CHAPTER 17

CONGRUENT TRANSFORMATION IN TERNARY SYSTEMS

Congruently melting phases in ternary alloy systems are of three kinds, namely, (1) the pure components, (2) binary intermediate phases of congruent characteristic, and (3) ternary intermediate phases that melt and transform without composition change. Intermediate ternary phases may be either congruently or incongruently melting. The latter melt by class III four-phase reaction, but the former behave as pure substances and may, at times, be considered as components of an alloy system. Many of the ternary intermediate phases have compositions approximating simple ratios of the three kinds of atoms concerned and are often referred to as *ternary compounds*, but as with binary alloys, the use of the term *compound* in this connection has been in disfavor. No sharp distinction is recognized at present between phases that occur with simple proportions of the three components and those that do not, so that the more general term *ternary intermediate phase* is preferred.

Quasi-binary Systems

When a congruently melting intermediate phase occurs in a ternary system, it sometimes happens that this phase forms a *quasi-binary system* with one of the other components. The example given in Fig. 17-1 shows a quasi-binary system existing between the intermediate δ phase of the binary system AB and the C component of the ternary system. A vertical section taken along the line joining these two compositions will be, in all respects, equivalent to a binary phase diagram (Fig. 17-2). All tie-lines in two-phase fields will lie in the plane of the section, and three-phase equilibrium will be represented by a single horizontal line. No four-phase equilibrium can occur in the quasi-binary section. All alloys behave as though binary in their structural response to temperature change.

The quasi-binary section divides the ternary diagram into two independent portions just as a congruently melting and transforming binary phase divides the binary diagram into independent parts. This condition is more clearly evident in the isothermal sections of Fig. 17-3 than in the space diagram itself. A dotted line has been drawn between the C corner

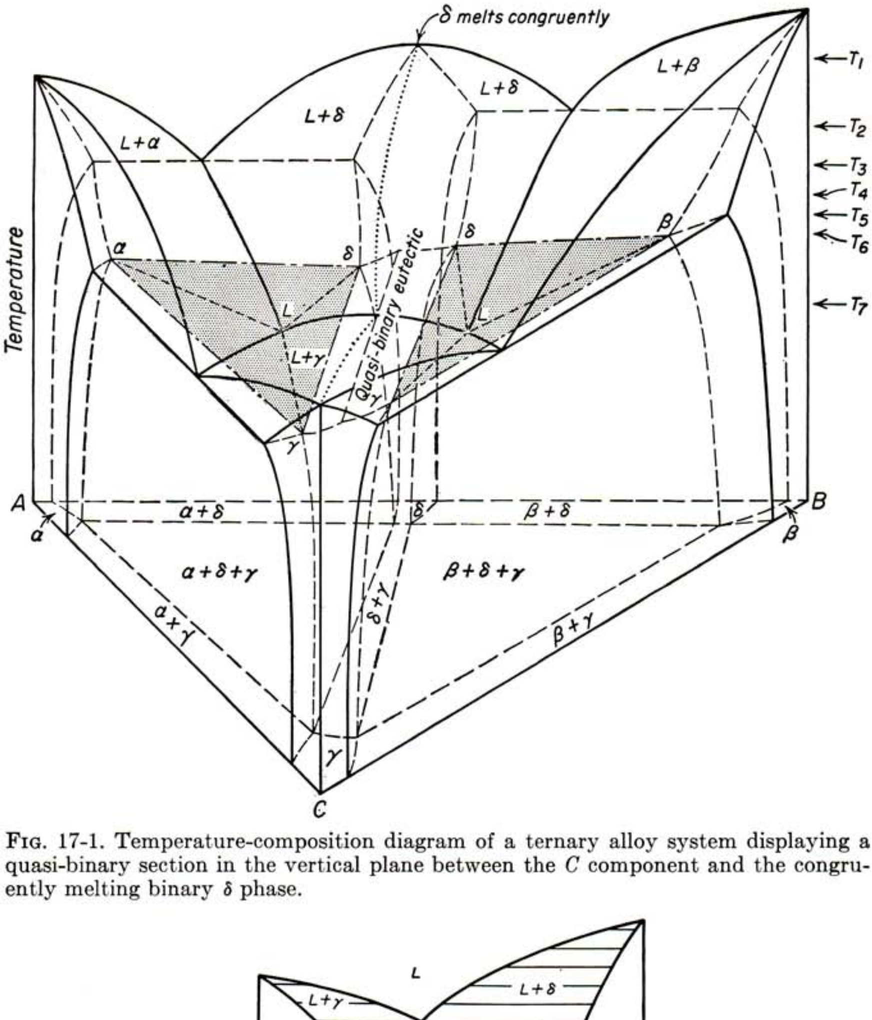

FIG. 17-1. Temperature-composition diagram of a ternary alloy system displaying a quasi-binary section in the vertical plane between the C component and the congruently melting binary δ phase.

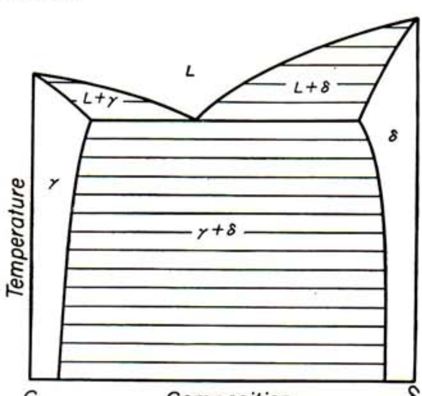

FIG. 17-2. A quasi-binary section from Fig. 17-1 has tie-lines in the plane of the section in all two-phase regions.

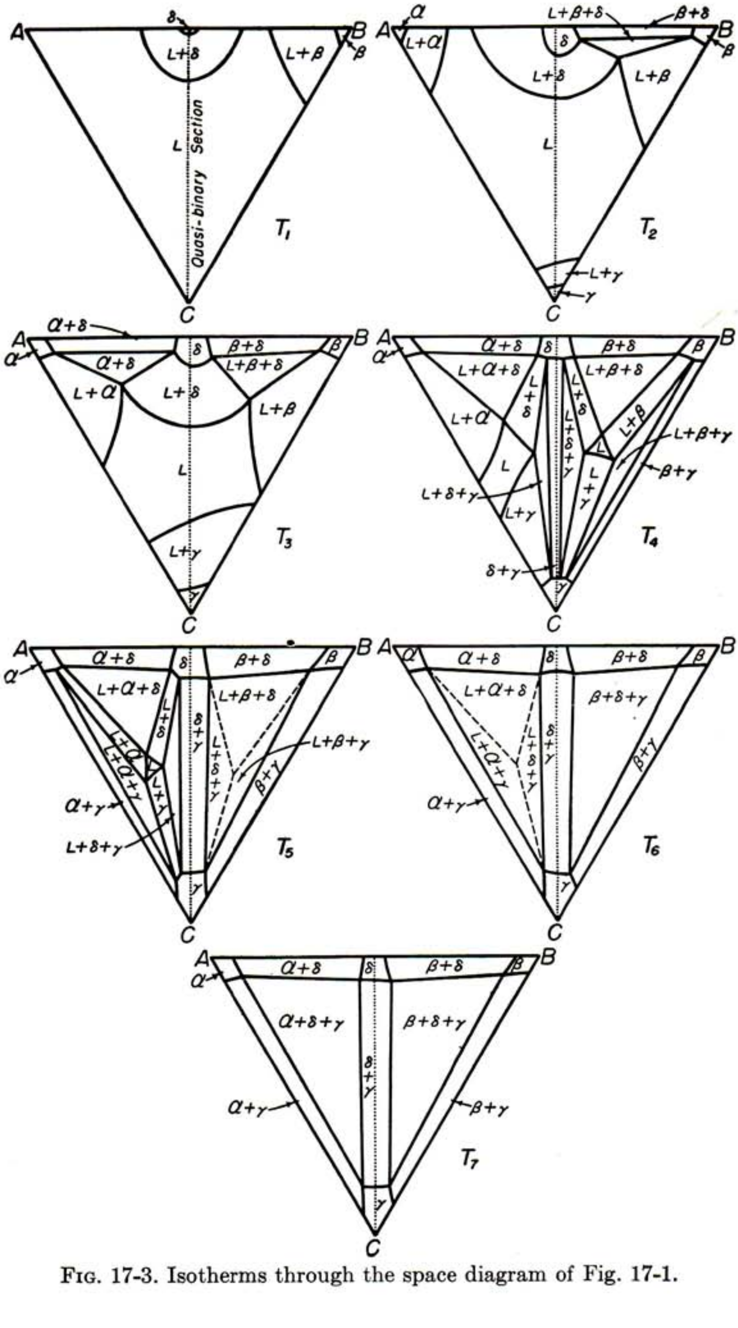

Fig. 17-3. Isotherms through the space diagram of Fig. 17-1.

of each isotherm and the opposite intermediate binary phase δ. Upon either side of the dotted line the complete configuration of a ternary eutectic diagram, such as that illustrated in Fig. 14-3, is found.

In the isotherm at T_4, Fig. 17-3, it can be seen that there is a region designated $L + \gamma + \delta$ on each side of the quasi-binary section. Both of these regions originate upon the quasi-binary eutectic isotherm

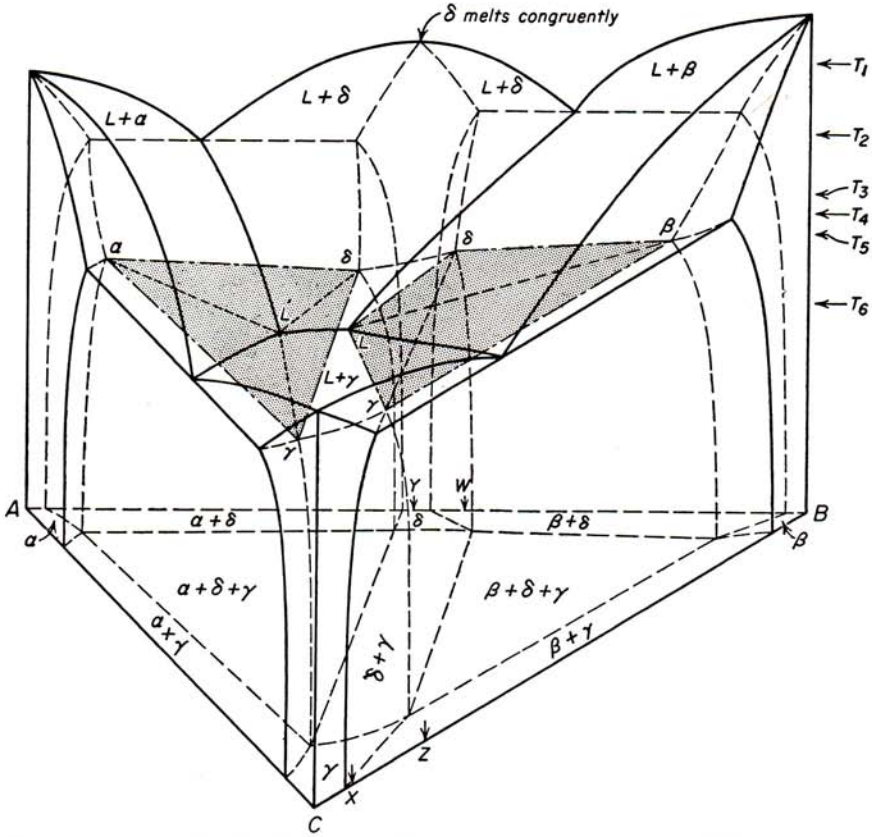

FIG. 17-4. Temperature-composition space diagram having a congruently melting intermediate phase but no quasi-binary section.

$(L \rightarrow \gamma + \delta)$, which occurs at the maximum temperature of equilibrium among these three phases. It will be recalled from Chap. 13 that a three-phase region, passing through a temperature maximum, is reduced to a single line at the maximum. The liquidus surface upon the two sides of the quasi-binary section forms a saddle astride the quasi-binary eutectic composition; see the liquidus projection of this diagram in Fig. 17-8*a*. It would be possible to have the quasi-binary eutectic correspond to a minimum in the ternary liquidus surface if the $L + \gamma + \delta$ regions pased through a minimum instead of a maximum as in Fig. 13-31. This could occur if class II four-phase reactions were substituted for the class I reactions shown in Fig. 17-1. The existence of a congruently melting intermediate phase in a ternary system by no means guarantees that a quasi-binary system will exist. A contrary case involving the same phases in the

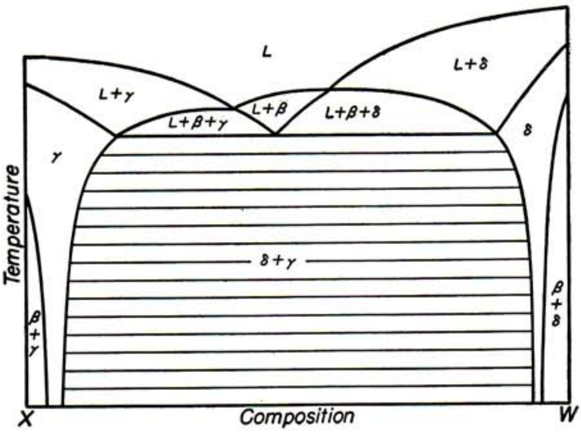

Fig. 17-5. Isopleth from the space diagram of Fig. 17-4.

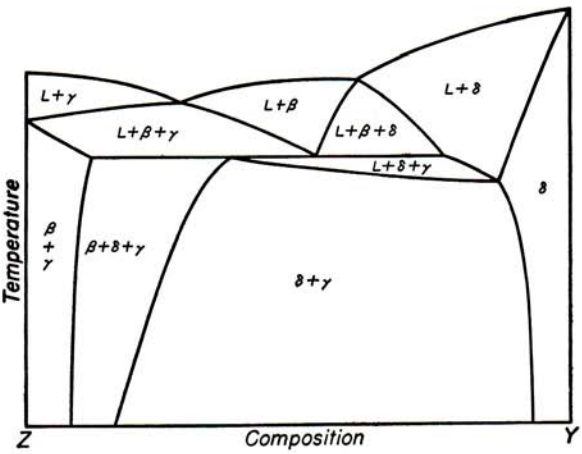

Fig. 17-6. Isopleth from the space diagram of Fig. 17-4.

same binary configuration appears in Fig. 17-4. Here there is no quasi-binary section (Fig. 17-7). A class II four-phase reaction isotherm $L + \beta + \gamma + \delta$ crosses the isopleth between the γ and δ phases (see T_4 in Fig. 17-7). Tie-lines are found in the isopleth of Fig. 17-5 only in the $\gamma + \delta$ field. Those of the $L + \beta$, $L + \gamma$, and $L + \delta$ fields lie at an angle to the plane of the section. Three-phase equilibrium is represented by areas, i.e., the areas $L + \beta + \gamma$ and $L + \beta + \delta$. Alloys of this series are not set apart from those on either side of the vertical section by their binary behavior but behave as ternary alloys.

The diagram of Fig. 17-5 has, as a matter of fact, been drawn in the most favorable way to place as many as possible of the tie-lines in the isopleth. It has been assumed in making the drawing that the $\gamma\delta$ tie-line

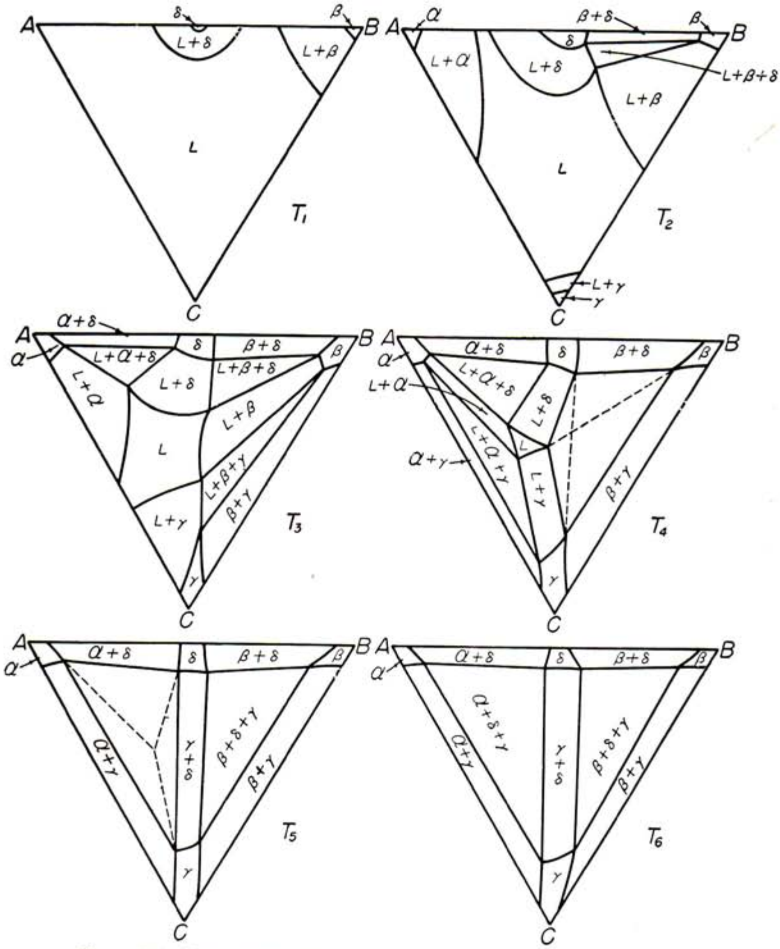

FIG. 17-7. Isotherms through the space diagram of Fig. 17-4.

of the class II four-phase reaction plane lies exactly in the vertical section. It is not necessary that this condition obtain. If the vertical section crosses the four-phase isotherm at random, the isopleth might appear somewhat as in Fig. 17-6, where no tie-lines exist anywhere in the section. The relative likelihood of tie-lines running parallel to the $\gamma\delta$ section in the several two-phase fields can be ascertained most easily by reference to the isotherms of Fig. 17-7. Here it can be seen that tie-lines in the $L + \beta$ field will lie almost perpendicular to the section while those in the other two-phase fields lie at various angles. Certain tie-lines in the $L + \gamma$, $L + \delta$, and $\gamma + \delta$ fields might, by chance, lie in the section. No maximum or minimum of three-phase equilibrium occurs in the vertical section; the liquidus valleys pass this vertical plane without inflection as can be seen in Fig. 17-8*b*.

Quasi-binary equilibrium can exist also between congruently melting ternary intermediate phases and other components (Fig. 17-9). One ternary intermediate phase is shown forming three quasi-binary systems,

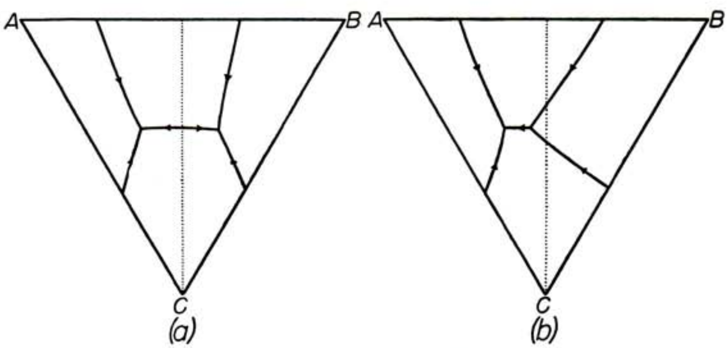

FIG. 17-8. Liquidus valleys from the two foregoing space diagrams: (*a*) Fig. 17-1 and (*b*) Fig. 17-4.

one with each of the terminal components. This divides the space diagram into three independent sections; three separate ternary eutectic systems are shown (see also Fig. 17-10). These three quasi-binary systems are identical in all characteristics with those formed by binary intermediate phases.

Division of the Ternary Diagram

A single quasi-binary system divides the ternary system into two parts. Two quasi-binary systems divide the ternary into three parts, three quasi binaries divide the ternary into four parts, and so on (see Fig. 17-11). The maximum number of quasi-binary sections is equal to the number of congruent binary intermediate phases. This is true regardless of the manner in which the sections are selected; for example, compare drawings *b* and *c* or *d*, *e*, and *f* in Fig. 17-11. The maximum number of independent ternary systems n into which the main ternary diagram is thus divided is equal to the number of binary intermediate phases b plus 1:

$$n = b + 1$$

By reference to Fig. 17-12*a*, *b*, and *c*, it can be seen that one ternary intermediate phase can give rise to three quasi-binary systems and that the maximum number of independent ternary systems into which the diagram is thus divided is equal to twice the number of ternary intermediate phases t plus 1:

$$n = 2t + 1$$

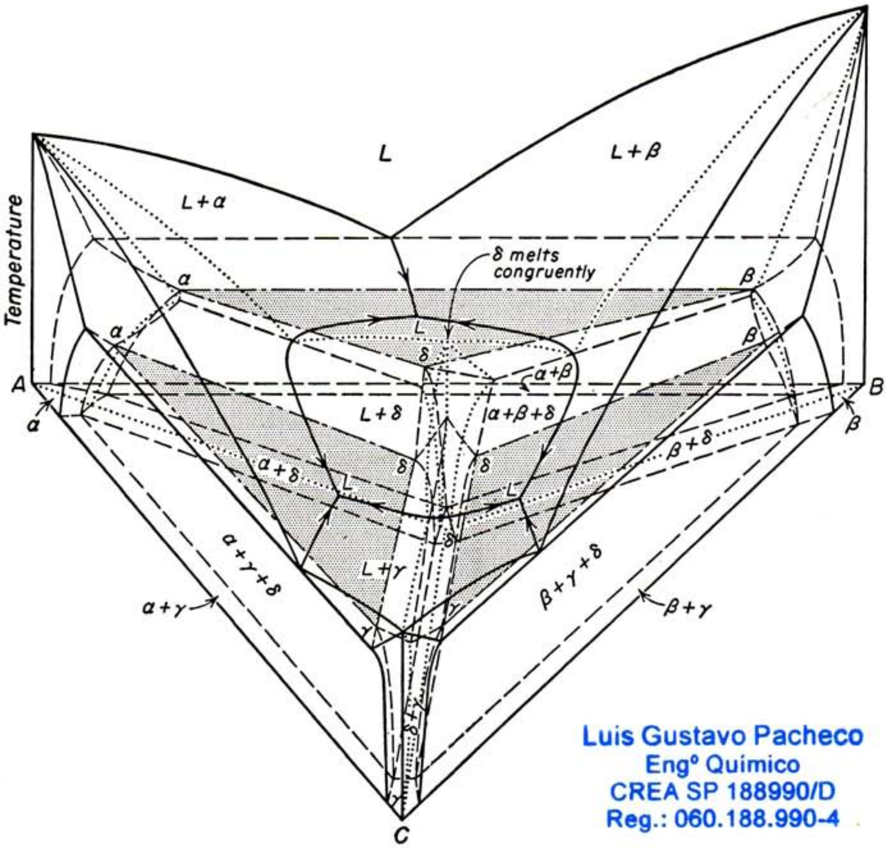

FIG. 17-9. Temperature-composition diagram of a system having a congruently melting ternary intermediate phase that forms quasi-binary sections with each of the three components.

Where binary and ternary intermediate phases occur in the same ternary system,

$$n = b + 2t + 1$$

In the drawing of Fig. 17-12*f* there are two ternary and one binary intermediate phases:

$$n = 1 + 2 \times 2 + 1 = 6$$

This rule is of interest in the construction of ternary diagrams but finds its greatest usefulness in the checking of isotherms. Here it is unnecessary to consider whether or not the intermediate phases are congruently melting, for the conditions at the temperature of the isotherm alone are concerned. Let n be the number of three-phase tie-triangles in the isotherm,

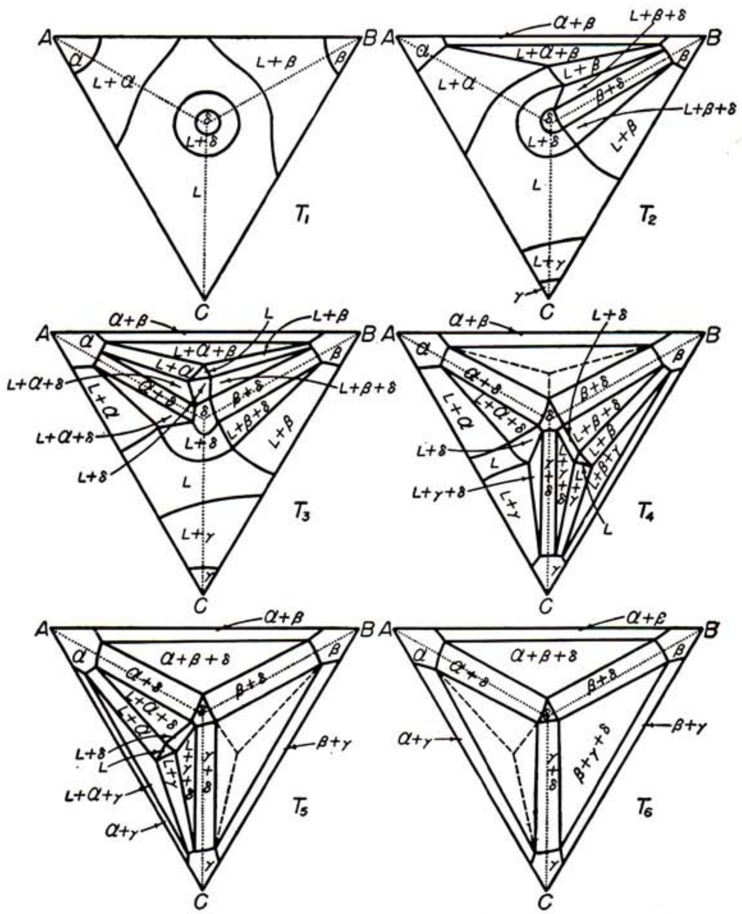

FIG. 17-10. Isotherms through the space diagram of Fig. 17-9.

b the number of binary phases (including all phases that touch the edge of the diagram, except the terminal phases), and t the number of phases occurring wholly within the diagram. Then the number of three-phase regions will be equal to the number of binary phases plus twice the number of ternary phases plus 1. In applying this rule it is necessary to make an exception of phases which are isomorphous across the ternary diagram. For each isomorphous phase one three-phase region must be

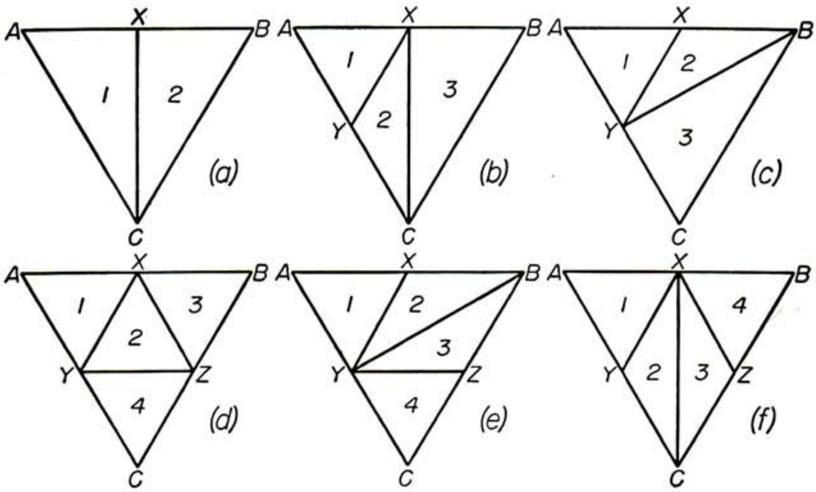

FIG. 17-11. Possible arrangement of quasi-binary sections in the presence of one (*a*), two (*b* and *c*), and three (*d*, *e*, and *f*) binary intermediate phases.

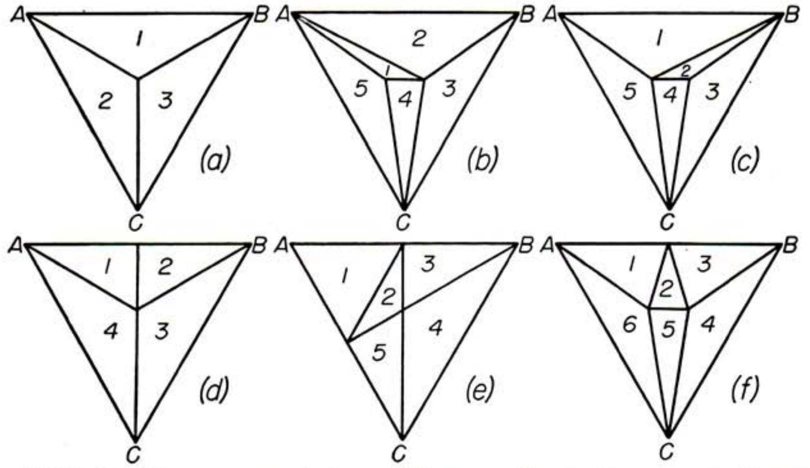

FIG. 17-12. Possible arrangement of quasi-binary sections in the presence of one (*a*) and two (*b* and *c*) ternary intermediate phases, and combinations of one binary and one ternary intermediate phase (*d*), two binary and one ternary intermediate phase (*e*), and one binary and two ternary intermediate phases (*f*).

subtracted from the result of the above computation. Where one phase is isomorphous with more than one other binary phase, the number of isomorphous systems is one less than the number of binary phases participating.

Thus, in section T_4 of Fig. 17-3 there are two binary phases (δ and L) and one ternary phase (L).

$$n = 2 + 2 \times 1 + 1 = 5$$

Five tie-triangles can be counted in the isotherm. In section T_2, Fig. 17-3, there are two binary (δ and L) and no ternary phases, but the L phase is isomorphous in two limbs.

$$n = 2 + 0 + 1 - 2 = 1$$

Only one three-phase region is found in this section.

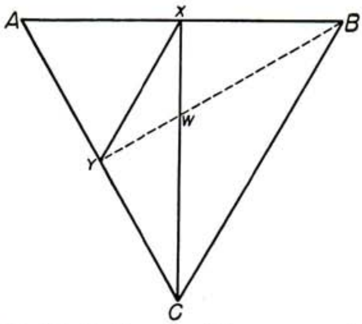

FIG. 17-13. Illustrating the "clear-cross principle."

The "Clear-cross Principle"

It has been shown in Figs. 17-11 and 17-12 that with a given number of intermediate phases, the quasi-binary sections can be arranged in several different ways. This is illustrated in Fig. 17-13, where the quasi-binary sections may be either XY and XC or XY and YB. Obviously, both XC and YB cannot exist; at least one of these two must be false.

An experimental procedure, known as the "clear-cross principle," has been devised to ascertain which of two quasi-binary systems (if either) is real. An alloy of composition W, lying on the intersection of the two potential quasi-binary sections, is made. After homogenization to establish equilibrium, the alloy is examined to determine the phases present. If only X and C are found, then the quasi-binary section XC is real and the section YB is false. If phases Y and B alone are found, then section YB is real and XC is false. But if three phases are found, neither is real.

Some Other Examples of Congruency

Congruent melting of ternary isomorphous solid solutions at compositions of maximum or minimum melting temperature has been mentioned in Chap. 12. A corresponding congruent transformation within the solid state is also possible. This may involve an order-disorder type of transformation as explained in Chap. 7. Likewise, quasi-binary behavior extends to equilibria wholly within the solid state.