

CHAPTER 12

TERNARY ISOMORPHOUS SYSTEMS

Ternary systems are those having three components. It is not possible to describe the composition of a ternary alloy with a single number or fraction, as was done with binary alloys, but the statement of two independent values is sufficient. Thus, the composition of an iron-chromium-nickel alloy may be described fully by stating that it contains 18% chromium and 8% nickel. There is no need to say that the iron content is 74%. But the requirement that two parameters must be stated to describe ternary composition means that two dimensions must be used to represent composition on a complete phase diagram.

The external variables that must be considered in ternary constitution are, then, temperature, pressure, composition X , and composition Y . To construct a complete diagram representing all these variables would require the use of a four-dimensional space. This being out of the question, it is customary to assume pressure constant (atmospheric pressure) and to construct a three-dimensional diagram representing, as variables, the temperature and two concentration parameters. In any application of the phase rule, therefore, it should be recalled that one degree of freedom has been exercised in the initial construction of the three-dimensional diagram by electing to draw it at 1 atmosphere of pressure.

Three-dimensional diagrams are usually so plotted that the composition is represented in the horizontal plane and the temperature vertically (see Fig. 12-4). Two-dimensional sections through this space model may be taken *horizontally* (isothermally) at various temperature levels or *vertically*. Since two-dimensional sections are more convenient than space models, their use is preferred. The selection and construction of such sections will be considered at length in this and subsequent chapters.

The Gibbs Triangle

Because of its unique geometric characteristics, an equilateral triangle provides the simplest means for plotting ternary composition. Other types of axes that have been used from time to time will not be discussed in this book. On the *Gibbs triangle*, which is an equilateral triangle, the

three pure component metals are represented at the corners, A , B , and C , Fig. 12-1. Binary composition is represented along the edges, i.e., the binary systems AB , AC , and BC . And ternary alloys are represented within the area of the triangle, such as at point P in Fig. 12-1.

If lines are drawn through point P parallel to each of the sides of the triangle, it will be found that these have produced three smaller equilateral triangles: aaa , bbb , and ccc . The sum of the lengths of the nine sides of these three triangles is equal to the sum of the lengths of the three sides of the major triangle ABC within which they are inscribed, or the sum of the lengths of one side from each of the minor triangles is equal to the length of one side of the major triangle: $a + b + c = AB = AC = BC$. Also, the sum of the altitudes of the minor triangles is equal to the altitude of the major triangle: $a' + b' + c' = AX$.

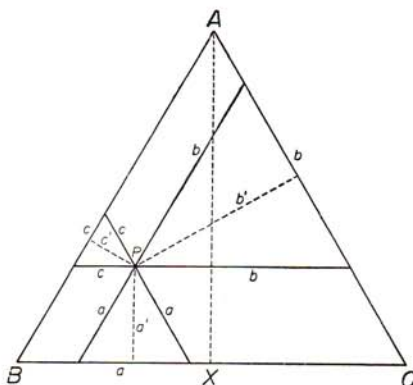


FIG. 12-1. The Gibbs triangle.

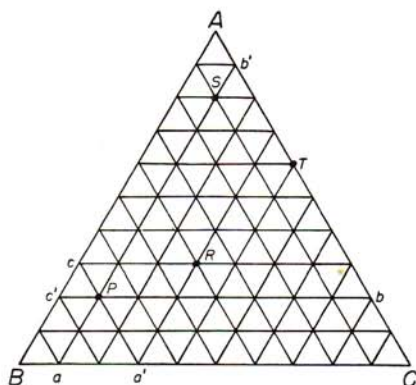


FIG. 12-2

If one side of the Gibbs triangle be divided into 100 equal parts, representing 100% on the binary composition scale, it will be found that the same units can be used to measure the composition at point P . Let the length a represent the percentage of A in P , the length b the percentage of B , and the length c the percentage of C . Since these lengths total the same as one side of the Gibbs triangle and together they must equal 100%, it is evident that 1% has the same length, whether measured along an edge of the diagram or along any inscribed line parallel to an edge. A similar result could be obtained by using altitudes, but this is less convenient. It should be noted that in either case, the percentage of A is measured upon the side of P away from the A corner and similarly with B and C .

For convenience in reading composition, an equilateral triangle may be ruled with lines parallel to the sides (Fig. 12-2). Composition may then be read directly, for example, $P = 20\% A + 70\% B + 10\% C$. At point P the percentage of A is represented by the line Pa (or equivalently Pa'),

which is 20 units long; the percentage of B by the line Pb (or Pb'), 70 units long; and the percentage of C by the line Pc (or Pc'), 10 units long. Other examples shown in Fig. 12-2 are $R = 30\% A + 40\% B + 30\% C$, $S = 80\% A + 10\% B + 10\% C$, and $T = 60\% A + 0\% B + 40\% C$.

Tie-lines

It can be shown that if any two ternary alloys are mixed together, the composition of the mixture will lie on a straight line joining the original two compositions. This is true regardless of the proportions of the two

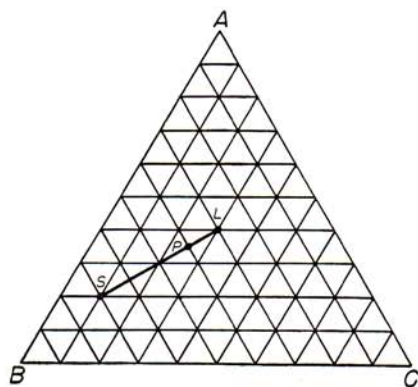


FIG. 12-3

alloys in the mixture. Conversely, if an alloy decomposes into two fractions of differing composition, the compositions of the two portions will lie on opposite ends of a straight line passing through the original composition point. The truth of this statement may be tested by reference to the example illustrated in Fig. 12-3. Points S and L represent two ternary alloys of respective composition: $20\% A + 70\% B + 10\% C$ and $40\% A + 30\% B + 30\% C$. Suppose that one part of S

is mixed with three parts of L and the mixture is analyzed. The analytical result must, of course, be

$$\begin{aligned} 0.25 \times 20\% A + 0.75 \times 40\% A &= 35\% A \\ 0.25 \times 70\% B + 0.75 \times 30\% B &= 40\% B \\ 0.25 \times 10\% C + 0.75 \times 30\% C &= 25\% C \end{aligned}$$

As can be seen by inspection of Fig. 12-3, this composition lies at P , which is a point on the straight line connecting S and L . No matter what compositions had been chosen or in what proportions they had been mixed, the total composition would have occurred on the line joining the two original compositions.

It will be evident that the line SL has the characteristics of a *tie-line*; it is both isobaric and isothermal, because it lies in the composition plane which is drawn perpendicular to the temperature axis and corresponds to the case of constant atmospheric pressure (i.e., would be drawn perpendicular to the pressure axis if a fourth dimension were available). The lever principle is applicable to this line as is indicated in the above demonstration. Hence, the line SL might represent the condition of an alloy of composition P which is partially frozen, at the temperature

under consideration, and consists of 25% solid of composition S and 75% liquid of composition L :

$$\%S = \frac{PL}{SL} \times 100 \quad \text{and} \quad \%L = \frac{SP}{SL} \times 100$$

The Space Diagram

A temperature-composition (TXY) diagram of an isomorphous system appears in Fig. 12-4. The composition plane forms the base of the figure, and temperature is measured vertically. Here, the liquidus and solidus

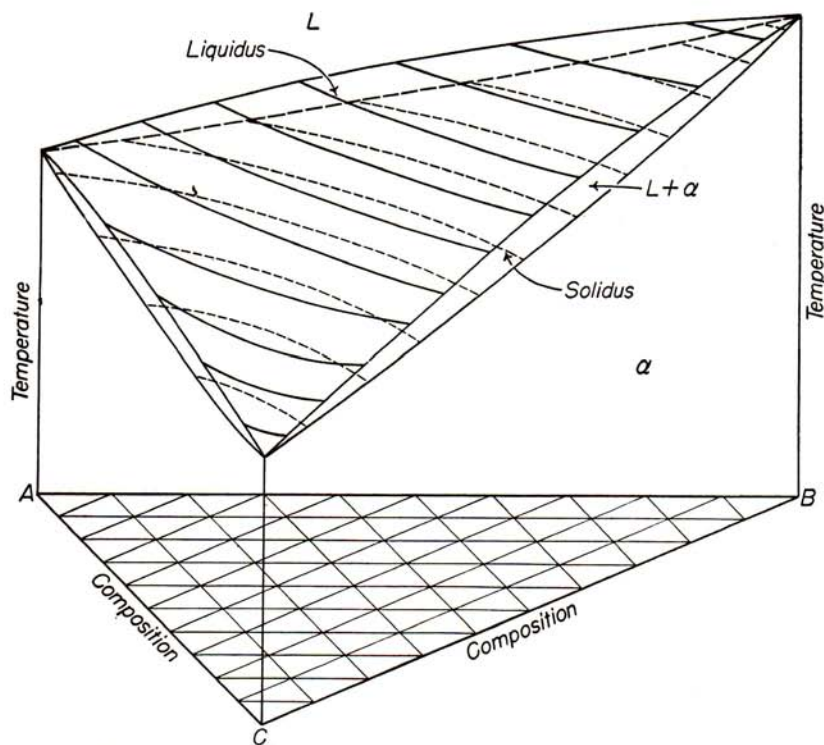


FIG. 12-4. Temperature-composition space diagram of a ternary isomorphous system.

become surfaces bounding the $L + \alpha$ space. Above the liquidus, all alloys are fully molten; below the solidus, all are completely solid. As in binary systems, the two-phase region $L + \alpha$ is composed of tie-lines joining conjugate liquid and solid phases. In the ternary system, however, the tie-lines are not confined to a two-dimensional area but occur as a bundle of lines of varying direction, but all horizontal (isothermal), filling the three-dimensional two-phase space.

Isothermal Sections

The location of the tie-lines can be visualized more easily by reference to isothermal (horizontal) sections cut through the temperature-composition diagram at a series of temperature levels. The three isotherms presented in Fig. 12-6 are taken at the temperatures designated T_1 , T_2 , and T_3 in Fig. 12-5. It will be seen that the first tie-line on each edge of the

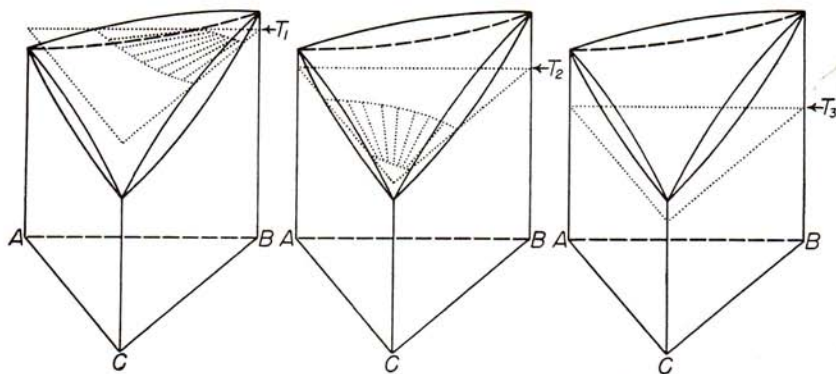


FIG. 12-5. Development of isotherms shown in Fig. 12-6.

$L + \alpha$ region is the bounding line of the figure; it is, in other words, the binary tie-line at the temperature designated. The directions of tie-lines lying within the figure vary "fanwise" so that there is a gradual transition from the direction of one bounding tie-line to that of the other. *No two tie-lines at the same temperature may ever cross.* Beyond this nothing

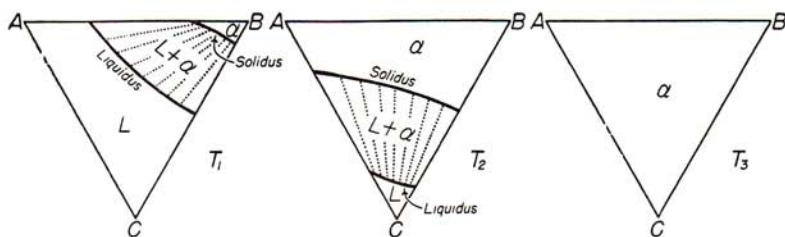


FIG. 12-6. Isotherms through the ternary isomorphous phase diagram, as derived from Fig. 12-5.

can be said of their direction, except, of course, that they must run from liquidus to solidus. Other than those on the edges of the diagram, none points toward a corner of the diagram unless by mere coincidence. It is necessary, therefore, to determine the position and direction of the tie-lines by experiment and to indicate them on the ternary phase diagram. Few of the published ternary diagrams show them because of a lack of

sufficient data. There are a few cases, however, in which more intensive studies have been conducted and the tie-lines are recorded.

Isothermal sections such as those shown in Fig. 12-6 generally provide the most satisfactory means for recording ternary equilibria in two dimensions. In them the various structural configurations assume their simplest forms. The method becomes cumbersome, to be sure, when many isotherms are required to delineate the structure of the space diagram, but no alternate means has been devised to overcome this difficulty. Orthographic sketches of the space model are convenient for showing the general plan of the ternary diagram in a qualitative way, but they are not well adapted to the recording of quantitative data.

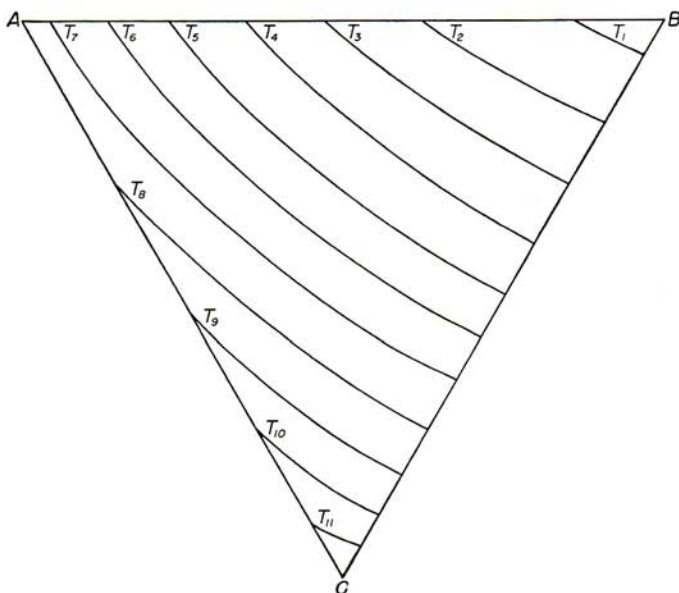


FIG. 12-7. Liquidus projection of the diagram shown in Fig. 12-4.

It is possible in certain cases to telescope a group of isotherms into a single diagram. For example, the isothermal lines which were used to delineate the liquidus surface in Fig. 12-4 may be projected onto a plane, such as the base of the diagram, giving the *liquidus projection* presented in Fig. 12-7. Each line is derived from a separate isotherm, and its temperature should therefore be indicated upon the line. In like manner the solidus (and other surfaces in more complex diagrams) may be presented as projections. Except in very simple systems, this scheme achieves only a minor condensation of the data, and it suffers from the handicap that tie-lines and other relationships existing among the parts of the diagram cannot be presented.

Vertical Sections (Isopleths)

Because of their seeming resemblance to binary diagrams, vertical sections, also known as *isopleths*, have been widely used. The sections selected are usually (1) those radiating from one corner of the space diagram and, therefore, representing a fixed ratio of two of the components

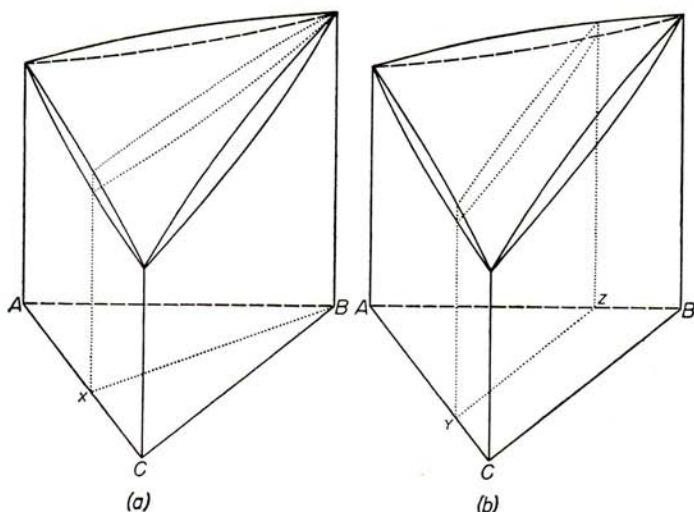


FIG. 12-8. Development of the isopleths shown in Fig. 12-9.

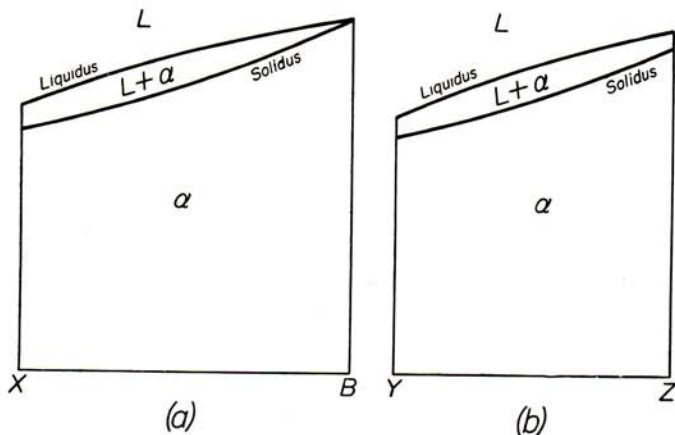


FIG. 12-9. Isopleths through an isomorphous system, derived from Fig. 12-8.

(Figs. 12-8a and 12-9a) or (2) those parallel to one side of the space diagram, representing a constant fraction of one of the components (Figs. 12-8b and 12-9b). It will be observed that the $L + \alpha$ region is open at its ends except where it terminates on the B component. From vertical sec-

tions the liquidus and solidus temperatures for any of the alloys represented can be read. It is not possible, however, to represent tie-lines on these sections, because no tie-line can lie in either section except by coincidence. In general, the tie-lines pass through the $L + \alpha$ region at an angle to the plane of the section. Consequently, it is not possible to record equilibria within the $L + \alpha$ region by the use of vertical sections. Sometimes this is a matter of little consequence, when, for example, the section lies so close to one side of the space diagram that the tie-lines may be presumed to lie *approximately* in the section. For this reason, vertical sections continue to be of some use, though they are gradually being displaced by isothermal sections in the literature of alloy constitution. Certain vertical sections in complex diagrams (the quasi-binary sections) do contain all tie-lines and will continue to be used; these are discussed in Chap. 17.

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Application of the Phase Rule

Within the one-phase spaces of the ternary diagram, the L and α regions of Fig. 12-4, the equilibria are quadrivariant; i.e., there are four degrees of freedom.

$$P + F = C + 2$$

$$1 + 4 = 3 + 2$$

These are pressure, temperature, concentration X , and concentration Y . The pressure was chosen when the diagram was taken at 1 atmosphere of pressure. It remains to verify the correctness of representing the one-phase regions by volumes in the space diagram by ascertaining if an independent choice of temperature and two concentration values will describe a fixed equilibrium.

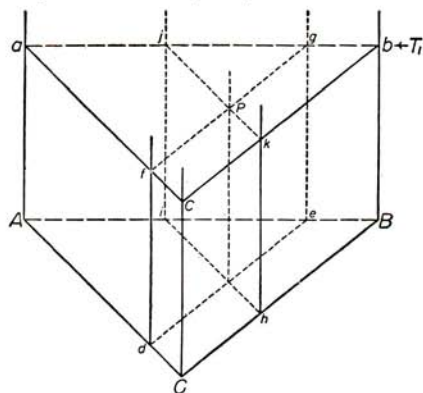


FIG. 12-10

Consider the diagram in Fig. 12-10; this figure represents a portion of the α field of Fig. 12-4, the liquidus and solidus having been removed. Let it be required that in addition to adjusting the pressure at 1 atmosphere, the temperature is to be established at T_1 and the composition at 20% A and 40% B . A horizontal plane abc , representing a choice of temperature, is passed through the diagram at T_1 . Next, one condition of composition is selected by erecting a vertical plane $defg$ parallel to the BC side and one-fifth of the distance from this side to the A corner. This plane intersects the T_1 isotherm along the line fg . At this juncture it can be seen that the equilibrium is not yet

fully described, because any one of many alloys having 20% *A* can exist as the α phase at 1 atmosphere of pressure and at temperature T_1 . If a second vertical plane *hijk*, parallel to the *AC* side of the diagram and two-fifths of the distance from this side to the *B* corner, is erected, it will intersect the T_1 isotherm along the line *jk* and will cross the line *fg* at *P*. Thus, a unique point (point *P*) has been designated by the exercise of four degrees of freedom. It will be evident from the argument that has been followed that the phase rule in no way limits the shape of the one-phase regions.

When two phases coexist at equilibrium in a ternary system, there can be only three degrees of freedom:

$$\begin{aligned} P + F &= C + 2 \\ 2 + 3 &= 3 + 2 \end{aligned}$$

The system is ternariant. Pressure being fixed, there remain but two degrees of freedom, which can be temperature and one concentration value or two concentration values. Both of these possibilities will be explored. First, the choice of temperature and one concentration value will be examined.

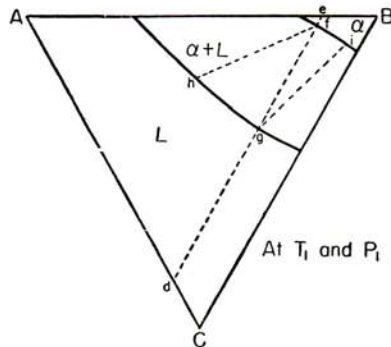


FIG. 12-11

Let a temperature be selected such that two-phase equilibrium may occur, for example, T_1 in Figs. 12-5 and 12-6. This isotherm is reproduced in Fig. 12-11. Two degrees of freedom have now been exercised, namely, pressure and temperature; a *single statement* concerning the composition of one of the phases should complete the description of a specific equilibrium. Therefore, let it be specified that the liquid phase shall contain 15% *A*. All alloys containing 15% *A* are represented on the isotherm by the dashed line *de*. This line includes, however, only one composition of liquid which can be in equilibrium with the solid phase, namely, the composition *g*, where the dashed line crosses the liquidus. Thus, the composition of the liquid phase is described completely, and the composition of the conjugate solid is identified by the corresponding tie-line at point *i* on the solidus. Had it been specified, instead, that the α phase should contain 15% *A*, then the composition of the solid would have been given at point *f* and that of the conjugate liquid at *h*.

Two statements concerning the composition should serve also to identify the temperature and composition of both phases. This case is illustrated in Fig. 12-12. It has been specified that the liquid phase shall

contain 5% *B* and 10% *C*. Two vertical planes have been erected, one at a constant *B* content of 5% and the other at a constant *C* content of 10%. These intersect in the vertical line L_1P which intersects the liquidus at L_1 . This point on the liquidus lies in the isothermal section $abcd$ and is associated with a specific composition of the α phase at α_1 by means of the tie-line $L_1\alpha_1$. Thus, the composition of the liquid phase, the composition of the solid phase, and the temperature of the equilibrium have all been established. Obviously, the same result could have been obtained by designating two concentration parameters for the solid phase or one each for the liquid and solid phases.

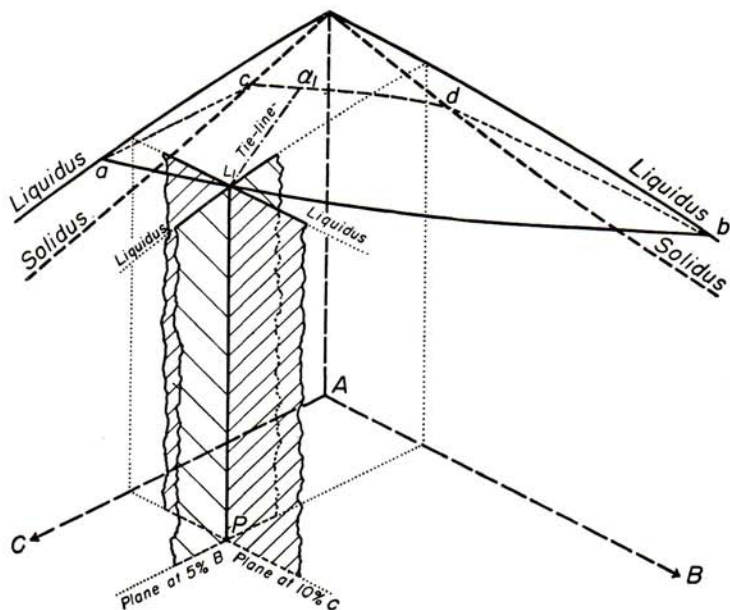


FIG. 12-12

From these demonstrations it will be apparent that the only construction of a two-phase region consistent with the phase rule is one in which there are two conjugate bounding surfaces existing within the same temperature range and upon which every point of one is connected by a horizontal tie-line with a unique point on the other.

Equilibrium Freezing of Solid-solution Alloys

The course of equilibrium freezing of a typical alloy of a ternary isomorphous system may be followed by reference to Fig. 12-13. Beginning at a temperature within the liquid field and cooling at a rate that is

“infinitely” slow, to permit the maintenance of equilibrium, the alloy of composition X will begin to freeze when the liquidus surface is reached at temperature T_1 . Here the liquid L_1 is in equilibrium with crystals of composition α_1 . As the solid grows, the liquid composition will change in a direction away from the α_1 composition, following a curved path down the liquidus surface $L_1L_2L_3L_4$. At the same time the α composition approaches the gross composition X along curved path $\alpha_1\alpha_2\alpha_3\alpha_4$. The tie-line, at each temperature, passes through the X composition, joining the

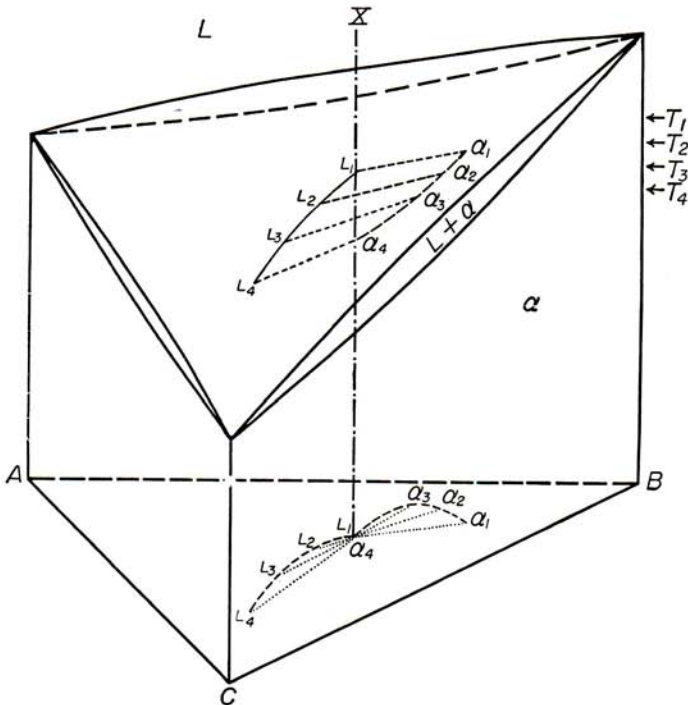


FIG. 12-13. Path of composition change of the liquid L and solid α phase during the freezing of a solid-solution alloy.

conjugate compositions of L and α . Hence the tie-line lies in a different direction at each successive temperature.

Inscribed upon the base of the diagram of Fig. 12-13 is a projection of the tie-lines and the paths of composition variation of the liquid and solid phases. The liquidus path starts at the X composition and ends at L_4 , while the solidus path starts at α_1 and ends at X . All tie-lines, α_1L_1 , α_2L_2 , α_3L_3 , and α_4L_4 , pass through X . The same information is presented in somewhat more realistic fashion in Fig. 12-14, where the complete isotherm for each of the temperatures from T_1 to T_4 is given. In these draw-

ings it becomes apparent that the curved paths of the solid and liquid compositions result from the turning of the tie-lines to conform with the liquidus and solidus isotherms at successively lower temperatures.

Natural Freezing of a Solid-solution Alloy

In natural freezing, the ternary solid solution departs from the course of "equilibrium" freezing in much the same way and for the same reason as does the binary solid-solution alloy. Diffusion fails to maintain the

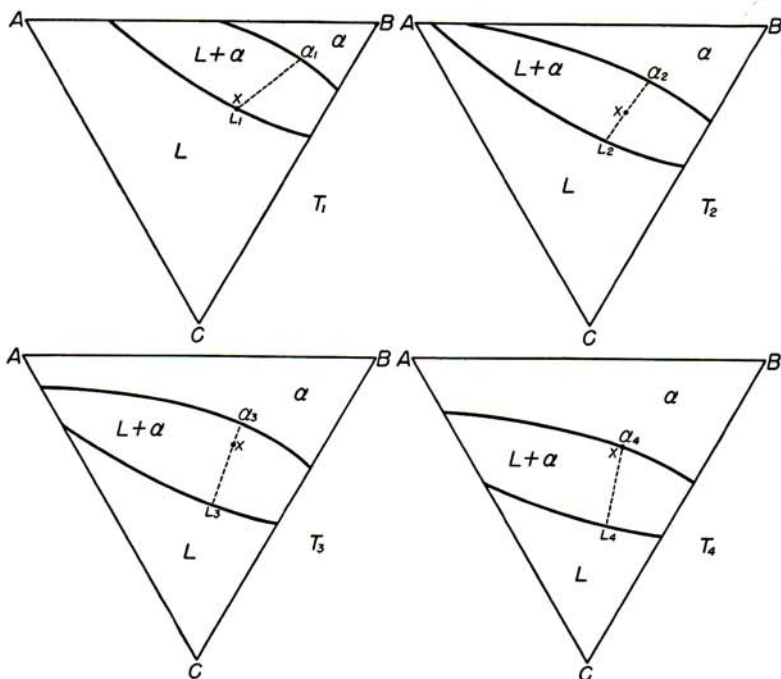


FIG. 12-14. Illustrating the progress of the "equilibrium freezing" of a ternary isomorphous alloy.

equilibrium compositions, so that a cored solid solution is produced and the temperature range over which freezing takes place is increased. This process is illustrated in Figs. 12-15 and 12-16, where the tie-line connecting the average solid and average liquid compositions is dashed. This line must, of course, pass through the gross composition X . Because both the solid and liquid phases present at the interface where freezing is in progress differ in their compositions from the corresponding averages, the solid tie-lines (solid lines in Fig. 12-16) representing "equilibria" at the front of freezing do not in general pass through the X composition except

at the start of the process. The average α composition must, obviously, change more gradually than does the α in contact with liquid, and the average composition of the liquid phase must similarly lag behind the composition change at the freezing front. Thus, the "average" tie-line

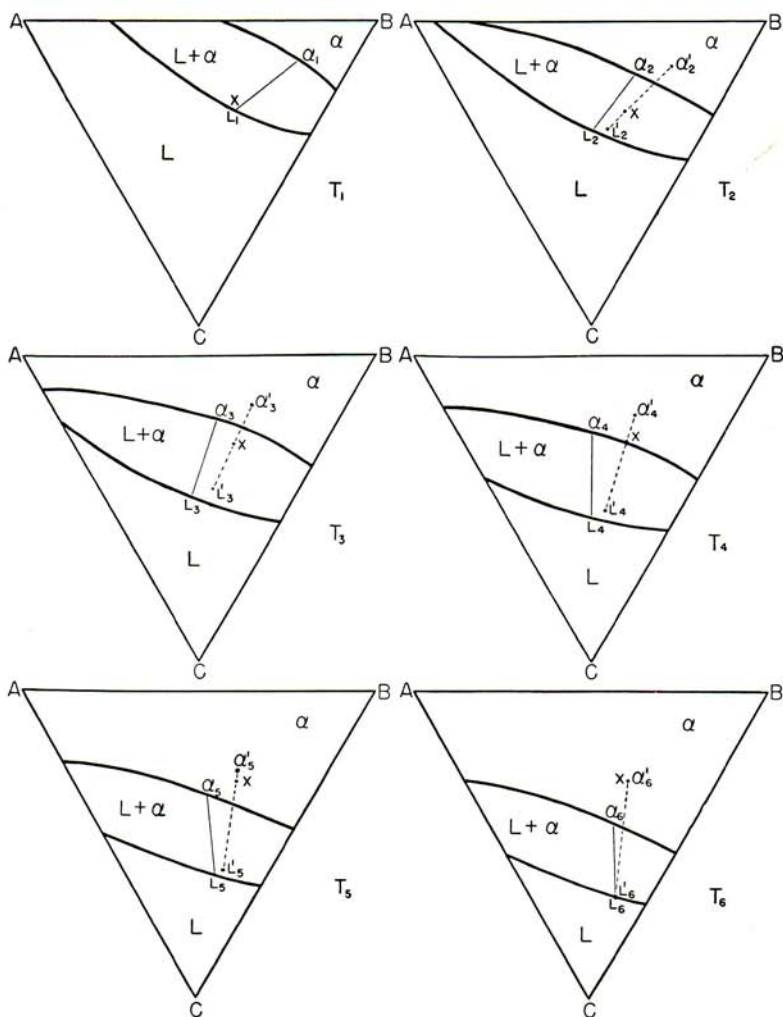


FIG. 12-15. Illustrating the progress of natural freezing of a ternary isomorphous alloy.

turns less with each step in cooling, shows an excess of liquid over the equilibrium quantity at each temperature, and proceeds to lower temperatures than are possible under equilibrium conditions. When the "average" composition of α coincides with X , the alloy is frozen. The

coring produced in this way is complicated by the curved path of freezing on the solidus, but this complication is not apparent in the microstructure, which is indistinguishable from that of binary coring (Fig. 3-9b).

A homogenizing heat treatment may be used to reduce composition differences as with binary alloys. The selection of a suitable heat-treating temperature involves the same considerations as those cited for the simpler case. Liquefaction, too, may result from overheating in a manner analogous to liquation in binary alloys, being complicated only by the curved path of liquid composition that must be followed during melting

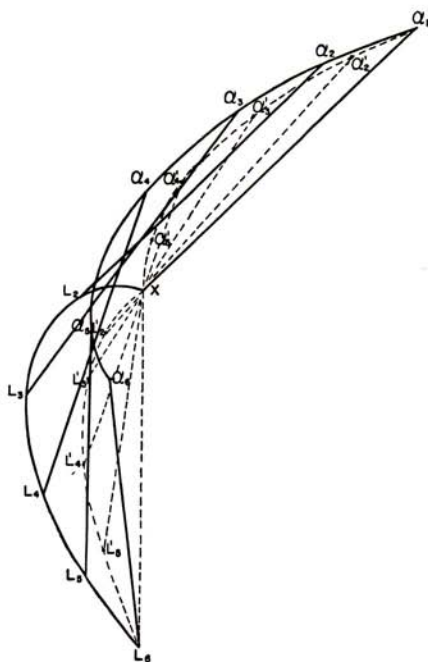


Figure 12-16. Tie-lines from the six isotherms of Fig. 12-15 superimposed.

and the curved path of solid composition followed during subsequent freezing. Changes of physical properties resulting from coring and subsequent heat treatment are likewise similar in kind.

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Maxima and Minima

Maxima and minima in ternary isomorphous systems are of two kinds, namely, (1) those occurring at a binary face of the diagram (Fig. 12-17) and (2) those occurring at a ternary composition (Fig. 12-18). In either case the liquidus and solidus meet at the maximum or minimum point. Where maxima or minima occur both at binary and at ternary composi-

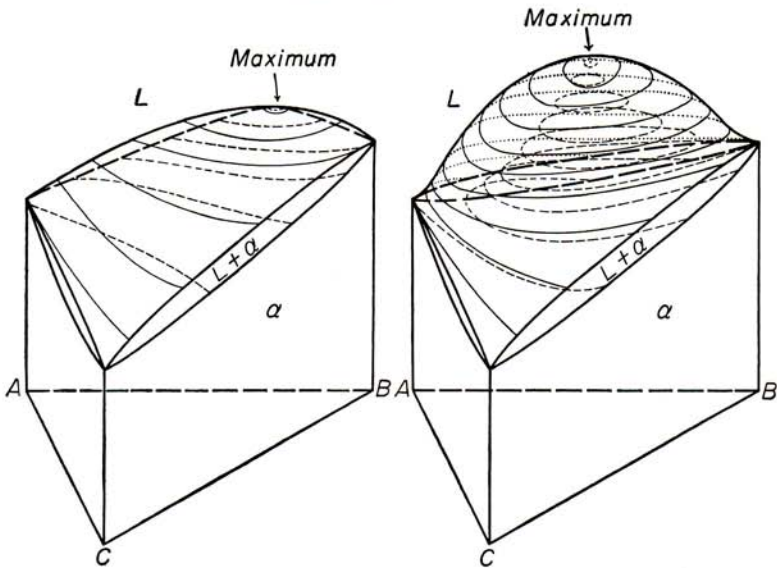


FIG. 12-17. Isomorphous ternary system with a maximum melting point in the binary system AB .

FIG. 12-18. Isomorphous ternary system with a maximum melting point in ternary space.

tions, the liquidus and solidus meet at both points, but not between the points. As with binary systems the alloys of maximum or minimum melting are congruently melting and may, if desired, be treated as components.

PRACTICE PROBLEMS

1. Sketch the solidus projection corresponding to the liquidus projection of Fig. 12-7.
2. How should the shapes of the composition paths of the α and L phases during freezing (Fig. 12-13) vary as the gross composition X approaches the BC side of the diagram, the AB side, the AC side, the C corner, the B corner, and the A corner?
3. Draw isothermal sections corresponding to the temperatures at which liquidus contours are shown in Fig. 12-17; the same for Fig. 12-18.
4. Draw isopleths through the space diagram of Fig. 12-17 as follows: (a) from C through the maximum in the binary system AB , (b) from 50% $B + 50\%$ C through the maximum in AB , (c) from C to 50% $A + 50\%$ B , (d) along the line of constant B content 50%; using the space diagram of Fig. 12-18, draw isopleths (e) from C through the temperature maximum to the AB side of the figure, (f) from C to the AB side, passing slightly to the right of the maximum.