

Principles of phase diagrams

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From the thermodynamic basis for phase equilibria, various types of phase diagram are developed and their characteristics described. The following types of diagram are distinguished: state diagram, property diagram, potential phase diagram, molar phase diagram, and phase diagrams with a mixture of variables. Projections and sections of such diagrams are also examined. Finally, phase diagrams for constrained equilibria are discussed.

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INTRODUCTION

Phase diagrams were put on a scientific basis through Gibbs' thermodynamic treatment of heterogeneous equilibria.¹ Following Gibbs, many researchers examined the shape of phase diagrams in great detail, making extensive use of the Gibbs phase rule, and also of more sophisticated thermodynamic considerations. Bakhuis Roozeboom² and Schreinemakers³ deserve special mention. The basic principles of phase diagrams were thus well established by around 1910.

The extensive experimental work on phase equilibria in alloys, which started in the 1920s, resulted in a revived interest in phase diagrams and in definitions of some new rules for construction.⁴⁻⁶ Today it is again possible to see a revived interest in phase diagrams, caused particularly by the application of computer techniques to the calculation of phase diagrams. Such calculations are based upon thermodynamic principles and should automatically result in theoretically correct phase diagrams. One might think that this fact should decrease the need for a deeper understanding of phase diagrams. However, there are several reasons why this need is instead increasing:

- (i) in producing an efficient program for the calculation of phase diagrams, it may be helpful to apply a deep understanding of their topology
- (ii) the time taken to write a program and the time needed to run it in the calculation of a phase diagram may be decreased if one does not require the computer to do everything, but also relies upon some manual work
- (iii) the computer can produce new or unusual types of section or projection of phase

diagrams, which may require some deep understanding for a correct interpretation.

In view of such reasons, it may be justified again to review the principles of phase diagrams. Such a review will now be given, and an attempt will be made to make the discussion as general as possible. However, in the discussions of thermodynamics, only one kind of work will be considered, that against a hydrostatic pressure. Furthermore, all surface effects will be disregarded. Topological aspects will be discussed frequently. As a general reference to the application of topology to phase diagrams, a paper by Prince⁷ may be used.

STATE DIAGRAMS

From thermodynamics, the following expression for the change of the internal energy of a system from an initial state can be derived:

$$dU = T dS - P dV + \sum_i^c \mu_i dn_i - D d\xi \quad \dots \quad (1a)$$

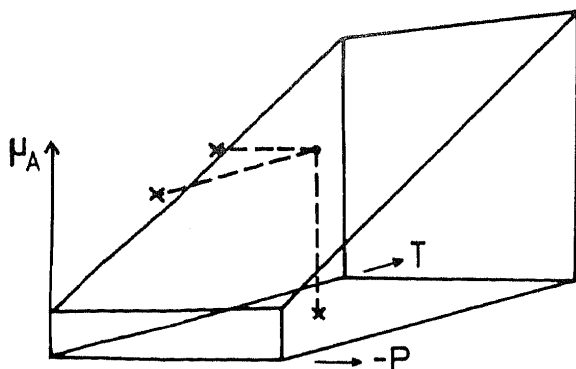
where i represents the different components and their number is denoted by c . D is the driving force for an irreversible, spontaneous reaction inside the system, and ξ measures the extent of such an internal reaction. In chemical literature, D is called affinity and is denoted by A .⁸ $D d\xi$ must be positive for a spontaneous reaction. When treating states of equilibrium and so-called reversible changes between such states, one omits the term $D d\xi$. On the right-hand side of equation (1a) there remain $c+2$ extensive variables (S, V, n_i) and $c+2$ intensive variables (T, P, μ_i). Of all these variables, $c+2$ are independent, and equation (1a) has been constructed after choosing all the extensive variables as independent. Equation (1a) can be written in a condensed form by denoting all the extensive variables by X^i and their conjugate intensive variables by Y^i . For convenience, $D d\xi$ is omitted from the summation. The condensed form is then:

$$dU = \sum Y^i dX^i - D d\xi \quad \dots \quad (1b)$$

It should be noticed that the intensive variable representing the pressure is $-P$ in this general scheme. As a consequence, $-P$ will be used in many of the diagrams to be presented below.

In the set of independent variables used in equation (1), each extensive variable can be exchanged for its conjugate intensive variable, and new thermodynamic functions are thus introduced – for instance, the Gibbs energy G , which is defined as $U - TS + PV$, from which:

$$dG = -S dT + V dP + \sum \mu_i dn_i - D d\xi \quad \dots \quad (2)$$



1 Property diagram for unary system with one phase; properties of this phase are represented by a surface

This new function also has $c+2$ independent variables, 2 intensive and c extensive ones, in addition to ξ .

It is well known that an attempt to replace all the extensive variables with their conjugate intensive variables does not result in a new thermodynamic function, but in a relation between the intensive variables:

$$0 = -S dT + V dP - \sum n_i d\mu_i - D d\xi \quad \dots (3a)$$

This relation gives a convenient method of examining whether a certain change could take place spontaneously, by studying whether $D d\xi$ is positive or not:

$$D d\xi = -S dT + V dP - \sum n_i d\mu_i \quad \dots (3b)$$

Suppose a system is at equilibrium with respect to all possible internal reactions. Then $D = 0$, and a variation of the potentials produced by actions from the outside must obey the following relation, known as the Gibbs-Duhem relation:

$$S dT - V dP + \sum n_i d\mu_i = 0 \quad \dots (4a)$$

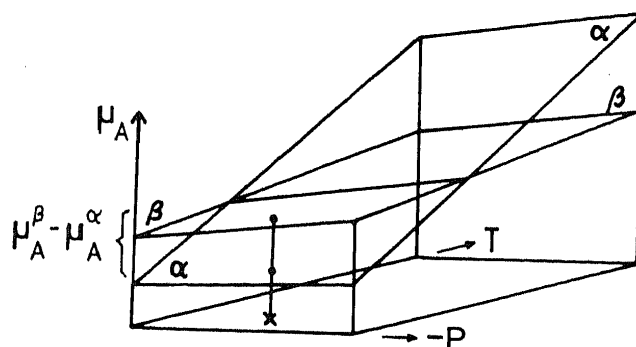
or, in the condensed form:

$$\sum X^i dY^i = 0 \quad \dots (4b)$$

The $c+2$ intensive variables are thus related, and only $c+1$ of them can be regarded as independent. This is a result of the fact that the value of an intensive variable is independent of the size of the system, and that the size cannot be defined by a set of values of intensive variables. It may thus be concluded that the state of a system is completely defined by giving the values of $c+2$ variables and requiring that at least one of them is extensive. One may, for instance, select $c+1$ intensive variables and the size of the system itself n , represented by the total number of atoms. The state is thus defined by giving a point in a $(c+2)$ -dimensional diagram. Such a diagram represents all the possible states, and may be called a *state diagram*. When discussing the properties of materials, one is usually not interested in the size of the system. The state is then sufficiently well described by $c+1$ intensive variables, and the state diagram can be constructed with $c+1$ axes.

PROPERTY DIAGRAMS

The set of $c+1$ axes can be selected from the $c+2$ intensive variables by omitting any one of them. It



2 Property diagram for unary system with two phases; $\mu_A^\beta - \mu_A^\alpha$ is driving force for $\beta \rightarrow \alpha$

may sometimes be useful to use a diagram with all $c+2$ intensive axes, whereupon the Gibbs-Duhem relation results in a surface (or hypersurface if $c > 1$) which represents the thermodynamic properties of the system. Such a diagram, with the surface included, may be regarded as a *property diagram*, and one for a unary system is illustrated in Fig. 1. From any point on the surface, a normal to any side of the diagram may be drawn. The projected point defines the state in terms of $c+1$ of the variables, and the side of the diagram, having $c+1$ axes, may be regarded as a state diagram. The position of the point on the normal gives the value of the omitted variable, i.e. the property. In the present discussion μ_A will always be omitted from the definition of the state, and μ_A is thus the property that will primarily be discussed. It is then convenient to rewrite the Gibbs-Duhem relation by moving the term $n_A d\mu_A$ to the left-hand side. By also dividing by n_A , the expression

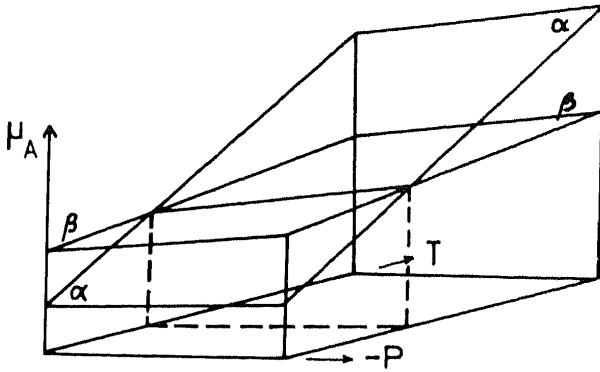
$$d\mu_A = -S_m dT + V_m dP - \sum_{i=1}^{c-1} x_i d\mu_i = - \sum_{i=1}^{c+1} X_m^i dY^i \quad \dots (5)$$

is obtained, where S_m , V_m , and x_i are all molar quantities, and are represented by the same notation X_m^i . They are here counted per mole of A rather than the usual mole of all components. By applying the fundamental equation (1) to a system with one mole of A atoms, it is possible to obtain, for reversible reactions, the expression

$$dU_m = T dS_m - P dV_m + \sum_{i=1}^{c-1} \mu_i dx_i = \sum_{i=1}^{c+1} Y^i dX_m^i \quad \dots (6)$$

since $x_A = 1$ and $dx_A = 0$. Component A is thus omitted from the summation in equation (6) as well as that in equation (5). Both equations have $c+1$ independent variables. In order to distinguish between the independent variables used in equation (5) and those used in equation (6), which are all intensive quantities, the former ones will be called 'potentials' and the latter ones 'molar quantities', a designation reminiscent of their close relation to extensive quantities.

With given values for the set of $c+1$ independent variables, it is possible to consider more than one possible atomic arrangement, in this context called 'phase'. Such a case, for a unary system where the surfaces, representing the properties of two such phases, intersect is illustrated in Fig. 2. If the values



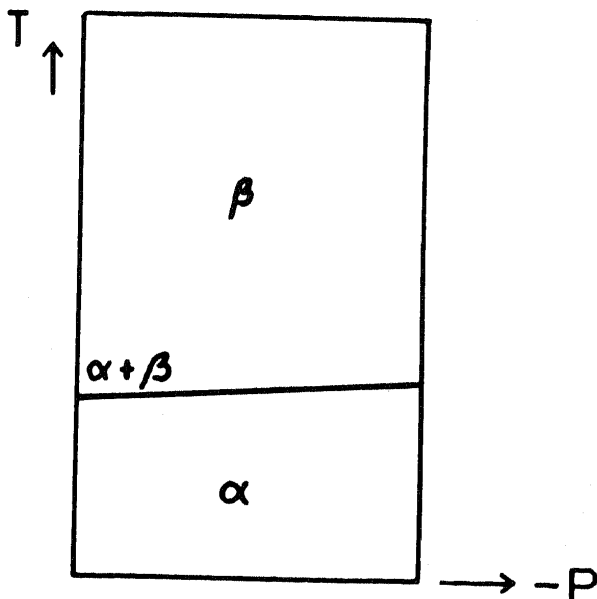
3 Construction of a phase diagram by projecting a property diagram; two phases can exist at line of intersection of their property surfaces

of $c+1$ independent variables, in this case T and $-P$, are fixed experimentally, the value of μ_A may be lower for the α -phase than for the β -phase. Equation (3) would then indicate that $D d\xi$ is positive for a change from β to α , and α would thus be the stable phase. Integrating over this change in the property diagram gives:

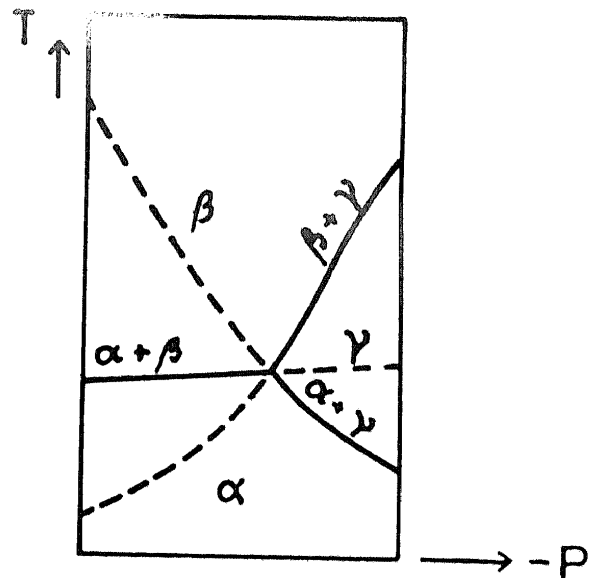
$$\int D d\xi / n_A = \mu_A^\beta - \mu_A^\alpha > 0 \quad \dots \dots \dots (7)$$

PHASE DIAGRAMS

It is only along the line of intersection of their property surfaces that the two phases α and β in Fig. 2 can exist together without a driving force for transformation from one to the other. The projection of this line on the side of the diagram, i.e. the state diagram, will separate two regions, where one phase or the other is stable (Fig. 3). A state diagram with such lines is called a *phase diagram* (Fig. 4). The two regions may be called one-phase fields, and the line may be called a two-phase field if the definition of the word field is generalized to mean a geometrical element of any dimensionality. It is evident that the



4 Simple phase diagram obtained by construction shown in Fig. 3



5 Unary phase diagram with three phases; broken lines are metastable extrapolations of two-phase equilibria

phase diagram may be regarded as the projection of a property diagram on a state diagram.

In German a phase diagram is often called state diagram (Zustandsdiagramm), but here 'state diagram' will be reserved to mean the coordinate system in which the phase diagram is plotted.

It is easy to see that the surface representing the properties of a third phase may intersect with the previous surfaces in the property diagram, and in the phase diagram one may obtain a point where all three phases can co-exist in equilibrium, a three-phase field (Fig. 5). The dashed lines represent metastable extrapolations of the two-phase fields, representing equilibrium states if the third phase is absent for some reason. It is evident that such extrapolations go into the one-phase field for the new phase. It is also evident that all angles between stable lines must be less than 180° .

Since the phase diagram is obtained simply by adding some new information to the state diagram, it also has $c+1$ axes, and it is evident that the dimensionality of the one-phase fields, i.e. the variance of the one-phase equilibria, is the same. It is easy to see that the variance of higher-order phase equilibria decreases by one unit for each additional phase, i.e.

$$v = c + 2 - p \quad \dots \dots \dots (8)$$

This is the Gibbs phase rule, in which c is the number of components and p is the number of phases. The variance v is often called the number of degrees of freedom. The rule is based upon the fact that the Gibbs-Duhem relation can be applied to each phase. Since all the independent variables in the Gibbs-Duhem relation are intensive, the Gibbs phase rule can be applied most easily to phase diagrams plotted with the intensive variables T , $-P$, and μ_i on the axes. Other types of phase diagram will be discussed below, and the present type will be called *potential phase diagrams*, because the intensive variables T , $-P$, and μ_i may be regarded as potentials. This word implies

that they must have the same value in all parts of a system at equilibrium.

POTENTIAL PHASE DIAGRAMS PROPERTIES OF POTENTIAL PHASE DIAGRAMS

The topology of potential phase diagrams is very simple. It has been illustrated in Fig. 5 for the simple case of a unary system, and it is easy to include new phases. The important thing to realize is that it is extremely unlikely that there will be an additional phase in the unary system which has such properties that its surface in the property diagram would go through the point of intersection of the three previous phases. This possibility will be completely neglected, and this is in agreement with the Gibbs phase rule, which predicts a variance of -1 for the case of four phases in a unary system. Even the most complicated phase diagram for a unary system is thus composed of surfaces representing divariant one-phase fields, lines representing monovariant two-phase fields, and points representing invariant three-phase fields. Such a diagram is built from a combination of elementary units such as the one shown in Fig. 5. In this respect, it is closely related to the two-dimensional arrangement of grains in a polycrystalline, single-phase sheet material. Smith⁹ has discussed the topology of a two-dimensional array of grains, and his conclusions also hold for a two-dimensional potential phase diagram. The following derivation is taken from his discussion; it will be modified below when treating different cases.

Euler has given the following topological rule for a network of lines on a closed surface, such as the surface of a sphere:

$$\mathcal{C} - \mathcal{E} + \mathcal{P} = 2 \quad (9)$$

\mathcal{P} is the number of polygons formed by the lines, i.e. one-phase fields or grains; \mathcal{E} is the number of lines, i.e. edges of the polygons, which may represent two-phase fields or grain boundaries; and \mathcal{C} is the number of points of intersection, which may represent three-phase fields or grain corners. Since each edge is shared by two polygons:

$$2\mathcal{E} = \sum n\mathcal{P}_n \quad (10)$$

where \mathcal{P}_n is the number of polygons with n edges, or corners. For the network of lines now under consideration, three polygons meet at each corner, giving the expression:

$$3\mathcal{C} = \sum n\mathcal{P}_n \quad (11)$$

Inserting these expressions and $\mathcal{P} = \sum \mathcal{P}_n$ into equation (9) gives:

$$\sum (6-n)\mathcal{P}_n = 12 \quad (12a)$$

When applying Euler's rule to a planar network of lines, Smith⁹ obtained a value of 6, rather than 12, because he chose not to regard the space outside a closed network as a polygon.

The average number of edges per polygon \bar{n} is obtained as:

$$\bar{n} = n\mathcal{P}_n / \sum \mathcal{P}_n = 6 - 12 / \sum \mathcal{P}_n \quad (12b)$$

and for a network of many polygons, the average number approaches 6.

It is always necessary to limit the consideration of a phase diagram or an array of grains to a certain region, and one usually selects a rectangular frame. The four corners of the frame will be considered to be corners where two edges meet. The left-hand side of equation (11) is then changed to $3\mathcal{C} - 4$ and the right-hand side of equation (12a) to 4. Suppose there are m intersections between lines, representing two-phase fields or grain boundaries, and the sides of the frame. The surrounding space is then a polygon with $m+4$ edges. By omitting that polygon from the summation, the expression

$$\sum' (6-n)\mathcal{P}_n = m+2 \quad (13)$$

which may be more convenient to use, is obtained.

In addition to the topological conditions, there is an important geometrical condition which must be obeyed. For a grain structure, the balance of surface tensions requires that each of the angles formed at a corner must be less than 180° . This implies that the extrapolation of a boundary between two grains must fall inside the third grain. As already mentioned, this rule also holds for phase boundaries, and is illustrated in Fig. 5. It is often referred to as the 180° rule, but of course, the physical reason for its existence is quite different.

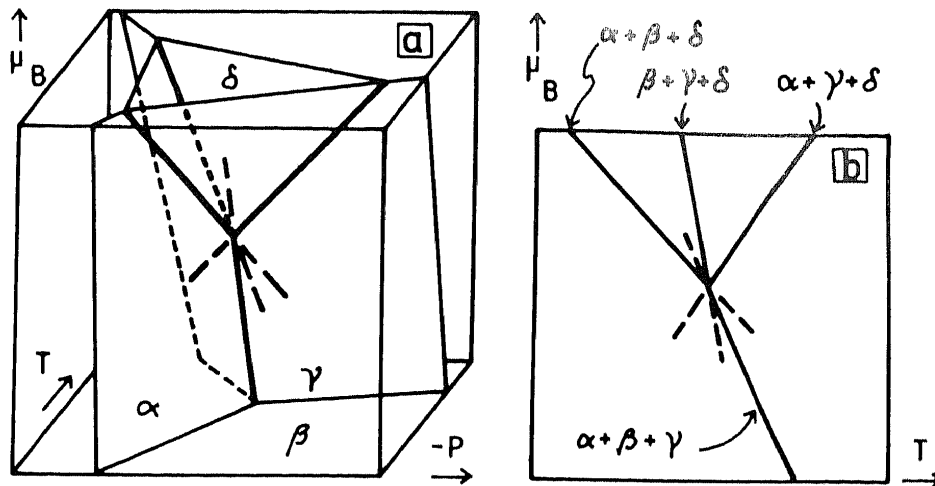
POTENTIAL DIAGRAMS IN HIGHER-ORDER SYSTEMS

The three-dimensional potential phase diagram of a binary system will now be considered, again choosing μ_A as the dependent potential. In view of equation (8), the variance of the three types of phase equilibria, already discussed, will increase by one unit, and a four-phase equilibrium will appear as a point (Fig. 6a). Again, the remote possibility that an additional, fifth phase has such properties that it can take part in the phase equilibrium which is already invariant will be neglected. A complicated binary phase diagram is thus simply composed of elementary units of the type shown in Fig. 6a. This is the same unit from which the three-dimensional arrangement of grains in a polycrystalline, single-phase material is constructed. Smith⁹ has discussed the topology of such arrays of grains, and most of his conclusions are valid for potential phase diagrams. In such cases, the Euler rule is modified by the number of polyhedral bodies \mathcal{B} :

$$\mathcal{C} - \mathcal{E} + \mathcal{P} - \mathcal{B} = 0 \quad (14)$$

It is not possible to derive an expression similar to equation (12a) in terms of \mathcal{B} from which the average number of sides (neighbours) can be calculated. It has been shown that it is 14 for each grain in a special regular arrangement of grains; however, in the actual cases found in nature, the arrangement is less regular, and the average number of sides is less than 14. It is most probable that the same will hold for the one-phase fields in phase diagrams.

Each of the sides of a one-phase field in a three-dimensional diagram is a polygon, and Euler's rule can be applied to the two-dimensional network covering the surface of a one-phase field. For a one-phase



a diagram with three potential axes; one-phase fields meet two and two at surfaces, three and three at lines, and all four at a point; extrapolation of each three-phase line goes into one-phase field of fourth phase; b projected diagram; extrapolations are arranged so as to reveal directions of two-phase surfaces

6 Binary phase diagram with four phases; compare Fig. 18

field with 14 sides, equation (12a) yields:

$$14(6 - \bar{n}) = 12$$

$$\Rightarrow \bar{n} = 5\frac{1}{7}$$

For a one-phase field with 12 sides, an average of exactly five corners is obtained for the polygonal sides. Studies of actual grain structures in nature have shown not only that the average is close to five, but that polygons with five sides are most common.

The 180° rule in two-dimensional grain structures and potential phase diagrams has its equivalent in three dimensions. It is illustrated by the extrapolated lines in Fig. 6a, and states that the extrapolation of a line of intersection between three grains or one-phase fields falls within a fourth grain or one-phase field. This implies that in a two-dimensional projection, such as Fig. 6b, all angles must be less than 180°.

In the general case, the elementary unit can be described by the number of various geometrical elements which intersect. The type of geometrical element can be defined by giving the number of phases in equilibrium p , or the variance obtained from equation (8). Each element of variance v_b can be regarded as the intersection between a number of elements of variance v_a , where $v_b < v_a$. This number n can be evaluated from the expression

$$n = \binom{p_b}{p_a} \left[\frac{p_b!}{p_a!(p_b - p_a)!} \right] = \binom{c+2-v_b}{c+2-v_a} \quad (15)$$

This relation is here given without proof. Its validity can be tested by application to various cases. As an example, it is possible to calculate the number of surfaces $v_a = 2$ that meet at the point $v_b = 0$ in the binary diagram in Fig. 6a:

$$n = \binom{2+2-0}{2+2-2} = \binom{4}{2} = 6$$

The number of volumes that meet at surfaces in a ternary system is obtained as:

$$n = \binom{3+2-1}{3+2-3} = \binom{4}{2} = 6$$

PROJECTIONS OF POTENTIAL PHASE DIAGRAMS

In order to show a three-dimensional phase diagram in two dimensions, one may use projections. Figure 6b is the projection of the phase diagram in Fig. 6a on the $T-\mu_B$ plane. One can still see and distinguish the various points and lines, but the one-phase volumes are reduced by one dimension and overlap with the projected two-phase surfaces.

Equilibria with more than four phases can appear in systems with more than two components, and the complete phase diagram of such a system will have more than three axes. As a consequence, such a phase diagram can only be visualized by projection, and in order to obtain a two-dimensional picture, one must project at least twice. In any case, such a two-dimensional picture will also show points and lines for the two highest-order phase equilibria. All other phase fields in this picture are two-dimensional, and many may overlap one another.

In order to adapt the Gibbs phase rule to projections of phase diagrams, it is necessary to introduce the number of projections N_{pr} . The number of axes R in the final diagram is equal to $c+1 - N_{pr}$, and one obtains, from equation (8):

$$v = R + N_{pr} + 1 - p; \quad p \geq 1 + N_{pr} \quad \dots \quad (16)$$

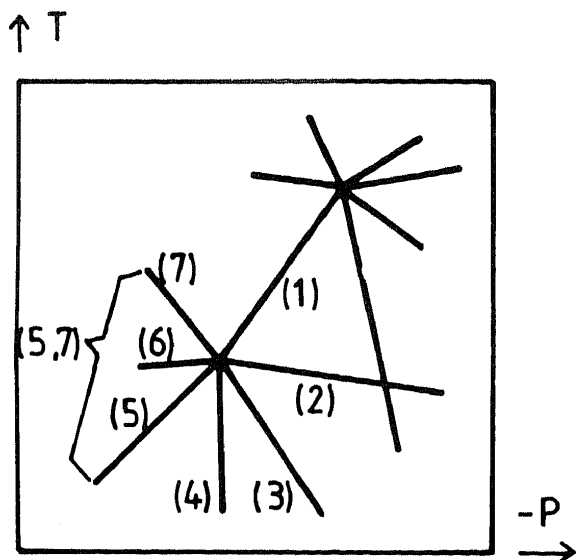
$$v = R; \quad p \leq 1 + N_{pr} \quad \dots \quad (17)$$

Phase fields with $p < 1 + N_{pr}$ will thus overlap phase fields with $p = 1 + N_{pr}$, and cannot easily be shown in the diagram.

In a quinary system, each point is the intersection of lines to a number of

$$n = \binom{5+2-0}{5+2-1} = \binom{7}{6} = 7$$

The point represents an invariant equilibrium between seven phases and the lines represent equilibria between six phases. It is self-evident that one can form seven such equilibria by omitting each one of the seven phases. A two-dimensional projection of



7 Projection of quinary phase diagram obtained by projecting in directions of chemical potentials of four components. Two invariant, seven-phase equilibria are shown. For one, phases are numbered 1–7, and adjoining six-phase lines are identified by omitted phase in parentheses; five-phase surface extending between lines (5) and (7) is identified by the two omitted phases in parentheses

such a phase diagram is shown in Fig. 7. It is obtained by projecting the complete phase diagram four times in the directions of the chemical potentials of all components except one. Of course, all seven linear phase fields belonging to each invariant equilibrium can be seen. Following a procedure used by Schreinemakers, each of the linear phase fields radiating from a point is here identified by giving, in parentheses, the omitted phase.

In Fig. 7, line (2) intersects a line radiating from another invariant equilibrium. It must be realized that this point of intersection does not represent an invariant phase equilibrium; in a three-dimensional projection, one would see that the two lines pass each other on different levels. In the complete potential phase diagram, all the geometrical elements discussed represent phase fields of various types. It is important to notice that, on projection, geometrical elements that are not phase fields may be formed; this point of intersection is an example.

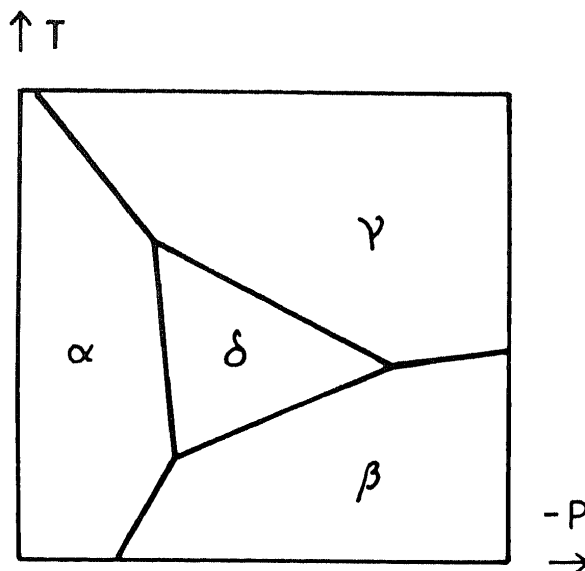
Each invariant point in a quinary system is also the intersection of surfaces to a number of

$$n = \binom{5+2-0}{5+2-2} = \binom{7}{5} = 21$$

Such a surface represents an equilibrium between five phases and extends between two of the six-phase lines in a manner similar to the two-phase surfaces in Fig. 6a. The five phases are those that are common to the two lines. The five-phase equilibria can thus be identified by giving, in parentheses, the two omitted phases. The five-phase equilibrium between phases 1, 2, 3, 4, and 6 is thus marked as (5, 7) in Fig. 7.

SECTIONS OF POTENTIAL DIAGRAMS

Another way to present the phase diagram of a higher-order system is to make sections at constant



8 Section of potential phase diagram in Fig. 6a at constant μ_B ; in general, the four-phase equilibrium will not appear in a section

values of some of the potentials. As an example, a section of Fig. 6a at a constant value of μ_B is shown in Fig. 8.

The Gibbs phase rule can be modified to apply to equipotential sections simply by subtracting the number of sectionings N_s . Since the number of axes R in the final phase diagram is now equal to $c+1-N_s$, suitable modification of equation (8) gives:

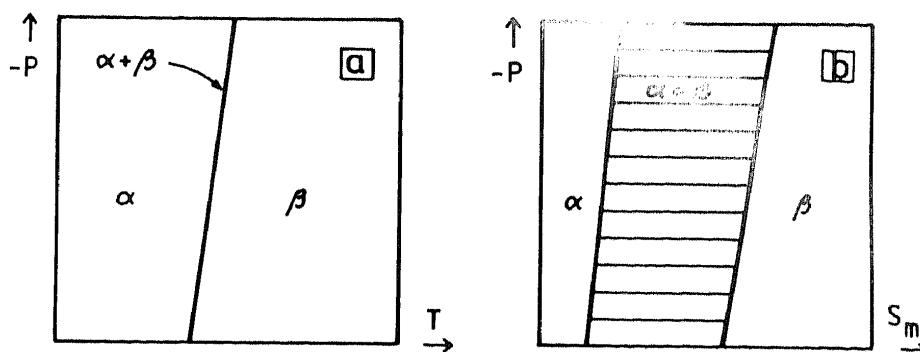
$$v = c + 2 - p - N_s = R + 1 - p \quad \dots \dots \dots (18)$$

According to this equation, the invariant equilibrium in the complete phase diagram would have a variance of -1 after one sectioning and should not show up in the section. It could be objected that the section in Fig. 8 could have been placed exactly through the four-phase point in Fig. 6a; however, this possibility will be neglected for the same reason put forward in neglecting the remote possibility of having an additional phase in equilibrium with phases which already form an invariant equilibrium. The argument that it will never be possible in practice to choose exactly the right value to intersect a point may be used in this context. (When discussing sections that go exactly through the point representing an invariant equilibrium, Palatnik and Landau⁶ call them irregular sections.)

It is evident from Fig. 8 that a diagram obtained by one sectioning has the same topology as a diagram for a system with one component less. This observation can be generalized in the light of equation (18), and it may be concluded that the topology of a diagram obtained with or without sectionings depends only upon the final number of axes R .

The topology of a diagram may be discussed in terms of the number of various elements which intersect. By inserting p from equation (18) into equation (15), the more general form

$$n = \binom{p_b}{p_a} = \binom{R - v_b + 1}{R - v_a + 1} \quad \dots \dots \dots (19)$$



9 Appearance of two-phase field between two one-phase fields in unary system, when a molar quantity is introduced instead of its conjugate potential

is obtained, where v_a and v_b are now the variances of the geometrical elements in the final phase diagram.

It is important to notice that the topology of an equipotential section is the same whether T or $-P$ or a chemical potential μ_i is kept constant. From a mathematical point of view, all potentials are equivalent.

It is sometimes convenient to reduce the number of axes in a phase diagram by first sectioning and then projecting. Equations (16) and (17) also apply to such cases, but equation (19) does not.

MOLAR PHASE DIAGRAMS

What happens if the potentials in a phase diagram are replaced by their conjugate molar quantities will now be examined. It should first be noticed that the two variables in a conjugate pair both increase or both decrease if one moves through a stable one-phase field at constant values of all the other molar quantities. As a consequence, the one-phase fields have the same general shape in a molar diagram as in a potential diagram. However, phases in equilibrium with each other will no longer fall on the same point, but will be separated by a distance equal to the difference in their molar quantity. It is common to connect such points by tie lines, as illustrated in Fig. 9.

It may seem self-evident that the one-phase fields will separate from each other, thus leaving room for the two-phase field with its tie lines, when a molar quantity is introduced as an axis instead of its conjugate potential. This can be proven by applying the Gibbs-Duhem relation in the form given by equation (5). Consider first two phases which are initially in equilibrium with each other. The system is then moved from equilibrium by changing the value of one potential Y^j , keeping the other potentials in the summation constant. Applying equation (5) to each of the two phases and taking the difference gives:

$$(X_m^{j\beta} - X_m^{j\alpha}) dY^j = d(\mu_A^\alpha - \mu_A^\beta) \quad (20)$$

Suppose β is the phase favoured by an increased Y^j value. Applying equation (7) to the case where β becomes stable for positive dY^j gives:

$$X_m^{j\beta} - X_m^{j\alpha} = \frac{d(\mu_A^\alpha - \mu_A^\beta)}{dY^j} > 0 \quad (21)$$

It is self-evident that the two one-phase fields will move apart by a distance $X_m^{j\beta} - X_m^{j\alpha}$ when X_m^j is intro-

duced as an axis instead of Y^j . Since $X_m^{j\beta}$ is larger than $X_m^{j\alpha}$ according to equation (21), it can be seen that the one-phase fields will actually separate and leave room for the two-phase field in between, $X_m^{j\beta} - X_m^{j\alpha}$ being the length of the tie line. As an example, Fig. 9 shows the effect of introducing S_m instead of T in a unary system. The pressure axis is shown in the diagrams, but the pressure is kept constant during the change; thus, all the tie lines are horizontal.

A similar diagram would apply when the molar content x_B is introduced instead of μ_B in a multicomponent system. To show the result in a two-dimensional diagram, one may use a section at constant values of T , μ_C , μ_D , etc. The length of the tie lines will be $x_B^\beta - x_B^\alpha$, and that length will be a positive quantity. However, it is important to notice from equation (5) that x_B is here defined as n_B/n_A . When the ordinary mole fraction is used, it may happen that the tie lines have a negative length, whereupon the two one-phase fields will overlap in a thin region. The same may happen for other molar quantities if they are not defined in the proper way, i.e. by dividing the extensive quantity with n_A .

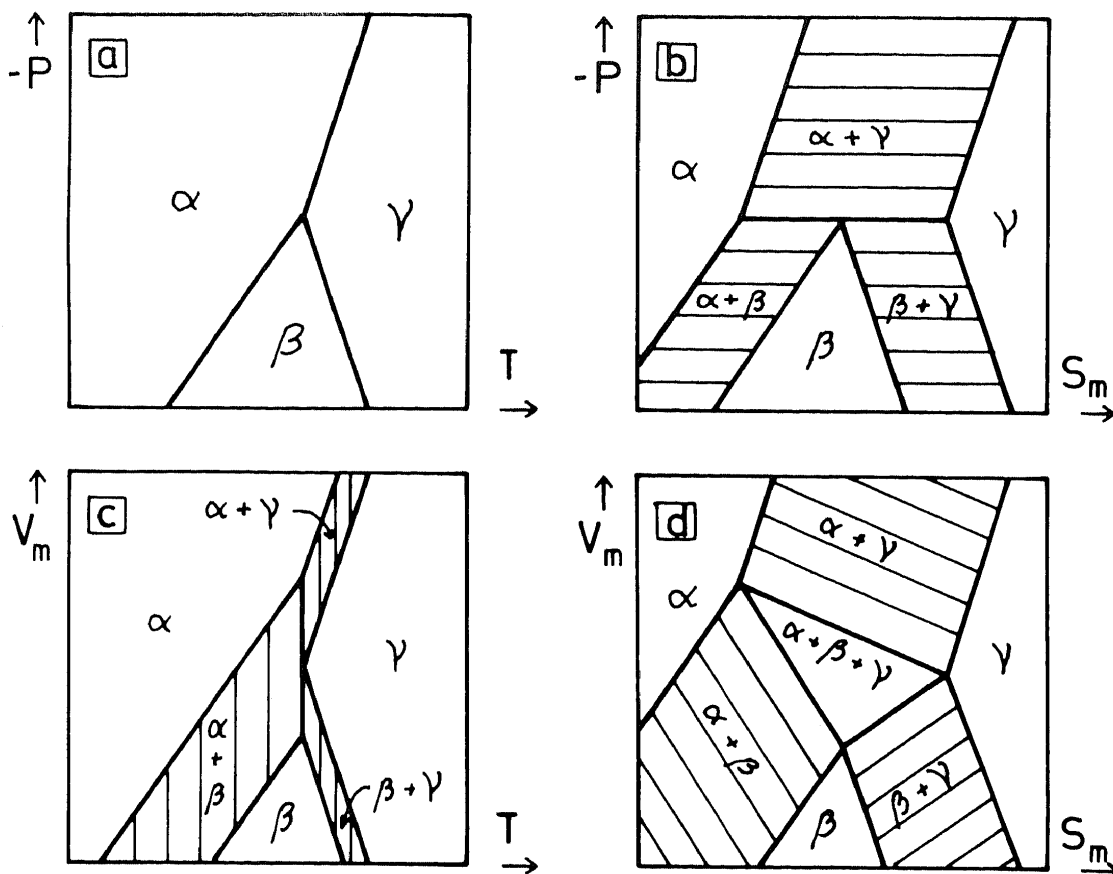
The manner in which a unary phase diagram with an invariant phase equilibrium changes when two molar quantities are introduced is shown in Fig. 10. It can be seen that the variance of each phase field increases by one unit for each molar quantity being introduced, until it is equal to the number of axes in the phase diagram. Thus, the number of molar quantities which are used as axes in the final diagram N_{ma} , and also the number of molar quantities which have been kept constant during sectioning N_{ms} , should be added to equations (16) and (17). On the other hand, the number of molar quantities in the direction of which a projection has been made should not be added, because in this case it makes no difference whether the potential or the molar quantity is used. Equations (16) and (17) are thus modified as follows:

$$v = R + N_{pr} + N_{ma} + N_{ms} + 1 - p;$$

$$p \geq 1 + N_{pr} + N_{ma} + N_{ms} \quad (22)$$

$$v = R; \quad p \leq 1 + N_{pr} + N_{ma} + N_{ms} \quad (23)$$

The length of tie lines has already been calculated above. It is also relevant to discuss their shape. If their whole purpose were to connect two points, they could be given any shape, but they are always drawn as straight lines. This is not trivial, as will now be shown.



10 Increase of variance of phase fields by one unit for each molar quantity, until variance is equal to number of axes

A point in a two-phase field in a molar diagram represents a mixture of the two phases. If f^α and f^β are the fractions of α and β , defined as n^α/n and n^β/n , the molar volume of the mixture is given by:

$$V_m = \frac{V}{n} = \frac{V^\alpha + V^\beta}{n} = \frac{V^\alpha}{n} \frac{n^\alpha}{n} + \frac{V^\beta}{n} \frac{n^\beta}{n} \\ = f^\alpha V_m^\alpha + f^\beta V_m^\beta \quad \dots \quad (24)$$

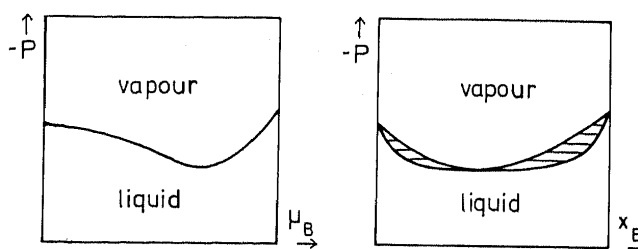
Similarly:

$$S_m = f^\alpha S_m^\alpha + f^\beta S_m^\beta \quad \dots \quad (25)$$

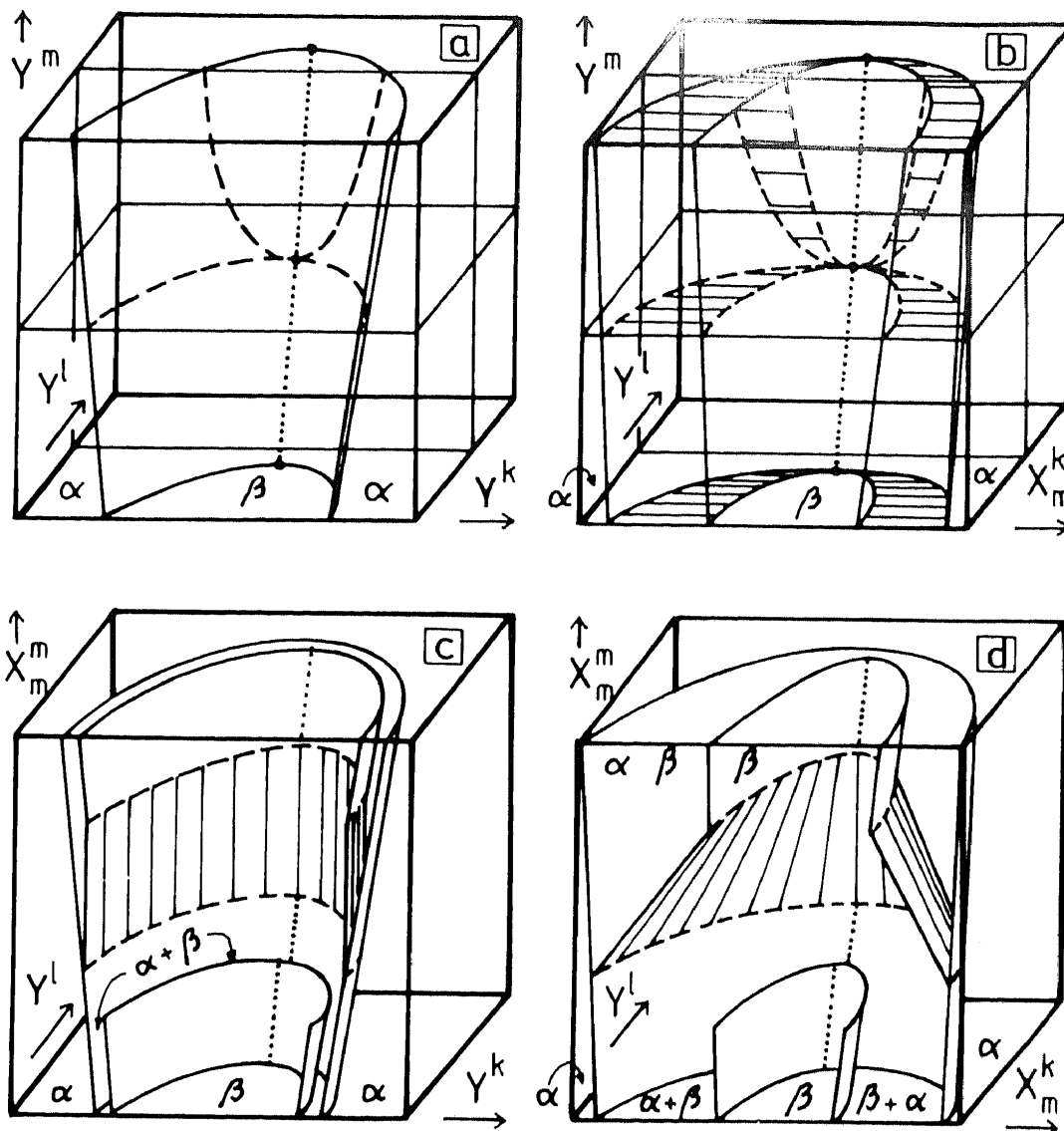
It follows that the mixture falls on the straight line between the points representing the individual phases. By making the tie lines straight, it is thus possible to make any point on a tie line representative of a mixture of the two phases represented by its end points; the fractions of the two phases can be evaluated from the position of the point relative to the end points, this relationship usually being expressed in terms of the so-called lever rule. Of course, this conclusion is valid only if all the molar quantities have been defined in the same way, i.e. with the same definition of n . This is ascertained if all the molar quantities are defined through equation (5), which is obtained by dividing equation (4) by n . One may choose n as the total number of atoms, as the number of A atoms, or in many other ways. It should be emphasized that this derivation of the lever rule applies to molar diagrams of any number of dimensions. It also applies to property diagrams with molar quantities on the axes.

POINTS OF EXTREMUM FOR TWO-PHASE EQUILIBRIA

The rule that two one-phase fields are separated from each other by a positive distance, when the proper molar quantity is used, is not as trivial as it may appear. It was discovered experimentally by Konovalov¹⁰ when measuring the vapour pressure of liquid solutions of water and various organic substances. In addition, he found two cases with a pressure maximum and realized that the liquid and vapour must have the same composition at such a point. A case of this type is shown in Fig. 11, and it is evident that it is simply due to the fact that the molar quantity which is used x_B replaces a potential whose axis happens to be parallel to a tangent to the linear two-phase field in the potential diagram. Other than that, the system has no unique properties at that point.



11 Isothermal section of phase diagram for binary system, showing a point of maximum pressure; at that point, the two phases must have the same value of x_B



a a three-dimensional potential phase diagram; points of tangency for lines parallel to Y^k -axis are marked with dotted line; *b* as *a*, but with Y^k replaced by its conjugate molar quantity X_m^k ; phases still coincide along dotted line; *c*, *d* as *a* and *b*, respectively, but with Y^m replaced by its conjugate molar quantity X_m^m ; phases along dotted line have separated, but still fall on same value of X_m^k in *d*

12 Effect of replacing potentials by their conjugate molar quantities in three-dimensional phase diagram with curved two-phase surface in potential diagram

Its importance stems simply from the fact that composition is often used as an experimental parameter. For this reason, such a point is often given a special name, azeotropic or congruent point, because a system undergoes an azeotropic or congruent transformation on passing through it.

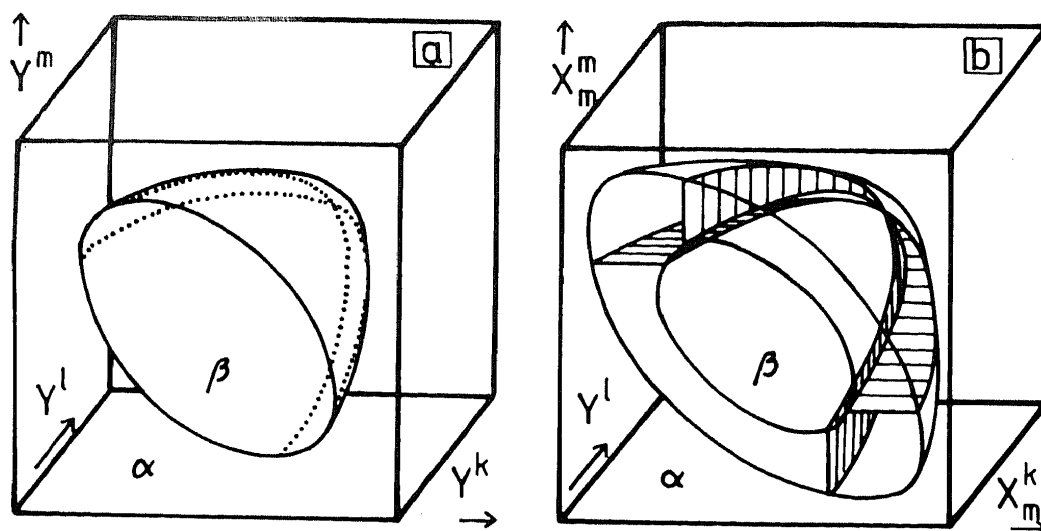
It is evident that the Konovalov rule does not only apply to composition. It may be generalized as follows: suppose that a linear two-phase field in a Y^k - Y^l diagram, determined at constant values of all the other potentials except μ_A , shows a Y^l maximum or minimum; at the point of extremum, the two phases must have the same value of X_m^k .

A third potential Y^m will now be added to the consideration. A possible shape of a curved two-phase surface in the three-dimensional potential phase diagram is shown in Fig. 12*a*. Points of tangency for tangents parallel to the Y^k -axis are marked with a dotted line. Any such point represents an extremum

value in sections parallel to the Y^k -axis. This is demonstrated in a horizontal section. The same equilibrium after introducing X_m^k instead of Y^k is shown in Fig. 12*b*. The one-phase fields are now separated, except at the points of tangency. At each such point the two phases have the same value of X_m^k , in agreement with the generalized Konovalov rule.

In Fig. 12*a* there is also a vertical section, and again the point of tangency represents an extremum value. This is a geometrical consequence, but it is also a necessary consequence of the generalized Konovalov rule. If two phases in equilibrium have the same value of X_m^k , the two-phase equilibrium must give an extremum for all other potentials. The vertical section in Fig. 12*b* looks just like the horizontal section.

The effect of introducing a molar quantity on another axis is shown in Figs. 12*c* and *d*. The two



a three-dimensional potential phase diagram; dotted lines represent points of tangency for lines parallel to Y^k and Y^m axes; point of tangency for vertical Y^k - Y^m plane is at intersection of these lines, and is a maximum for Y^l ; b as a, but with Y^k and Y^m replaced by their conjugate molar quantities X_m^k and X_m^m ; vertical and horizontal lines are tie lines corresponding to points of tangency in a; α and β have same values of X_m^k and X_m^m at point of tangency of X_m^k - X_m^m plane

13 Effect of replacing potentials by their conjugate molar quantities in three-dimensional phase diagram with curved two-phase surface in potential diagram

phases at the points of extremum will separate, but will still have the same X_m^k value.

A case where there is a point of tangency for a plane parallel to the Y^k - Y^m plane is shown in Fig. 13a. That point represents an extremum value for the potential on the third axis, Y^l . As demonstrated in Fig. 13b, the two phases must have the same value of X_m^k , as well as X_m^m , at that point. This diagram could, for instance, apply to the equilibrium between a ternary intermetallic phase and a melt at constant pressure. Y^l would then be the temperature and X_m^k and X_m^m the mole fractions x_B and x_C . At the point of extremum, the two phases would have the same values of x_B and x_C ; they thus have the same composition, meaning that the extremum point is a congruent transformation point.

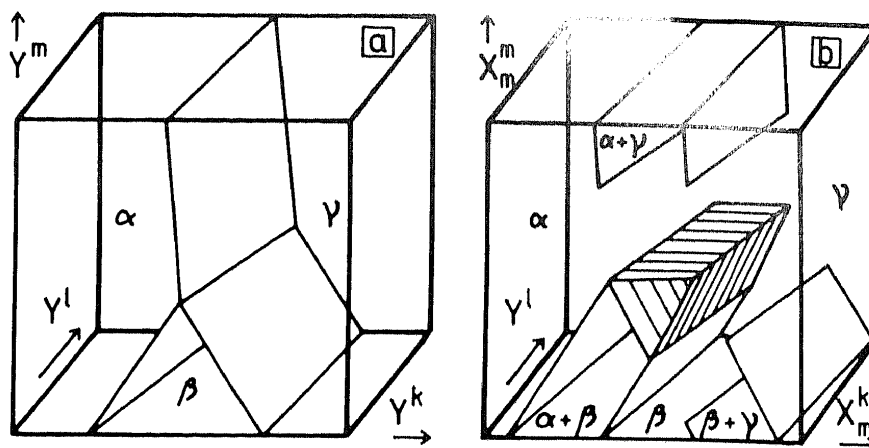
The Konovalov rule may thus be generalized further. Suppose a two-phase field in an n -dimensional potential diagram shows an extremum in one of the potentials. At the point of extremum, the two phases have the same value for all the molar quantities, conjugate to the remaining potentials in the diagram. If these molar quantities define the composition completely, the point of extremum is a congruent transformation point. Furthermore, consider any other potential in addition to the n potentials included in the diagram. This potential has been kept at a constant value in the diagram. If one attempted to vary such a potential, yet still retaining the two phases in equilibrium, one would find that the additional potential also has an extremum. Its extremum value is equal to the previous constant value if the potential that primarily showed an extremum is now kept constant at the value of that extremum.

POINTS OF EXTREMUM FOR HIGHER-ORDER EQUILIBRIA

A linear three-phase field in a three-dimensional potential diagram (Fig. 14a) will now be considered.

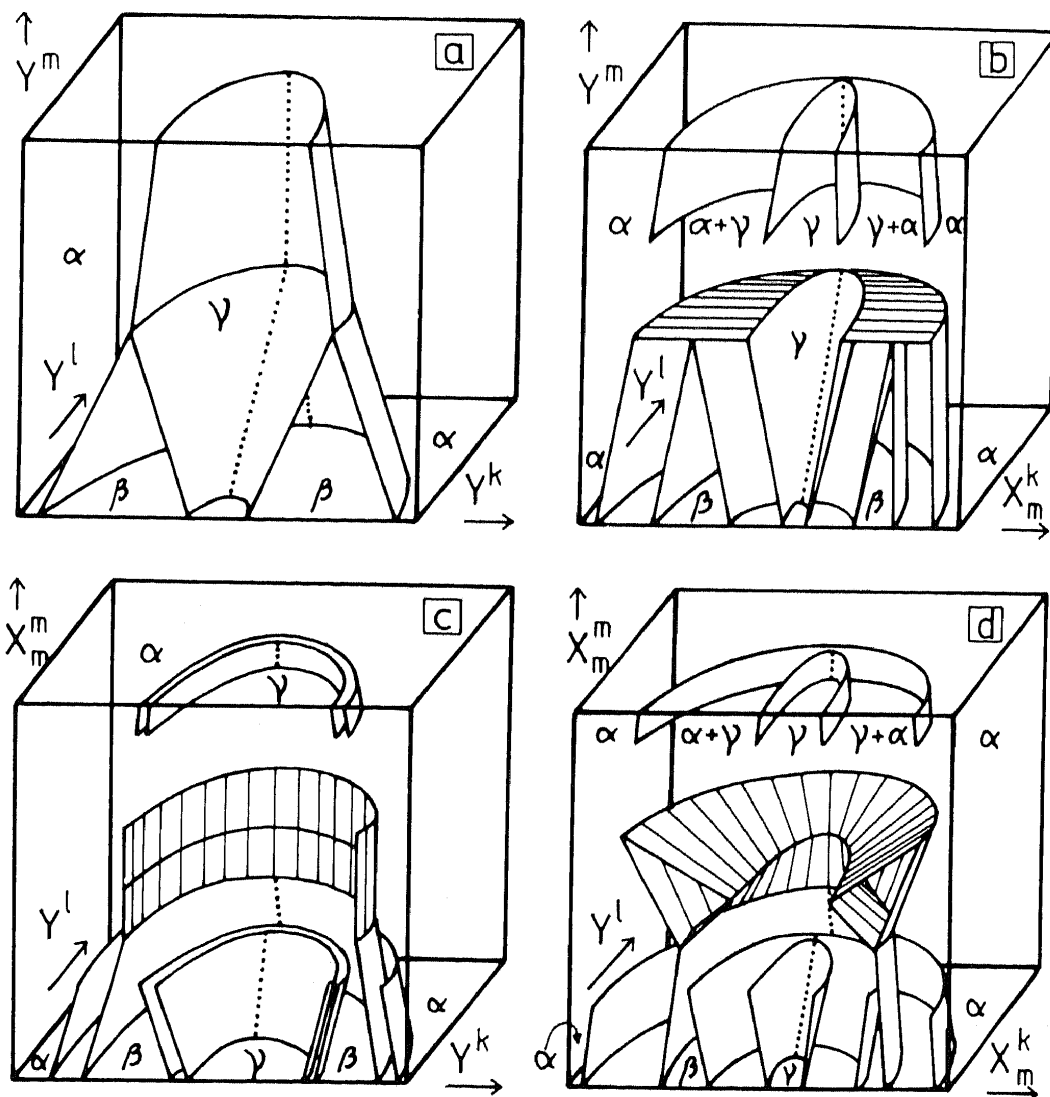
The result of introducing two molar quantities is illustrated in Fig. 14b. In order to show the three-phase field better, parts of two two-phase fields have been removed. Consider next the case where the three-phase line in the potential diagram is curved and has a maximum in one of the potentials Y^l . For the sake of simplicity, it will be assumed that the tangent to the three-phase line at the point of maximum Y^l is parallel to the Y^k -axis (Fig. 15a). The diagram is modified as shown in Fig. 15b when X_m^k is introduced instead of Y^k . It is evident that the three phases in equilibrium have the same X_m^k value at the maximum point, but fall on a straight line in all other cases. It is shown in Fig. 15c how the original diagram is modified when another molar quantity X_m^m is introduced instead of Y^m . In this case, the three phases in equilibrium always fall on a straight line, at the maximum as well as everywhere else. Finally, the modification when both these molar quantities are introduced at the same time is shown in Fig. 15d. The three-phase line then opens up into a triangular prism, such as the one shown in Fig. 14. However, in the present case, the three-phase line is bent and, at the maximum point, the triangular cross-section has degenerated into a line.

In the general case, the tangent to the three-phase line at the point of maximum Y^l in Fig. 15a is not parallel to the Y^k -axis, but has a different direction in the Y^k - Y^m plane. This case can be illustrated simply by choosing a new coordinate system in Fig. 15a, obtained by rotating the present one around the Y^l -axis. This will not change the construction of Fig. 15d, because the new X variables can be obtained as linear combinations of the present ones. It is thus possible to conclude that the three phases will fall on a straight line in the X_m^k - X_m^m diagram obtained by sectioning at an extremum value of Y^l for the three-phase equilibrium. On the other hand, Fig. 15b and c will be modified; in particular, Fig. 15b will no longer show a point of contact between the three phases.



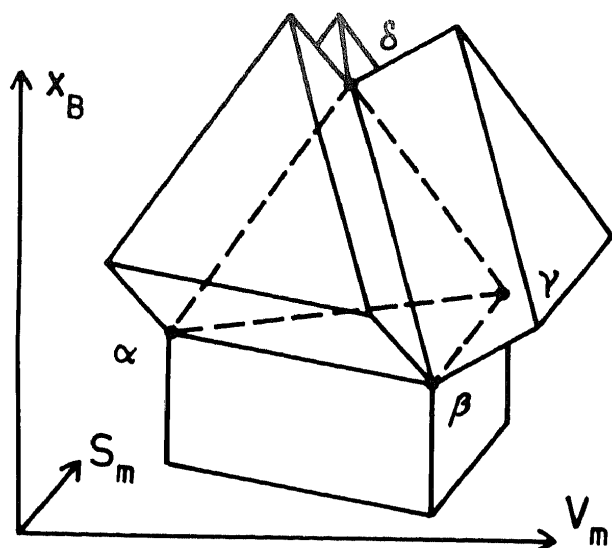
a three-dimensional potential phase diagram; *b* as *a*, but with Y^k and Y^l replaced with their conjugate molar quantities X_m^k and X_m^l ; three-phase line has opened up into triangular prism (parts of two-phase fields have been removed to show three-phase field better)

- 14 Effect of replacing potentials by their conjugate molar quantities in three-dimensional phase diagram with three-phase line in potential diagram



a three-dimensional potential phase diagram; at point of maximum Y^l , tangent to three-phase line happens to be parallel to Y^k -axis; *b*, *c* as *a*, but with either Y^k or Y^m replaced by their conjugate molar quantities X_m^k or X_m^m , respectively; three-phase equilibrium is shown with tie lines; *d* as *a*, but with both Y^k and Y^m replaced by their conjugate molar quantities; three-phase line has opened up into bent triangular prism, but at point of maximum Y^l , tie triangle degenerates into straight line

- 15 Effect of replacing potentials by their conjugate molar quantities in three-dimensional phase diagram with curved three-phase line in potential diagram; dotted lines represent points of tangency to three two-phase surfaces parallel to Y^k -axis (parts of two-phase fields have been removed for simplicity in *b*, *c*, and *d*)



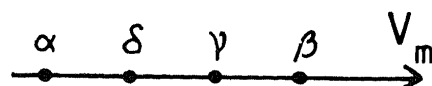
16 Four-phase equilibrium in diagram with three molar axes, shown with dashed lines; diagram has tetrahedral form, but is covered by triangular prisms representing three-phase equilibria

Most of the practical applications of the above result concern extrema in temperature and pressure in ternary systems. One may, for instance, study a three-phase equilibrium at constant pressure, using T , μ_B , and μ_C as experimental variables. If one finds a temperature maximum on the three-phase line, then one knows that the three phases are there co-linear in the composition triangle. From this fact it also follows that the three-phase equilibrium has a pressure extremum for the same compositions.

The same reasoning can be applied to higher-order phase equilibria, but the visibility is then lost, and one must use analytical methods. Usually, a four-phase equilibrium in a diagram with three molar axes has the form of a tetrahedron. This is demonstrated in Fig. 16, which is constructed from Fig. 6a. The tetrahedron is covered by triangular prisms representing the one-dimensional three-phase fields in Fig. 6a. The hidden edges of the tetrahedron are shown with dashed lines. In some cases, the tetrahedron is degenerated, and the four phases in a diagram such as Fig. 16 would fall on a plane. This happens when the four-phase equilibrium has an extremum value for a fourth independent potential. In the same way, the five phases in a five-phase equilibrium would fall in the same three-dimensional volume in four-dimensional molar space when the five-phase equilibrium has an extremum for a fifth independent potential.

With reference to equations (5), (20), and (21), it has been emphasized that the present discussion is based upon the definition of all molar quantities in terms of dividing the extensive quantities by the number of A atoms, when μ_A is treated as the dependent variable among the potentials. However, when the final conclusion concerns the positions of phases in the complete compositional space, one can transform the mole fractions, defined relative to A, to the ordinary mole fractions.

The results for three-phase equilibria are closely related to the Alkemade rule for three-phase triangles.¹¹ All the results may be described by a



17 Relative positions of four phases along V_m -axis introduced instead of $-P$ -axis through invariant equilibrium in Fig. 6a

further generalization of the Kononov rule. Suppose a p -phase field in an R -dimensional potential diagram ($R \geq p$) shows an extremum in one of the potentials. At the point of extremum, the p phases have values for the $R-1$ molar quantities, conjugate to the remaining potentials, which fall in a $(p-2)$ -dimensional section of the $(R-1)$ -dimensional molar space. Suppose the R -dimensional diagram to be an equipotential section for an additional potential. If one starts to vary that potential under the same phase equilibrium, keeping the first potential constant at its extremum value, it will be found that the constant value of the new potential in the original diagram is also an extremum value.

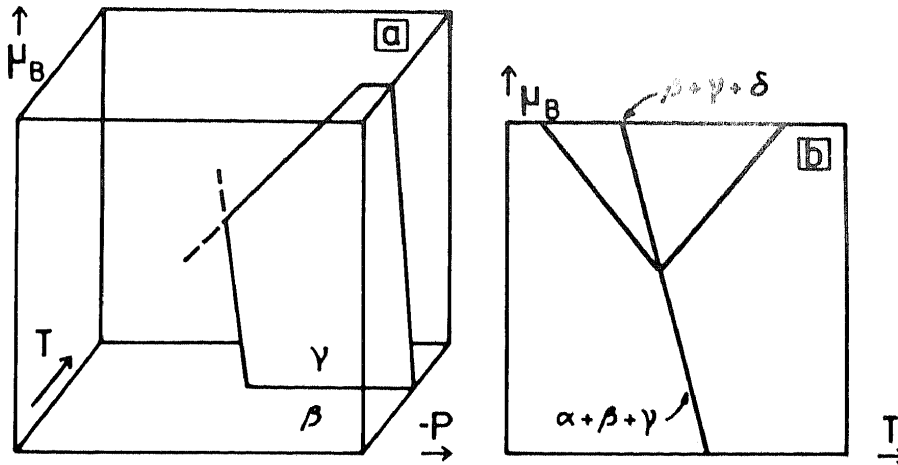
The rules concerning points of extremum for phase equilibria can be derived algebraically. The geometric method was chosen here because it forms the basis for a discussion of the topology of projected potential phase diagrams in the next chapter.

TOPOLOGY OF PROJECTIONS OF POTENTIAL PHASE DIAGRAMS

As demonstrated by Figs. 5 and 6, the elementary units of potential diagrams are very simple from the topological point of view. In this sense, the projections of such diagrams are more interesting. This is evident if one considers the dashed extrapolations in Fig. 6a and in the projected picture Fig. 6b. Between the lines in Fig. 6b there are two extrapolations in one case, one extrapolation in two cases, and no extrapolation in one case. In fact, this is the only way to draw four lines in different directions and obey the 180° rule. It is evident that, in the projected direction, the four phases are related to each other in different ways. This phenomenon will now be examined.

If potential axes are chosen for the complete, three-dimensional phase diagram of a binary system, the four phases of an invariant equilibrium will fall at one point. If a molar quantity is introduced, say, X_m^I instead of Y^I , then the four phases will fall on a line, just as the three phases in the three-phase equilibrium in Fig. 10a fall on a line in Fig. 10b. In that case, it is easy to see in what order the phases arrange themselves along the line: β must be placed between α and γ , otherwise there will be some overlapping of the one-phase fields. Using the same reasoning, it is easy to see in which order the four phases of Fig. 6a will arrange themselves when a molar quantity is introduced. One simply looks at the directions of the two-phase surfaces. Their relative positions along a V_m -axis introduced instead of the $-P$ -axis through the invariant phase field in Fig. 6a are demonstrated schematically in Fig. 17.

When the phase diagram of Fig. 6a is projected in the P -direction and the picture given in Fig. 6b is formed, much information is lost. However, the information regarding the order of arrangement along the



18 Modification of Fig. 6 by rotation of $\beta + \gamma$ surface until it is parallel to $-P$ -axis; in $-P$ projection, $\beta + \gamma + \delta$ and $\alpha + \beta + \gamma$ lines will now coincide, and their extrapolations will not be visible

projected direction when the molar quantity is introduced is not lost, because some conclusions can still be drawn regarding the directions of the two-phase surfaces. They are situated between the three-phase lines. For example, the $\beta + \gamma$ surface goes from the $\beta + \gamma + \delta$ to the $\alpha + \beta + \gamma$ line in Fig. 6b. It is thus possible to get an impression of which way the $\beta + \gamma$ surface is leaning, relative to the direction of projection.

Suppose one could gradually change the properties of the system in such a way that the $\beta + \gamma$ surface in Fig. 6a would rotate around an axis roughly parallel to the μ_B -axis. One could thus make the two lines $\beta + \gamma + \delta$ and $\alpha + \beta + \gamma$ in the projection approach each other without changing the topology of the projected diagram. At the moment of coincidence, one has a situation such as that illustrated in Fig. 18a in three dimensions and in Fig. 18b in the projection. The $\beta + \gamma$ surface is now parallel to the direction of projection. If the $\beta + \gamma$ surface is not planar, the projected lines will not be straight. If they still coincide at the invariant point, the surface is there parallel to the direction of projection, i.e. parallel to the $-P$ -axis. It is thus possible to apply the Konovalov rule, as developed for Fig. 12a and b, and conclude that the β and γ phases have the same value of V_m at the invariant equilibrium if the $-P$ projections of the $\alpha + \beta + \gamma$ and $\beta + \gamma + \delta$ lines coincide when they meet at the four-phase point. Evidently, before the gradual rotation of the $\beta + \gamma$ surface the β and γ phases must have been neighbours along the V_m line in Fig. 17.

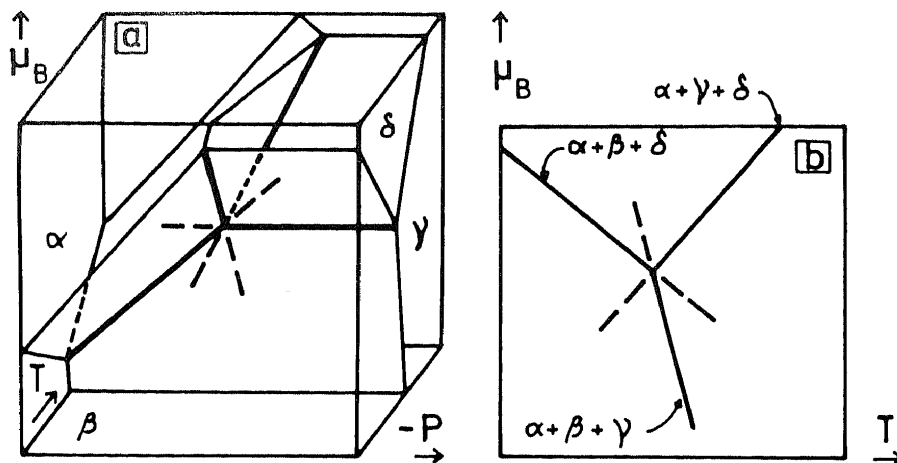
From Fig. 6b, it can be seen that it is also possible to make the $\alpha + \gamma + \delta$ and $\alpha + \beta + \delta$ lines approach each other after a rather large, gradual rotation, without changing the topology of the projected diagram. The α and δ phases must also be neighbours. Finally, it is also possible to make the $\beta + \gamma + \delta$ and $\alpha + \gamma + \delta$ lines approach each other. In this case they will overlap, because they will go in the same direction, rather than in opposite directions. However, it is still possible to conclude that the γ and δ phases must also be neighbours. The only way to arrange the four phases relative to one another is thus the one illustrated in Fig. 17. It is also possible to conclude that the lines must be arranged relative to one

another as shown in Fig. 6b, or by its mirror image, when the V_m values of the four phases are arranged as shown in Fig. 17.

It is interesting to note that the two neighbours which were identified when the two three-phase lines overlapped, the γ and δ phases, are situated between the other phases. The correctness of this conclusion can be tested by inspecting Fig. 6a. It is also interesting to note that one can make the $\alpha + \beta + \delta$ and $\alpha + \beta + \gamma$ lines in Fig. 6b approach each other without changing the topology, and it would thus seem that the α and β phases should also be neighbours. However, the 180° rule prevents these two lines from coinciding.

As an example of a possible application, a ternary system studied at constant pressure is now considered. The phase equilibria could then in principle be represented in a three-dimensional diagram such as Fig. 6a. However, if the phase equilibria are studied by measuring two potentials (T and μ_B) only, one would only obtain a projection similar to Fig. 6b. Suppose a diagram of the form of Fig. 18b is obtained when the data for four three-phase lines are plotted in the T - μ_B diagram. There is one more independent variable, although it has not been measured. Assume that it is μ_C ; the diagram in Fig. 18b should then be regarded as a μ_C projection. Since two of the three-phase lines seem to coincide, it is possible to identify two phases which must have almost the same value of x_C . However, it should be remembered that x_C is defined by dividing n_C by n_A . As a consequence, it makes no difference whether μ_A is regarded as the dependent variable and μ_C as the projected one or vice versa. The conclusion from Fig. 18b is that the β and γ phases in the invariant equilibrium have the same n_C/n_A ratio.

The binary case will now be reconsidered, and what happens if three of the four phases have the same V_m value will be investigated. The monovariant equilibrium between these three phases would have two phases in common with each of the other three monovariant equilibria. In the P projection one would thus expect the line corresponding to the first monovariant equilibrium to coincide with all three of the other lines. However, these other lines should not coincide with one another, because they do not



a three-dimensional potential phase diagram; *b* projection of diagram in *a* parallel to $-P$ -axis

- 19 Modification of Fig. 6 by rotating entire diagram until $\beta + \gamma + \delta$ line is parallel to $-P$ -axis; all three surfaces, $\beta + \gamma$, $\gamma + \delta$, and $\delta + \beta$, are then parallel to $-P$ -axis. In $-P$ projection, $\beta + \gamma + \delta$ will degenerate to a point, and will thus coincide with all the other lines without them coinciding with one another

have two phases of the same V_m value in common. How these conditions can be satisfied is demonstrated by Fig. 19, which holds for a system obtained by gradually changing the properties of the system shown in Fig. 6*a* in such a way that the whole picture is rotated until the $\beta + \gamma + \delta$ line points in the $-P$ direction. All three of the adjoining two-phase surfaces ($\beta + \gamma$, $\gamma + \delta$, and $\delta + \beta$) are then parallel to the $-P$ -axis, as they should be if the phases β , γ , and δ have the same V_m value. The projection is shown in Fig. 19*b*; it shows only three three-phase lines, because the fourth, the $\beta + \gamma + \delta$ line, is perpendicular to the plane of this diagram, and has thus degenerated to a point.

One cannot rotate the picture of Fig. 6*a* in such a way that three of the lines coincide in the projection. If such a case was found, it would mean, for instance, that α and β must have the same value of the molar quantity conjugate to the projected potential, but so must β and γ , and also γ and δ . As a consequence, all four phases must have the same value, and not only three, but all four, of the monovariant lines must coincide in the projection.

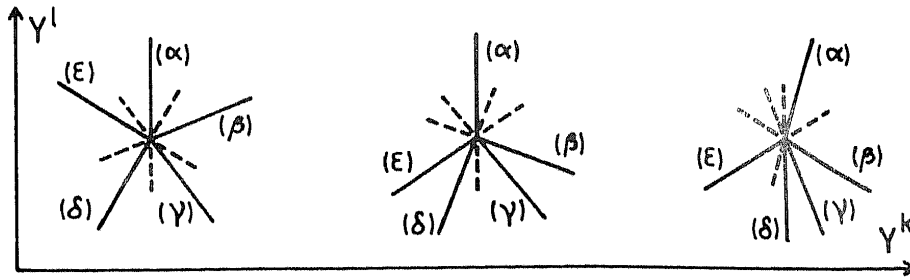
PROJECTIONS OF HIGHER-ORDER INVARIANT EQUILIBRIA

This kind of topological examination may be extended to higher-order invariant equilibria, although the visibility is then lost. However, it has been shown by analytical methods¹²⁻¹⁴ that the same principles that have been derived here by inspection apply. A four-dimensional phase diagram must be projected twice in order to yield a two-dimensional picture, and it may show an invariant five-phase equilibrium and five adjoining four-phase lines. If no lines coincide, they can arrange themselves in three different ways, as illustrated in Fig. 20. For a closer discussion of the phases taking part in the five-phase equilibrium, the two potentials on the axes will be kept constant at the values of the invariant point, while the two projected potentials will be replaced by their conjugate molar quantities. The five phases will fall on different points on the plane formed by the two molar

quantities, and Fig. 21 illustrates the arrangement of the phases in the three different cases. Three phases may here be regarded as neighbours if their points can be connected to form a triangle with no other point inside and if the triangle can be changed into a line without any one of its points moving inside any other such triangle. If two lines in the projected potential phase diagram coincide, then the three common phases fall on a straight line in the molar diagram.

A five-dimensional phase diagram must be projected three times in order to yield a two-dimensional picture, and the six phases in an invariant equilibrium will be arranged in certain ways in the three-dimensional space formed by three molar quantities.

The rule relating the coincidence of lines in a projected potential phase diagram to the positions of the common phases in the space formed by the molar quantities was called the 'Coincidence theorem' by Morey. From the above discussion of the binary case, its close connection with the Konovalov rule is evident. In view of the fact that the Konovalov rule can be generalized, it may also be possible to generalize the coincidence theorem. This may be demonstrated by the following example. Suppose that two of the points, α and δ , in the first picture of Fig. 21 coincide. Then δ , α , and γ fall on a line, and lines (β) and (ϵ) in Fig. 20 should coincide. However, β , δ , and α would also fall on a line, and so lines (γ) and (ϵ) in Fig. 20 should also coincide. As a consequence, all three lines, (β), (γ), and (ϵ), should coincide. It is thus possible to generalize the coincidence theorem as follows. Consider a two-dimensional projection of an R -dimensional potential diagram. It may have an invariant equilibrium involving $R+1$ phases. From this point, $R+1$ monovariant equilibria, each with R phases, radiate. The theorem concerns the positions of the phases in the $(R-2)$ -dimensional space formed by the molar quantities conjugate to the projected potentials. If r of the phases fall in an $(r-2)$ -dimensional section through that space, then the monovariant equilibria, which contain the r phases, coincide in the two-dimensional projection. Their number is $R+1-r$.



20 Possible diagrams obtainable by projecting an $Y^k-Y^l-Y^m-Y^n$ phase diagram in Y^m and Y^n directions; points represent invariant five-phase equilibria; the five lines emanating from each point represent four-phase equilibria, and are identified by giving omitted phase in parentheses; broken lines are metastable extrapolations

The information contained in the projected diagram can also be used to predict the nature of the monovariant equilibria close to the invariant point. Suppose that the ε -phase is the vapour phase. The (ε) line in Fig. 20 would then represent the four-phase equilibrium between condensed phases, and Fig. 21 shows their relative positions. If an experiment is carried out under constant values of X_m^m and X_m^n , then Fig. 21 shows the character of the phase transformation occurring when one changes the Y^k and Y^l potentials in such a way that one crosses the (ε) line in Fig. 20. In the left-hand case, one obtains $\alpha + \beta \rightleftharpoons \delta + \gamma$, but in the other two cases $\alpha \rightleftharpoons \beta + \gamma + \delta$, because α is there situated inside the β - γ - δ triangle. It may thus be concluded that the character of a four-phase transformation obtained by changing the temperature at constant pressure may be predicted from a projected potential diagram involving an additional phase, for instance a gas, and an additional potential, for instance the pressure.

TOPOLOGY OF MOLAR PHASE DIAGRAMS

In a complete diagram with only molar quantities on the axes, their number N_{ma} is equal to $c + 1$, and all the phase fields have the same variance as the diagram has axes, since equation (23) is satisfied for all phase fields. Because $N_{pr} = N_{ms} = 0$, equation (23) becomes:

$$p \leq 1 + N_{pr} + N_{ma} + N_{ms} = 2 + c \quad (26)$$

The topology of such a diagram is fairly simple, although more complicated than that of a potential

diagram. A two-dimensional molar diagram is composed of units obtained by a modification of the elementary unit shown in Fig. 5. Its modification is illustrated in Fig. 10, where Fig. 10a shows the initial unit and Fig. 10d the modified unit. It is interesting to note that the topology of the one-phase fields is unchanged, and for a diagram with many phases, the average number of sides for the one-phase fields must thus approach six. As shown in Fig. 10d, the number of sides of the three-phase fields is always three. By combining two units, it is easy to see that the two-phase fields will always have four sides. In addition to these rules, an expression for the average number of sides for all the phase fields may be derived, starting from Euler's rule, equation (9). Equation (10) still holds, but equation (11) must be replaced by the following, since four lines now meet at each corner:

$$4C = \sum nP_n \quad (27)$$

Equation (9) will thus give:

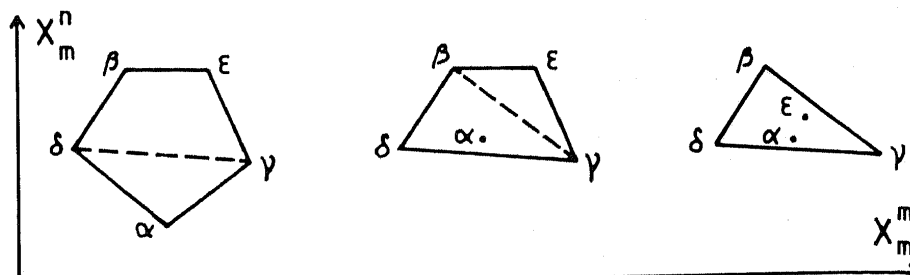
$$\sum (4 - n)P_n = 8 \quad (28)$$

The average number of sides of all the phase fields is thus obtained as

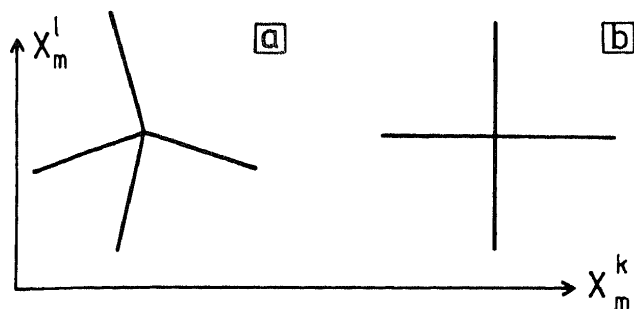
$$\bar{n} = \sum nP_n / \sum P_n = 4 - 8 / \sum P_n \quad (29)$$

In a molar phase diagram with many phases, the value of the last term can be neglected, and thus the average number of sides of the phase fields approaches four.

For a two-dimensional phase diagram which is limited by a rectangular frame, the rule takes a simpler form. Suppose there are m intersections between lines



21 Schematic picture of positions of five phases from Fig. 20 in $X_m^m-X_m^n$ plane at constant values of Y^k and Y^l which give invariant equilibrium. Change occurring when lines (ε) and (β) in left-hand picture are rotated to approach each other can be illustrated by moving point α towards straight line between δ and γ ; middle picture is obtained by letting (ε) and (β) lines pass one another, thus making point α cross δ - γ straight line; right-hand picture is obtained by letting (α) and (δ) lines rotate and pass one another, whereupon ε will cross β - γ line



a elementary unit; b topological equivalence of unit in a

22 Elementary unit of two-phase molar phase diagram and its topological equivalence

in the molar phase diagram and the sides of the frame. Counting these intersections as corners, including the four corners of the diagram, and taking into account the fact that only three polygons meet at m corners and only two polygons at 4 corners gives the expression:

$$4(\mathcal{C} - m - 4) + 3m + (2 \times 4) = \sum n\mathcal{P}_n \quad \dots (30)$$

Equation (9) will thus give:

$$m + \sum (4 - n)\mathcal{P}_n = 0 \quad \dots (31)$$

On omitting the surrounding space, which has $m + 4$ sides, from the summation of polygons, the expression

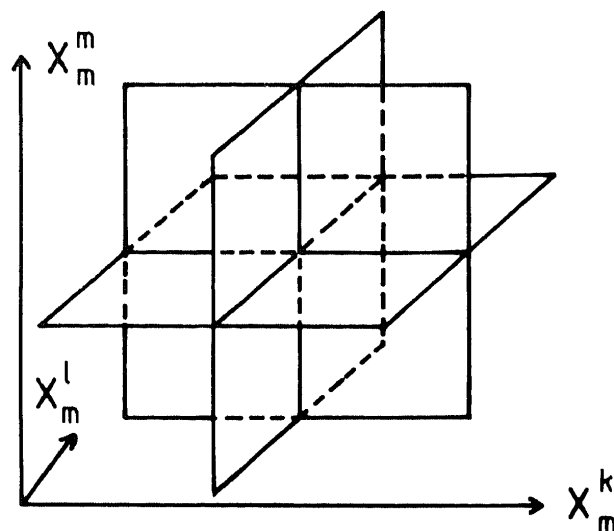
$$\sum' (4 - n)\mathcal{P}_n = 0 \quad \dots (32)$$

is obtained. The average number of sides for the phase fields is thus exactly four, independent of the size of the network.

At the beginning of this chapter, it was stated that all phase fields have the same variance in a diagram with only molar quantities. However, this rule is not obeyed when there is some stoichiometric constraint in a phase. Suppose the molar content of a component cannot vary in a phase. When the chemical potential for this component is replaced by its molar content, the one-phase field will contract and lose one dimension. When discussing the topology of phase diagrams, it is helpful simply to assume that there is a small variation of composition in such phases.

PHASE BOUNDARIES

Since all the phase fields in a molar diagram have the same variance as the diagram has axes, it is evident that all other geometrical elements, surfaces, lines, and points in a three-dimensional diagram, are not phase fields. They separate phase fields and may be called phase boundaries. When discussing the topology of a molar phase diagram in terms of the phase boundaries, it is possible and convenient to choose a smaller elementary unit which has only one corner. Such a unit for a two-dimensional molar diagram is shown in Fig. 22a; two phase fields meet at each line, and four phase fields meet at the point. Topologically, Fig. 22a can be represented by two intersecting lines (Fig. 22b), and a complicated, two-dimensional molar diagram by a network of crossing lines. The rule that the average number of sides of the phase fields is four thus seems very natural, because one can form a diagram containing only rectangles by using two families of parallel lines.



23 Topological equivalence of elementary unit in three-dimensional molar phase diagrams; Fig. 16 is composed of four such units

It can be seen by inspection of the three-dimensional diagram in Fig. 16, that it is possible to divide it into four identical, elementary units, each composed of a point where eight phase fields meet, although only four of them are shown in Fig. 16. The one-phase field and the three two-phase fields are omitted. Also, six linear phase boundaries radiate from these points. They are shown for the β and δ points in Fig. 16. It was pointed out by Palatnik and Landau⁶ that, topologically, this elementary unit can be represented by three intersecting planes (Fig. 23). Evidently, the topology of a complicated three-dimensional molar diagram can be represented by a system of intersecting surfaces.

In the general case, the elementary unit can be described by the number of various geometrical elements which meet. The dimensionality of these elements will be denoted by a and b . Palatnik and Landau gave the following equation for the number of elements with a dimensionality a which meet at an element of dimensionality b in a molar phase diagram with R axes:

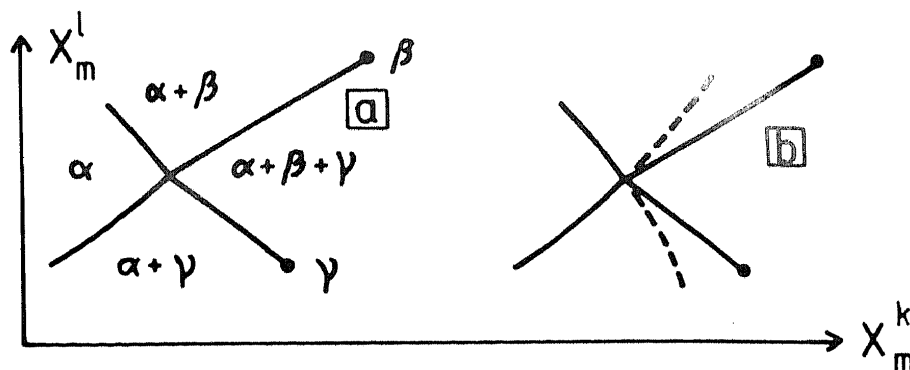
$$n = 2^{a-b} \binom{R-b}{a-b} \quad \dots (33)$$

Masing⁴ observed that the number of phases will change by one unit when one crosses a boundary with $b = R - 1$, i.e. a surface in a three-dimensional diagram or a line in a two-dimensional molar diagram; the latter case is illustrated in Fig. 24a. Palatnik and Landau⁶ were able to generalize Masing's boundary rule and to give it a mathematical formulation:

$$D^+ + D^- = R - b \quad \dots (34)$$

where D^+ and D^- are the number of phases that appear and disappear, respectively, as one crosses the boundary. This rule will be referred to as the 'MPL boundary rule' (after Masing, Palatnik, Landau).

The elementary unit of a two-dimensional molar diagram is subject to two important geometrical rules. One is the 180° rule. Of the three extrapolations given



24 Elementary unit of two-dimensional molar phase diagram obeying Schreinemakers' rule

in Fig. 5, two should appear in Fig. 24, since the form of the one-phase fields is essentially preserved when molar quantities are introduced instead of potentials, but they cannot enter the one-phase field, because of the 180° rule. A possible case is shown in Fig. 24b, where both extrapolations have been placed inside the two-phase fields. However, the 180° rule does not determine whether they should actually fall inside the two-phase fields or the three-phase field. This question was examined by Schreinemakers³ when studying isobaric-isothermal sections of ternary diagrams. He found that the extrapolations must either both fall inside the three-phase field or fall one inside each of the two two-phase fields. His rule can be generalized, as will be seen below.

In a potential phase diagram, all geometrical elements of the same dimensionality represent the same kind of phase fields. This is not the case in molar diagrams. There, all the phase fields will have the same dimensionality of $a = R$, although they represent equilibria between different numbers of phases, from 1 to $c + 2$. All elements of a lower dimensionality will be boundaries between phase fields with different numbers of phases. It may be interesting to calculate how many phase fields with p phases meet at a boundary of dimensionality b . This number is given by

$$n_p = \binom{R-b}{p-d} \quad \dots \quad (35)$$

where d is a new parameter which serves to distinguish between different kinds of boundary of the same dimensionality b . The d parameter can have any value from 1 to $c + 2 - R + b$. As an example, take the linear boundaries, $b = 1$, in Fig. 10d. It is a two-dimensional diagram ($R = 2$) for a unary system, ($c = 1$), and d will thus vary from 1 to $1 + 2 - 2 + 1 = 2$. For $d = 1$:

$$n_1 = \binom{2-1}{1-1} = \binom{1}{0} = 1$$

$$n_2 = \binom{2-1}{2-1} = \binom{1}{1} = 1$$

This is thus a boundary between a one-phase field and a two-phase field. For $d = 2$:

$$n_2 = \binom{2-1}{2-2} = \binom{1}{0} = 1$$

$$n_3 = \binom{2-1}{3-2} = \binom{1}{1} = 1$$

This is a boundary between a two-phase field and a three-phase field. Examples of both kinds of linear boundary are shown in Fig. 10d. As another example, consider the linear boundaries ($b = 1$) in Fig. 16. It is a three-dimensional diagram ($R = 3$) for a binary system ($c = 2$), and d will thus vary from 1 to $2 + 2 - 3 + 1 = 2$. For $d = 1$:

$$n_1 = \binom{3-1}{1-1} = \binom{2}{0} = 1$$

$$n_2 = \binom{3-1}{2-1} = \binom{2}{1} = 2$$

$$n_3 = \binom{3-1}{3-1} = \binom{2}{2} = 1$$

This is thus a boundary where one one-phase field, two two-phase fields, and one three-phase field meet. For $d = 2$:

$$n_2 = \binom{3-1}{2-2} = \binom{2}{0} = 1$$

$$n_3 = \binom{3-1}{3-2} = \binom{2}{1} = 2$$

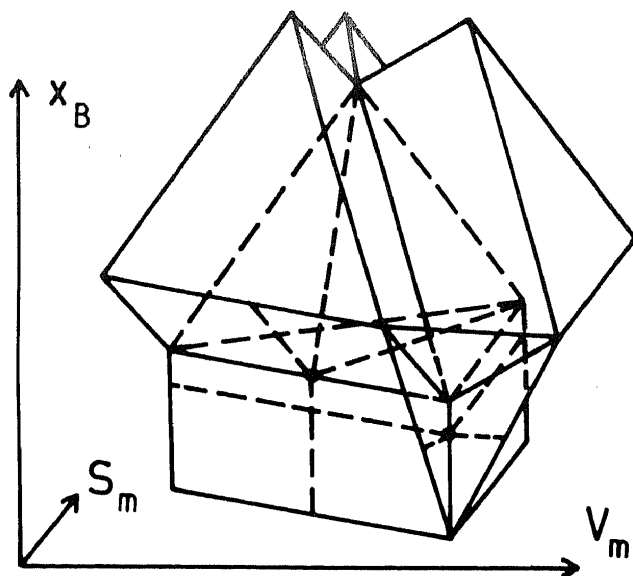
$$n_4 = \binom{3-1}{4-2} = \binom{2}{2} = 1$$

This is a boundary where one two-phase field, two three-phase fields, and one four-phase field meet. Examples of both kinds of linear boundary are shown in Fig. 16.

By these examples, it is demonstrated that d is numerically identical to the smallest number of phases in any of the phase fields meeting at the boundary.

SECTIONS OF MOLAR PHASE DIAGRAMS

Sections of molar phase diagrams are quite useful and are in common usage. Since all phase fields in a molar phase diagram have the same variance as the phase diagram has axes, all kinds of phase field may show up in a section. The topology of the sections is simplified if it is again assumed that it will not be possible to place a section through a point. The topology of a section will then be the same as the topology of a complete phase diagram with one component less. This fact is evident from equation (33), since the values of $R - b$ and $a - b$ do not change on



25 Two sections through phase diagram in Fig. 16; sections are shown with broken lines. Two-dimensional boundaries of β -phase field in Fig. 16 have been added here, and one section goes through two of them

sectioning. As an example, two sections through Fig. 16 are indicated in Fig. 25. In each case, the section gives the same arrangement of lines as in Fig. 22a. Furthermore, the MPL boundary rule applies to the sections, since $R - b$ does not change. However, there is one difference between a section and a complete phase diagram of a system with fewer components, which can be illustrated with the help of equation (35). As already emphasized, R and b will both decrease by one unit on sectioning, and $R - b$ will thus remain unchanged. However, the number of components c does not change, and the range of d values is thus larger in a sectioned, higher-order system than in a lower-order system. For a diagram obtained by sectioning N_{ms} times at constant values of molar quantities, d may have integral values from 1 to

$$d_{\max} = c + 2 - R + b = 1 + N_{ms} + b \quad (36)$$

since the number of axes R is now equal to $c + 1 - N_{ms}$. In the case discussed earlier in this chapter, phase fields meeting at points ($b = 0$), as in Fig. 22a, were considered. For one sectioning, $d_{\max} = 2$, and there should thus be two different kinds of point, having d equal to 1 or 2. Of course, this is the same result obtained in the complete phase diagram for phase fields meeting at lines ($b = 1$), because that is where the points are formed by the sectioning of lines. There are thus two different kinds of line in Fig. 16, although topologically they look the same. This was also demonstrated by the second example discussed in connection with equation (35).

Whether the Schreinemakers rule applies to points with different values of d will now be considered, starting by investigating a point on the intersection between two boundaries of the type where one new phase appears. The MPL boundary rule, equation (34), indicates that such boundaries have $b = R - 1$. In a three-dimensional diagram, such boundaries

would be surfaces, since they have $b = 3 - 1 = 2$. In Fig. 25 two such points have been marked. Comparison with Fig. 16 shows that one is on the boundary of the β phase field, while the other is on the boundary of the $\alpha + \beta$ phase field; consequently, they have $d = 1$ and 2, respectively. For each such point there will be two tie lines going to the two new phases. No matter how many dimensions the phase diagram has, it is, in principle, possible to make a two-dimensional section through the three points, although, as pointed out above, it is extremely unlikely that such a section can be made in practice. However, in such a section there will be four lines radiating from the point of interest – the two straight tie lines and the sections through the two boundaries, which may be curved. These sections are indicated in Fig. 25. Thus, exactly the same arrangement as that illustrated in Fig. 24a will be obtained, whether α in this figure represents one or more phases.

Since what is now being considered is a phase diagram constructed with molar quantities only, a discussion of thermodynamic properties should be based upon the internal energy. For reversible changes, equation (1) yields

$$dU = T dS - P dV + \sum_1^c \mu_i dn_i = \sum_1^{c+2} Y^i dX^i \quad (37)$$

It is here convenient to regard the entropy and volume as components, whose amounts are expressed by S and V , and whose chemical potentials are T and $-P$. The introduction of $c + 2$ new components instead of the old ones will now be effected by selecting this many points in the state diagram. They will each be identified by a subscript j , and their positions in the state diagram are given by sets of X^i values, which will be denoted by X_j^i . The amount of such a component will be expressed by the number of atoms n_j , and, as usual, the molar quantities are obtained as X_j^i/n_j , which will here be denoted by x_j^i . In terms of the old set of components, any system can be characterized by giving the X^i values, and that description can be transformed to the new set of components by the relation

$$X^i = \sum_j X_j^i = \sum_j x_j^i n_j \quad (38)$$

With a fixed set of new components, x_j^i are fixed and, for a small movement of the system in the state diagram,

$$dU = \sum_i Y^i dX^i = \sum_i Y^i \sum_j x_j^i dn_j = \sum_j dn_j \sum_i Y^i x_j^i \quad (39)$$

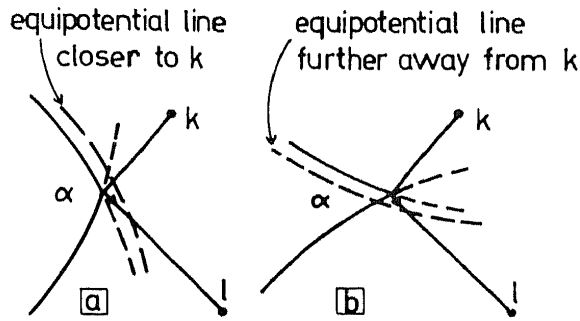
It is thus possible to regard $\sum_i Y^i x_j^i$ as the chemical potential of the new component j :

$$\mu_j = \sum_i Y^i x_j^i = \frac{\partial U}{\partial n_j} \quad (40)$$

For these generalized chemical potentials, the following relation is then obtained:

$$\frac{\partial \mu_l}{\partial n_k} = \frac{\partial^2 U}{\partial n_k \partial n_l} = \frac{\partial \mu_k}{\partial n_l} \quad (41)$$

Consider now a system represented by the point on two boundaries, discussed above, including the end-points of the two tie lines in a set of new components,



a the two phase boundaries both extrapolate outside α -k-l triangle when $\partial\mu_k/\partial n_l = \partial\mu_l/\partial n_k > 0$; b both extrapolate inside the triangle when $\partial\mu_k/\partial n_l = \partial\mu_l/\partial n_k < 0$

26 Proof of Schreinemakers' rule

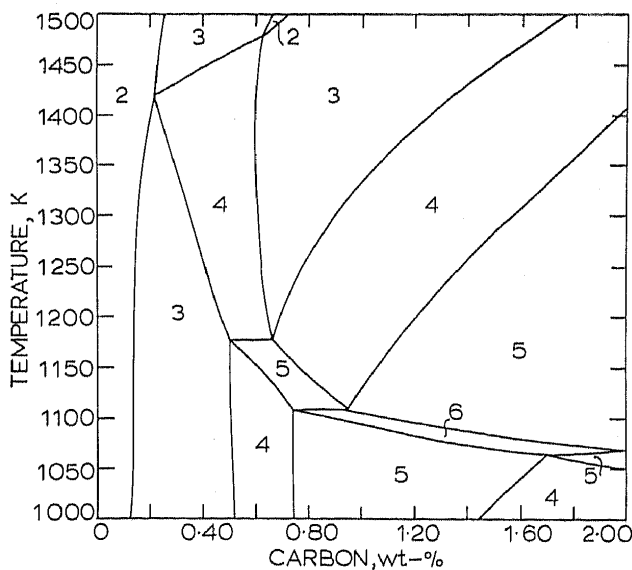
these points being designated k and l (see Fig. 26). At the point under consideration, one of the two boundaries represents equilibrium with k, and is thus an equipotential line for k. If it extrapolates outside the α -k-l triangle, the potential of k must increase on moving closer to the point l, because this path intersects equipotential lines for k situated closer to the point k, i.e.

$$\frac{\partial\mu_k}{\partial n_l} > 0 \quad \dots \dots \dots (42)$$

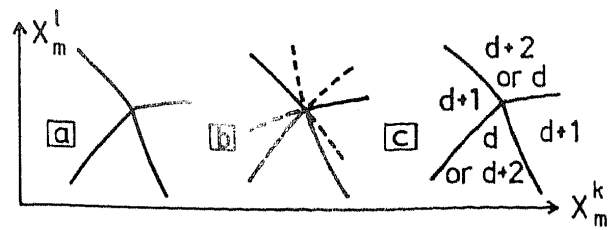
Then, from the above relation,

$$\frac{\partial\mu_l}{\partial n_k} > 0 \quad \dots \dots \dots (43)$$

from which the second boundary must also extrapolate outside the α -k-l triangle. On the other hand, if



27 Calculated phase diagram for system with eight components; complete phase diagram has two potential axes and seven molar axes, and has been sectioned at one constant potential (pressure) and six constant molar quantities (molar contents); Schreinemakers' rule holds at all intersections; numbers given are number of phases in each phase field; after Ref. 15



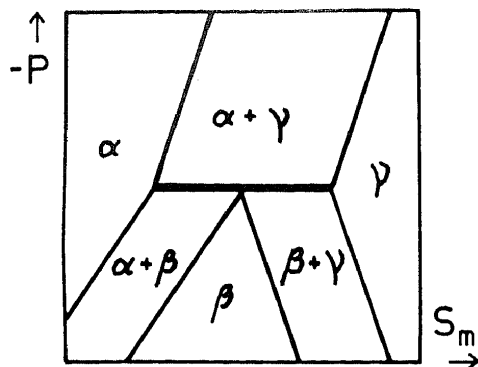
28 Use of Schreinemakers' rule to decide which phase fields have equal numbers of phases

the k boundary extrapolates into the triangle, a movement towards the point l will intersect equipotential lines for k further away from the point k. Both derivatives must then be negative, and both boundaries must extrapolate into the triangle. It has thus been shown that the extrapolations of the two phase boundaries under consideration must either both fall outside the highest-order phase field or both fall inside it, in agreement with Schreinemakers' rule. It may be emphasized that the rule also holds for equipotential sections. In order to prove it in such a case, one must use a thermodynamic function which allows the corresponding potentials to be kept constant; for instance, T and $-P$ in the case actually considered by Schreinemakers. The above reasoning must then be applied to the Gibbs energy, instead of the internal energy.

In the derivation of the Schreinemakers rule it is essential that the two boundaries of the highest-order phase field are straight lines. This will be true for all sections of phase fields with $p = R + N_{\text{max}} + 1$; for instance, the four-phase field in Fig. 25. In general, it will not be true in other cases. However, experience shows that the Schreinemakers rule is obeyed in most cases, and it may be used as a convenient guide when other information is lacking. As an example, the result of a computer-operated calculation of a section through an eight-component system is presented in Fig. 27. The rule is satisfied at all the corners in this diagram, in spite of the fact that it has one potential axis.

Usually, the Schreinemakers rule is used to predict the directions of phase boundaries. On the other hand, if the phase boundaries are given - for instance, from calculation or experiment - the rule can then be used to decide the number of phases in the various phase fields. Suppose the arrangement in Fig. 28a is given, but the numbers of phases in the four phase fields are not known. One should then extrapolate all the lines; two phase fields will then contain one extrapolation each, and these phase fields will be opposite one another. According to Schreinemakers' rule, these will be the phase fields with the same number of phases, $d + 1$ in Fig. 28c. Of the other two phase fields, one will contain two extrapolations and the other none. These phase fields will contain one phase more and one phase less than the others, respectively. However, the rule does not allow us to tell which has more and which less. It would be possible to predict the number of phases in all the phase fields of Fig. 27 by this method, if it were known that the phase field to the very left has two phases.

It is interesting to note that most of the polygons in Fig. 27 have four sides. It seems that this number



29 Phase diagram from Fig. 10b, reproduced without tie lines; thick line represents $(\alpha + \beta + \gamma)$ one-dimensional phase field

is not only the required average value, as shown above, but may also be the predominating number in sections of molar phase diagrams.

MIXTURES OF VARIABLES

It is very common to include potentials as well as molar quantities in the set of independent variables. The topology of the resulting phase diagrams can be very complicated. However, there is an important exception. It has been shown that sectioning at a constant potential gives a diagram with the same topology as a lower-order potential phase diagram. If molar quantities are then introduced on all the remaining axes, the topological rules for a molar diagram are obeyed, and this is also true after further sectioning at constant values of some molar quantities. The topological rules for molar diagrams may thus be applied, even if sectioning has been made at constant values of a mixture of potentials and molar quantities. The only requirement is that molar quantities are used on all the remaining axes. It is even possible to relax this requirement somewhat, because one can apply the MPL boundary rule to the phase diagram in Fig. 27, in spite of the fact that it has one potential axis. This is possible because all the phase fields have the same variance as the diagram has axes, which is actually all that is required. The maximum number of phases allowed in any phase field in order for topological rules of molar diagrams to apply can easily be calculated from equation (23). For the system shown in Fig. 27, $p \leq 1 + N_{ma} + N_{ms} = 1 + 1 + 6 = 8$, although actually this value is never reached, since there is a maximum of six phases in any phase field in Fig. 27.

The more difficult cases, where all the phase fields do not have the same variance as the diagram has axes, will now be discussed. Palatnik and Landau⁶ made it quite clear that the MPL rule was derived for purely molar phase diagrams. Nevertheless, they tried to apply it to phase diagrams with one or two potential axes, but encountered some difficulty in connection with phase fields of a lower variance than the phase diagram has axes. In order to explain the difficulty, they regarded such a phase field as degenerate. In the present paper, the potential phase diagram has been used as the starting point, and it hardly makes sense to regard phase fields of a lower variance as degenerate when they have the correct value accord-

ing to the Gibbs phase rule. In order to avoid confusion with the nomenclature of Palatnik and Landau, the term 'phase field' was chosen here, instead of the more common term 'phase region', which was used by Palatnik and Landau. In the present nomenclature, phase fields in a diagram may have different variances, and, for any particular case, one can evaluate the variance from equations (22) and (23).

To solve their problem, Palatnik and Landau suggested that their rule should not be applied to a phase diagram with potential axes until the phase diagram had been modified to resemble a phase diagram with only molar axes. This means that all the phase fields should be expanded until they are characterized by variances that are numerically equal to the number of axes of the phase diagram.

Zhou¹⁶ has recently discussed this problem and proposed a solution that does not involve expansion. He emphasized the importance of making a distinction between different kinds of line in the phase diagrams, and even applied his method to phase fields which are not in direct geometrical contact, but only connected through their contacts to different points of an invariant phase equilibrium. His method thus seems to have some characteristics in common with that using potential phase diagrams.

For the present discussion, it seems sufficient to use the MPL rule. This can be applied successfully without expanding any phase fields, if it is used only for contacts between two phase fields, where at least one has the same variance as the phase diagram has axes, and not used for phase fields separated by a third phase field. With these restrictions, the MPL rule can even be applied to a purely potential phase diagram.

As an example, consider the $-P-S_m$ phase diagram in Fig. 10b, which is reproduced in Fig. 29 without tie lines. All the boundaries between phase fields are drawn with thin lines. The thick line represents a three-phase field, $\alpha + \beta + \gamma$. The MPL rule cannot be applied to the β and $\alpha + \gamma$ phase fields, because they are separated by the $\alpha + \beta + \gamma$ phase field. For the contact between β and $\alpha + \beta + \gamma$, the rule gives

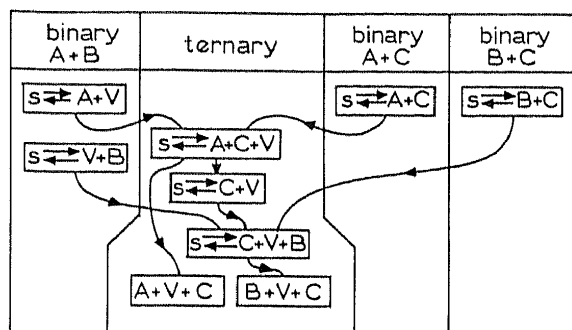
$$b = R - (D^+ + D^-) = 2 - 2 = 0 \quad \dots \quad (44)$$

in agreement with the fact that the two phase fields meet at a point. For the contact between $\alpha + \gamma$ and $\alpha + \beta$:

$$b = R - (D^+ + D^-) = 2 - (1 + 1) = 0 \quad \dots \quad (45)$$

This is also correct, because the two phase fields do not make contact along the thick horizontal line, where they are separated by the $\alpha + \beta + \gamma$ three-phase field, but only at the left end-point of the horizontal line.

Evidently, it is valuable to be able to distinguish between phase fields and boundaries. It will also be helpful to be able to predict the variance of a phase field for a known number of phases. This is given by equations (22) and (23), which can be applied to mixtures of variables and to various types of section and projection. These equations should be supplemented by a rule for calculating the maximum number of phases in any phase field in a certain section, since this number cannot be evaluated from equation (22) by putting $v = 0$, because it is not certain that there



30 Scheil diagram reproduced from Ref. 4; this is, in effect, a simplified projection of a potential phase diagram

can be an invariant phase field in the section. It is easy to see that each molar quantity that is used as an axis in the final section has increased the variance of the highest-order phase field in the section by one unit. The number of molar axes in the section is denoted by N_{ma} , and this is equal to the variance for the highest-order phase field, i.e.

$$v = N_{ma} \quad (46)$$

Thus, from equation (22),

$$p_{max} = R + N_{pr} + N_{ms} + 1 \quad (47)$$

It should be reiterated that N_{ms} represents the number of molar quantities that have been kept constant during sectioning.

SCHEIL DIAGRAMS

By tradition, most phase diagrams are produced with temperature as the vertical axis and composition on the horizontal plane, keeping the pressure constant at 1 atm. For a ternary system, one would thus need a three-dimensional diagram, which is difficult to show in two dimensions. In order to show the main features of such a system, one sometimes uses a 'reaction scheme', of the form suggested by Scheil.¹⁷ A simple example, taken from Masing,⁴ is reproduced in Fig. 30. It is worth emphasizing that this is really a projection of a potential diagram, such as the one shown in Fig. 6b. However, no effort has been made to draw it to scale. The important aim is to show the series of reactions that occurs in the system with decreasing temperature. The relative popularity of the Scheil diagram may be taken as an indication of the advantage of potential phase diagrams as a complement to temperature-composition phase diagrams.

As demonstrated in Fig. 30, the lines in the potential diagram are reproduced in the Scheil diagram. Each point is substituted by a box, which not only gives the phases in the invariant equilibrium, but also indicates the way in which they react when the temperature is lowered. It should be emphasized that, in some cases, the character of the reaction depends upon how the amount of a phase has been defined, and this information should thus be given together with the diagram. Sometimes there is also a box indicating the reaction taking place along a line, but this may be misleading, since the lines represent monovariant equilibria, in which phases may change their compositions with temperature; thus, the

character of the reaction may depend upon the average composition of the system.¹⁸⁻²⁰

PHASE DIAGRAMS TO SUIT EXPERIMENTAL VARIABLES

The tradition of preferring temperature-composition phase diagrams is a result of the fact that temperature and composition are the most common experimental variables. From suitable experiments, one can get direct information on that type of diagram, and from the diagram one can make direct predictions of the result of a new experiment. When computerized phase diagrams become available, the situation may change. The thermodynamic information will be stored in a data bank, and the computer will be able to calculate and plot any type of phase diagram or any special quantity of interest. In fact, the computer only needs to calculate the various phase equilibria once, whereupon the customer can ask to have the information plotted in various ways using potential or molar axes, sections or projections. If the customer knows that he is only interested in a particular section, it would, of course, save time to limit the calculation to that section.

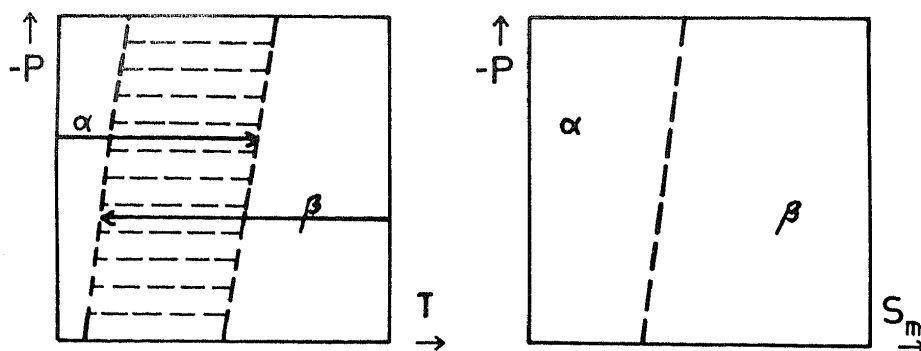
Even though it is most common to control temperature and composition in experiments, there are other possibilities. For instance, in carburization, one may control the chemical potential of carbon, and, in understanding the progress of carburization in an alloyed steel, it may be most convenient to use the carbon potential as one of the axes. In other cases, one may control the heat flow out of the system, rather than the temperature. It would then be convenient to use the enthalpy, rather than temperature, as one of the axes. Enthalpy has not been mentioned as one of the possible variables in the definition of the state of a system. However, it can always be evaluated from the variables already discussed, and it can be used to replace any variable which affects its value. There are many thermodynamic quantities that could be used, and it is possible to choose any such variable when plotting a diagram after the calculation of the various phase equilibria, because the choice of variables does not normally affect the nature of the equilibria. However, it should be emphasized that the proof, given by equations (20) and (21), that one-phase fields move apart when a molar quantity is introduced as an axis instead of a potential, only holds for a pair of conjugate variables. In addition to the pairs already discussed (T/S_m , $-P/V_m$, and μ_i/x_i), one may define new pairs by rearranging the fundamental equation (1) to give

$$-dS = -\frac{1}{T} dU - \frac{P}{T} dV + \sum \frac{\mu_i}{T} dn_i - \frac{D}{T} d\xi \quad (48)$$

Thus, U_m may be used as an axis instead of $-1/T$, which is equivalent to T . For any other substitution, there is a slight chance of obtaining some overlap between sets of two one-phase fields.

PHASE DIAGRAMS FOR CONSTRAINED EQUILIBRIA

In some cases, the experimental conditions are such that the system does not attain the ordinary equilibrium. So-called constrained equilibria fall in this



a potential phase diagram; note overlap of two-phase fields; b as a, but with T replaced by its conjugate molar quantity S_m ; broken line represents notional equilibrium between α and β in adiabatic conditions

31 Phase diagram for system in constrained equilibrium (adiabatic conditions)

category. An example is diffusionless transformation in alloys at low temperatures. Such a reaction requires a special thermodynamic calculation, although it is based on information in the data bank which is used in the calculation of ordinary equilibria. As another, more hypothetical, example, one might mention adiabatic transformations, and this type will now be discussed in some detail.

Suppose that a system is thermally insulated and that all reactions inside the system must be adiabatic. In this discussion, the practical difficulties in such an experiment will be neglected, attention being directed towards exploring the consequences of such conditions. As before, the discussion will be limited to reversible reactions; it is known from thermodynamics that these will be isentropic under adiabatic conditions. It is thus possible to consult an equilibrium phase diagram, such as Fig. 9b, and ask where α and β would be found under the constrained equilibrium conditions of equal entropy. This is probably somewhere close to the middle of the $\alpha + \beta$ two-phase field, where both phases are metastable if the constraints are relaxed. It is possible, by calculation, to find a line representing α and β in equilibrium under such conditions, i.e. a linear two-phase field (see Fig. 31b). Consider next how that two-phase field would look in the $-P-T$ phase diagram. Of course, when α and β are subject to the same pressure and have the same entropy, they cannot have the same temperature, and a two-phase field will appear in the $-P-T$ phase diagram. However, in this case, there is no separation of the two one-phase fields; they have moved in the other direction and now overlap (see Fig. 31a). This demonstrates that the fact that one-phase fields in a potential diagram separate and leave room for a two-phase field between them when a conjugate molar quantity is introduced is not trivial. Instead it is a characteristic of complete equilibrium. All constrained equilibria result in overlapping one-phase fields in the potential phase diagram.

SUMMARY

Various types of phase diagram have been discussed. From a topological point of view, the diagrams with potential axes are simplest. All the geometrical elements in such a diagram are phase fields, the dimensionalities of which are given by the Gibbs

phase rule. One can use projection or sectioning to present a multidimensional phase diagram.

In a projected potential phase diagram, obtained by projecting n times, phase fields with less than $n + 2$ phases may overlap, and it will be difficult to distinguish between them.

Each time a preceding section of a potential phase diagram is sectioned, the variance of a phase field decreases by one unit, until it becomes a point. On the next sectioning, it will usually disappear.

Phase diagrams with only molar quantities as axes have a relatively simple topology. All the phase fields have variances that are numerically equal to the number of axes on the phase diagram, and all geometrical elements of lower variance are boundaries between phase fields. The numbers of phases in two phase fields meeting at a boundary are related by the MPL rule. At a boundary where four phase fields make contact, the directions of adjoining boundaries are governed by a generalized version of the Schreinemakers rule.

Sections of molar phase diagrams are useful and obey the MPL rule. The Schreinemakers rule is of considerable value here, but is not strictly valid.

Phase diagrams with a mixture of potential and molar axes are common. They may be difficult to interpret, especially after sectioning, because it is not always evident whether a particular geometrical element is a phase field or just a boundary between phase fields. The MPL rule holds if two conditions are fulfilled: first, it can only be applied to two phase fields separated by a boundary which is not a third phase field; and second, it can be applied only if at least one of the phase fields has a variance numerically equal to the number of phase-diagram axes.

The 'reaction scheme' diagram of Scheil is a simplified version of a projection of a potential phase diagram.

Phase diagrams can also be constructed for conditions of constrained equilibria. Potential phase diagrams will show overlapping one-phase fields under such conditions.

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