how they determine the arrangement of all the stable and metastable univariant and divariant equilibria where they intersect at an invariant point in P-T space, and finally to understand the relationship of this arrangement to the positions of the participating phases in composition space (“chemography”).

Non-Degenerate Ternary Systems

Applying the Gibbs phase rule and Equation 1 to a non-degenerate ternary system ($n=3$) of 5 phases, it becomes obvious that this system may include an invariant assemblage consisting of 5 phases which is the intersection of 5 univariant assemblages of 4 phases each and 10 divariant assemblages of 3 phases each. In composition space, each divariant assemblage is represented by a triangle whose three vertices are the compositions of the three phases that coexist in the divariant equilibrium. We will show representations of stable configurations in composition space, chemographs, by plotting only the triangles representing stable divariant assemblages at particular P, T conditions. The P-T diagram may thus show an invariant point, also known as a quintuple point, and 5 univariant lines with their stable and metastable portions. Apart from the invariant point and univariant lines, it is also possible to graphically identify the 10 sectors representing the divariant assemblages on the P-T diagram. A set of rules identified by Schreinemakers is particularly useful at this point in order to proceed further with the graphical representation of the information gathered thus far on a P-T diagram. Using Schreinemakers rules, the relative locations of the univariant curves can be determined such that even a simple hand-drawing based on little experimental data can accurately constrain certain key features of actual unknown P-T diagrams. This is important

because, although many univariant lines and their respective invariant points have been experimentally determined for both naturally occurring and synthetic systems, it is an enormous amount of tedious and often expensive work to fully map the P-T diagram of a multi-component chemical system. In some cases key parts of the diagram may be beyond the conditions that can be achieved experimentally. It is equally true that calculations of phase stability, for example from density functional theory or other *ab initio* methods, are tedious and expensive and it is very helpful to have a tool for confidently constructing complete, topologically correct, diagrams based on the minimum number of calculations.

Consider a ternary system involving 5 phases, A, B, C, D, and E. The first step in the construction of the P-T diagram is to determine the location of a univariant line and to correctly label the sides of the stable portions of this line according to the reaction it represents.

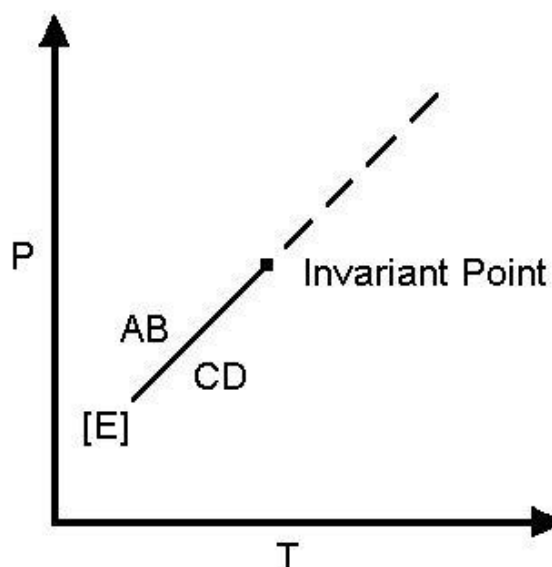


Figure 1: Univariant line [E] representing reaction $A+B=C+D$ (phase E not involved). The stable portion of the univariant line is shown as a solid line while the metastable portion is shown as a dashed line.

Figure 1 shows an example of the correct labeling of a univariant line which represents the reaction $A+B=C+D$. In addition, phase E (shown in square brackets), which does not participate in the reaction, has been used to identify this univariant line. Since (see above) each univariant assemblage is found by deleting exactly one phase from the invariant set, identifying each univariant curve by the missing phase is unique and convenient.

The relative locations of the other univariant lines [A], [B], [C], and [D] can now be determined based on Schreinemaker's rules. This set of rules is best explained here through a real example using the MgO-Al₂O₃-SiO₂ ternary system in the vicinity of the invariant point where the 5 coexisting phases are (A) forsterite, Mg₂SiO₄, (B) sillimanite, Al₂SiO₅, (C) cordierite, Mg₂Al₄Si₅O₁₈, (D) spinel, MgAl₂O₄, and (E) clinoenstatite, MgSiO₃. Based on their compositions, these 5 phases can be depicted in a ternary composition plot (Figure 2). Although these particular five phases

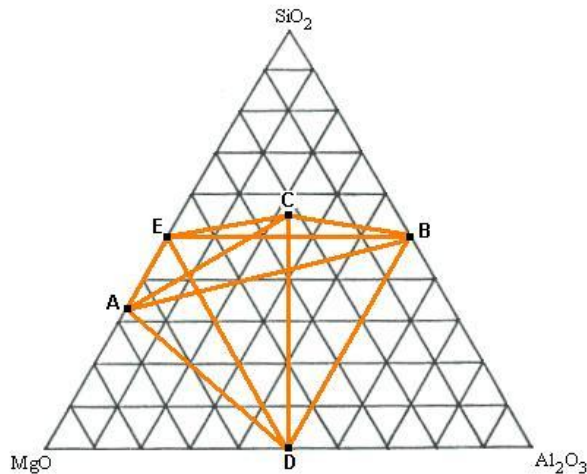


Figure 2: Chemograph of the MgO-Al₂O₃-SiO₂ ternary system at the quintuple point. (A) forsterite, Mg₂SiO₄, (B) sillimanite, Al₂SiO₅, (C) cordierite, Mg₂Al₄Si₅O₁₈, (D) spinel, MgAl₂O₄, and (E) clinoenstatite, MgSiO₃

significant solid solution in this ternary system, even if we used phases that could vary in composition, there would still be a unique set of compositions for each phase where they coexist at the invariant point. The geometrical arrangement of these coexisting compositions is called the chemography of the invariant point, and the figure generated by connecting them with straight lines is called a chemograph. Each line drawn between phases implies that they are in equilibrium with each other. At the invariant point, equilibrium between phase A and phases B, C, D, and E is represented by 4 such lines; this is repeated for all other phases to generate a fully connected chemograph which shows that invariance does involve all phases coexisting at equilibrium with one another.

In a non-degenerate ternary system of 5 phases, the compositions of the phases at the invariant point are chemographically related to one another in 3 possible arrangements: pentagonal with all interior angles less than 180° (Figure 3a),

quadrilateral as defined by four phases with the remaining phase being an interior point not falling on the diagonals (Figure 3b), and triangular as defined by three phases with the remaining two phases being interior points which are neither collinear with any of the points of the triangle nor coincident with each other (Figure 3c). The

Non-Degenerate Ternary System of 5 Phases (Invariant Point)

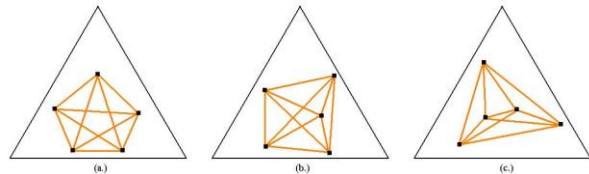


Figure 3: Possible arrangements of five phases in a non-degenerate ternary system. (a.) Pentagonal with all interior angles less than 180°, (b.) Quadrilateral with an interior point not falling on the diagonals, and (c.) Triangular with interior points neither collinear with any of the vertices of the triangle nor coincident with each other.

conditions where three or more phases plot along a line or where two or more phases plot at a common point are called degeneracies and they will be examined later in another review paper.

In the MgO-Al₂O₃-SiO₂ ternary system, the compositions of the five phases defined above at the invariant point define a distorted but nevertheless convex pentagon (Figure 2). Figure 4a shows the chemographs which represent one of the five univariant reactions, A+B=C+D (phase

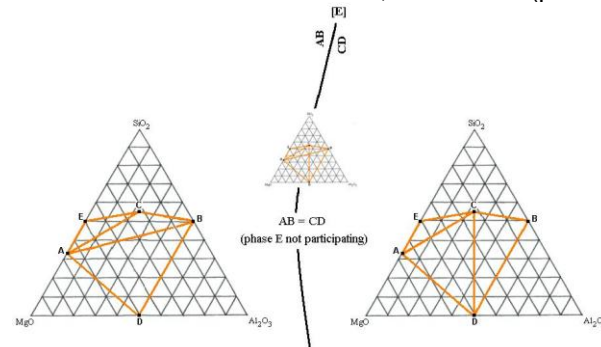


Figure 4a

E not participating). On the chemograph for the AB side of the reaction where phases A and B are in equilibrium with each other, a total of 3 divariant assemblages can be seen. That is, of the ten possible triangles that can be made up from all the straight lines drawn in Figure 2 for the invariant assemblage, only three remain stable in this region of the (P,T) space. The divariant assemblage (B,D) is indicated by a triangle showing coexistence between phases A, C, and E at equilibrium; the divariant assemblage (D,E) is indicated by the coexistence of phases A, B, and

C at equilibrium; the divariant assemblage (C,E) is indicated by the coexistence of phases A, B, and

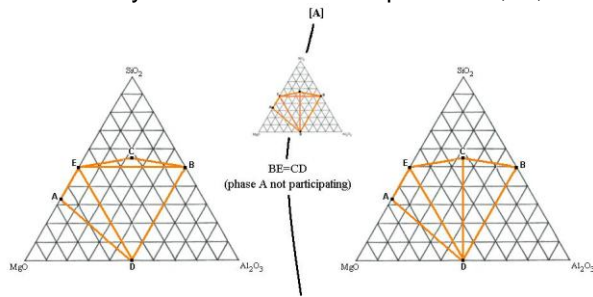


Figure 4b

D at equilibrium. As the reaction proceeds from equilibrium between phase A and B to equilibrium between C and D, there exists a set of pressures and temperatures that forms the univariant line [E], whereby all four phases A, B, C, and D exist in equilibrium. On the other hand, on the opposite (CD) side of the reaction, equilibrium between phases A and B is replaced by equilibrium between C and D. Here the chemograph shows triangles for the stable divariant assemblages (B,D), (B,E) and (A,E). This kind of reaction is termed a “tie-line flip” since the line representing equilibrium between A and B, one of the diagonals

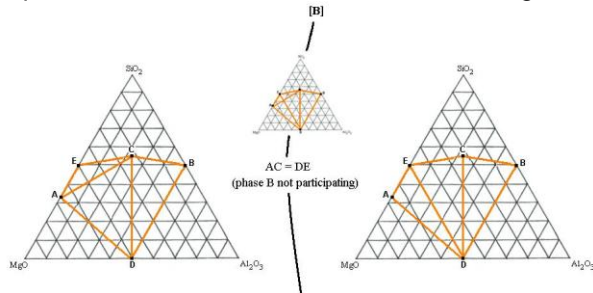


Figure 4c

of the ABCD quadrilateral, has literally been flipped to the other diagonal, representing equilibrium between C and D. We may also refer to this kind of univariant reaction as a “non-terminal” reaction, since all four of the participating phases retain a stability field on both sides of the reaction (only the pairs of coexisting phases change). The other 4 univariant reactions, $B+E=C+D$ (phase A not participating), $A+C=D+E$ (phase B), $A+B=D+E$ (phase C), and $A+C=B+E$ (phase D) for the $MgO-Al_2O_3-SiO_2$ ternary system are shown in Figures 4b, 4c, 4d, and 4e respectively. We note that, for the chemography of the selected phases, all five univariant reactions are non-terminal, tie-line flip reactions. This is evident in that each subset of four phases forms a quadrilateral whose diagonals can flip across the univariant reaction. This is a necessary

consequence of the five phases forming a convex

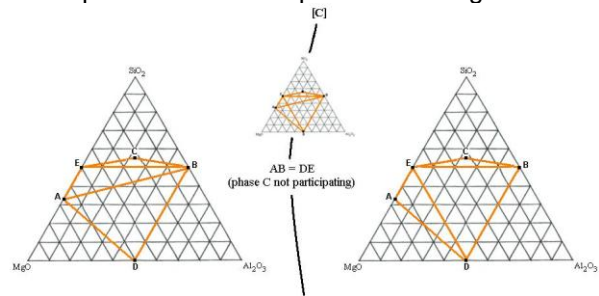


Figure 4d

pentagon – removing any point from a pentagon leaves a quadrilateral.

We may furthermore note that the chemograph of stable three-phase triangles shown at right on Figure 4a is identical to that shown at left on Figure 4c. Likewise, the chemograph on the right of Figure 4c matches that on the right of Figure 4b. The left of Figure 4b matches the right of Figure 4d. The left of Figure 4d matches the right of Figure 4e. And the left of Figure 4e matches the left of Figure 4a. This hints at the arrangement of

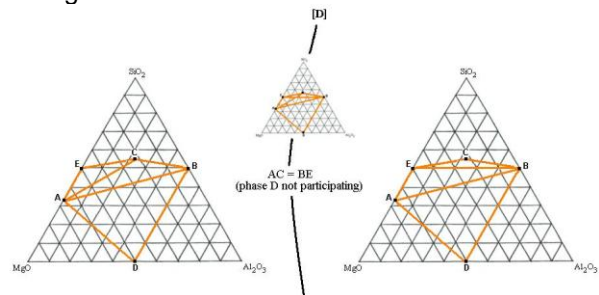


Figure 4e

these reactions where they meet at an invariant point. We can travel around the circle, changing stable triangles each time we cross one of these reactions, and arrive back at the original configuration. Depending which way we go around the circle, then, we can encounter the stable reactions in the order [B], [A], [C], [D], [E] or in the order [E], [D], [C], [A], [B]. No other sequence is legal.

Schreinemakers Rules

In the words of Schreinemakers (F.A.H. Schreinemakers, 1915): 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. This statement is referred to as the

“fundamental axiom” (E-An Zen, 1966), and holds true as long as the univariant curves under discussion arise from the intersection of Gibbs free-energy surfaces. It is a topological statement about the properties of continuous surfaces in three-dimensional space. That is, if an assemblage is divariant then its Gibbs energy can be expressed as a function of two variables, P and T. By the phase rule, fixing these two variables is sufficient to determine all other properties, such as phase compositions, and especially the value of G. So divariant assemblages are represented by well-defined surfaces in G(P,T) space. The fundamental axiom simply states that where two such surfaces intersect (that is, have equal value of G) along some curve in (P,T), that one surface is higher than the other (“less metastable”) on one side of the line and the other surface is higher on the opposite side of the line. That is, two intersecting surfaces interchange their relative height.

A univariant line represents the common equilibrium of some number of divariant assemblages (four, in the ternary case). Essentially, the fundamental axiom means that each of these divariant assemblages can only be stable on one side of the univariant line; it must be metastable on the other side. If the univariant is itself stable (that is, there is no other divariant assemblage, beyond those defining the univariant, with lower G), then each of its constituent divariant assemblages must indeed be stable on one side of the univariant line (and metastable on the other). If the univariant line is itself metastable relative to some other divariant assemblage, then all the divariant assemblages making up the univariant are metastable on both sides, but they still interchange their relative stability across the univariant line.

Take, for example, the univariant reaction represented in Figure 4e. This reaction involves equilibrium among the four phases ABCE (phase D is absent) and so it can also be described as an equilibrium among the four divariant assemblages ABC, ABE, ACE, and BCE; these may also be labeled by the phases absent from each of these groups: (D, E), (C, D), (B, D) and (A, D). We find from the chemographic analysis above that two of these assemblages, ABC and ACE, can be stable on the left side of Figure 4e – that is, the triangles bounded by the three vertices corresponding to their phase compositions are plotted on the chemograph at left – but are absent from the chemograph on the right. On the other hand, the remaining two divariant assemblages (triangles),

ABE and BCE, appear on the right side but are absent on the left.

From the fundamental axiom, three further important conclusions can be drawn for an n-component system of n+2 phases.

Conclusion 1:

On a P-T diagram, the stable divariant assemblage (M,N) is bounded by the univariant lines [M] and [N] and where these lines meet at an invariant point, the sector between them occupied by the stability region of (M,N) occupies no more than 180°. In addition, the stable portion of all n+2 univariant lines about the invariant point forms n+2 sectors, all less than or equal to 180°, occupied by one or more divariant assemblages, one of which is unique to the sector. This is known as the 180° rule.

Conclusion 2:

Any divariant assemblage whose stability sector extends across the univariant line [J] (stable or metastable) contains the phase J. The opposite of this statement is, however, not true. A divariant assemblage that contains phase J need not necessarily extend across the stable or metastable portions of univariant line [J]. This is known as the overlap rule.

Conclusion 3:

Consider a univariant line [J] that separates the P-T space into two sides and represents a certain reaction $A+B+C+\dots=M+N+O+\dots$. When any other univariant line involving all but one of these phases plus phase J crosses the first reaction, it must change from stable to metastable and the metastable end of the univariant lines [M], [N], [O]... must lie on the side of [J] representing phases M, N, O, ... Likewise, of course, the metastable ends of the univariant lines [A], [B], [C], ... must lie on the side of [J] where $A+B+C+\dots$ is relatively more stable. We shall call this the half-plane rule. The application of this rule for the arrangement of univariant lines is illustrated in Figure 5 for a ternary system containing five phases J, K, L, M, and N. For the univariant line [J] representing reaction $K+L=M+N$, the stable portions of univariant line [M] must lie on the KL side at positions such as 1, 2, and 3 (all of which are located within the sector marked by the black arrow) with their metastable portions lying at the MN side. The univariant line [N] is arranged in a similar way to that of univariant line [M], and all positions are allowed as long as the metastable

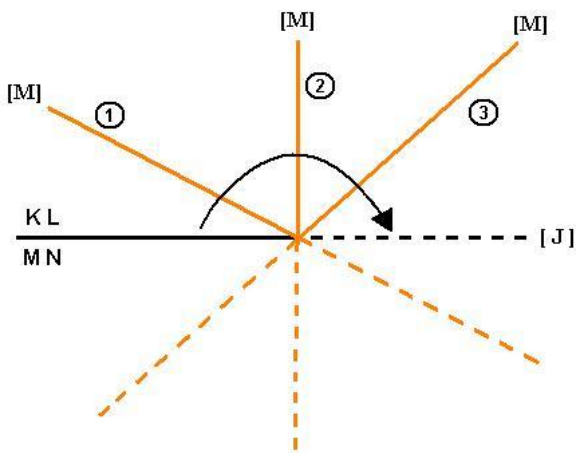


Figure 5: Application of Schreinemaker's half-plane rule determines that the metastable portions of univariant line [M] must lie on the MN side of univariant line [J].

extension is on the side containing phase N (i.e. the MN side). Although at this stage the relative position of the [M] and [N] reactions has not been determined, this also follows from the half-plane rule once the reactants and products of these reactions are known, which is determined by the chemography. In short, knowing the chemography of the coexisting phases, successive application of the half-plane rule determines, schematically, the entire layout of the stable and metastable univariant reactions about the invariant point.

This set of three conclusions from the fundamental axiom forms the very basis of Schreinemaker's rules, which govern the steps involved in the mapping out of the approximate locations of all univariant lines as well as the relationships of all divariant assemblages on a P-T diagram. The following section completes the P-T diagram of the MgO-Al₂O₃-SiO₂ ternary system by locating all other univariant lines according to the Schreinemaker's rules discussed so far for a scenario when the locations of two univariant lines are determined through experiments.

Construction of P-T Diagrams Based on Schreinemaker's Rules

Arrangement 1: Convex Pentagon

Figure 6 is an incomplete P-T diagram of the MgO-Al₂O₃-SiO₂ ternary system consisting of 5 phases which are namely (A) forsterite, Mg₂SiO₄, (B) sillimanite, Al₂SiO₅, (C) cordierite, Mg₂Al₄Si₅O₁₈, (D) spinel, MgAl₂O₄, and (E) clinoenstatite, MgSiO₃.

Figure 6 shows two univariant lines [C] and [E], obtained from experiments. The univariant line [C] shown in the figure, for example, is a best-line fit from experimental data to the reaction forsterite + sillimanite = spinel + clinoenstatite (A+B = D+E). The compositions of these phases determine the stoichiometry of the reaction; that is, in order that this be a balanced chemical reaction we must have forsterite + sillimanite on one side and spinel + clinoenstatite on the other (in fact, the balanced reaction is 2 forsterite + sillimanite = spinel + 3 clinoenstatite, but for our purposes the numerical values of the stoichiometric coefficients do not matter; only their sign). Through observation of reaction progress direction in experiments taken from both sides of the univariant line [C], it is easy to determine the AB side and the DE side. The univariant line [E], on the other hand, represents the reaction forsterite + sillimanite = cordierite + spinel (A+B=C+D). When these two univariant lines are plotted in (P,T) space, we see that they appear to intersect, suggesting the existence of an invariant point. Furthermore, we can immediately check that our experimental data are valid by testing the form of this intersection against Schreinemaker's rules (see Figure 6). Indeed the metastable part of reaction [C] lies on the CD side of reaction [E] and the metastable part of reaction [E] lies on the DE side of reaction [C], so the arrangement does satisfy the half-plane rule. Also, the phase pair A+B, and hence also the divariant assemblages ABC, ABD, and ABE, have their stability sector bounded in Region 2 on Figure 6, which occupies less than 180°, so the

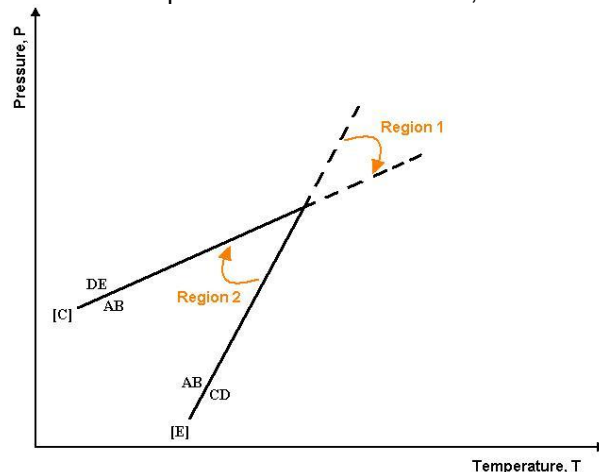


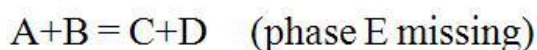
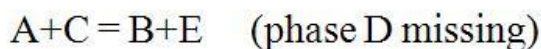
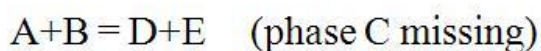
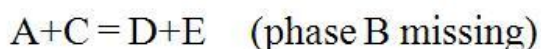
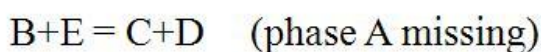
Figure 6: An incomplete P-T diagram of the MgO-Al₂O₃-SiO₂ ternary system in which two univariant lines [C] and [E] are obtained experimentally.

arrangement satisfies the 180° rule. These are the

only checks we can make at this stage, but the arrangement appears legal. This is a good example of the application of Schreinemakers rules to verify that experimental data are topologically valid.

Moreover, despite considerable efforts to obtain the locations of these two univariant lines, the locations of the other three univariant lines [A], [B] and [D] are still unknown. Many further experiments would be required to determine the locations of these remaining univariant curves; some of these experiments might need to extend beyond the P, T or time range where the experiments are considered practical in the laboratory. The application of Schreinemakers rules at this point will allow the construction of a fully mapped P-T diagram that provides important information on the arrangement of the remaining univariant lines.

The five univariant reactions are as follows: (Equation 5)



Equation #5

Applying conclusion 3, Schreinemakers half-plane rule, for the arrangement of univariant lines from the previous section, we can be certain that the metastable portion of the univariant line [D] is located within Region 1 which extends between the metastable portions of univariant lines [C] and [E] (Figure 6). This is because, from conclusion 3, the metastable end of univariant line [D] must lie on the DE side of univariant line [C] and also on the CD side of univariant line [E]; only Region 1, where these sides overlap, satisfies both constraints. Reaction [D] has been added in this manner to Figure 7. Now, the stoichiometry of reaction [D] is forsterite + cordierite = sillimanite + clinoenstatite ($A+C = B+E$). Once again, the half-plane rule determines which side is which on the P-T plane. Based on the reactions already plotted, the A+C side must be the side where the

metastable extension of [C] is located, and the B+E side must contain the metastable end of [E]; hence B+E is the upper-left side in Figure 7.

Next, the location and reactant/product sides of the remaining two univariant lines [A] and [B] can easily be found by repeated application of the half-plane rule. The metastable portion of univariant line [A] must necessarily be found in a region representing an overlap of the phase A-containing sides of all the univariant lines so far plotted. This is Region 4 (Figure 7), representing

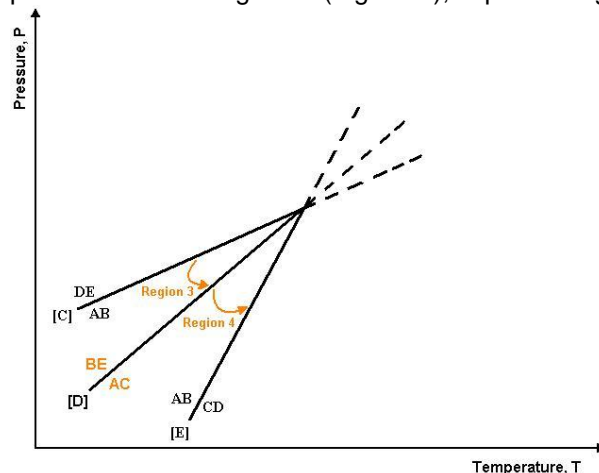


Figure 7: Determination of the location of univariant line [D] on the P-T diagram, and correct labeling of its AC and BE sides using the half plane rule.

the overlap of the AC side of univariant line [D] and the AB side of univariant line [E] (for consistency, we also note that Region 4 is on the AB side of reaction [C]). Similarly, the metastable portion of univariant line [B] is located in Region 3 where the AB side of univariant line [C] and BE side of univariant line [D] overlap. By drawing the

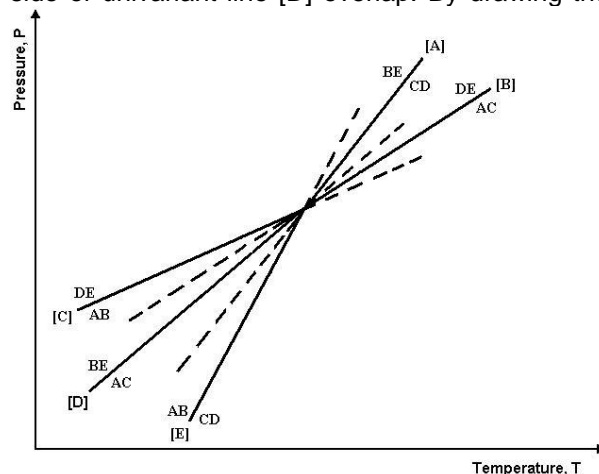


Figure 8: Fully mapped P-T diagram based on Schreinemakers rules.

remaining two univariant lines, and correctly

labeling the sides BE and CD for univariant line [A] and the sides AC and DE for univariant line [B], the relative locations of all five univariant lines for the MgO-Al₂O₃-SiO₂ ternary system is finally fully mapped out on the P-T diagram using Schreinemaker's rules (Figure 8). It so happens in this case that we can add reactions [A] and [B] in either order; in general, however, it is wise to sequentially add the reactions one at a time.

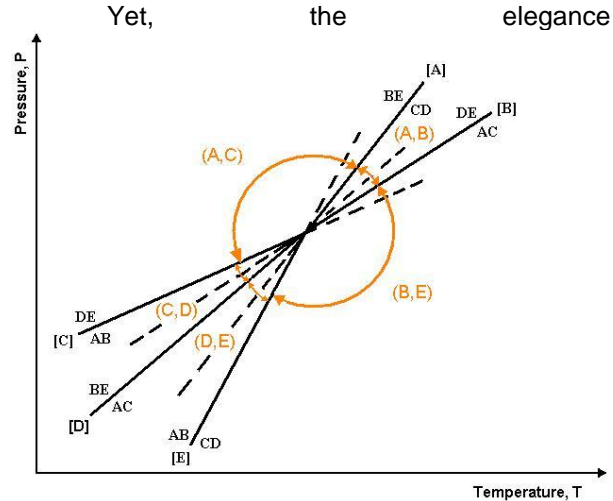


Figure 9a: Divariant assemblages (A, B), (A, C), (C, D), (D, E), and (B, E), all of which are unique to the five sectors formed by the univariant lines.

of the method of Schreinemaker does not stop here at the full construction of the P-T diagram; more information can be obtained through an analysis of the P-T diagram using conclusions 1 and 2 of Schreinemaker (the 180° rule and the overlap rule). From Equation 3 and the chemography of the five phases in Figure

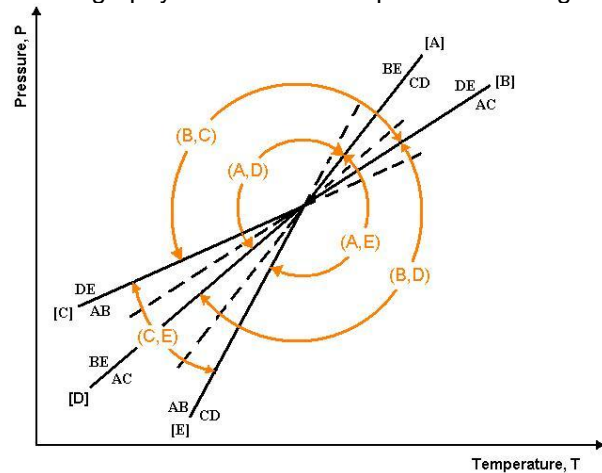


Figure 9b: Sectors occupied by the remaining five divariant assemblages (A, D), (A, E), (B, C), (B, D), and (C, E).

2, there are a total of 10 divariant assemblages namely (A, B), (A, C), (C, D), (D, E), (B, E), (A, D), (A, E), (B, C), (B, D), and (C, E). According to the 180° rule, the divariant assemblage (A, B) representing equilibrium between phases C, D and E, is represented by a sector spanning no more than 180° between univariant lines [A] and [B]. This is the direct result of the 180° rule and the fundamental axiom which dictates that the divariant assemblage of phases C, D and E is stable only up to but never crossing both univariant lines [A] and [B]. In addition, divariant assemblage (A, B) also belongs uniquely to one of the 5 sectors formed by the 5 univariant lines. Figure 9a shows the five unique sectors spanned by divariant assemblage (A, B) and the other four divariant assemblages (A, C), (C, D), (D, E), and (B, E). Conclusion 2, the overlap rule, is also observed here in our analysis. According to the overlap rule, divariant assemblage (A, B) contains phase D as one of its three equilibrium phases C, D, and E since the sector representing it extends across the metastable portion of univariant line [D]. The same can be observed for the remaining five divariant assemblages (A, D), (A, E), (B, C), (B, D), and (C, E) whose sectors are shown in Figure 9b. As another example, the sector for divariant assemblage (B, C) passes through the stable portions of univariant line [A] and the metastable portions of univariant lines [D] and [E]. Therefore, the stable divariant assemblage (B, C) must contain phases A, D and E.

We can complete our visualization of the

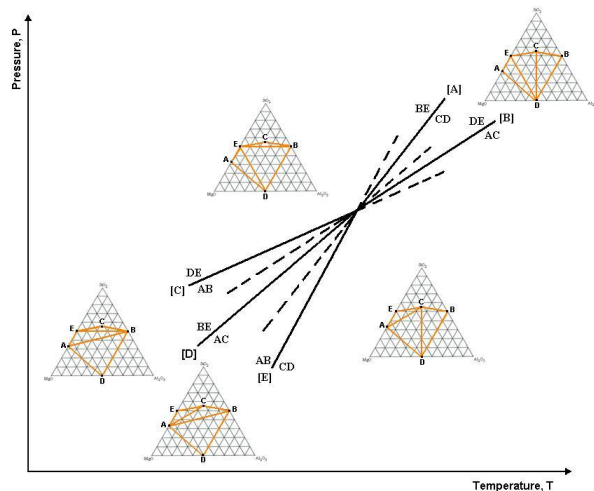


Figure 10: (Pentagonal Arrangement) Chemographs at each sector of the P-T diagram.

stable and metastable divariant assemblages everywhere around the invariant point by adding chemographs to each of the five sectors bounded by stable univariant reactions. On each of these

chemographs we draw a triangle for each stable divariant assemblage found in Figure 9. The result of this is Figure 10. Thus, for example, in the sector at high temperature and low pressure

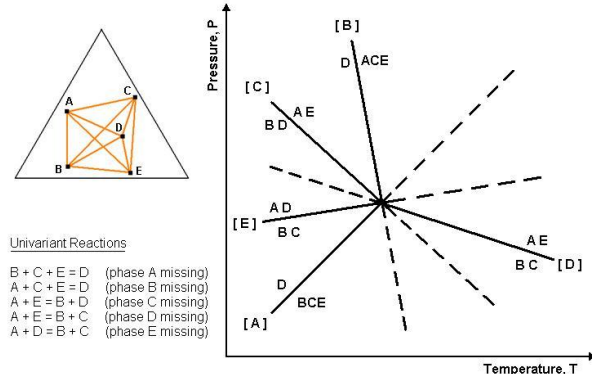


Figure 11: Fully-mapped P-T diagram for the quadrilateral arrangement of five phases.

(relative to the invariant point), there are three stable divariant assemblages (B, E), (A, E) and (B, D) since the sectors representing these stable assemblages extend across this sector of the P,T plot. This means that we expect that a rock equilibrated at such a (P,T) point will, depending on its bulk composition, contain either forsterite + cordierite + clinoenstatite, forsterite + cordierite + spinel, or cordierite + spinel + sillimanite. Under these (P,T) conditions, regardless of rock composition, we do not expect to find forsterite

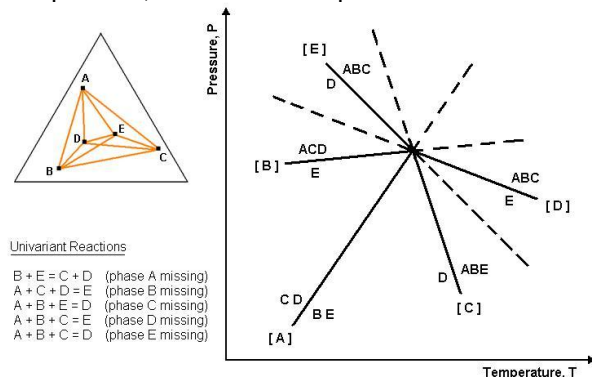


Figure 12: Fully-mapped P-T diagram for the triangular arrangement of five phases.

coexisting with sillimanite or clinoenstatite coexisting with spinel. Similar conclusions can be drawn for any region of (P,T) space by simply referring to the chemographs in Figure 10.

Arrangements 2 & 3: Quadrilateral and Triangular

We are now equipped with the necessary skills to analyze a ternary system whose chemography at the invariant point is governed by the quadrilateral or

triangular arrangement of the five phases. As in the treatment of the pentagonal case, we rely first on knowledge of the location of a certain univariant line from experimental data before proceeding on with the application of the half-plane rule for the construction of the remaining univariant lines on the P-T diagram. Using the 180° rule and the overlap rule, we can next proceed to identify the sectors bounded by the divariant assemblages.

Figures 11 and 12 show the fully-mapped P-T diagram of the quadrilateral case and the triangular case respectively; the construction of these is left as an exercise for the reader. Doing so requires an understanding of another form of univariant reaction, known as the terminal univariant reaction, in addition to the tie-line flip (or non-terminal univariant reaction) introduced earlier. Consider the univariant assemblage A, B, C and D (Figure 13) found in the chemograph of the triangular case in Figure 12 which represents the reaction $A+B+C=D$. This reaction is terminal since the stability field of phase D appears at the D side of the reaction and then disappears

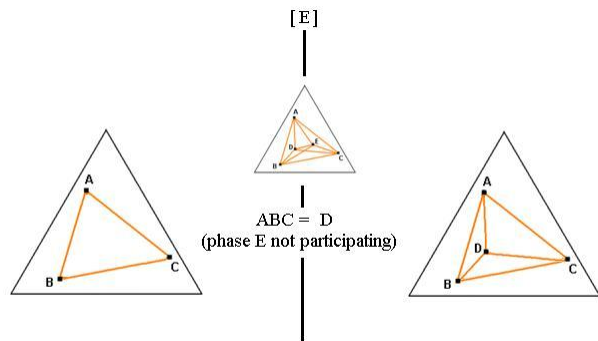


Figure 13: Terminal univariant reaction, $A + B + C = D$ (phase E).

at the ABC side. The univariant reactions for the quadrilateral and triangular cases can now be readily written to determine the kind of reaction for each of the five univariant lines in both cases before one proceeds to apply the method of Schreinemakers in the construction of the P-T diagram.

Conclusion

The fundamental axiom by F.A.H Schreinemakers results from the topology of intersection of Gibbs free-energy surfaces along a univariant line; it leads to important conclusions such as the 180° rule, overlap rule and half-plane rule all of which are collectively known as Schreinemakers rules. In this review, we have demonstrated the effectiveness of Schreinemakers rules in the

determination of the arrangement of univariant reactions about the invariant point and the construction of a fully mapped P-T diagram using one or more univariant lines obtained from experimental data. Schreinemakers rules are also useful in the analysis of the sectors spanned by all divariant assemblages. This allows one to determine the divariant assemblages which are stable (or metastable) at a given pressure and temperature by simply referring to the constructed P-T diagram. Apart from the pentagonal, quadrilateral, and triangular cases illustrated for a ternary non-degenerate system of five phases, Schreinemakers rules apply equally well and can yield insightful results for system containing degeneracies and any number of components, as is characteristic of real mineralogical systems. Even if the chemography exists in a space of too many dimensions to be drawn, linear algebra or trial and error allows one to determine the stoichiometry of the univariant reactions in a system of any number of components, and then knowing on which side of each reaction the phases appear, Schreinemakers rules can be applied just as we have demonstrated in the ternary system.

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