CHAPTER 19

MULTICOMPONENT SYSTEMS

From the standpoint of metallurgical practice, phase diagrams of alloy systems involving four and more elements are needed more than are the diagrams of simpler systems, because many of the alloys of commerce contain more than three elements added deliberately, and if the significant impurities are included in the count, the majority contain a still larger number of elements. It is unfortunate, therefore, that temperature-composition phase diagrams of four-component systems become extremely cumbersome and that those of more than four components are all complex to the point of being almost useless. About 40 quaternary systems (four components) have been investigated in part, none completely, and portions of perhaps a half dozen quinary systems (five components) have been studied. Hence, despite their complexity, it will be worth while to give the higher order systems some consideration, brief though it must necessarily be.

Quaternary Systems

In order to express the composition of a quaternary alloy it is necessary to state the percentage or fraction of three of its four components. The graphical representation of these three variables together with the pressure and temperature (PTXYZ) would require a five-dimensional space. A temperature-concentration (TXYZ) diagram of a four-component system would require the use of four dimensions. Since neither is possible, it is necessary to resort to either three-dimensional isothermal isobaric sections or isobaric isopleths in which temperature and one or two concentration variables are represented in two or three dimensions, respectively. Both approaches will be discussed in this chapter.

For the representation of the three composition variables in three dimensions, an equilateral tetrahedron is employed (Fig. 19-1). This figure has the same properties in three dimensions as has the equilateral triangle in two dimensions. Four lines originating upon any one (composition) point within the tetrahedron, each drawn parallel to a different edge to intersection with one of the four faces of the figure, will have a total length equal to that of one edge of the tetrahedron. From point P, lying within the tetrahedron $ABCD$, Fig. 19-1, a line has been drawn parallel with AD to its intersection with face BCD at point a; another line Pb has been drawn parallel to AB and ends upon point b in the face ACD; the line Pc is drawn parallel to AC and ends upon the face ABD; while Pd is drawn to ABC parallel to BD. The total length of these lines is equal to the length of any one of the edges such as AB. If, once more, the length of an edge be taken as 100%, then the composition at point P is represented by the lengths of the four lines:

$$\%A = Pa$$
$$\%B = Pb$$
$$\%C = Pc$$
$$\%D = Pd$$

Pure components are represented at the corners of the tetrahedron, binary mixtures along the six edges, ternary mixtures upon the four faces, and quaternary mixtures within the space of the tetrahedron.

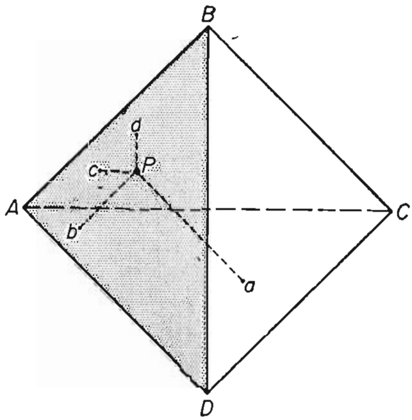


FIG. 19-1. Equilateral tetrahedron representing all possible compositions of the quaternary system $ABCD$. Point P represents a quaternary composition within the tetrahedron, its position being shown by the four dashed lines which terminate upon the four faces of the tetrahedron.

Were it mechanically feasible to do so, a three-dimensional grid for reading the composition of alloys, analogous to that employed with ternary diagrams in Fig. 12-2, might be constructed by passing regularly spaced planes through the tetrahedron parallel to each of its four faces. This is not practical, however, with a two-dimensional drawing of a space model. Consequently, there is little that can be done, short of making actual space models, to make four-component isotherms quantitative. Several schemes for reading composition in two-dimensional drawings of space figures have been proposed, but none has been found satisfactory. The principal usefulness of the three-dimensional isotherm is, therefore, in exhibiting the structure of the quaternary diagram in a qualitative way. Isopleths may then be used to advantage to give the temperature and compositions at points distributed upon the lines and surfaces depicted in the isotherms. This is a cumbersome procedure, indeed, but nothing better is at hand.

Representation of Equilibria in Quaternary Isotherms

According to the phase rule, there can be a maximum of five phases in equilibrium in a quaternary system after the pressure variable has been selected arbitrarily, thereby exercising one degree of freedom:

$$P + F = C + 2$$
$$5 + 1 = 4 + 2$$

Six distinct types of geometric construction are required to represent quaternary equilibria in isothermal sections. These are as follows:

One-phase equilibrium is represented in the isothermal tetrahedron by any space enclosed by two-phase boundary surfaces.

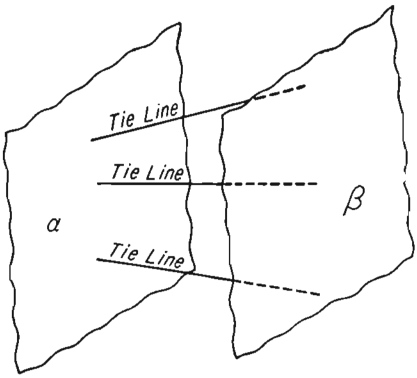


FIG. 19-2. Tie-lines in a space isotherm connect conjugate surfaces and may lie in any direction.

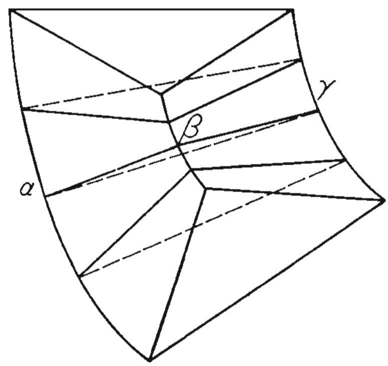


FIG. 19-3. Tie-triangles in a space isotherm connect three conjugate curves and may lie in any direction.

Two-phase equilibrium is represented in a space having two conjugate bounding surfaces connected at all points by tie-lines;[1] the tie-lines may run in any direction in the tetrahedral isotherm because every point in the figure is at the same pressure and temperature (see Fig. 19-2). Ruled boundaries of three-phase regions may partake in enclosing the two-phase space.

[1] This is true, of course, only of the isobaric isothermal section. In the (imaginary) TXYZ diagram tie-lines would connect two conjugate three-dimensional surfaces (i.e., conjugate volumes), tie-triangles would connect three conjugate *surfaces*, and tie-tetrahedra would connect four conjugate lines. In the complete PTXYZ diagram tie-lines would connect pairs of conjugate four-dimensional volumes, tie-triangles would connect sets of three three-dimensional volumes, tie-tetrahedra would connect sets of four conjugate surfaces, and the five-phase tetrahedra and hexahedra would connect sets of five conjugate curves. In drawing isopleths and projections these differences should be remembered.

Three-phase equilibrium is represented by three conjugate curves everywhere connected by tie-triangles;[1] these, too, may be oriented in any manner (see Fig. 19-3). Bounding surfaces of three-phase regions are shared with two-phase and four-phase regions.

Four-phase equilibrium is represented by a tie-tetrahedron[1] the four corners of which touch the four one-phase regions involved in the equilibrium. The tie-tetrahedron can have any shape that can be constructed by the use of four triangular faces of an assortment of dimensional ratios, and it may be oriented in any way (see Fig. 19-4). It should be noted that any ternary four-phase reaction plane, whether class I, II, or III, is the limiting (two-dimensional) case of a tetrahedron (three-dimensional). Figure 19-5 represents the development of a tetrahedron from the class I or III reaction triangle, and Fig. 19-6 illustrates the development of a tetrahedron from the reaction trapezium of class II.

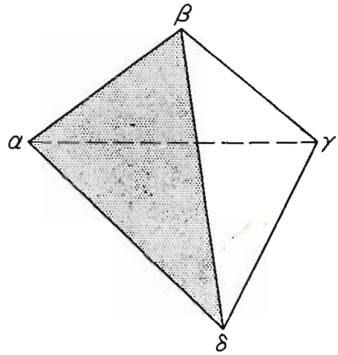


FIG. 19-4. Tie-tetrahedron associating the four phases α, β, γ and δ.

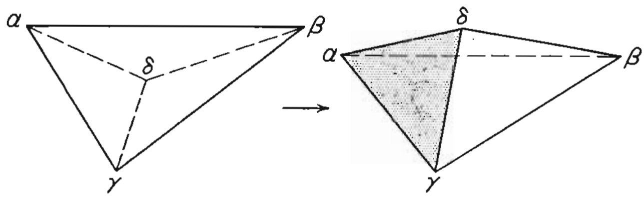


FIG. 19-5. Development of a tie-tetrahedron from the ternary class I, or class III, four-phase reaction triangle.

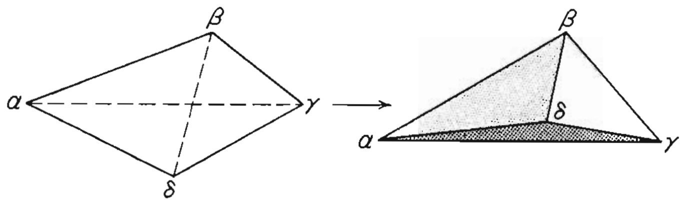


FIG. 19-6. Development of a tie-tetrahedron from the ternary class II four-phase reaction trapezium.

Five-phase equilibrium is represented by a tie-tetrahedron[1] (Fig. 19-7*a*) or a tie-hexahedron[1] (Fig. 19-7*b*), that is isothermal and, hence, can occur in only one of a series of isotherms taken at different temperatures. There are four classes of quaternary five-phase equilibrium, two of which

[1] See footnote, on opposite page.

are represented in Figs. 19-8 and 19-9 and the other two of which are the geometric inverse of the first two.

Class I five-phase equilibrium is represented by four four-phase tie-tetrahedra descending from higher temperature and joining to form the five-phase isothermal tetrahedron from which a single four-phase tie-tetrahedron descends to lower temperature. The fifth phase is represented at that point within the five-phase tetrahedron where the four

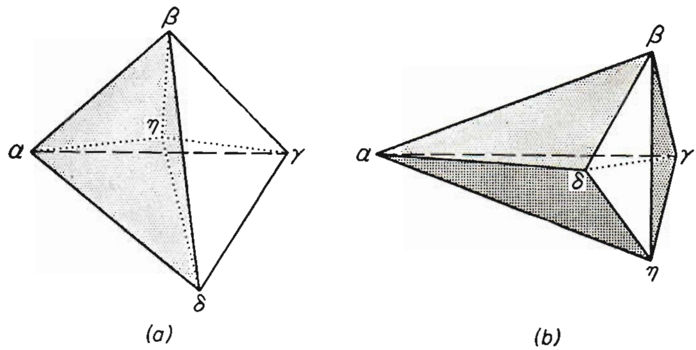


FIG. 19-7. Two possible kinds of space figures representing five-phase equilibrium: (*a*) tetrahedron, (*b*) hexahedron.

apexes of the four four-phase tetrahedra meet, as at η in Fig. 19-8. The quaternary eutectic is a reaction of the first class:

$$L \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \alpha + \beta + \gamma + \delta$$

as also is the quaternary eutectoid:

$$\alpha \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \beta + \gamma + \delta + \eta$$

There are in all 23 combinations of phases that may conceivably partake in this class of reaction.

Class II five-phase equilibrium is represented by three four-phase tie-tetrahedra descending from higher temperature and joining to form an isothermal tie-hexahedron at the five corners of which are represented the five phases that coexist in isothermal equilibrium. This figure divides into two tie-tetrahedra that descend to lower temperature (Fig. 19-9). The reaction is somewhat analogous to ternary class II four-phase reaction:

$$L + \alpha \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \beta + \gamma + \delta$$

There are 29 combinations of phases that could conceivably partake in class II five-phase equilibrium.

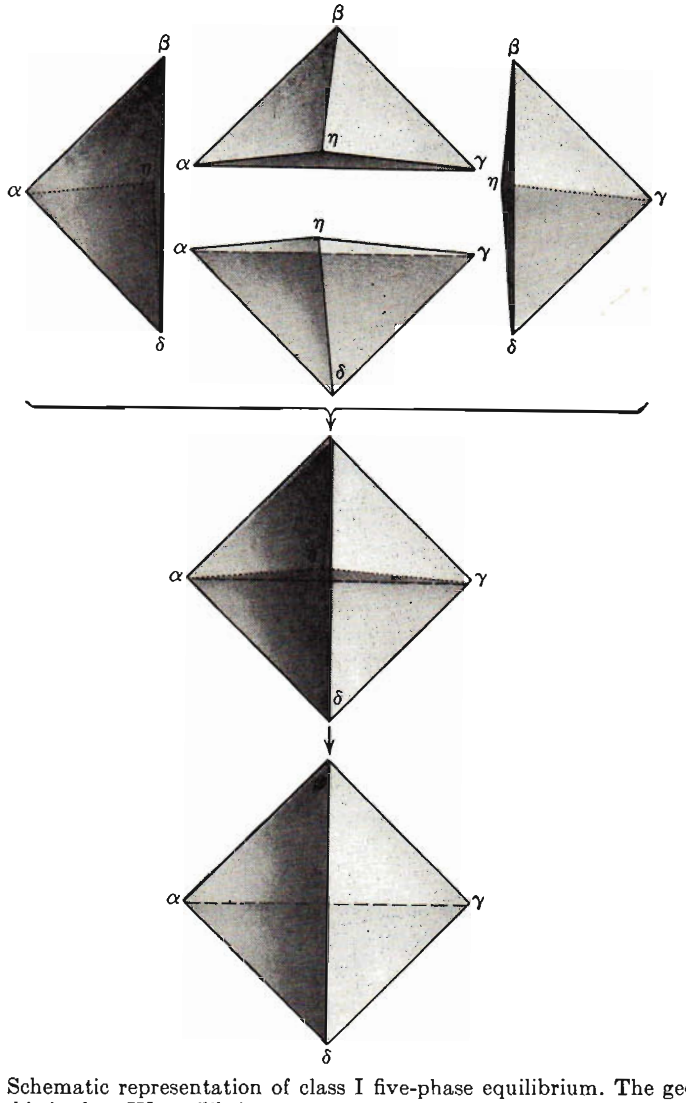


Fig. 19-8. Schematic representation of class I five-phase equilibrium. The geometric inverse of this is class IV equilibrium.

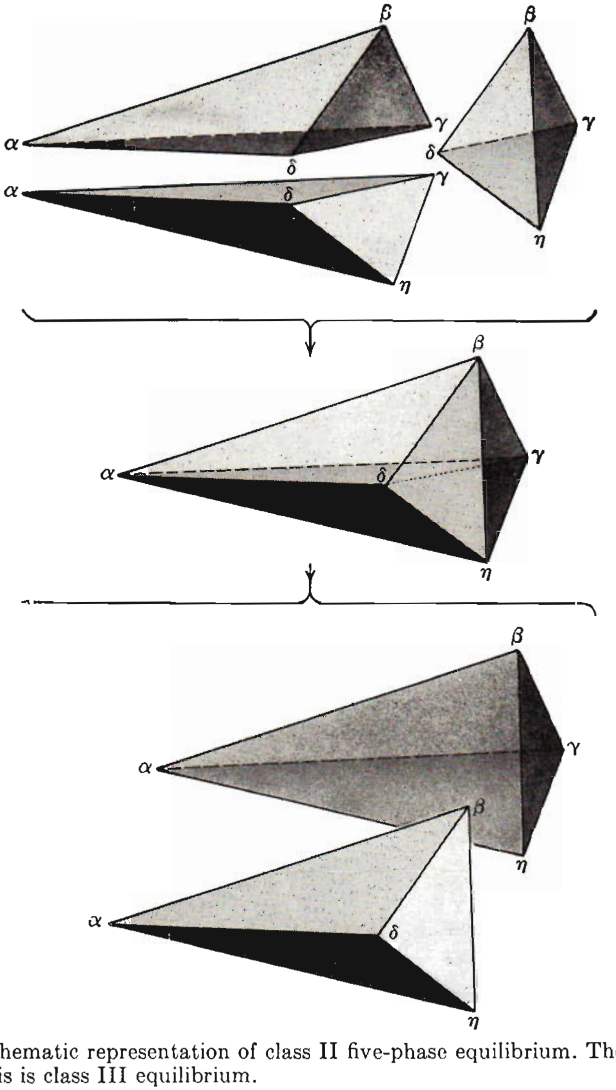


Fig. 19-9. Schematic representation of class II five-phase equilibrium. The geometric inverse of this is class III equilibrium.

Class III five-phase equilibrium is the inverse of class II equilibrium. Two tie-tetrahedra descending from higher temperature join to form an isothermal tie-hexahedron which then divides into three tie-tetrahedra that continue to lower temperature:

$$L + \alpha + \beta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \gamma + \delta$$

Class IV five-phase equilibrium is, similarly, the inverse of class I equilibrium. A single tie-tetrahedron descending from higher temperature becomes the five-phase tie-tetrahedron. Reaction to form a new phase divides the tetrahedron into four tetrahedral parts that proceed to lower temperature. This is the quaternary peritectic reaction:

$$L + \alpha + \beta + \gamma \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \delta$$

and the same reaction involving only solid phases is the quaternary peritectoid:

$$\alpha + \beta + \gamma + \delta \underset{\text{heating}}{\overset{\text{cooling}}{\rightleftharpoons}} \eta$$

Temperature-composition Sections

Isopleths in which a limited series of alloy compositions is represented, with the temperature variable, may be taken in a number of ways. For example, the composition with respect to one of the four components may be fixed, while the compositions of the other three are permitted to vary. Compositions designated by fixing the B content at 40% are contained in the plane triangle XYZ of Fig. 19-10. If this plane is made the base of a triangular prism, as in Fig. 19-17, coordinates resembling those employed in the construction of ternary space models are obtained. The diagrams so obtained often resemble ternary diagrams in a superficial way, but it should be remembered that they include only a small fraction of the alloys of the quaternary system and that tie-lines, tie-triangles, and tie-tetrahedra will not, in general, lie wholly within such a section but will extend through a series of such sections.

Another type of composition section in which the ratio of two of the components is held constant is shown in Fig. 19-11, where the plane ADX corresponds to a constant ratio of B and C. Such sections are useful chiefly in representing "quasi-ternary" equilibria, when X is a congruently melting intermediate phase that forms a simple ternary system with A and D. If a constant ratio is maintained between one of the components and two of the other components, the section appears as in plane AXY of Fig. 19-12. A quasi-ternary system between two intermediate phases and a component may be represented on this type of section.

Diagrams of sections that can be drawn in two dimensions are obtained by limiting the composition series to a single line through the quaternary composition tetrahedron. It is usual to take the lines parallel to one of the edges of the space figure as line XY in Fig. 19-13. This line represents all

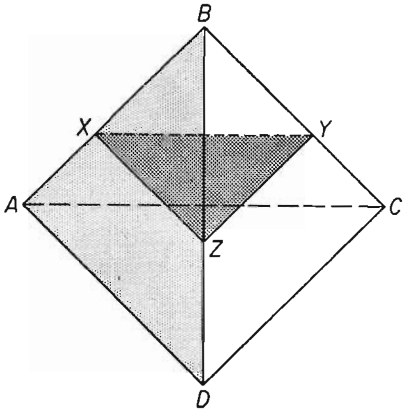


FIG. 19-10. Shaded section represents a system of alloys of a fixed B content.

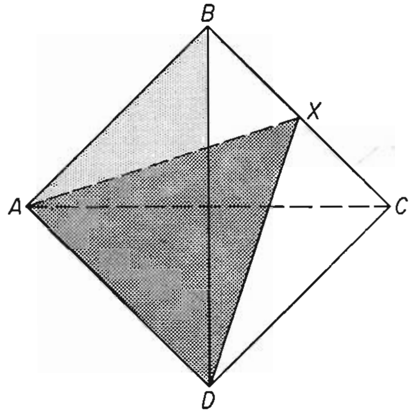


FIG. 19-11. Shaded section represents a system of alloys having a fixed ratio of the B and C components.

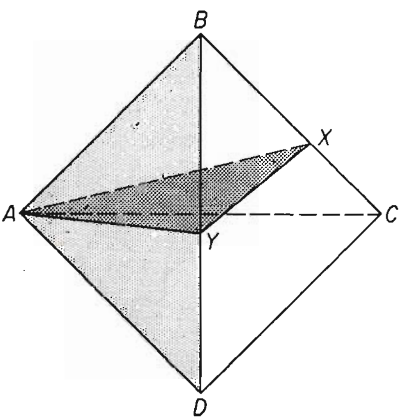


FIG. 19-12. Shaded section represents a system of alloys in which there is a fixed ratio between B and the sum of the C and D components.

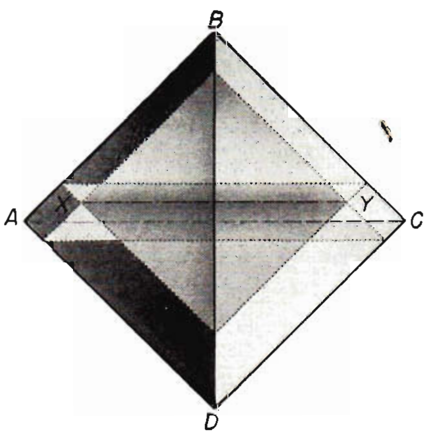


FIG. 19-13. Line XY, lying in a plane of constant B content, represents a constant D content in that plane; i.e., only the A and C contents vary along the line.

compositions containing 20% B and 10% D; the percentages of A and C then vary between 0 and 70. If this line is made the base line of a set of coordinates similar to those employed in the representation of binary equilibria, diagrams of the kind shown in Fig. 19-18 are obtained. Once again it must be emphasized that the several tie-elements are not generally included in such sections and that the compositions of the participating phases are indicated only in certain special cases.

Quaternary Isomorphous Systems

The best qualitative view of the equilibria in a quaternary isomorphous system is obtained from isotherms as in Fig. 19-14. The six tetrahedra in this illustration are arranged in order of descending temperature from T_1 to T_6. Component A melts above T_1, component C between T_3 and T_4,

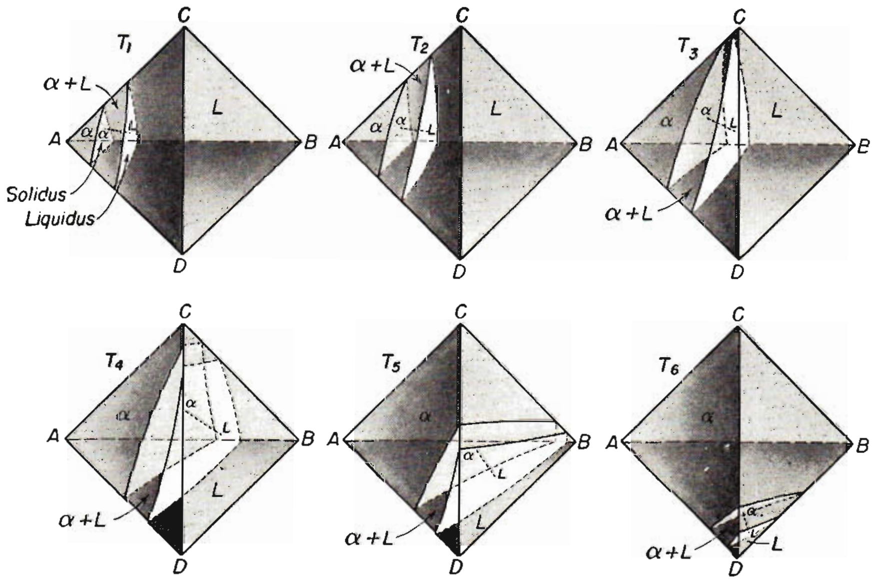


FIG. 19-14. Isotherms of a quaternary isomorphous system, temperature decreasing from T_1 to T_6.

component B between T_5 and T_6, and component D below T_6. Each isotherm shows a section of liquidus and a section of solidus. The liquidus and solidus surfaces sweep downward in temperature in successive isotherms from the melting point of A to that of D. At each component (corner of the tetrahedron) the liquidus and solidus meet. Tie-lines connect the conjugate liquid and solid phases at every point on this pair of surfaces. The short dotted lines in each isotherm, labeled "αL," are typical tie-lines included to show how these lines turn as the temperature is lowered. It should be noted that they are not necessarily horizontal as are the tie-lines in ternary space models, because the entire tetrahedron is isothermal. Tie-lines near the edges of the tetrahedron are nearly parallel with the edges, and the transition in direction is more or less

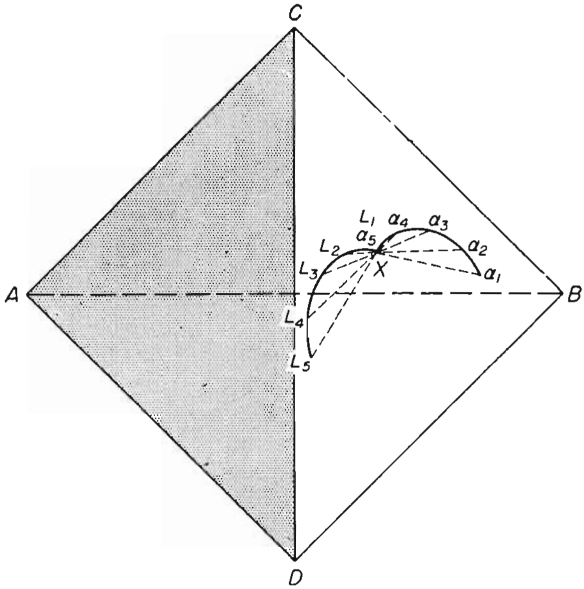


FIG. 19-15. Projection of the tie-lines involved in the freezing of a quaternary solid solution alloy of composition X.

regular in crossing the diagram. The usual lever principle is applicable to tie-lines in quaternary systems.

Freezing follows a curved path as shown in Fig. 19-15. This drawing is a liquidus and solidus "projection" analogous to that shown for the ternary case in Fig. 12-13. The gross composition of the alloy under consideration is indicated at X. Passing through point X is a series of tie-lines covering the temperature range of freezing. Freezing begins at T_1, with liquid and solid represented at the ends of the tie-line $\alpha_1 X$, and is completed at T_5, the tie-line XL_5. Coring is possible as in simpler systems, the microstructure of a cored quaternary solid solution being indistinguishable from that of binary and ternary alloys.

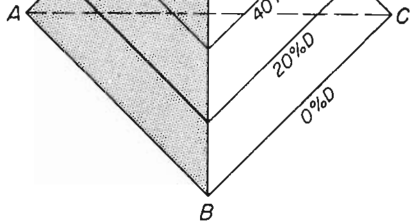


FIG. 19-16. Plan of composition sections represented in the space isopleths of Fig. 19-17.

A series of isopleths representing constant percentages of the D component, Fig. 19-16, is presented in Fig. 19-17. In order to show the relationship between these and the isothermal sections of Fig. 19-14, each

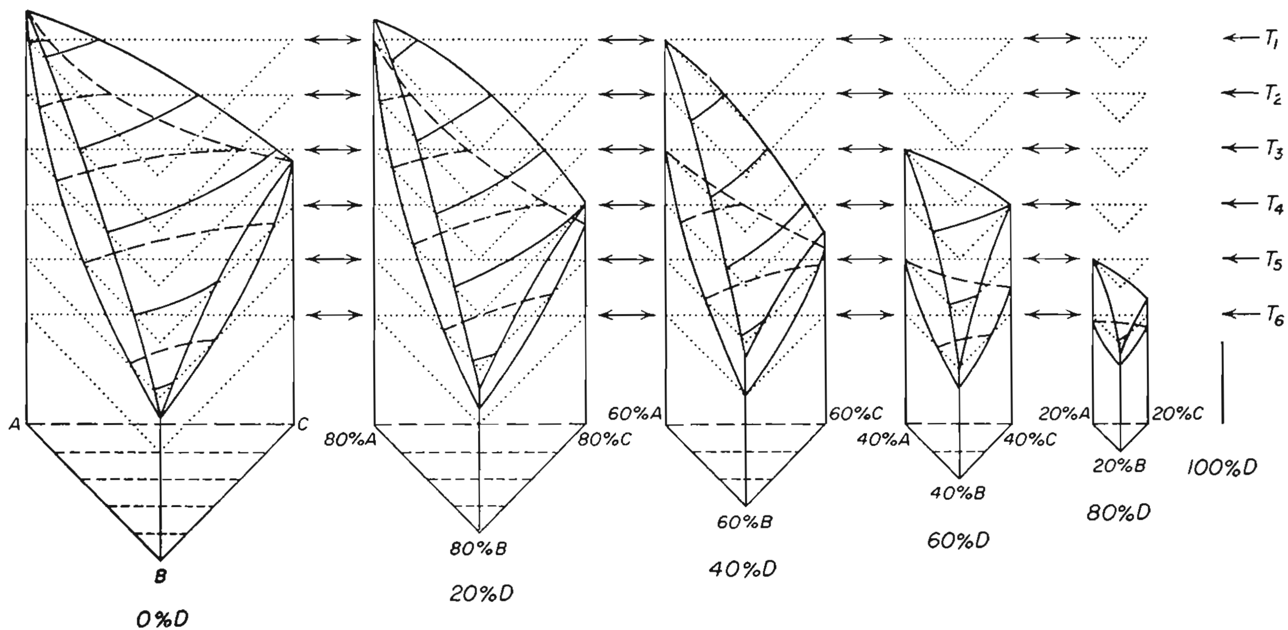


FIG. 19-17. Space isopleths through the quaternary isomorphous system illustrated in Fig. 19-14.

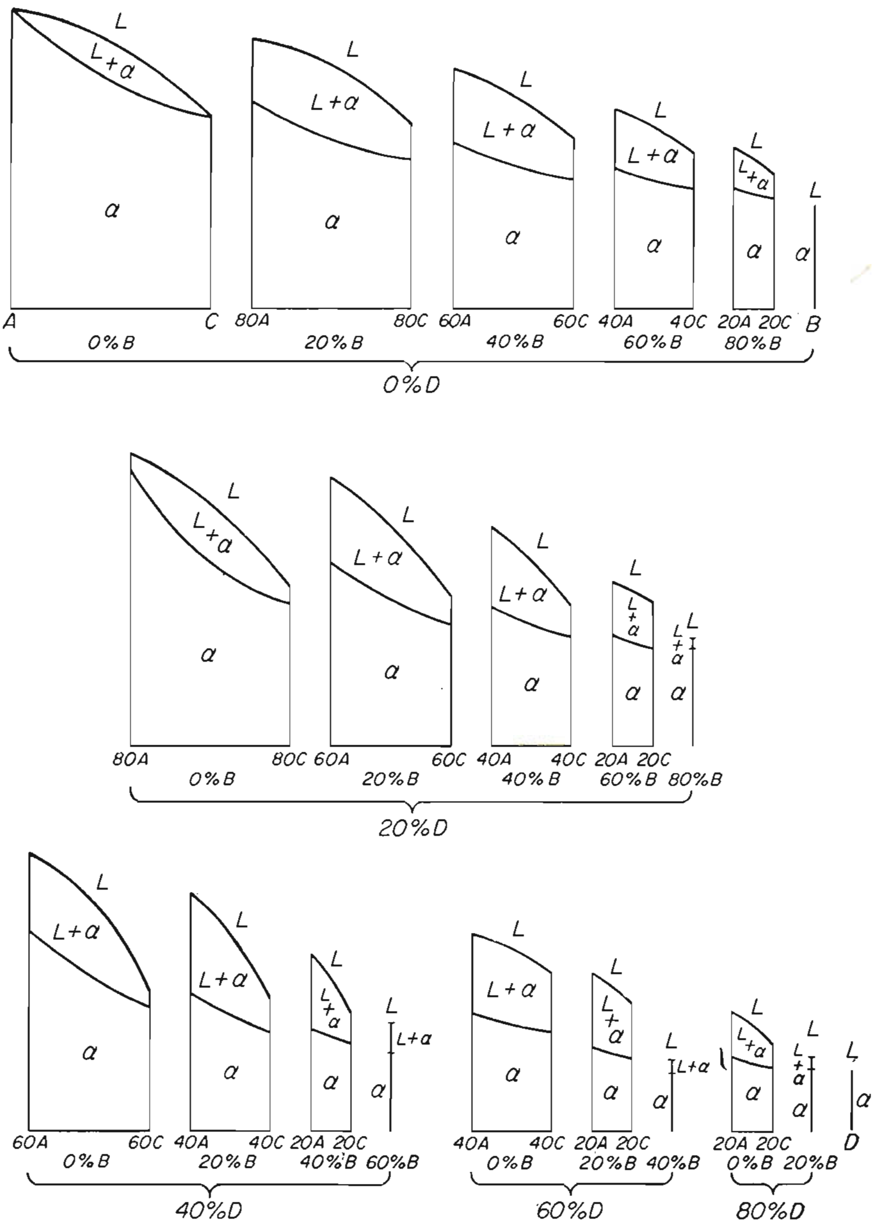


FIG. 19-18. Planar isopleths through the quaternary isomorphous system.

model has been intersected by horizontal dotted planes at the temperatures T_1 to T_6. The intersection of each of these planes with the liquidus and solidus surfaces corresponds in temperature and composition with an intersection of a plane, such as 20% D in Fig. 19-16, with the liquidus and solidus in one of the isotherms of Fig. 19-14. The isopleth on the left of Fig. 19-17 is, in fact, the ternary system ABC, and the liquidus and solidus meet at the three corners of the prism. All others are quaternary sections so that there is no meeting of liquidus and solidus at corners. At 100% D the section shrinks to a single line the height of which indicates the melting point of D.

With both the D and B contents held constant, the two-dimensional isopleths of Fig. 19-18 are obtained. The sections represented are indicated by the dashed lines drawn upon the base of each prism in Fig. 19-17 and also by the dashed lines in Fig. 19-19. Six series of these diagrams, representing 0, 20, 40, 60, 80, and 100% D, are presented in Fig. 19-18. Individual diagrams in each series represent constant B content at intervals of 20%. Liquidus and solidus temperatures corresponding to definite gross composition points may be measured on these diagrams, but the conjugate liquid and solid compositions cannot be associated.

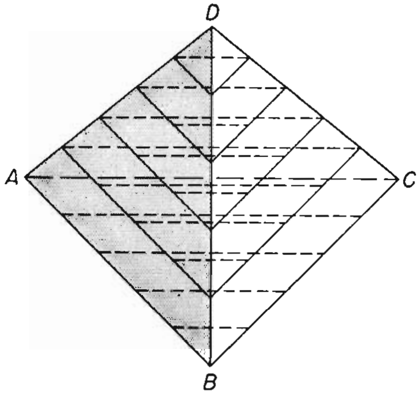


FIG. 19-19. Plan of composition series represented in the isopleths of Fig. 19-18.

Twenty-one separate sketches have here been used to depict the quaternary diagram at composition intervals of 20%. This is obviously an insufficiently complete survey for practical purposes. In order to decrease the composition intervals to 5%, which would be fairly satisfactory for practical uses, it would require the determination of 231 sections! There is little wonder that no fully determined quaternary diagrams are available.

An Example Involving Three-phase Equilibrium

An example of the representation of three-phase equilibrium without further complications may be found in a quaternary system in which three of the binary systems, AB, BC, and AC, are isomorphous and three, AD, BD, and CD, are of the simple eutectic type (Fig. 19-20). The first isotherm T_1, Fig. 19-20a, is taken at the BD binary eutectic temperature; the liquidus surfaces emerging from the B and D corners have just met on the line BD. At a slightly lower temperature T_2 tie-triangles $L + \beta + \delta$

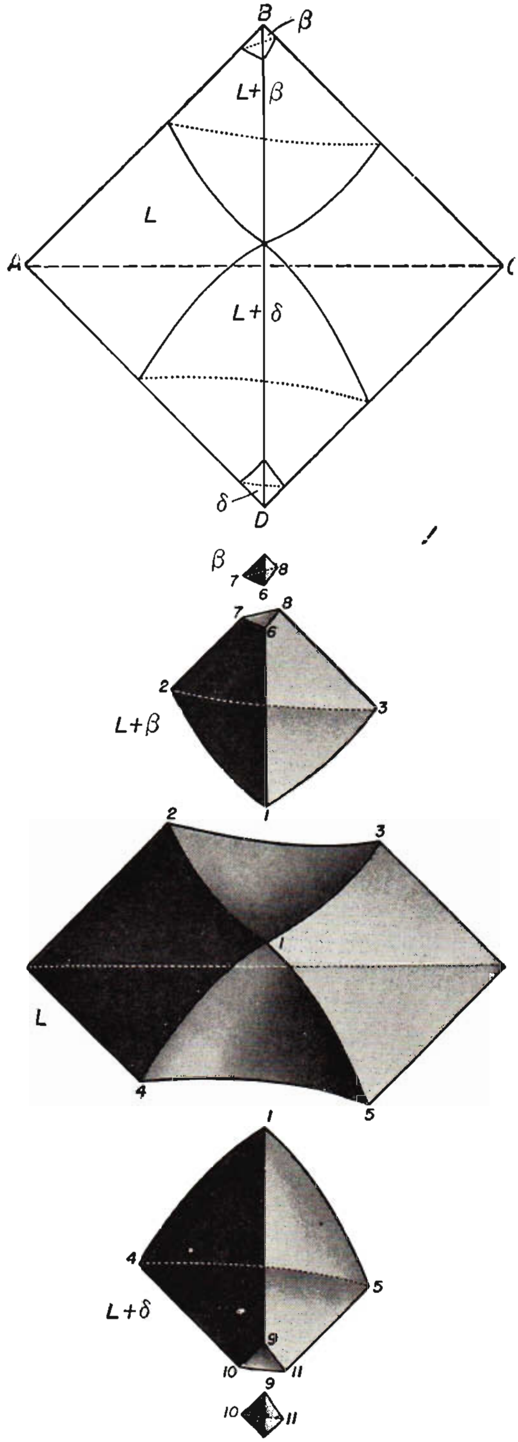


FIG. 19-20a. Six isotherms of a quaternary system in which the three-phase equilibrium $L + \beta + \delta$ sweeps through the diagram, with falling temperature, from the binary eutectic BD at T_1 to the binary eutectic AD, which lies between T_5 and T_6.

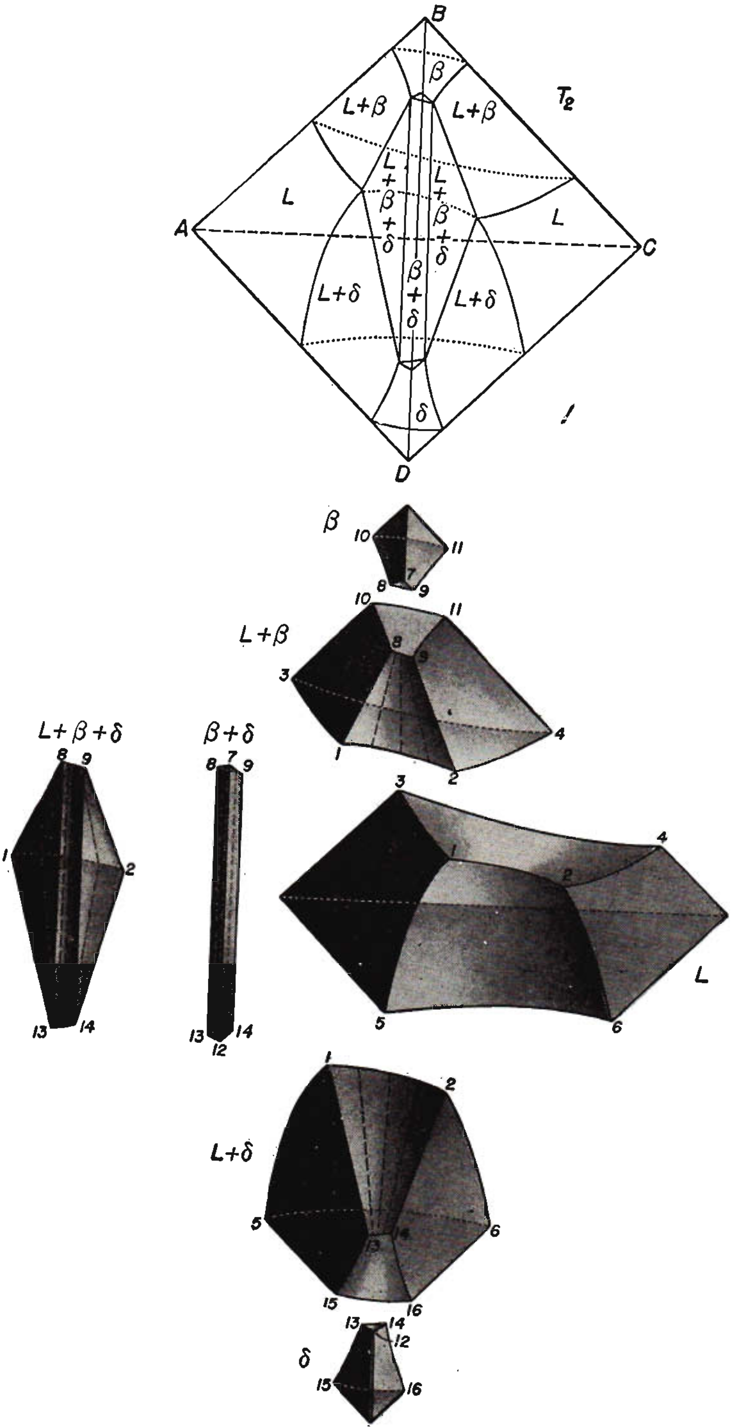
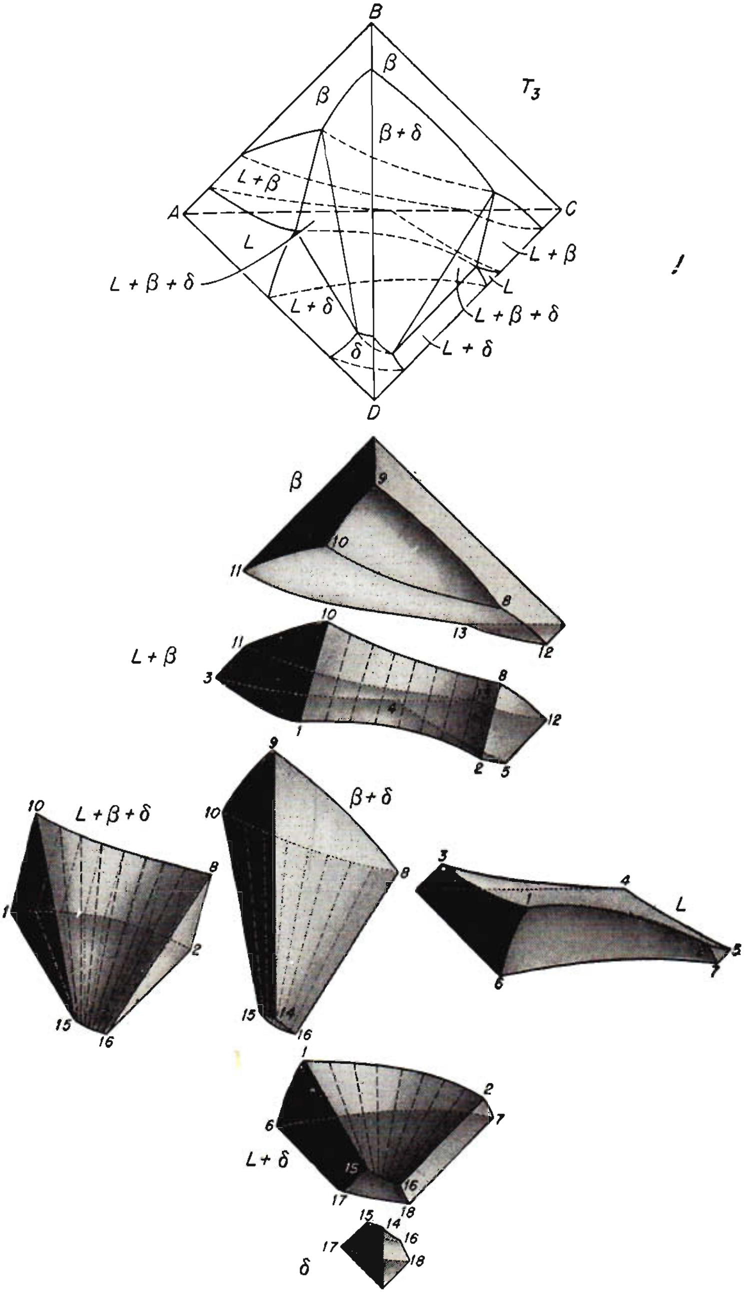

B
A
C
D
T_2
β
$L+\beta$
$L+\beta$
L
L
$L+\beta+\delta$
$L+\beta+\delta$
$\beta+\delta$
$L+\delta$
$L+\delta$
δ
β
$L+\beta$
$L+\beta+\delta$
$\beta+\delta$
L
$L+\delta$
δ

FIG. 19-20*b*.



B
β
T3
β
β + δ
L + β
A
C
L
L + β
L + β + δ
L
L + δ
L + β + δ
δ
L + δ
D
β
9
10
11
8
13
12
10
11
L + β
3
8
4
12
1
2
5
9
β + δ
10
L + β + δ
10
8
8
3
4
L
1
2
5
6
7
15
16
15
14
16
1
2
6
7
L + δ
15
16
17
18
15
14
16
17
18
δ

Fig. 19-20c.

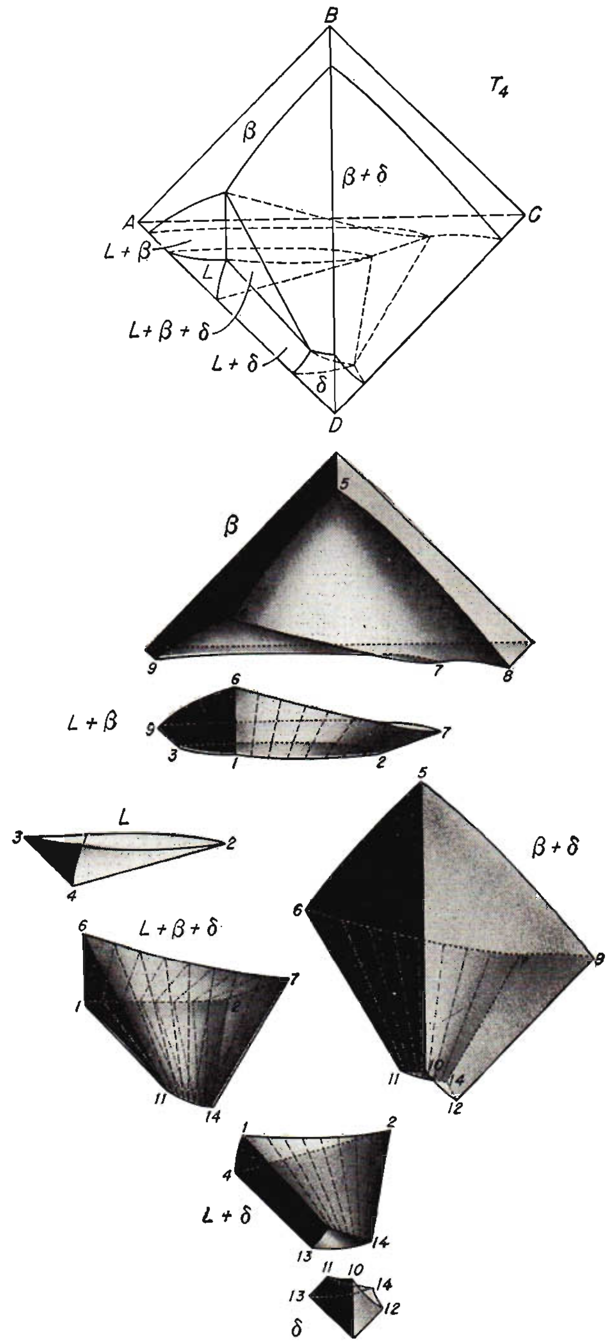


FIG. 19-20*d*.

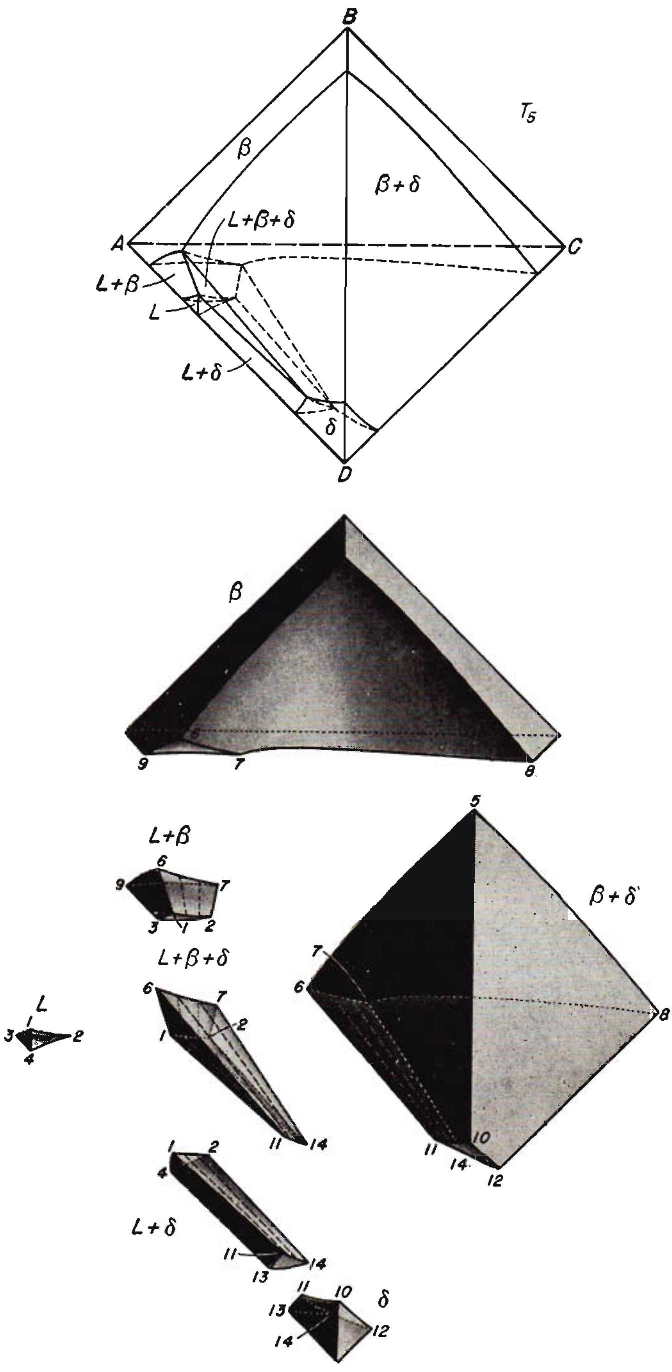

B
T_5
β
β+δ
L+β+δ
A
C
L+β
L
L+δ
δ
D
β
9
7
8
5
L+β
6
9
7
3
1
2
β+δ
L+β+δ
7
6
6
7
8
L
1
3
2
4
1
2
11
14
11
10
14
12
1
2
4
L+δ
11
14
13
11
10
δ
13
12
14

Fig. 19-20*e*.

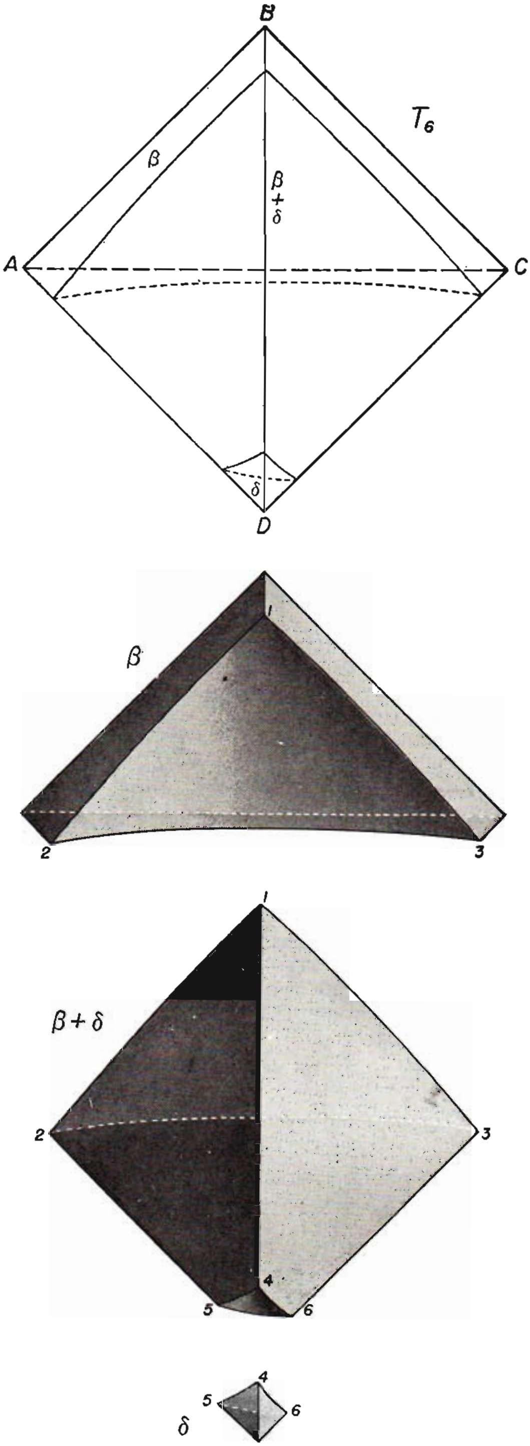


Fig. 19-20f.

are seen in the ternary faces ABD and BCD (see Fig. 19-20b). Indeed, these two faces appear very much the same as isotherm T_2 in Fig. 13-6. The three corners of the two tie-triangles in the ternary faces are connected point for point to form a solid space of triangular cross section (the space field $L + \beta + \delta$); i.e., the two liquid points are connected as are the two β points and the two δ points. This region is shown at the extreme left in the exploded model. An elongated region of $\beta + \delta$ lies between the BD edge of the diagram and the $L + \beta + \delta$ region, forming one surface of that region. Another surface of the three-phase region is formed by the top boundary of the $L + \delta$ region, and the third surface is the front boundary of the $L + \beta$ region. All these surfaces are inscribed with tie-lines in the exploded model; also, to aid the reader, the corners of the several regions are identified by numbers that correspond from region to region.

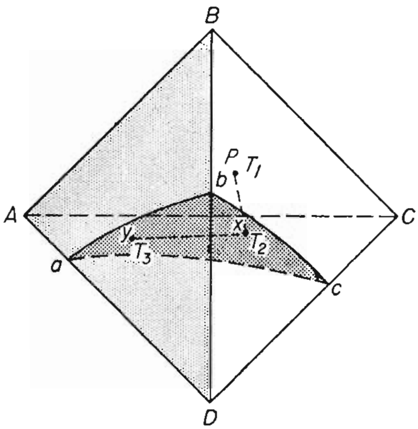


FIG. 19-21. Liquidus projection of the quaternary diagrams of Fig. 19-20. The shaded plane is the trace of all compositions of the liquid phase in three-phase equilibrium with β and δ, i.e., the quaternary equivalent of the ternary "liquidus valley." The dashed line represents the course of composition change of the liquid phase during the freezing of the alloy of initial composition P.

As the temperature continues to fall, the three-phase region becomes broader and approaches the lower face of the tetrahedron (see Fig. 19-20c). Between T_3 and T_4 it meets the binary eutectic of the system CD, where the terminal cross section of the region is reduced to a single line. From T_4, Fig. 19-20d, downward in temperature, the $L + \beta + \delta$ region no longer touches the BCD face of the tetrahedron, all alloys of this ternary system now being solid. It extends, instead, from the ACD face to the ABD face. Finally, between T_5, Fig. 19-20e, and T_6, Fig. 19-20f, the three-phase region ends in the $L + \beta + \delta$ binary eutectic line of the system AD, and the last of the liquid disappears. Below the AD eutectic the quaternary system is seen to be composed of only three regions, namely, β, δ, and $\beta + \delta$.

The course of freezing of a typical alloy may be followed with these isotherms, but a simpler view is obtained by the use of a "liquidus projection." The shaded surface *abc* in Fig. 19-21 represents the trace of the "liquidus valley" (i.e., trace of the line representing liquid on the $L + \beta + \delta$ region in Fig. 19-20) through the entire freezing range. Consider the behavior of a four-component alloy of composition P, which lies within the space of the tetrahedron between the BC edge and the surface *abc*. As freezing begins at T_1, the liquid will have the composition *P*. Primary crystals of β are rejected, and the liquid composition moves downward and forward, away from the *B* corner, with falling temperature, until at T_2 it reaches point *x* on the surface *abc*. Now a secondary separation of $\beta + \delta$ begins. The direction of shift of the liquid composition changes sharply and moves away from the *BD* edge along the surface *abc* to *y* at T_3, where the liquid is exhausted and the alloy is entirely solid. This alloy will have a microstructure which appears very similar to that of a binary hypoeutectic alloy (Fig. 4-8*b*) or of a ternary alloy involving only three-phase equilibrium (Fig. 13-9, 20°C). The coring will, of course, be more complex than appears in the microstructure, since there is variation with respect to four

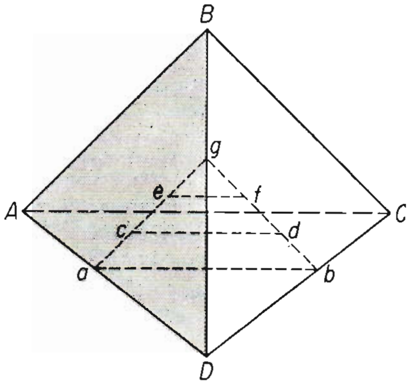


FIG. 19-22. Plan of isopleths shown in Fig. 19-23.

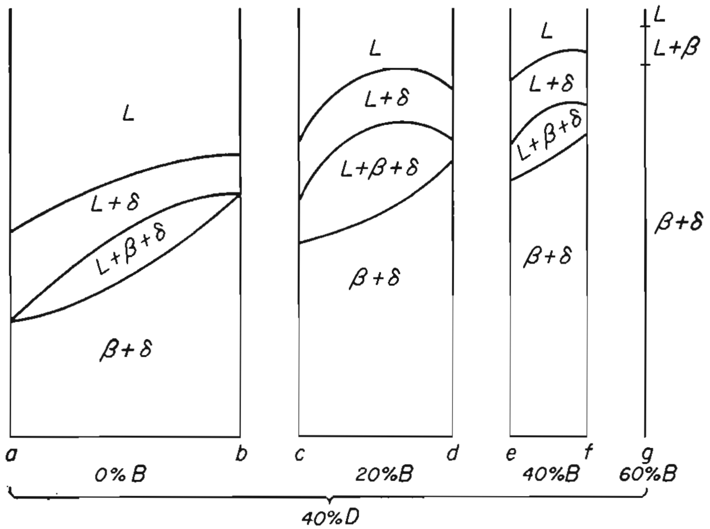


FIG. 19-23. Isopleths through the quaternary phase diagram of Fig. 19-20.

components. An analysis of the tie-triangles in this diagram will show that both of the solid phases must increase in quantity as the liquid diminishes during cooling. With other reactions combined in three-phase equilibrium, corresponding transformation characteristics can be developed as was done in the case of ternary alloys in Chap. 13.

In order to record actual temperatures of phase changes in this system, as with all quaternary alloys, it is necessary to employ a series of isopleths. A typical series taken at 40% D with fixed percentages of B in successive diagrams is given in Fig. 19-23. A key to the location of these sections appears in Fig. 19-22. The first diagram of the series a-b lies in the ternary system ACD and is normal for a vertical section through a ternary alloy. Succeeding sections are somewhat similar, though it should be noted that the three-phase field is not closed at the edges of the diagram.

A System Involving Four-phase Equilibrium

A simple example of four-phase equilibrium in a quaternary system is illustrated in the seven isotherms of Fig. 19-24. Among the six binary systems concerned, five are of the simple eutectic type and one (AC) is isomorphous; two of the four ternary systems are of the simple ternary eutectic type, while the other two involve no four-phase equilibria.

The first isotherm in Fig. 19-24a is taken at a temperature slightly below the BD binary eutectic at which the three-phase region $L + \beta + \delta$ originates. Just above the ABD ternary eutectic temperature, T_2 in Fig. 19-24b, three three-phase regions are seen growing toward a junction near the center of the ABD face of the tetrahedron. The junction is effected with the first appearance of four-phase equilibrium, $L + \alpha + \beta + \delta$, at the ternary eutectic temperature T_3, Fig. 19-24c. Point L of the ternary four-phase equilibrium now moves rapidly into the space diagram, while points α, β, and δ move slowly inward, Fig. 19-24d. Thus is created a tetrahedral figure representing quaternary four-phase equilibrium. Upon each of its four faces it meets a three-phase region, $\alpha + \beta + \delta$ originating upon the ABD face of the isotherm, $L + \alpha + \beta$ upon the ABC face, $L + \alpha + \delta$ upon the ACD face, and $L + \beta + \delta$ upon the BCD face.

As the temperature continues to fall, this four-phase tetrahedron sweeps through the space diagram (see T_5, Fig. 19-24e) approaching the BCD ternary eutectic (T_6, Fig. 19-24f). The last of the liquid vanishes as the four-phase tetrahedron closes to a plane and terminates upon the ternary eutectic isotherm at the BCD ternary eutectic temperature. At this and lower temperatures a three-phase region $\alpha + \beta + \delta$ crosses the space diagram from its ABD face to its BCD face (Fig. 19-24g).

Alloys of this system should be expected to develop structures similar to ordinary ternary eutectic alloys except that coring is possible in all constituents. A series of typical isopleths taken at 20% of the B component and with the quantity of the D component increasing in intervals of 20% in the series is given in Fig. 19-25. It will be noted that there are no isothermal (horizontal) boundaries anywhere in these diagrams.

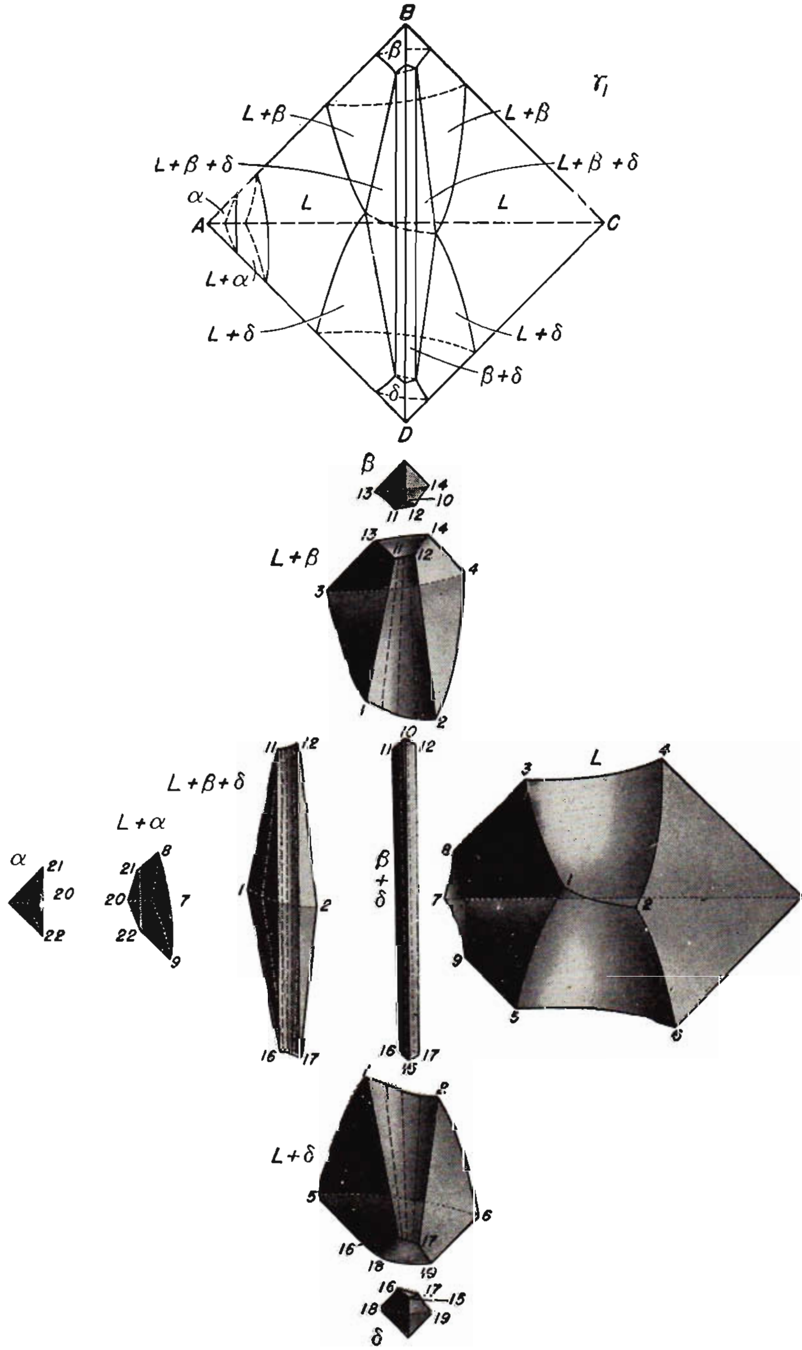


FIG. 19-24*a*. Seven isotherms from a quaternary system in which the four-phase equilibrium $L + \alpha + \beta + \delta$ sweeps through the diagram from the ternary eutectic *ABD* at T_3 to the ternary eutectic *BCD* between T_6 and T_7. The sequence of isotherms is from high temperature at T_1 to low temperature at T_7.

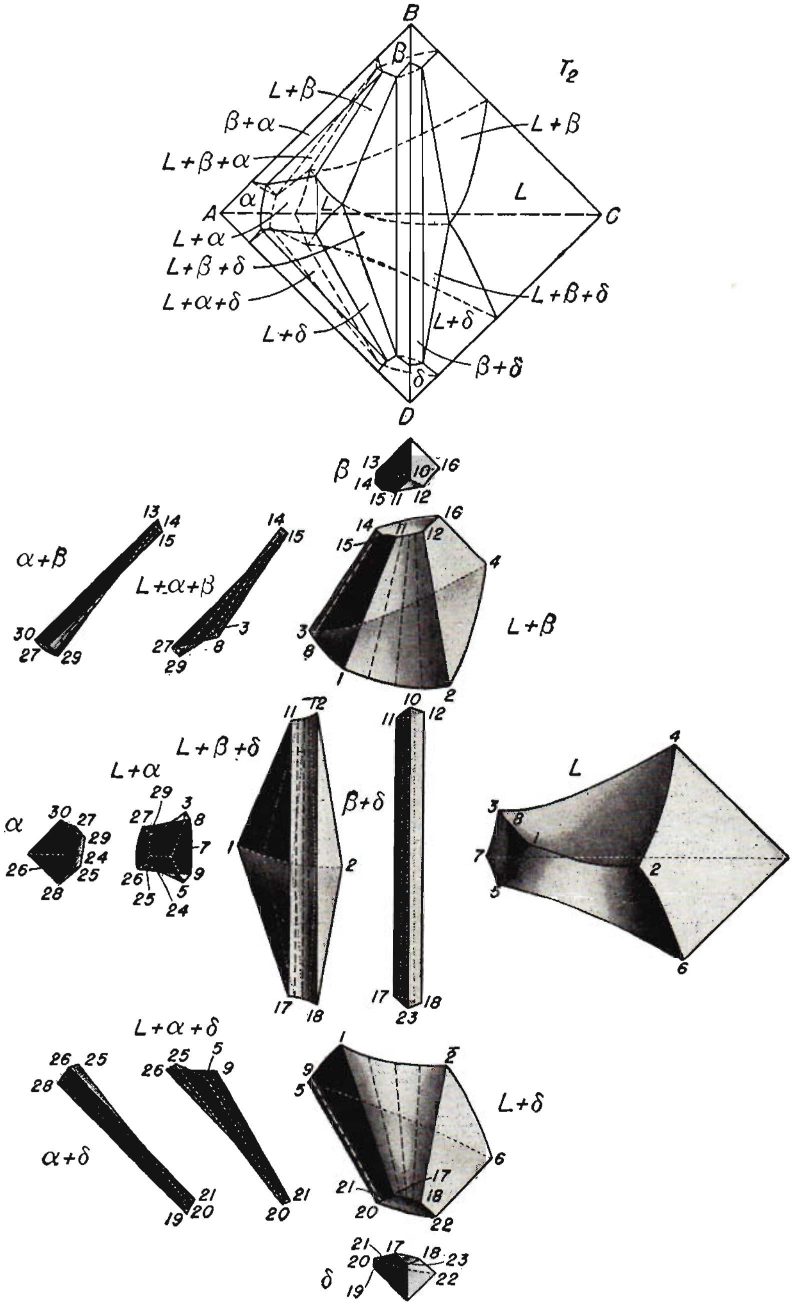


FIG. 19-24b.

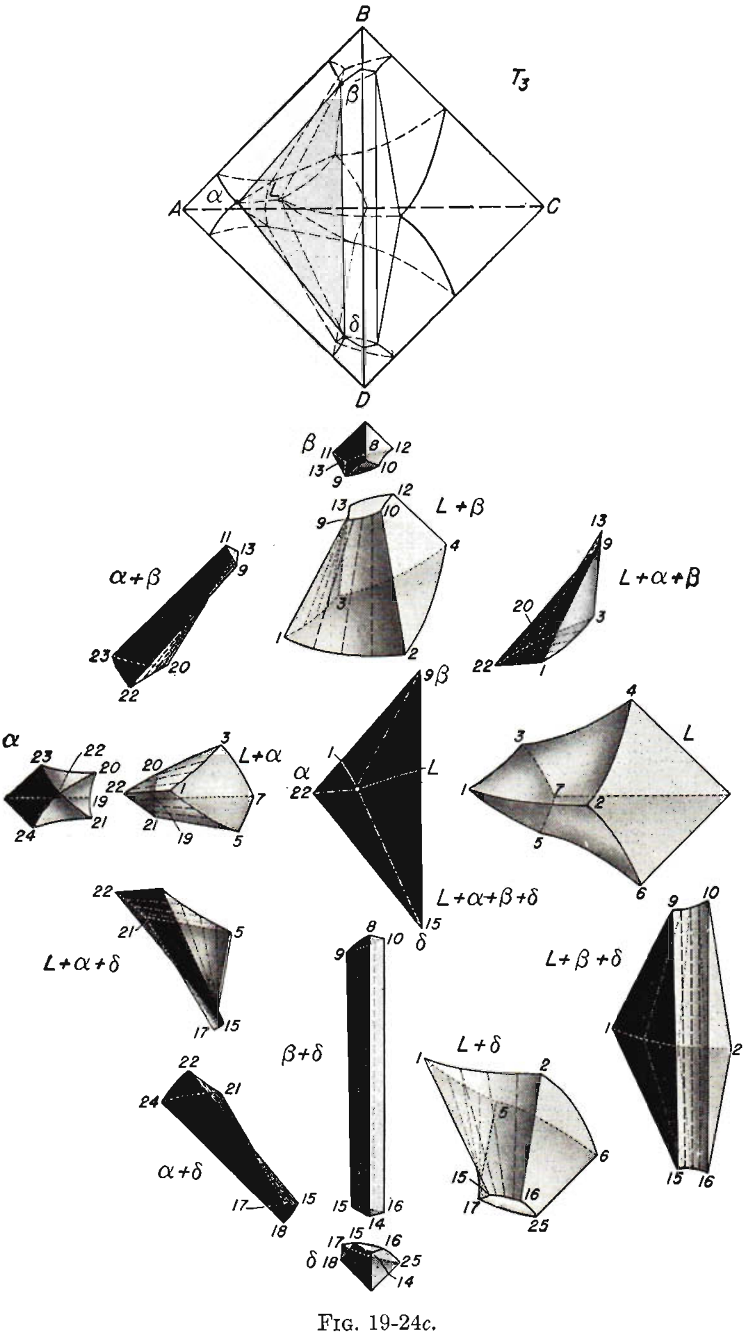


FIG. 19-24c.

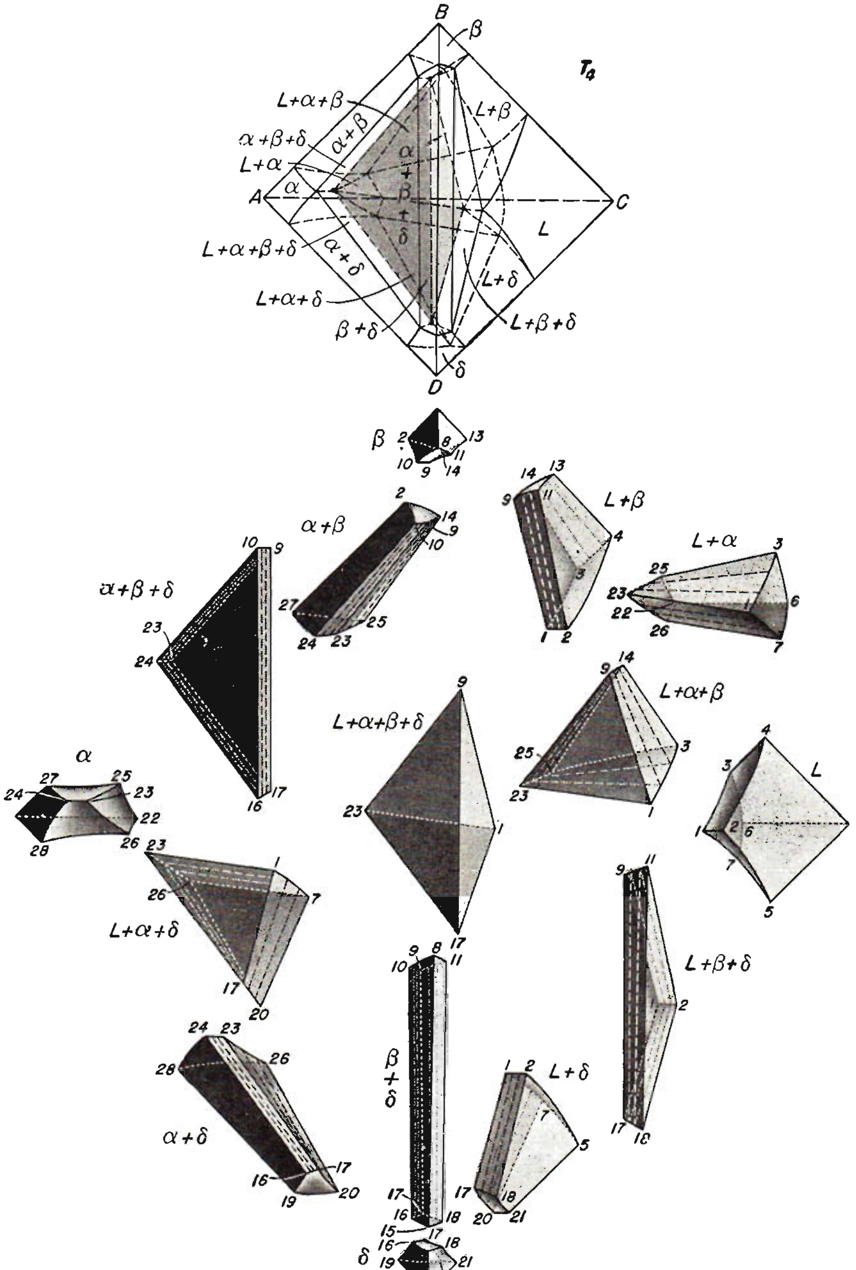
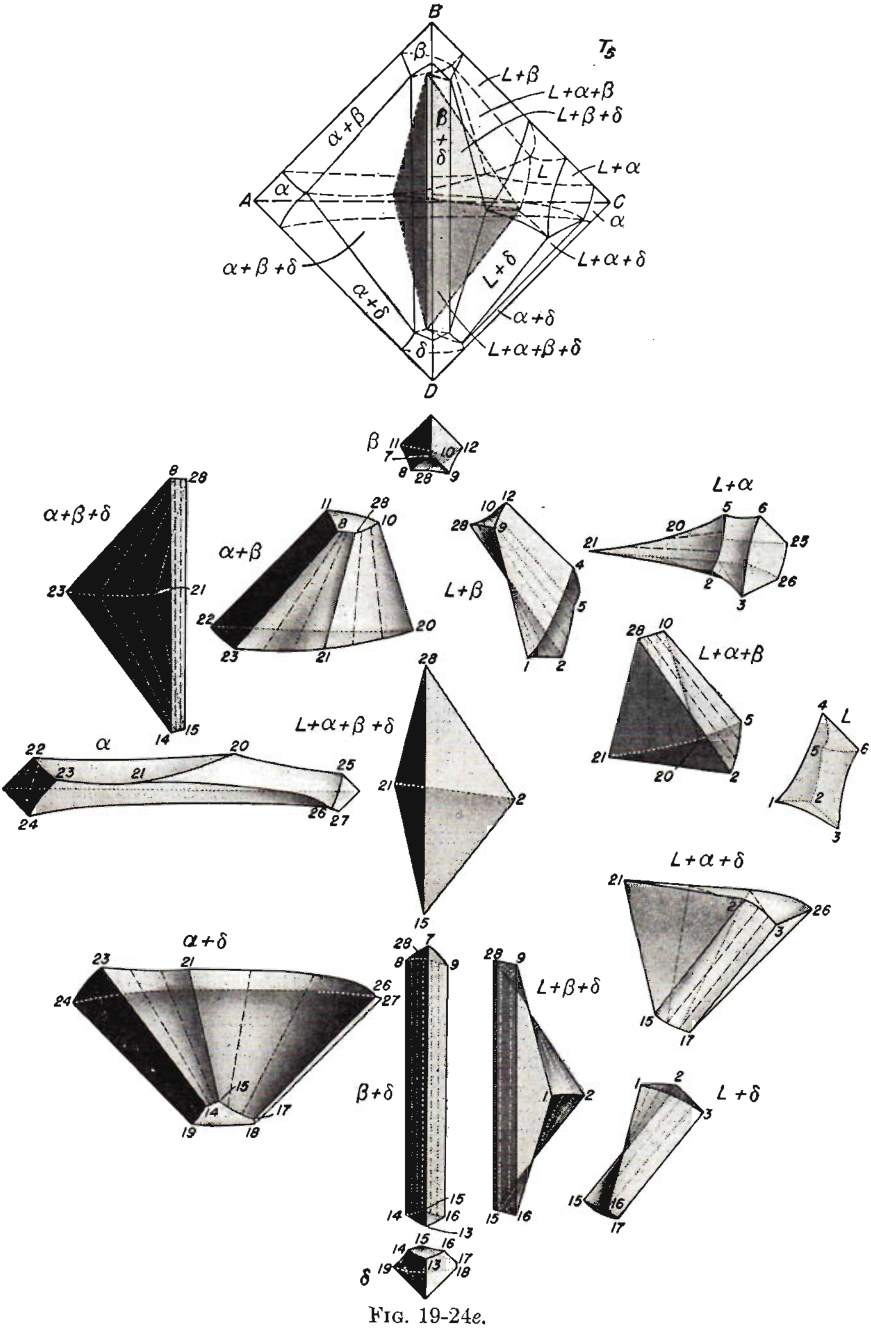

B
β
T_4
L+α+β
α+β+δ
α+β
L+α
L+β
α
A
C
L
L+α+β+δ
α+δ
L+α+δ
L+δ
β+δ
L+β+δ
δ
D
β
α+β
L+β
L+α
α+β+δ
L+α+β+δ
L+α+β
α
L
L+α+δ
L+β+δ
β
+
δ
L+δ
α+δ
δ

FIG. 19-24*d*.



B
T_5
β
$L+\beta$
$L+\alpha+\beta$
$L+\beta+\delta$
$\alpha+\beta$
$\beta+\delta$
L
$L+\alpha$
A
α
C
α
$\alpha+\beta+\delta$
$L+\alpha+\delta$
$L+\delta$
$\alpha+\delta$
$\alpha+\delta$
δ
$L+\alpha+\beta+\delta$
D
β
$\alpha+\beta+\delta$
$\alpha+\beta$
$L+\beta$
$L+\alpha$
$L+\alpha+\beta$
α
$L+\alpha+\beta+\delta$
L
$L+\alpha+\delta$
$\alpha+\delta$
$\beta+\delta$
$L+\beta+\delta$
$L+\delta$
δ

FIG. 19-24e.

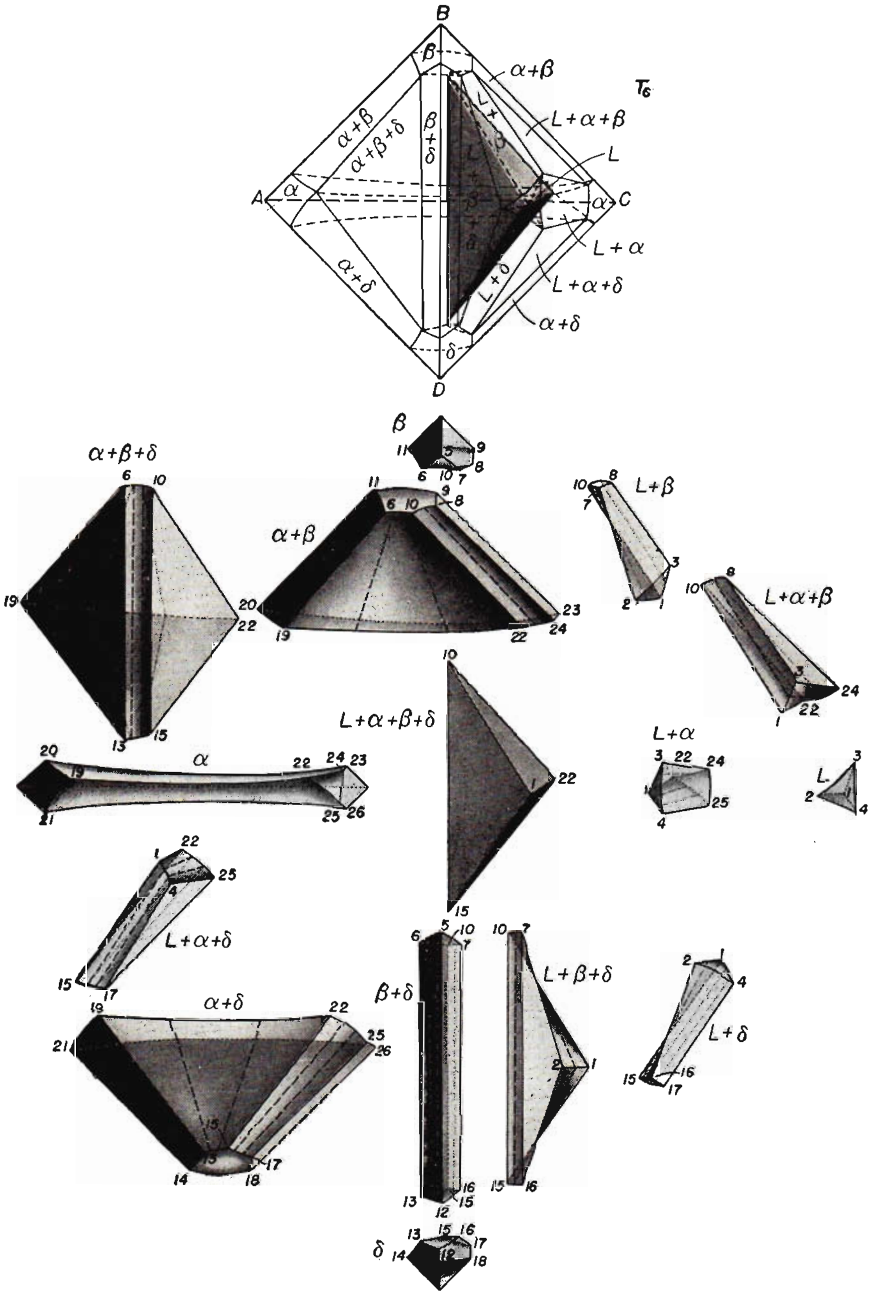

B
A
C
D
T_6
$\alpha+\beta$
$\alpha+\beta+\delta$
$\beta+\delta$
$L+\alpha+\beta$
L
$L+\alpha$
$L+\alpha+\delta$
$\alpha+\delta$
$L+\delta$
β
δ
α
$L+\beta$
$L+\alpha+\beta+\delta$
$L+\beta+\delta$

Fig. 19-24*f*.

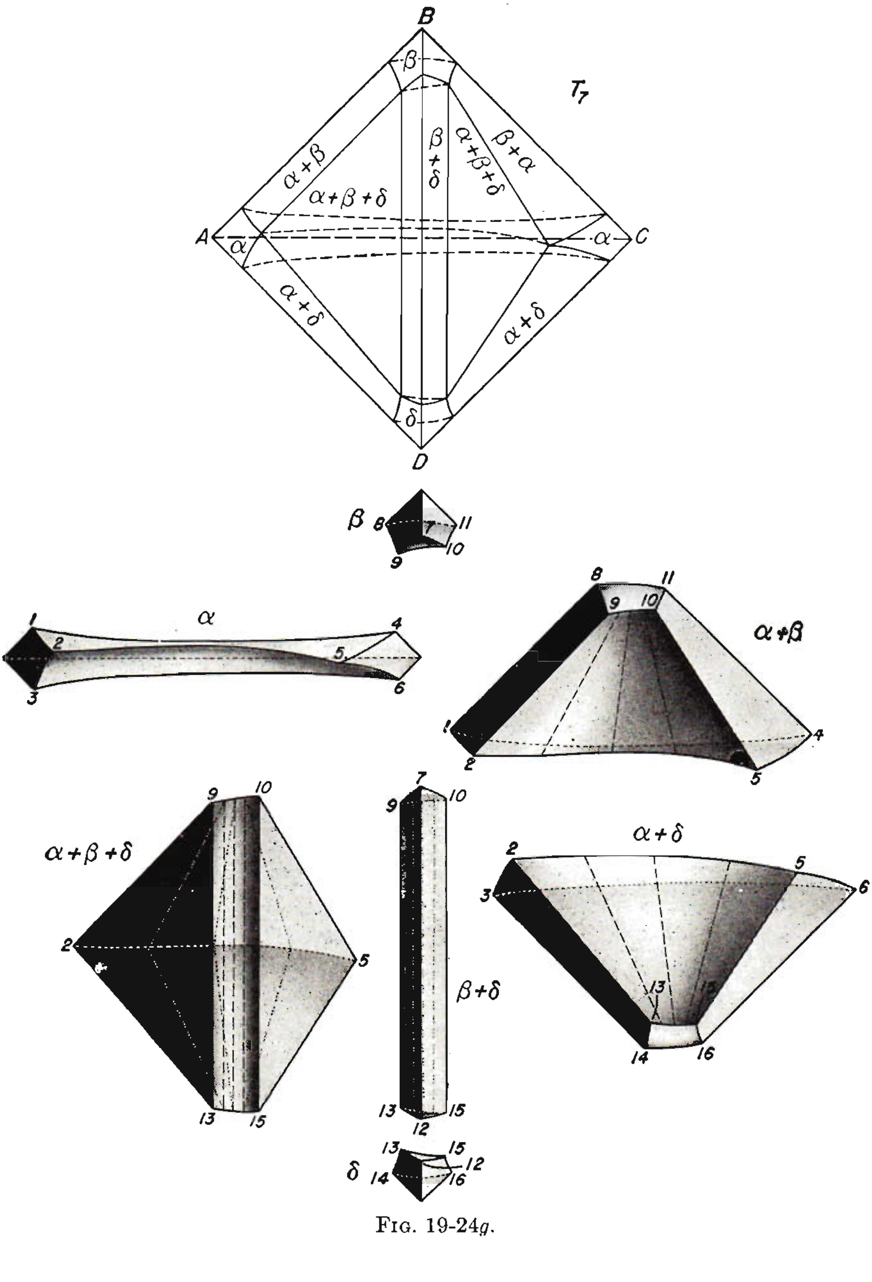


Fig. 19-24g.

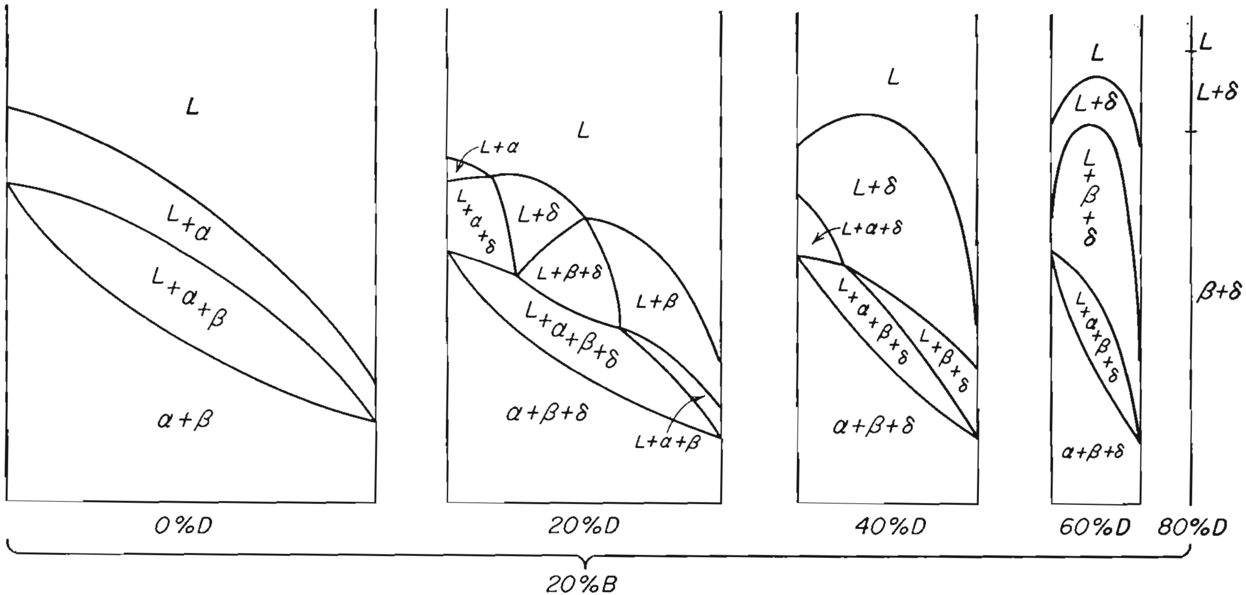


FIG. 19-25. Isopleths through the quaternary system shown in Fig. 19-24.

An Example of Class I Five-phase Equilibrium, A Quaternary Eutectic System

Five-phase equilibrium of the first kind may be exemplified by a *quaternary eutectic* system, Fig. 19-26. This rather complex diagram is, perhaps, best understood by comparing it with the foregoing example of four-phase equilibrium. Here, all the six binary systems are taken to be of the eutectic type, and all four ternary systems are of the simple ternary eutectic class. The first six isotherms of Fig. 19-26 record the progress of freezing the four ternary eutectics with the development of a four-phase tetrahedron corresponding to each. At T_2, Fig. 19-26*b*, the ternary eutectic of the system ABD is being approached. This reaction results in the formation of the tetrahedral region $L + \alpha + \beta + \delta$ that appears for the first time in section T_3, Fig. 19-26*c*. Between T_3 and T_4 the ACD ternary eutectic is passed, introducing the tetrahedral region $L + \alpha + \gamma + \delta$, Fig. 19-26*d*, and between T_4 and T_5 the ternary eutectic of the system ABC gives rise to the four-phase region $L + \alpha + \beta + \gamma$, Fig. 19-26*e*. All four-phase regions are present in section T_6, Fig. 19-26*f*, which is below all the ternary eutectic temperatures but above the quaternary eutectic temperature.

The liquid region at T_6 is enclosed wholly within the space of the isotherm, being outlined by six curved lines that join the liquid points of the four four-phase tie-tetrahedra. This region shrinks to a single point at the quaternary eutectic temperature T_7, Fig. 19-26*g*, where the four four-phase tetrahedra join to form the five-phase isothermal tetrahedron that is the *quaternary eutectic reaction isotherm*. Below T_7 the configuration of the diagram remains qualitatively constant, with a single tie-tetrahedron representing the equilibrium $\alpha + \beta + \gamma + \delta$.

The *quaternary eutectic point* is the point in composition that represents the last liquid to freeze. An alloy of this composition freezes isothermally with the simultaneous rejection of four solid phases. The resulting structure is illustrated for the quaternary eutectic alloy of the system bismuth-cadmium-lead-tin (approximately "Wood's metal") in Fig. 19-27. In this case, the bismuth, being present in major proportion, forms a matrix in which the other three phases are embedded. It is worthy of note that equilibrium is achieved in complex structures such as this without each phase necessarily making physical contact with every other phase. If α is in contact with β and the two are in mutual equilibrium, and if, at the same time, γ is in contact and in equilibrium with β, then α and γ will be in equilibrium with each other whether or not they touch each other in the microstructure.

Alloys of other than quaternary eutectic composition may freeze in a variety of ways. The pattern of freezing of a randomly selected quaternary

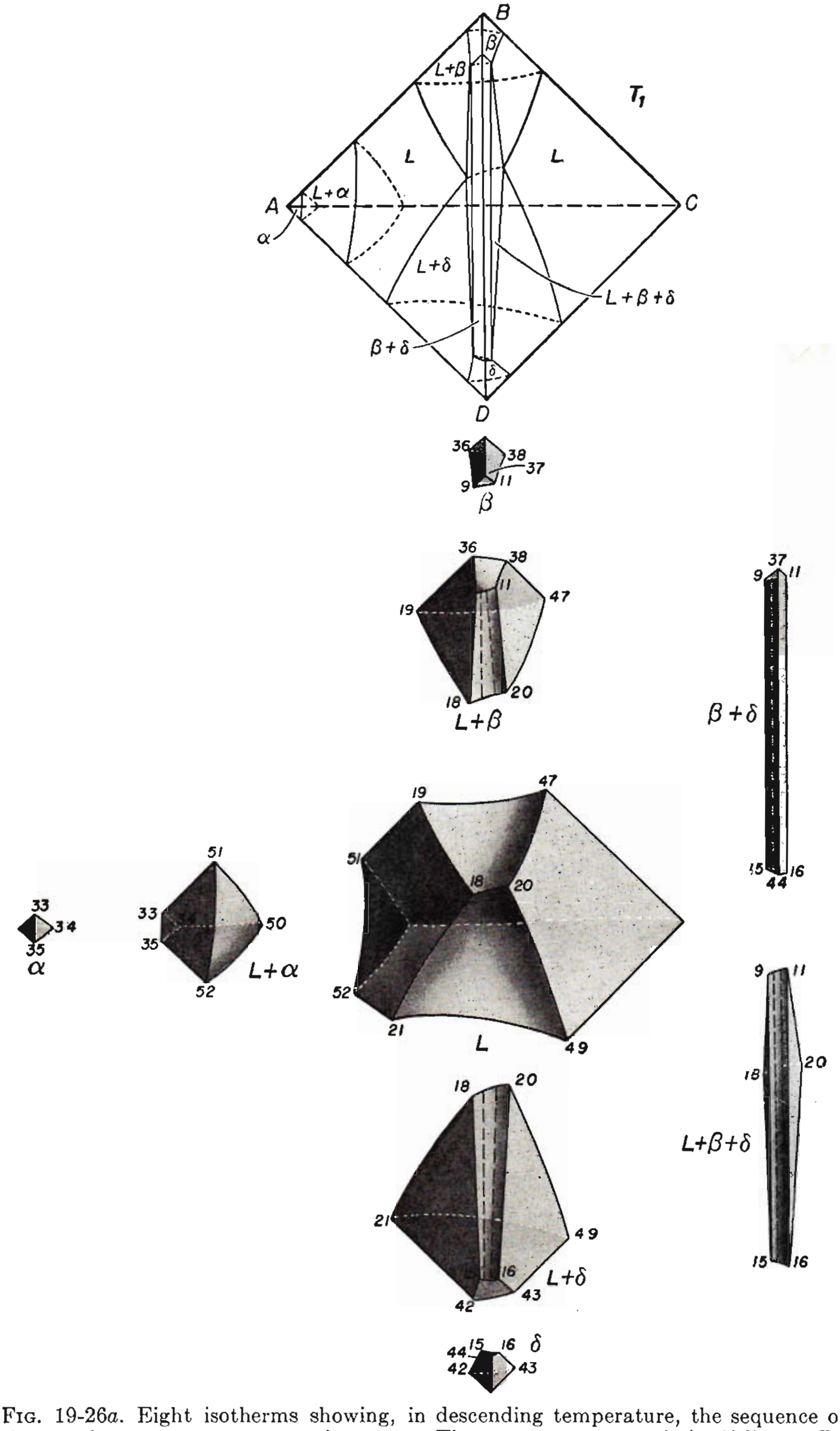


FIG. 19-26a. Eight isotherms showing, in descending temperature, the sequence of changes in a quaternary eutectic system. The quaternary eutectic itself lies at T_7, where the five-phase equilibrium $L + \alpha + \beta + \gamma + \delta$ is represented.

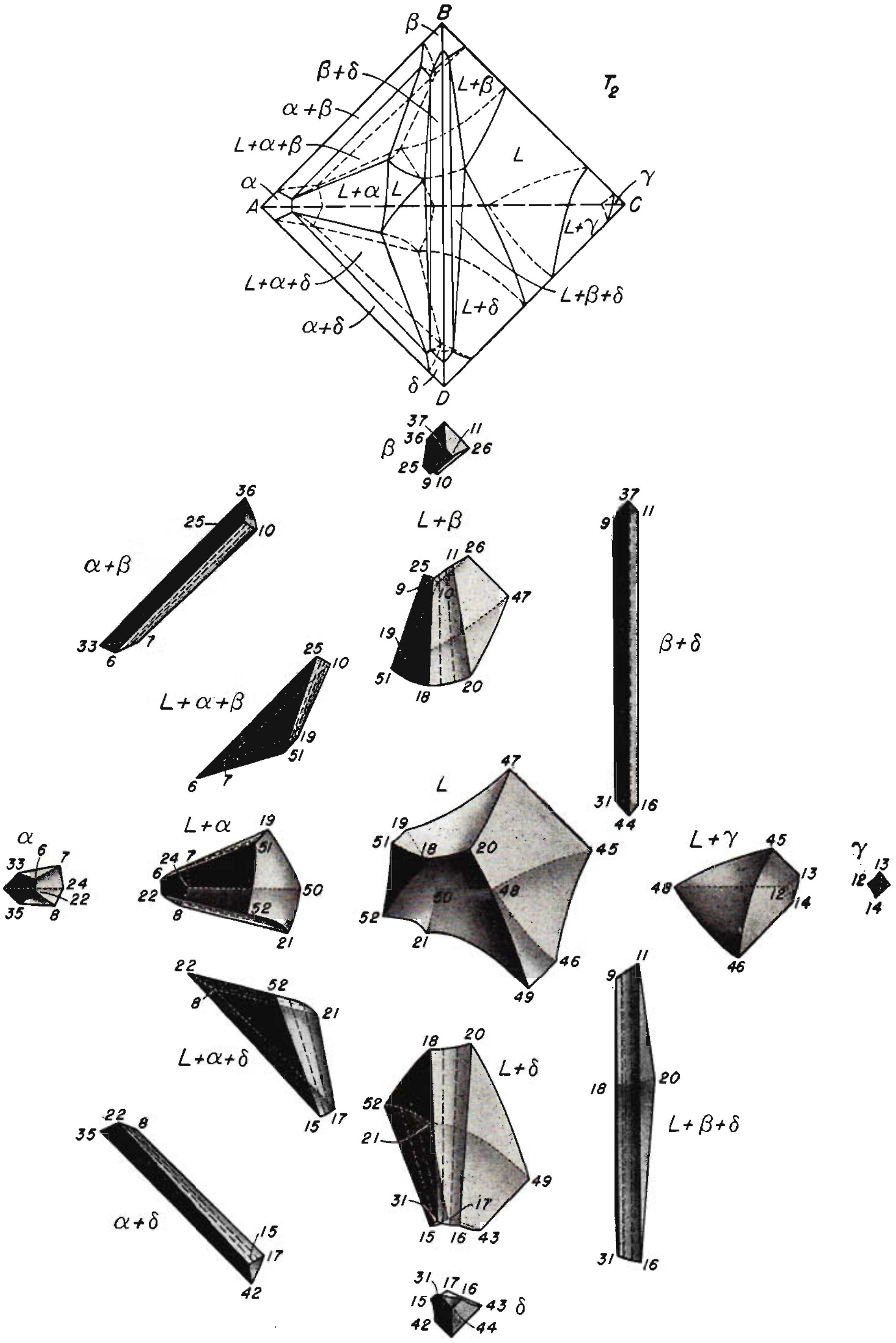


FIG. 19-26b.

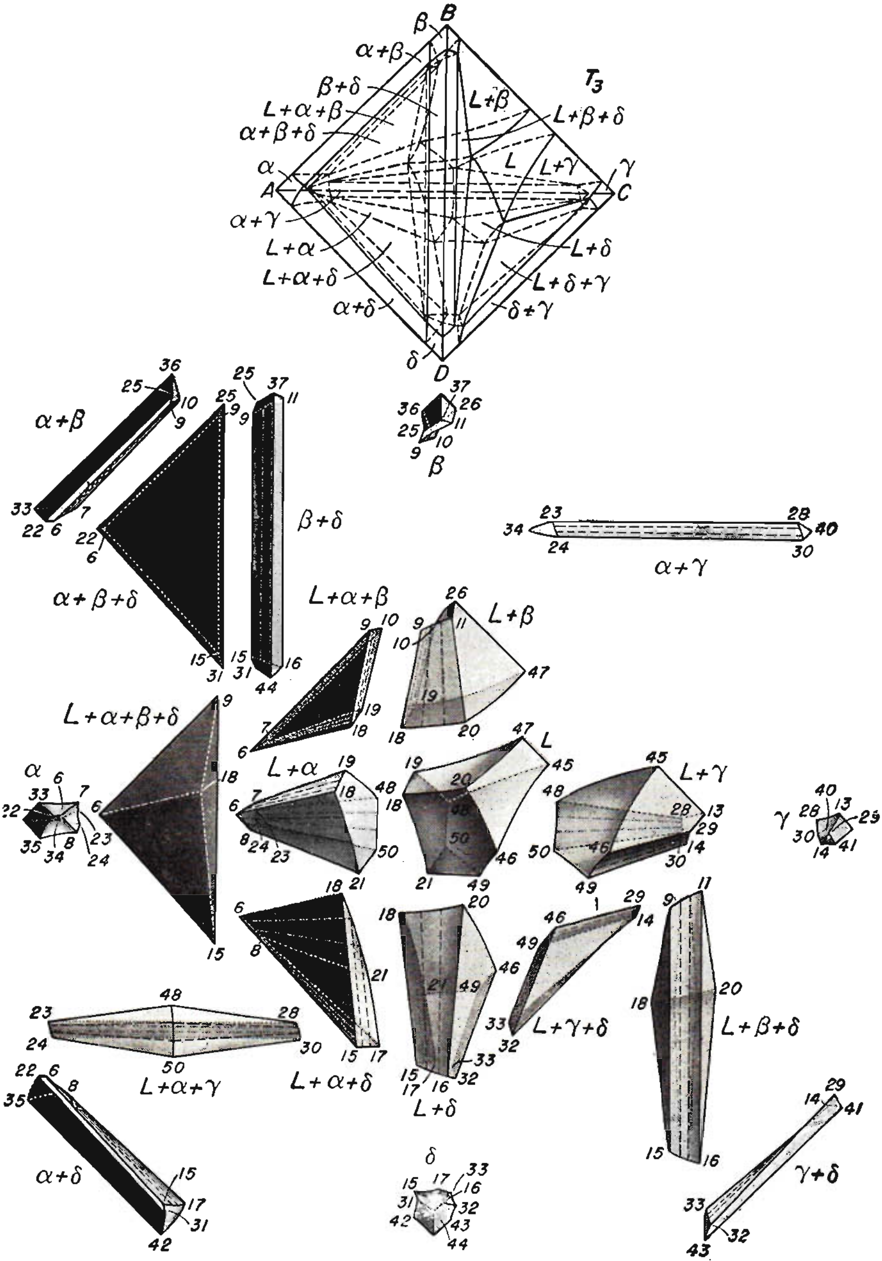


FIG. 19-26c.

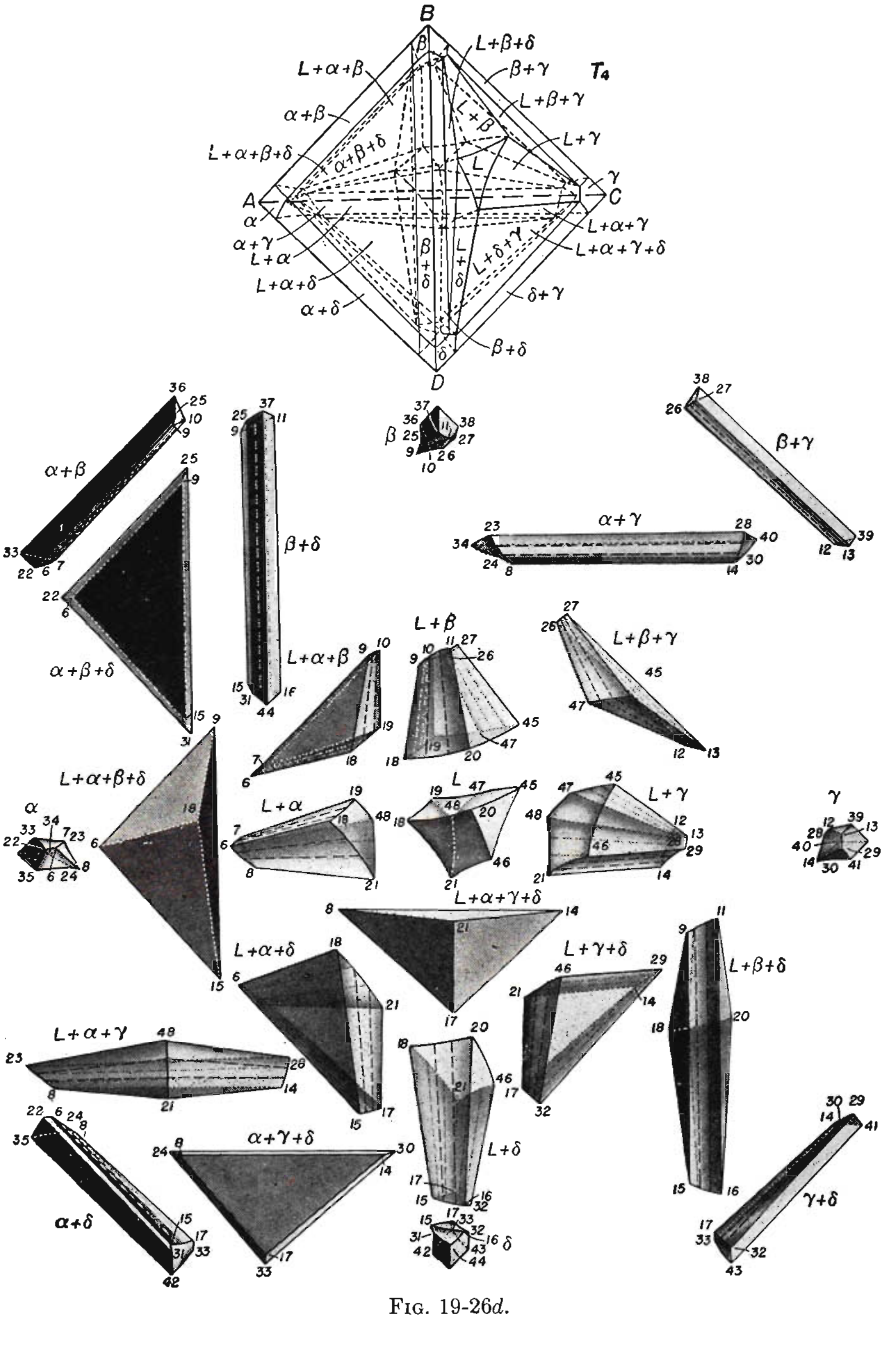

B
A
C
D
T_4
$L+\alpha+\beta$
$L+\beta+\delta$
$\beta+\gamma$
$L+\beta+\gamma$
$\alpha+\beta$
$L+\gamma$
$L+\alpha+\beta+\delta$
$\alpha+\beta+\delta$
$L+\alpha+\gamma$
$L+\alpha+\gamma+\delta$
$\alpha+\gamma$
$L+\alpha$
$L+\alpha+\delta$
$\alpha+\delta$
$\delta+\gamma$
$\beta+\delta$
$L+\delta+\gamma$
β
α
γ
δ
L
$L+\beta$
$L+\delta$
$L+\gamma+\delta$
$\alpha+\gamma+\delta$
$\gamma+\delta$

FIG. 19-26*d*.

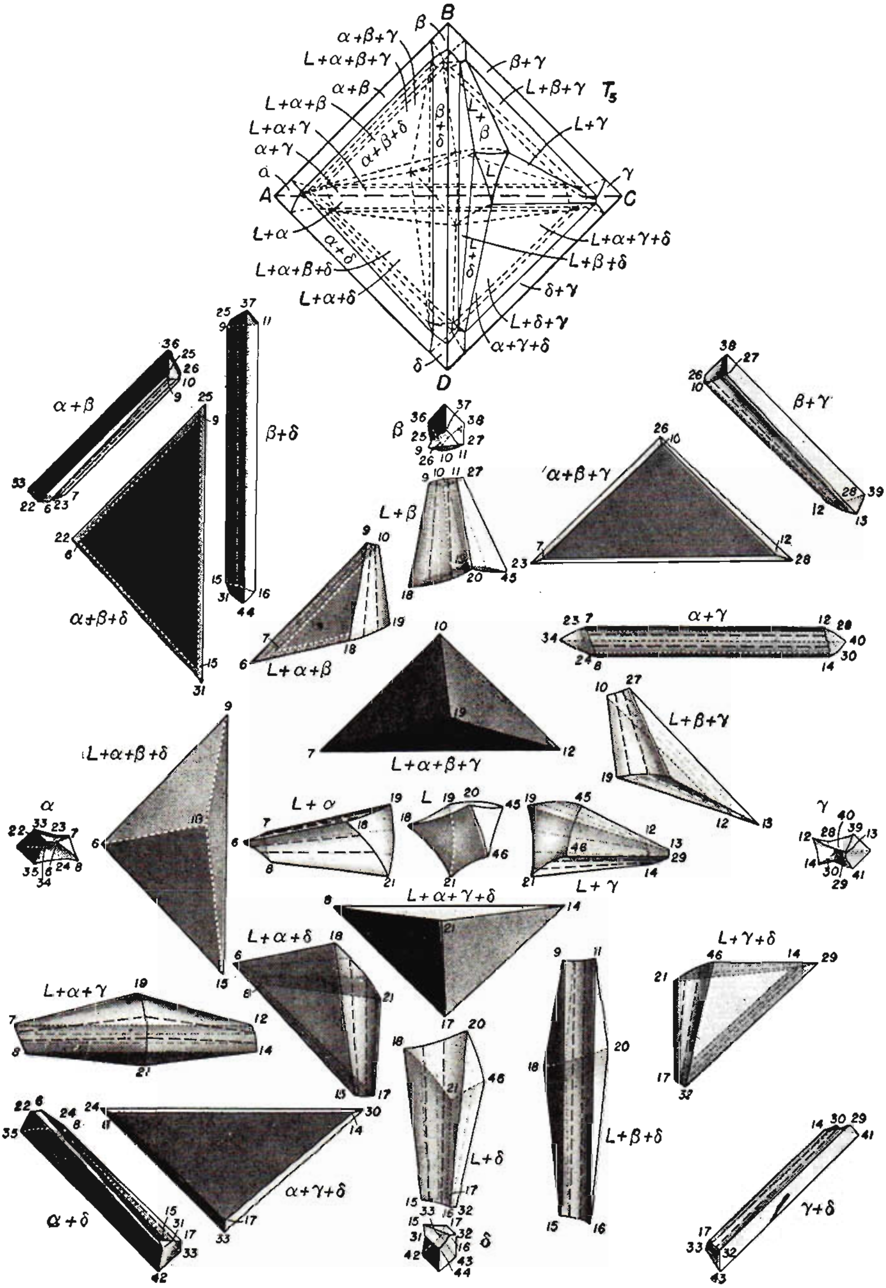

T5
α+β
β+δ
β
β+γ
α+β+γ
L+β
α+β+δ
L+α+β
α+γ
L+α+β+γ
L+β+γ
L+α+β+δ
α
L+α
L
L+γ
γ
L+α+γ+δ
L+α+δ
L+γ+δ
L+α+γ
L+β+δ
L+δ
α+γ+δ
α+δ
δ
γ+δ

Fig. 19-26e.

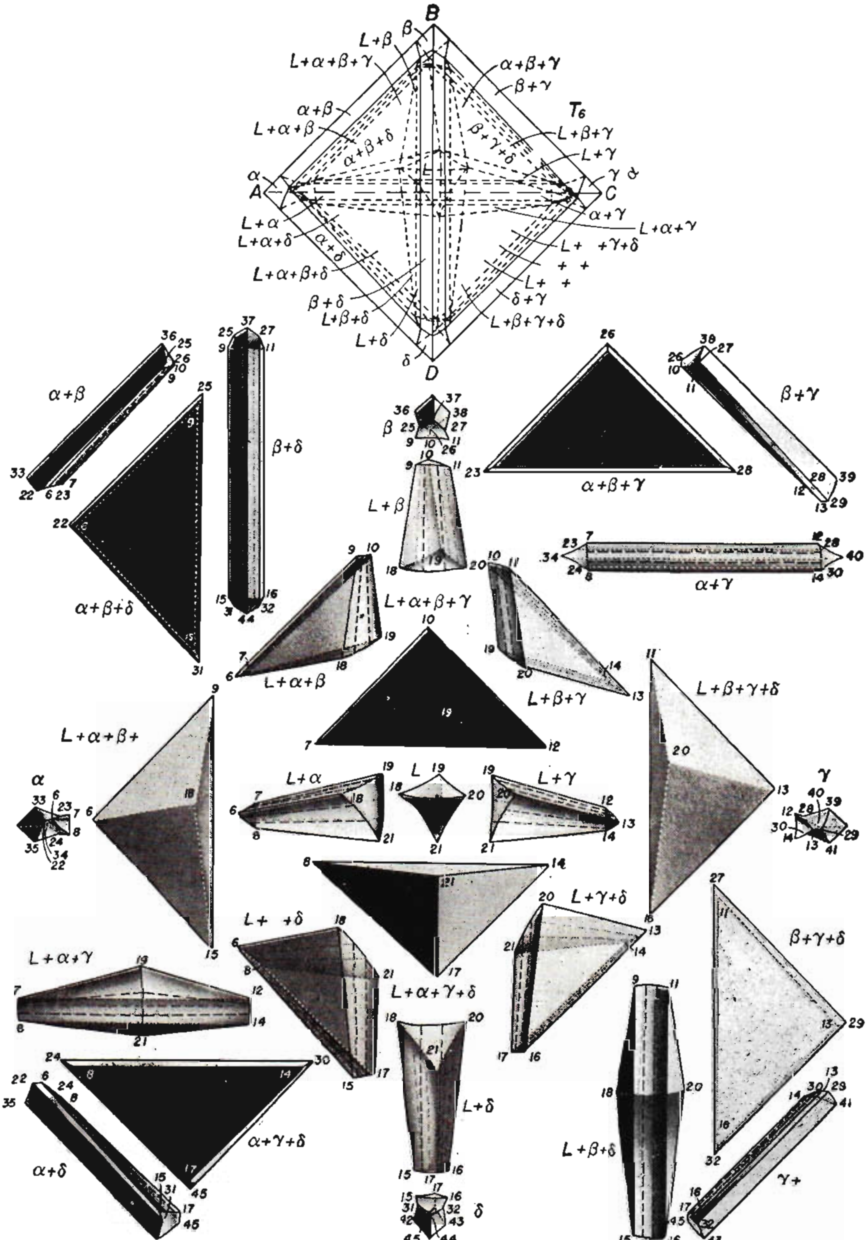

B
A
C
D
T6
L+β
β
L+α+β+γ
α+β+γ
β+γ
α+β
L+α+β
α+β+δ
β+γ+δ
L+β+γ
L+γ
α
γ
L+α
L+α+δ
α+δ
α+γ
L+α+γ
L+ +γ+δ
L+α+β+δ
β+δ
L+β+δ
L+δ
δ+γ
L+β+γ+δ
δ
α+β+δ
L+α+β+γ
L+α+β
L+β+γ
L+α+β+
L+α
L
L+γ
L+α+γ
L+ +δ
L+γ+δ
L+α+γ+δ
α+γ+δ
β+γ+δ
γ+

FIG. 19-26*f*.

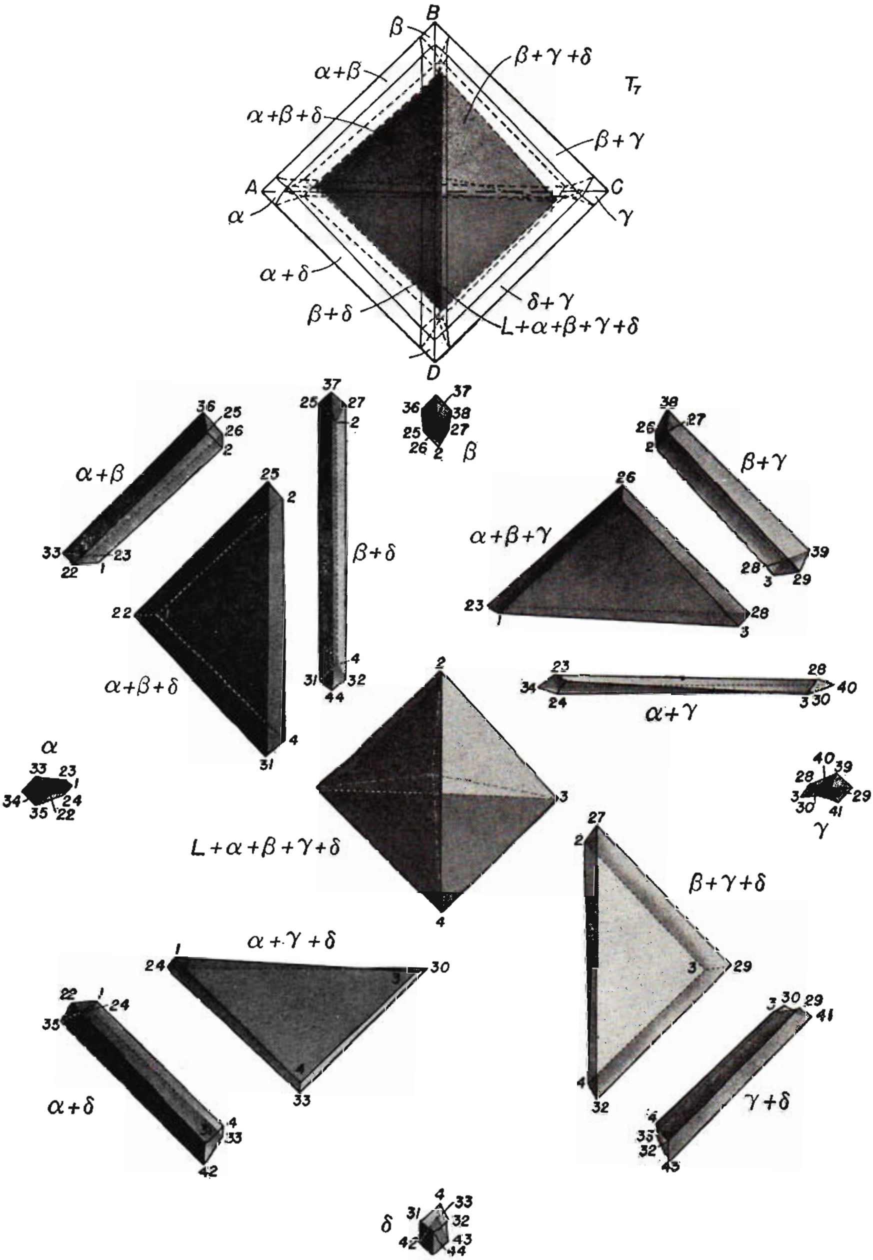

B
β
α+β
β+γ+δ
T_7
α+β+δ
β+γ
A
C
α
γ
α+δ
δ+γ
β+δ
L+α+β+γ+δ
D
α+β
β+δ
β
β+γ
α+β+γ
α+β+δ
α+γ
α
γ
L+α+β+γ+δ
β+γ+δ
α+γ+δ
α+δ
γ+δ
δ

FIG. 19-26g.

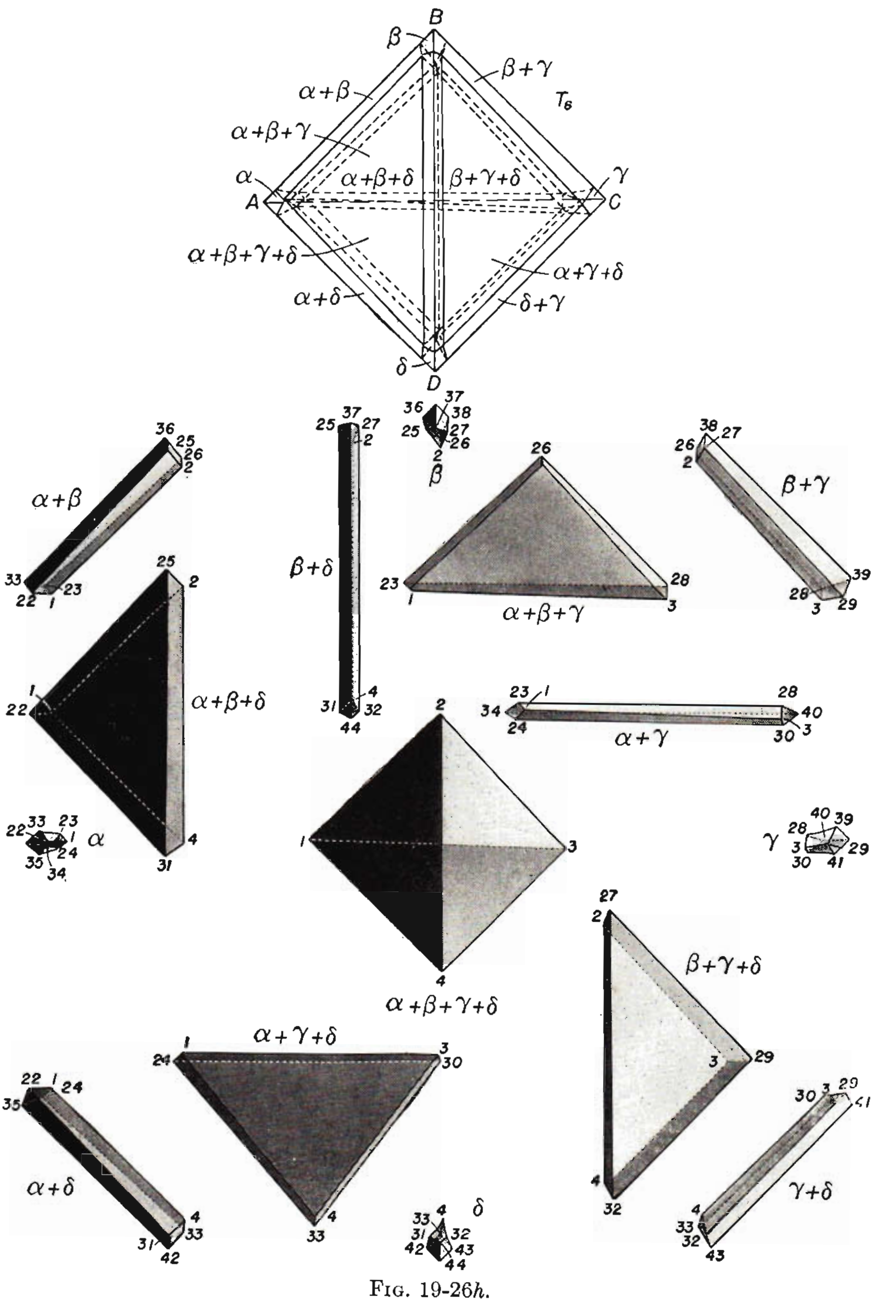

B
β
β+γ
α+β
T6
α+β+γ
α
α+β+δ
β+γ+δ
γ
A
C
α+β+γ+δ
α+γ+δ
α+δ
δ+γ
δ
D
α+β
β+δ
β
α+β+γ
β+γ
α+β+δ
α
α+γ
γ
α+β+γ+δ
β+γ+δ
α+γ+δ
α+δ
δ
γ+δ

FIG. 19-26h.

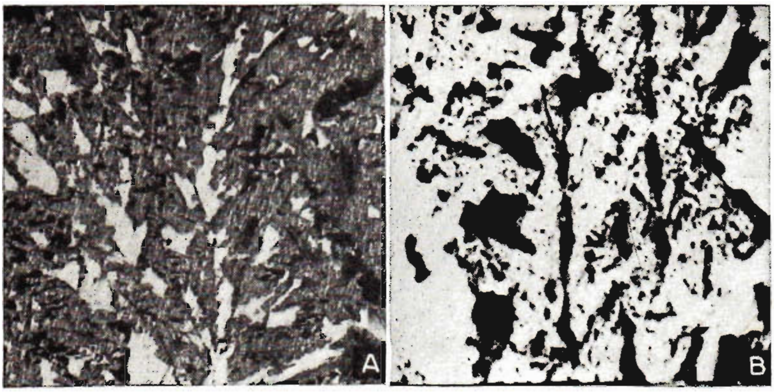


FIG. 19-27. Microstructure of the quaternary eutectic of the system bismuth-lead-tin-cadmium; the four phases are, respectively: bismuth (light-colored matrix, best seen in B); lead (small, dark, script-like particles, giving gray color to the matrix in A); tin (large, white masses, most evident in A); and cadmium (large, black particles). Magnification: A, 100; B, 500.

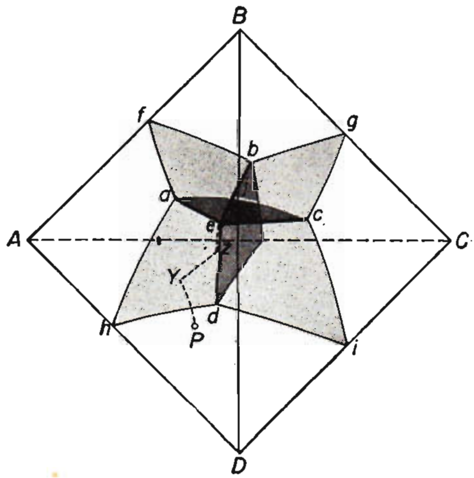


FIG. 19-28. Liquidus projection of the quaternary eutectic system. The dashed line, originating upon the composition of alloy P, traces the change in the composition of the liquid phase during the primary crystallization of δ (P to Y), the secondary crystallization of $\alpha + \delta$ (Y to Z), the tertiary crystallization of $\alpha + \gamma + \delta$ (Z to e), and the final freezing of the last liquid of eutectic composition e.

composition, such as P in Fig. 19-28, may be followed qualitatively by reference to a "projection of the liquidus valleys." Lines of ternary bivariant equilibrium involving the liquid phase (the liquidus valleys, for example, fa) are shown as light lines in the ternary faces of the tetrahedron of Fig. 19-28. Quaternary bivariant lines involving liquid, for example, ae, in the space of the diagram (the traces of the "liquid points" of the

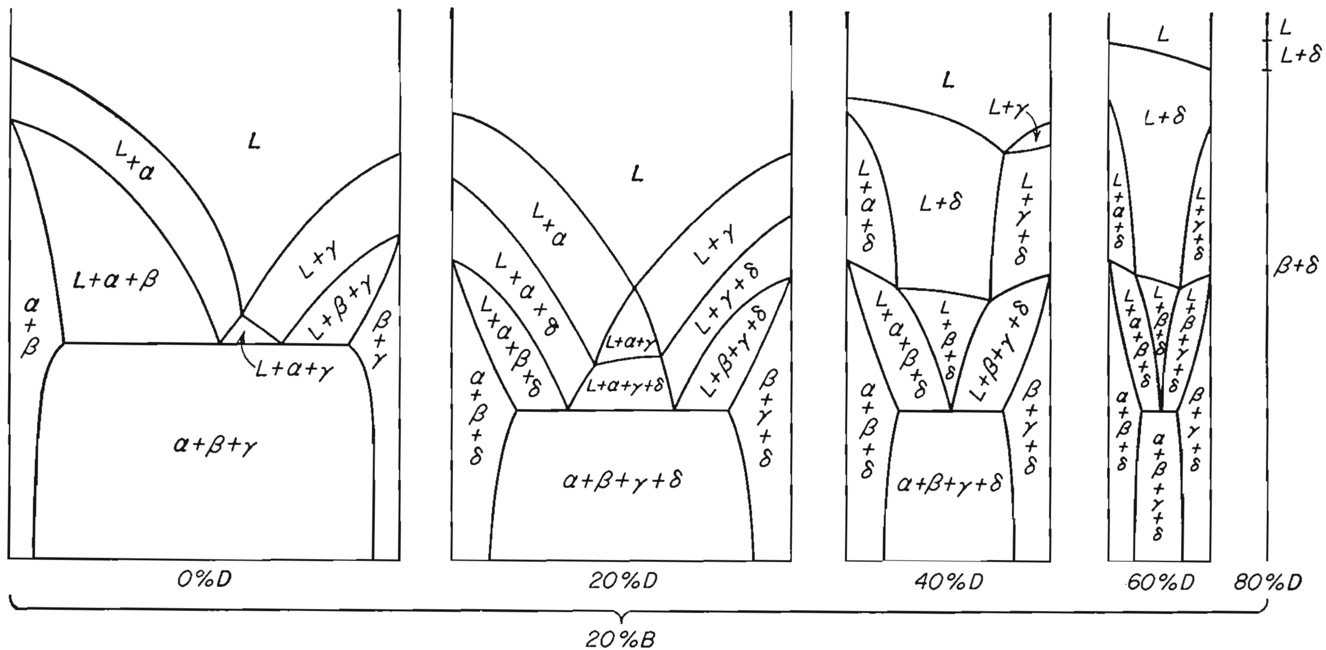


FIG. 19-29. Isopleths through the quaternary eutectic diagram of Fig. 19-26.

four tie-tetrahedra) are shown in heavy lines. These 16 lines enclose six tervariant surfaces, such as *haed*, representing the traces of the liquid points on three-phase equilibria involving liquid. The alloy of composition P first rejects primary δ, and the liquid composition moves away from the D corner of the diagram until it meets the surface *haed* at point Y. Here, α and δ freeze cooperatively as a two-phase secondary constituent and the liquid composition moves away from the AD edge of the diagram toward point Z. As the liquid reaches point Z, a tertiary constituent of $\alpha + \gamma + \delta$ commences to form. Now the liquid composition moves away from the ACD face along the line *de*. At the quaternary eutectic point e, any remaining liquid freezes isothermally to the quaternary eutectic constituent composed of $\alpha + \beta + \gamma + \delta$. Coring of the primary, secondary, and tertiary constituents is to be expected.

A series of isopleths is presented in Fig. 19-29. As in previous examples, the B content has been taken at 20% for the entire series, and successive diagrams represent constant quantities of D in intervals of 20%. Five-phase equilibrium, being isothermal in quaternary systems, is represented by a horizontal line in the three sections in which it appears. These drawings serve to illustrate a rule for identifying the phases represented in the various areas, a rule that will be increasingly useful as more complex sections are encountered. Every four-phase field is surrounded by three-phase fields (except along the eutectic isotherm) each of which includes three of the four phases of that region. Two-phase fields, similarly, contain only phases that appear in the three-phase fields with which they are in contact. This is an application of the general principle of the succession of fields stated in Chap. 18.

An Example of Class II Five-phase Equilibrium

The occurrence of five-phase equilibrium of the second kind is illustrated in Fig. 19-30. Four ternary eutectic systems are again produced by the four components of this quaternary system. In distinction with the previous example, however, one of the ternary eutectics (BCD) lies at a temperature below that of five-phase equilibrium. Four-phase tie-tetrahedra emerge in succession: from the ABD face $L + \alpha + \beta + \delta$ just above T_1, Fig. 19-30*a*; from the ABC face $L + \alpha + \beta + \gamma$ just above T_2, Fig. 19-30*b*; and from the ACD face $L + \alpha + \gamma + \delta$ just above T_3, Fig. 19-30*c*. These join at T_4 to form a class II five-phase tie-hexahedron representing equilibrium among L, α, β, γ, and δ, Fig. 19-30*d*. The hexahedron divides into two new tie-tetrahedra, one of which ($\alpha + \beta + \gamma + \delta$) persists to low temperature and the other terminates in the ternary eutectic reaction plane of the system BCD at a temperature between T_5 and T_6.

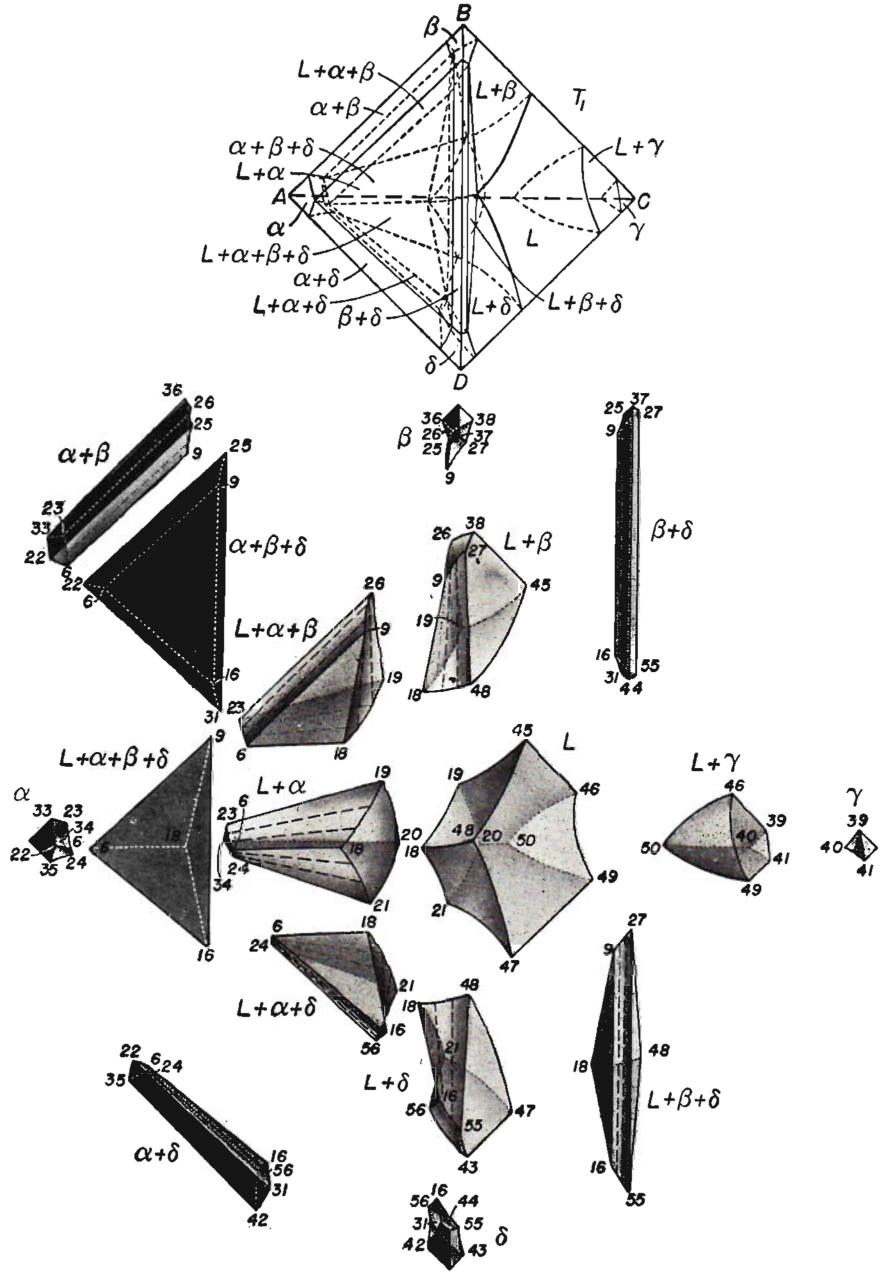
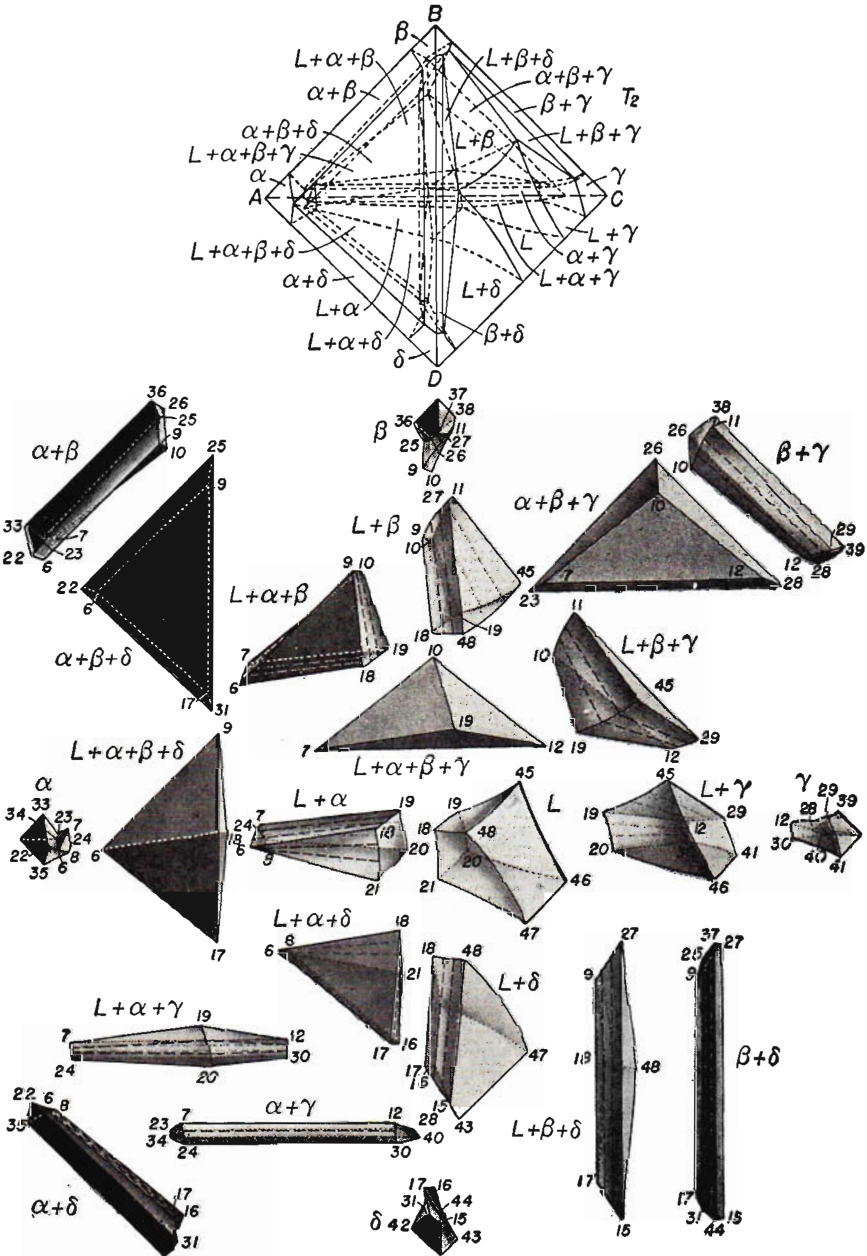
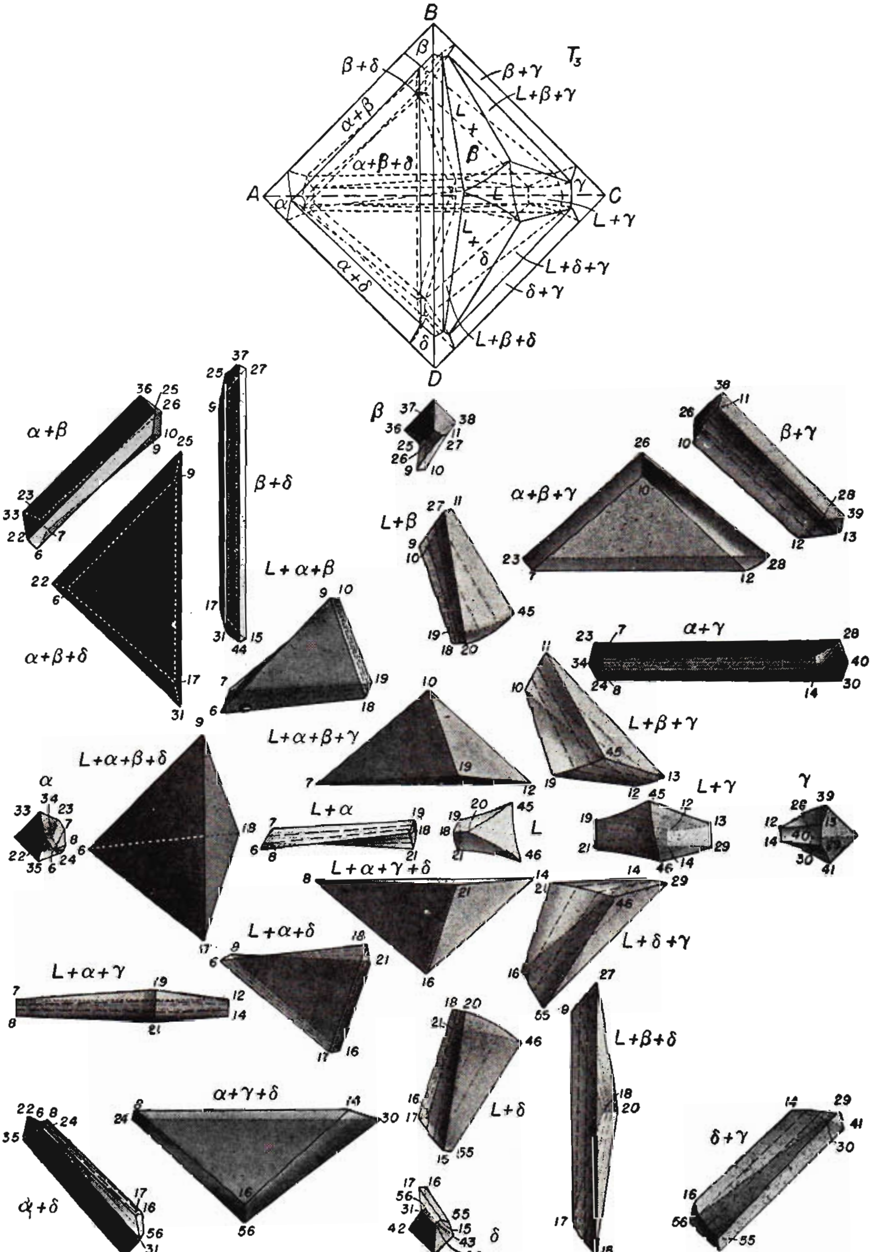


FIG. 19-30a Six isotherms through a quaternary system involving class II five-phase equilibrium. Four-phase tetrahedra, which originate upon the ternary eutectics of the three systems *ABD*, *ABC*, and *ACD*, join at T_4 to form the five-phase hexahedron $L + \alpha + \beta + \gamma + \delta$. Below T_4 there are only two four-phase equilibria, of which one terminates upon the ternary eutectic of the system *BCD* between T_5 and T_6 and the other $(\alpha + \beta + \gamma + \delta)$ persists to low temperature.



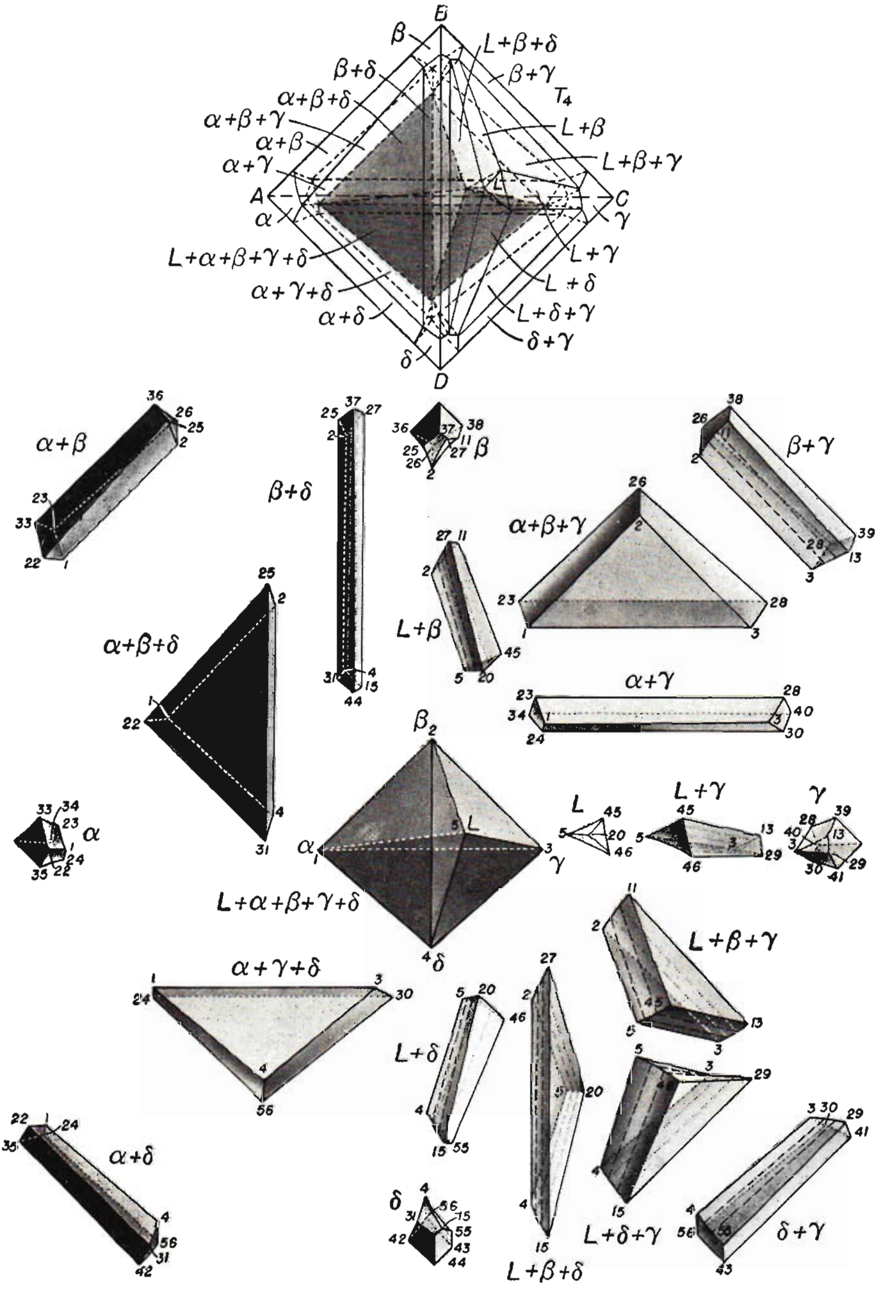
B
A
C
D
T_2
β
L+α+β
L+β+δ
α+β+γ
α+β
β+γ
α+β+δ
L+β+γ
L+α+β+γ
L+β
α
γ
L+γ
L+α+β+δ
L
α+γ
α+δ
L+α+γ
L+δ
L+α
L+α+δ
β+δ
δ

FIG. 19-30b.



B
A
C
D
T3
β
α
γ
δ
L
β+δ
β+γ
L+β+γ
α+β
L+β
α+β+δ
L+γ
L+δ
α+δ
L+δ+γ
δ+γ
L+β+δ
α+β+γ
α+γ
L+α+β
L+α+β+γ
L+α+β+δ
L+α
L+α+γ+δ
L+α+δ
L+α+γ
α+γ+δ

Fig. 19-30c.



B
A
C
D
T_4
β
β+δ
α+β+δ
α+β+γ
α+β
α+γ
α
L+α+β+γ+δ
α+γ+δ
α+δ
δ
L+β+δ
β+γ
L+β
L+β+γ
γ
L+γ
L+δ
L+δ+γ
δ+γ
L

Fig. 19-30d.

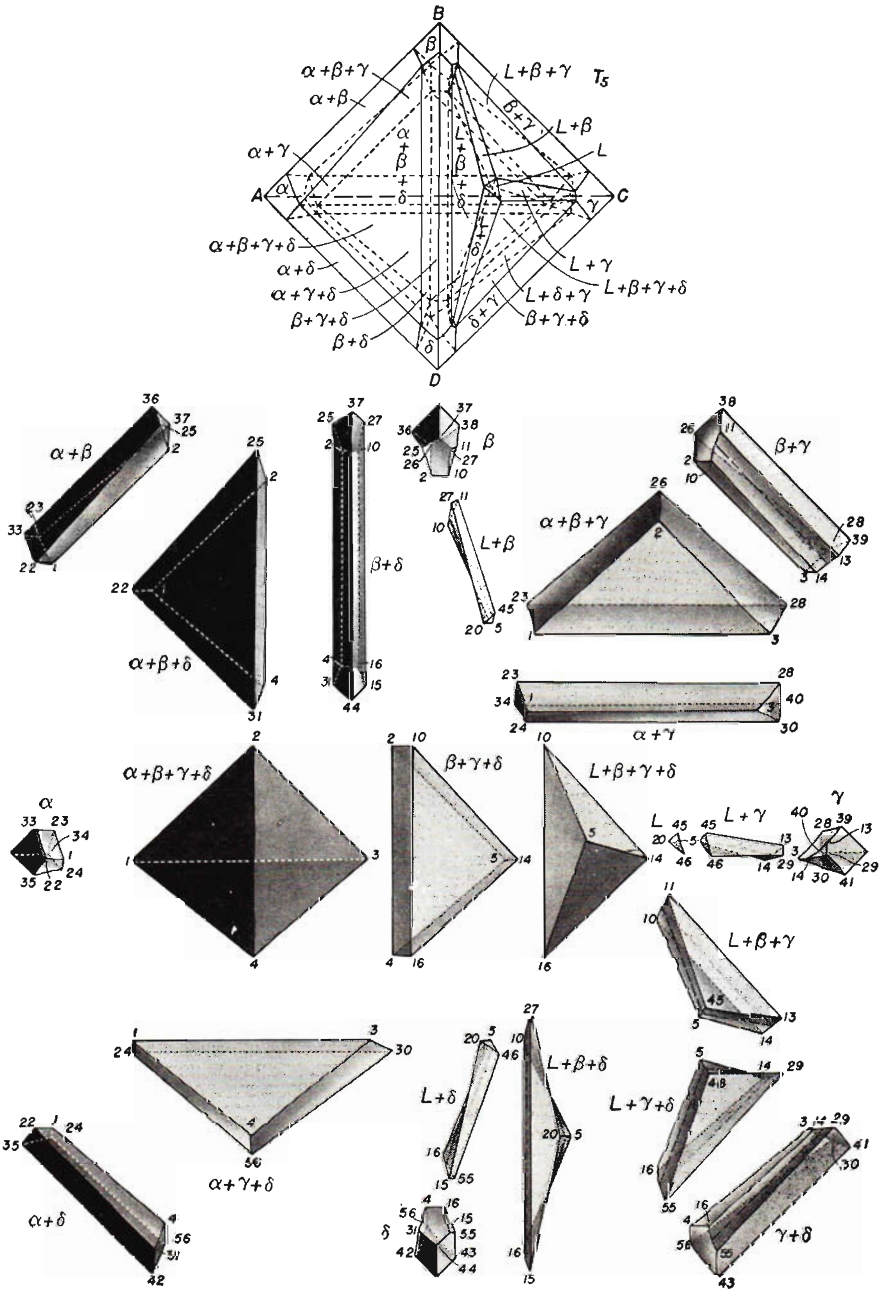

B
A
C
D
T_5
α+β+γ
α+β
α+γ
α+β+γ+δ
α+δ
α+γ+δ
β+γ+δ
β+δ
L+β+γ
β+γ
L+β
L
L+γ
L+β+γ+δ
L+δ+γ
δ+γ
β+γ+δ
α+δ
L+δ
β+δ
L+γ+δ
α+γ
γ+δ
L+β+δ
L+γ
γ
α
β
δ

FIG. 19-30e.

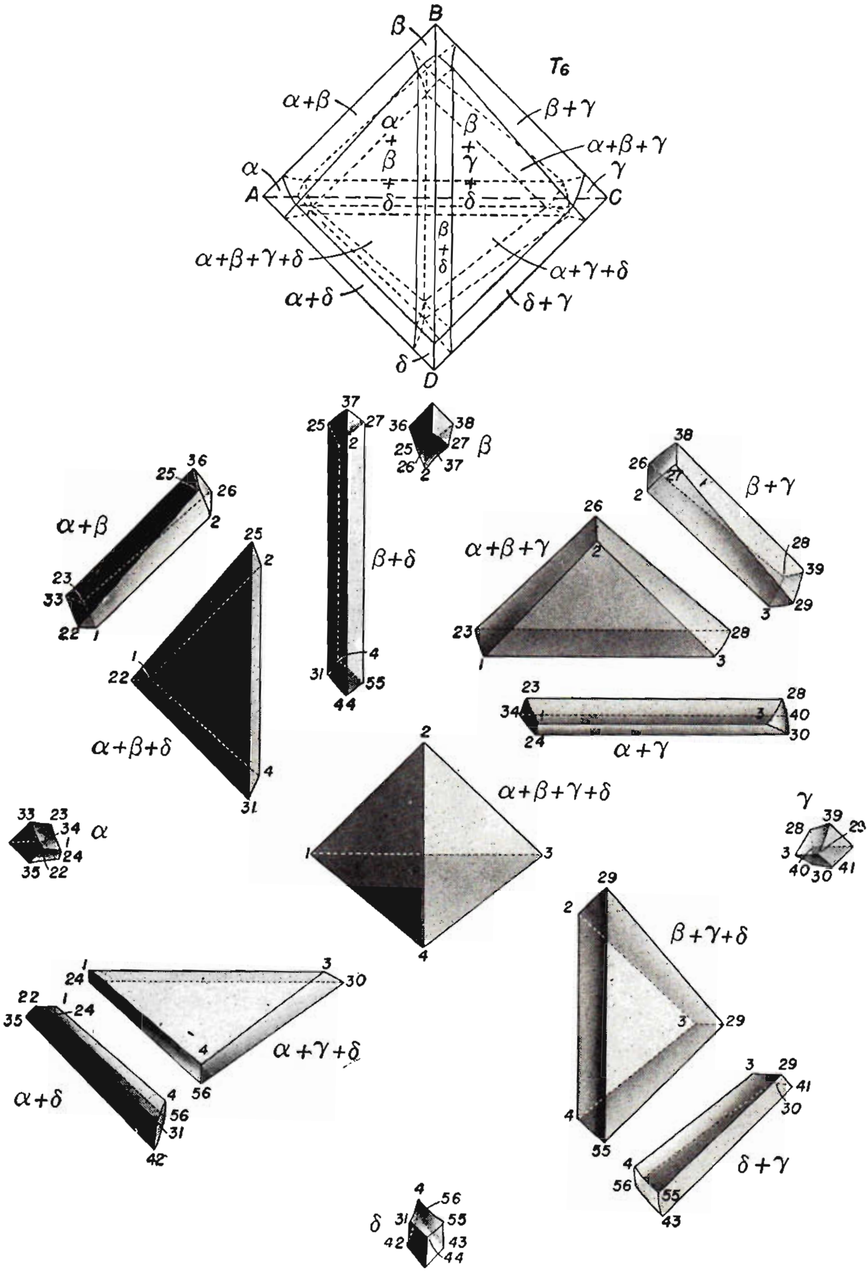


FIG. 19-30*f*.

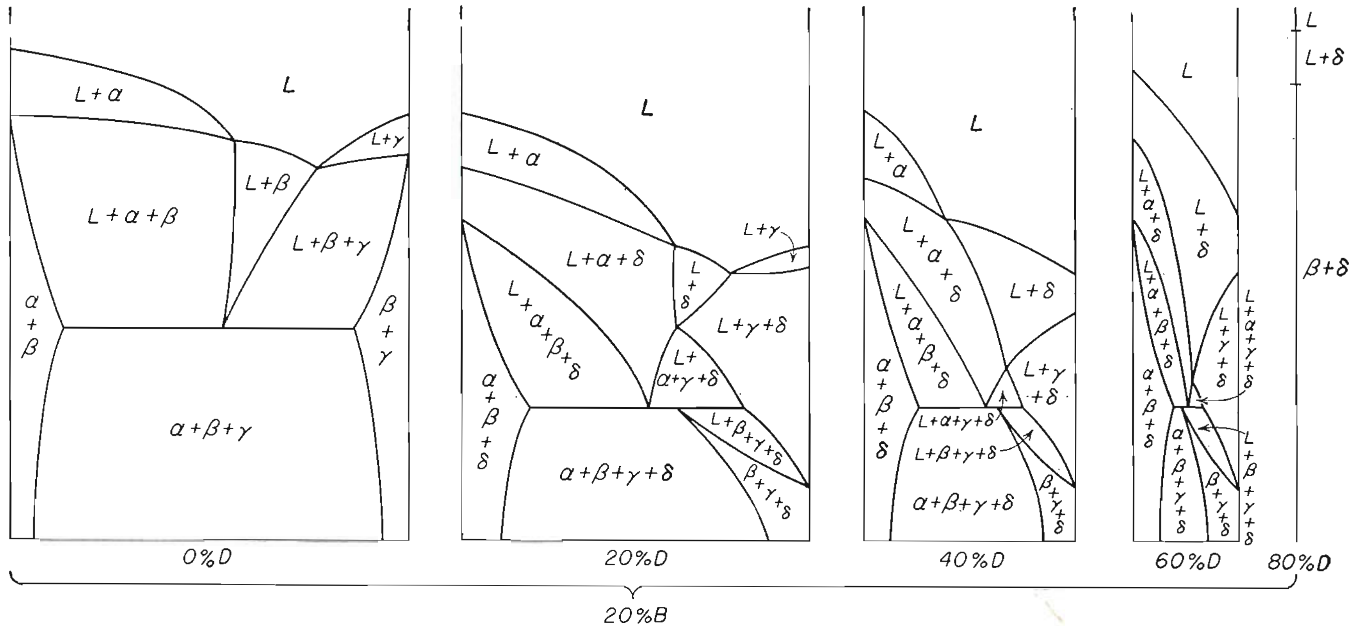


FIG. 19-31. Isopleths through the quaternary system shown in Fig. 19-30.

During class II five-phase reaction the quantities of three of the previously existing phases diminish while the other two gain:

$$L + \alpha + \beta \rightarrow \gamma + \delta$$

As with class II four-phase reaction in ternary systems, this type of transformation partakes of both eutectic and peritectic reaction. Hence, it is to be expected that notably incomplete reaction will usually be encountered with any but very slow rates of heating or cooling.

Some examples of two-dimensional isopleths are given in Fig. 19-31. These have been taken in a manner favorable for illustrating the form of the class II five-phase reaction isotherm. A four-phase field involving liquid, $L + \beta + \gamma + \delta$, approaches the reaction plane from the low-temperature side, while three others approach from the high-temperature side although only two of the latter are intersected by these isopleths.

Other Constructions in Quaternary Systems

Enough examples have now been presented to illustrate the main types of construction that appear in quaternary systems. Five-phase equilibria of the third and fourth kinds, being simply the inverse of the first two, require no detailed discussion. The methods of representing the various kinds of maxima and minima and of quasi-binary and quasi-ternary sections may be deduced with little difficulty by analogy with binary and ternary systems. It is evident that an enormous number of types of quaternary diagrams could be derived by combining the many varieties of binary, ternary, and quaternary equilibria that have been mentioned. Although arduous, the development of the phase diagram for any one of the many cases that have not been discussed should present no unsurmountable problems to one having a clear understanding of the types that have been considered.

Quinary Equilibrium

With five components the graphical representation of all compositions simultaneously is not possible, since a four-dimensional space would be needed for the purpose. This condition makes the use of isothermal sections impossible and effectively limits quinary diagrams to isopleths in which three of the four concentration variables are held constant. It will be obvious that a prodigious number of such sections would be required to present even a sparse survey of an entire quinary system. Existing surveys have been confined to narrow composition ranges.

From the phase rule it can be seen that a maximum of six phases can exist in equilibrium in a randomly selected quinary isobar. The quinary eutectic is of the form

$$L \rightleftharpoons \alpha + \beta + \gamma + \delta + \eta$$

Five kinds of six-phase isothermal equilibrium are to be expected in

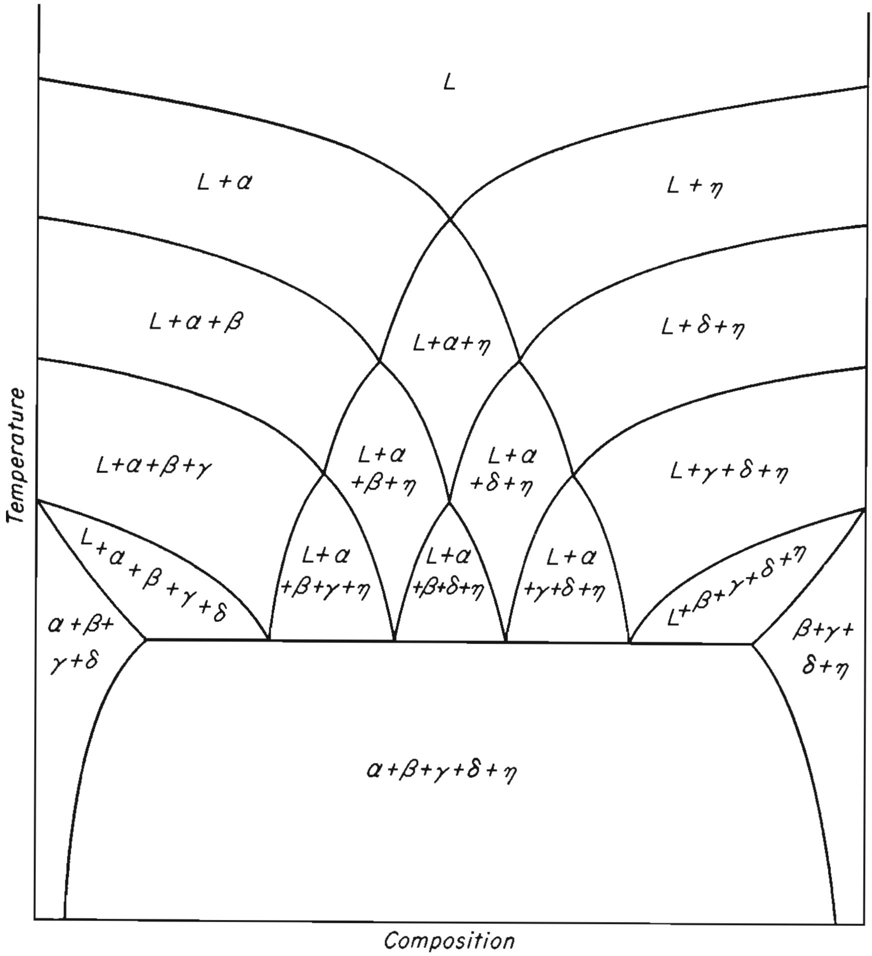


FIG. 19-32. An isopleth through a quinary eutectic system.

quinary systems. The other four are such as

$$L + \alpha \rightleftharpoons \beta + \gamma + \delta + \eta$$
$$L + \alpha + \beta \rightleftharpoons \gamma + \delta + \eta$$
$$L + \alpha + \beta + \gamma \rightleftharpoons \delta + \eta$$
$$L + \alpha + \beta + \gamma + \delta \rightleftharpoons \eta$$

An ideal section through a quinary eutectic diagram is given in Fig. 19-32. It will be seen that an alloy selected at random may freeze in as many as five stages, each producing a microconstituent with an additional phase up to five phases at the quinary eutectic temperature.

Higher-order Systems

Although practical difficulties make the use of higher-order phase diagrams, in which the composition variable is represented, virtually useless, it is interesting to speculate briefly on the nature of the constitution of the multicomponent systems. It can be seen from the foregoing survey of unary, binary, ternary, and quaternary systems that

1. The number of classes of univariant reaction is always equal to the number of components; there would be 10 classes of isothermal reaction in a decinary system.
2. A region representing x phases must always be bounded by regions representing $x - 1$ and $x + 1$ phases.
3. Other than the pattern of coring and the limits of solubility, no essential structural differences are produced in one-phase alloys as the number of components is increased or in two-phase alloys, and so on.

In general, multicomponent alloys that are composed predominantly of two components, not having the other components present in sufficient quantity to produce additional phases, may be treated as modified binary alloys. This is, in fact, what is always done in the establishment of binary diagrams, because absolutely pure metals can not be obtained or maintained for constitutional studies.