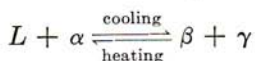# TERNARY FOUR-PHASE EQUILIBRIUM—CLASS II

There is another type of ternary four-phase equilibrium, known as *four-phase equilibrium of the second kind* or *class* II *four-phase equilibrium*, that has no direct equivalent in binary systems. It may be thought of as being intermediate between eutectic and peritectic reaction:

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

During heating or cooling, two phases interact to form two new phases.

The manner of representation of class II four-phase equilibrium in a space diagram is illustrated in Fig. 15-1, and isothermal sections through
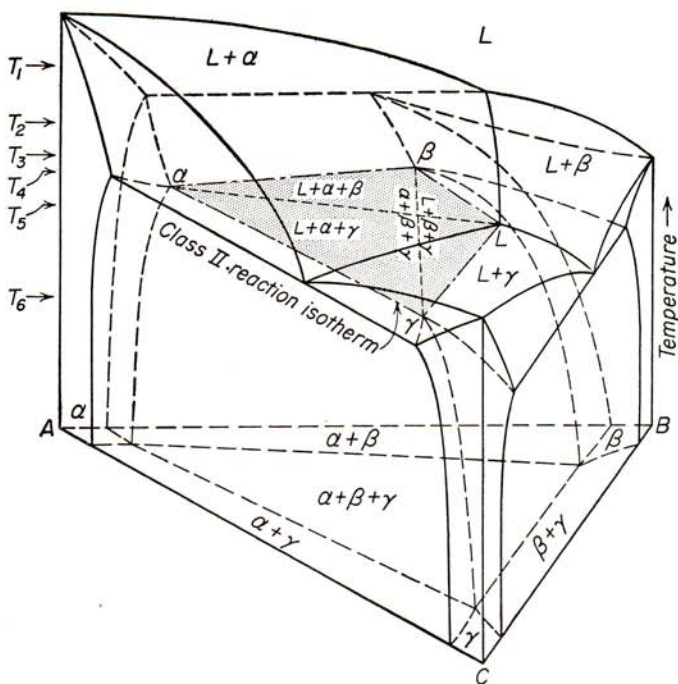

Fig. 15-1. Temperature-concentration diagram illustrating class II four-phase equilibrium.
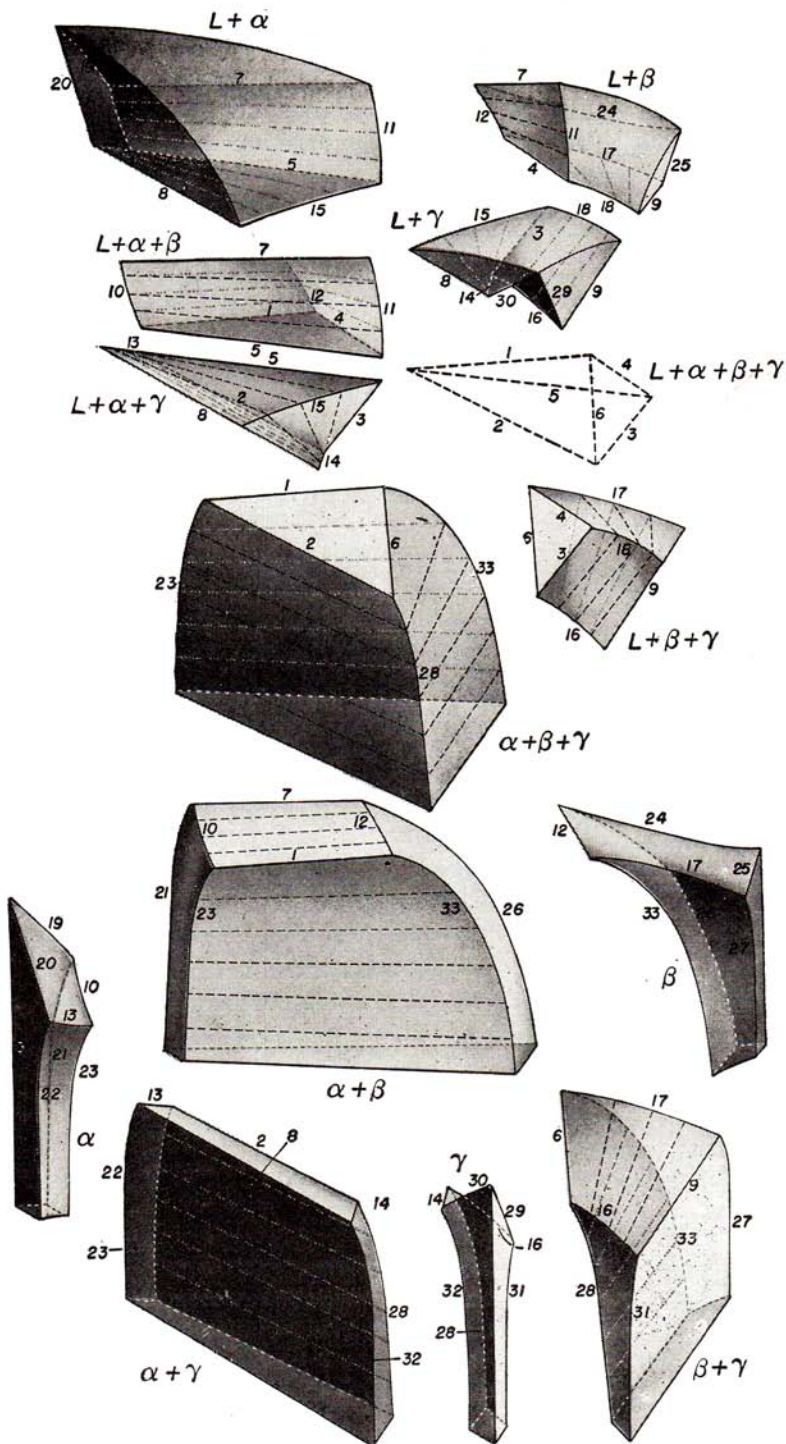
FIG. 15-2. Exploded model of the phase diagram of Fig. 15-1. The inscribed numbers identify edges that are identical lines on different segments of the model.

this diagram are given in Fig. 15-3. Further details are shown in the exploded model in Fig. 15-2. In these drawings it can be seen that *two* three-phase regions $L + \alpha + \beta$ and $L + \alpha + \gamma$ descend from higher temperature toward the four-phase reaction plane, where they meet to form a horizontal trapezium (kite-shaped figure) at the four corners of
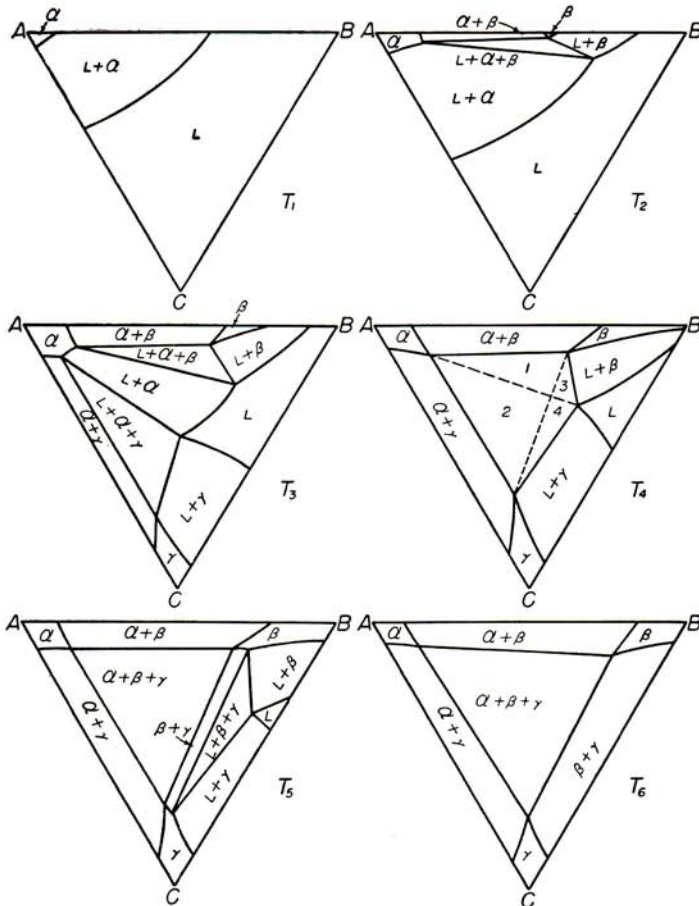

FIG. 15-3. Isotherms through the space diagram of Fig. 15-1.

which the four phases in equilibrium are represented: $\alpha + \beta + \gamma + L$. Beneath the four-phase reaction plane two new three-phase regions, $\alpha + \beta + \gamma$ and $L + \beta + \gamma$, originate and descend to lower temperature. Thus, the two tie-triangles, $L + \alpha + \beta$ and $L + \alpha + \gamma$, Fig. 15-4, join along a common tie-line αL to form the four-phase reaction trapezium, and this figure divides along the tie-line $\beta \gamma$ to form two new tie-triangles, $\alpha + \beta + \gamma$ and $L + \beta + \gamma$. An alloy occurring at the composition at

which these tie-lines cross (intersection of the dashed lines in the central sketch of Fig. 15-4) would be composed entirely of L and α just above the reaction temperature and entirely of β and γ just below the reaction temperature.

This construction conforms with the demands of the phase rule. Four-phase reaction should be univariant; the temperature and compositions of the participating phases should be constant at fixed pressure. These conditions are met, since the four-phase trapezium is horizontal (isothermal) and the one-phase regions touch it only at its four corners where a unique composition is thereby designated for each of the four phases.

Other than the four-phase reaction trapezium, this diagram involves no regions that have not been discussed in previous chapters. The one-, two-, and three-phase regions in this diagram are, in fact, identical in number and designation with those found in the ternary eutectic diagram.
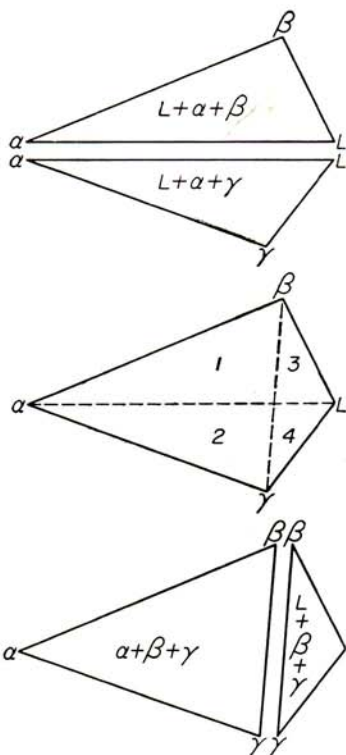

Course of Freezing of Some Typical Alloys

An examination of the course of freezing of several typical alloys should prove helpful in gaining an understanding of the nature of class II four-phase reaction. Four alloys designated 1, 2, 3, and 4 in the central drawing of Fig. 15-4 will be considered.

Fig. 15-4

It can be seen at once that these will undergo the following changes upon descending through the four-phase reaction temperature:

1. $L + \alpha + \beta \rightarrow \alpha + \beta + \gamma$
2. $L + \alpha + \gamma \rightarrow \alpha + \beta + \gamma$
3. $L + \alpha + \beta \rightarrow L + \beta + \gamma$
4. $L + \alpha + \gamma \rightarrow L + \beta + \gamma$

By reference to Fig. 15-3 it can be seen that alloy 1 begins freezing with a primary separation of the α phase followed by a secondary deposition of $\alpha + \beta$. Just above the four-phase reaction temperature the relative proportions of the three phases may be computed from the tie-triangle in

solid lines in Fig. 15-5:

$$\%\beta = \frac{X1}{X\beta} \times 100 \approx 50\%$$

$$\%\alpha = \frac{XL}{\alpha L}\frac{1\beta}{X\beta} \times 100 \approx 28\%$$

$$\%L = \frac{\alpha X}{\alpha L}\frac{1\beta}{X\beta} \times 100 \approx 22\%$$

Just below the four-phase reaction temperature

$$\%\beta = \frac{Y1}{Y\beta} \times 100 \approx 66\%$$

$$\%\alpha = \frac{Y\gamma}{\alpha\gamma}\frac{1\beta}{Y\beta} \times 100 \approx 18\%$$

$$\%\gamma = \frac{\alpha Y}{\alpha\gamma}\frac{1\beta}{Y\beta} \times 100 \approx 16\%$$

The percentage of α has decreased sharply, and the liquid has disappeared altogether, while the quantity of β has increased, and a substantial quantity of γ has appeared as a new phase. Some of the previously existing α has been consumed by reaction with liquid, as in *peritectic reaction*. The increase in the quantity of β, coincident with the appearance of γ, more nearly resembles *eutectic reaction*. This is what was meant by the opening statement to the effect that class II four-phase equilibrium occupies a position midway between the eutectic and peritectic types.

FIG. 15-5

Alloy 2 (Fig. 15-4) also begins freezing with a primary separation of the α phase, but the secondary crystallization will be of $\alpha + \gamma$ in this case instead of $\alpha + \beta$. If the tie-triangles were analyzed for this example, it would be found t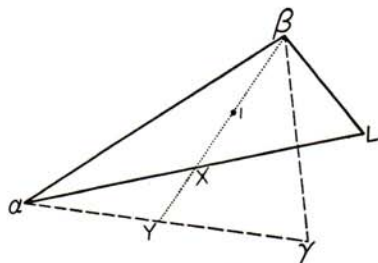hat at the four-phase reaction temperature, the liquid phase is wholly consumed and the α phase is partly redissolved to form a tertiary precipitation of $\beta + \gamma$.

The two alloys 3 and 4 which lie closer to the liquid corner of the four-phase trapezium differ from the foregoing pair of alloys in that the primary and secondary α crystals should be totally consumed if four-phase reaction goes to completion, while some of the liquid phase should remain to freeze as $\beta + \gamma$ at a lower temperature. In both alloys the primary constituent is α, although its quantity may be small because these com-

positions are close to the lower edge of the $L + \alpha$ field. The secondary constituent in alloy 3 will be $\alpha + \beta$, while that in alloy 4 will be $\alpha + \gamma$. Both will suffer a loss of α and of some liquid to form $\beta + \gamma$ in four-phase reaction, and the simultaneous crystallization of β and γ will continue at lower temperature until the supply of liquid is exhausted.

As with peritectic alloys the formation of reaction layers (envelopment) upon the α phase may be expected to interfere with the completion of reaction by hindering the diffusion that must take place to establish equilibrium. Consequently, an excess of the α phase is likely to persist and some liquid is likely to survive through four-phase reaction in all the alloys of this system. This will have the effect of minimizing the differences in structure among the several alloys.

Some examples of characteristic microstructures of lead-antimony-tin alloys that undergo class II four-phase reaction are presented in Fig. 15-6. Isothermal sections of the appropriate portion of the lead-antimony-tin phase diagram are given in Fig. 15-7. The compositions at which the four alloys represented in Fig. 15-6 occur are designated a, b, c, and d in the isotherm at 250°C in Fig. 15-7. Because no single etching technique serves to differentiate clearly among the β, δ, and γ phases of this alloy system, two pictures of each alloy are presented. The picture on the left, in each case, has been made by the use of an etch which blackens the δ phase and leaves the β and γ phases white, while the etch used in preparing the pictures on the right causes the δ phase to appear black, the γ phase gray to black, and the β phase white. Thus the β phase is white and the δ phase black in both pictures, while the γ phase is white in the pictures on the left and gray or black in the pictures on the right.

The large white squares are, in all cases, primary β. That they have been subject to "peritectic attack," especially in alloys b and d (pictures D and H), is evident from the penetration of the γ phase along their edges. In alloy c (pictures E and F) the primary constituent is γ, seen as typical dendrites, white in the picture on the left and black in the picture on the right. A two-phase constituent $\beta + \gamma$ forms secondarily in alloys a and c (pictures A, B, E, and F). The β of this constituent is largely destroyed during subsequent transformation and remains only as small white irregular specks in the background of the microstructure, being more plentiful in alloy a than in alloy c as should be expected. The secondary constituent in alloys b and d (pictures C, D, G, and H) is $\beta + \delta$. Here again, the secondary β is largely destroyed in subsequent reaction, being more plentiful in alloy b than in alloy d. Four-phase reaction, in all alloys, proceeds by the formation of finely divided $\delta + \gamma$ through reaction of liquid with β and, subsequently, by the direct decomposition of any remaining liquid into $\delta + \gamma$. This constituent appears as a mixture of very small black and white specks in the photographs on the left and of gray
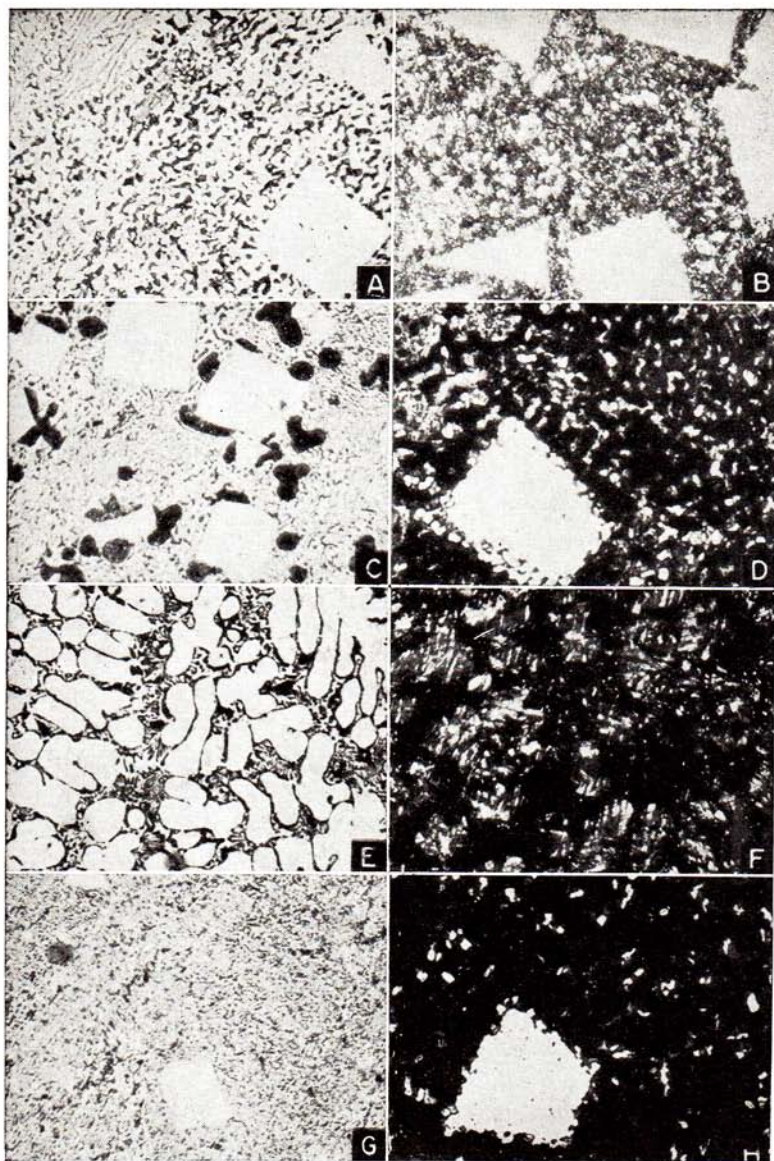
Fig. 15-6. Microstructure of cast alloys of compositions *a*, *b*, *c*, and *d*, designated in the first isotherm of Fig. 15-7. Two photomicrographs are required to show the structure of each alloy, because the γ phase is indistinguishable from the δ phase (black) in the pictures on the right and from the β phase (white) in the pictures on the left. In *a*, *b*, and *d* (pictures A, B, C, D, G, and H) the primary constituent is β which is partly redissolved in subsequent class II reaction, as shown by the serrated edges of the white squares. The primary constituent in alloy *c* (pictures E and F) is dendritic γ. Tin-rich alloys *a* and *c* (pictures A, B, E, and F) display a secondary crystallization of $\beta + \gamma$, while lead-rich alloys *b* and *d* (pictures C, D, G, and H) have an equivalent $\beta + \delta$ constituent. In all cases, class II reaction results in the formation of a finely divided tertiary constituent of $\gamma + \delta$. Magnification: A and B, 500; C, 250; D, 750; E and F, 250; G, 250 and H, 750.

and black specks, which can scarcely be differentiated, in the photographs on the right.

Other Examples of Class II Four-phase Equilibrium

Class II four-phase reaction appears to be relatively common in ternary alloy systems. Most of the examples on record are of the kind just described, in which one liquid and three solid phases participate. Similar reaction among four solid phases has been reported, however, in a
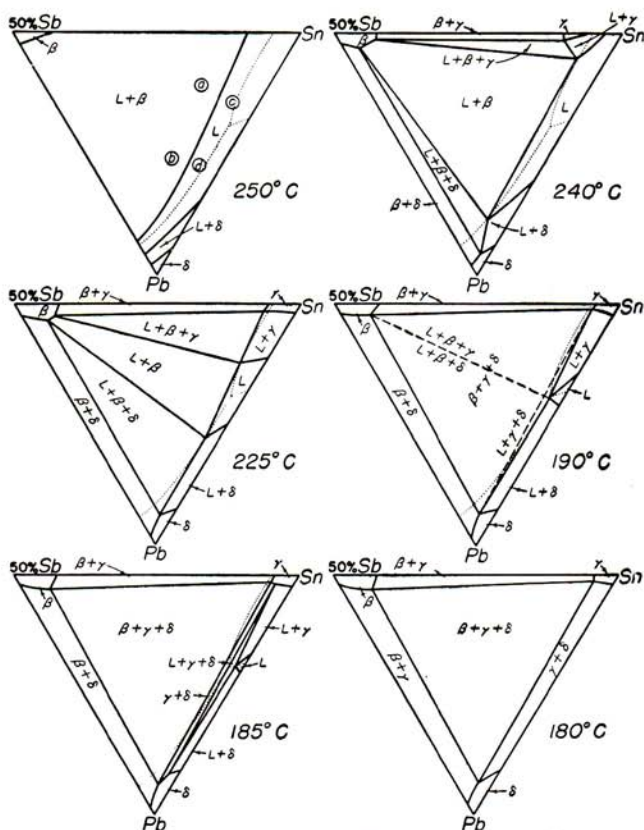

FIG. 15-7. Isotherms of the ternary system Pb-Sn-β (50% Sb + 50% Sn). The circled letters in the isotherm at 250°C indicate the compositions of the four alloys of which the microstructure is shown in Fig. 15-6.

number of systems, as have other combinations of phases in class II reaction. All conceivable combinations are listed in Table 4, Chap. 18, relatively few of which have as yet been observed in ternary alloy systems. Wherever such reaction does occur, however, the general principles outlined above should apply to its interpretation.

Some Vertical Sections

In vertical sections through the space diagram the class II four-phase reaction plane appears, of course, as a horizontal line (see Figs. 15-8, 15-9, and 15-10). Otherwise, there is little generalization possible in the construction of vertical sections. A section UV taken parallel to the AB
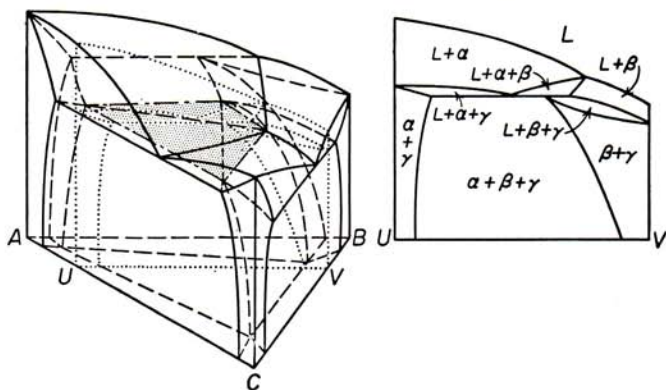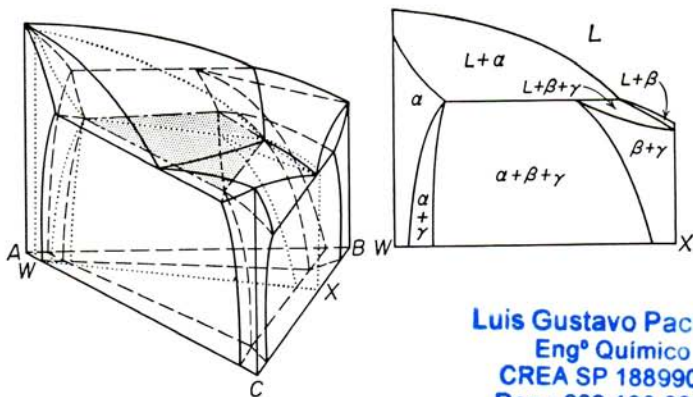

FIG. 15-8

FIG. 15-9

side of the space model is represented in Fig. 15-8. By shifting the plane of this section slightly so that it passes through the α and liquid compositions of the four-phase reaction, section WX of Fig. 15-9 is obtained. Here the $L + \alpha$ field rests upon the four-phase reaction line because αL is an element of the trapezium and also the lowest tie-line in the $L + \alpha$ field. Section YZ of Fig. 15-10 is taken parallel to the BC side of the diagram and illustrates the complexity of configuration that is sometimes encountered in vertical sections through this type of ternary diagram. Isothermal sections, Fig. 15-3, are much easier to understand in this case.
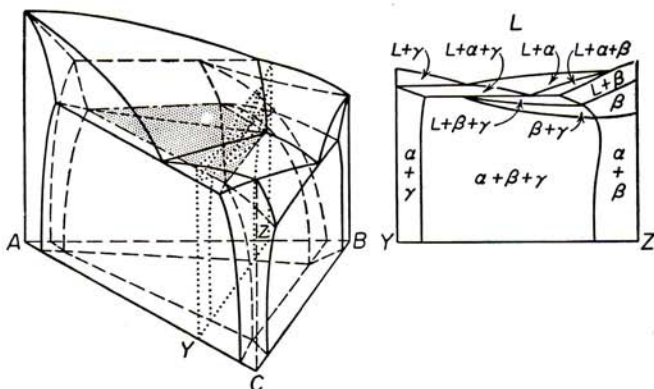
FIG 15-10

Heat Treatment of Alloys

There is little to be said concerning the relationships between the constitution of alloys of class II ternary four-phase systems and the structures produced by heat treatment that has not already been said in connection with the ternary eutectic system. The discussion with regard to Fig. 14-11 applies as well to alloys in the neighborhood of the A component in the diagram just considered. Similar relationships obtain in other alloys of this type of system, the most noteworthy difference being that liquation can occur below the temperature of four-phase reaction in any alloys containing both the β and the γ phase. These phases will melt together at the BC binary eutectic temperature (or somewhat above) if one or both are not dissolved prior to the attainment of this temperature.

PRACTICE PROBLEMS

1. How do the percentages of the several phases change during the class II transformation of composition 3 in Fig. 15-4? Of composition 4? If Class II transformation were to be suppressed altogether, as by rapid cooling or a very slow diffusion rate, how would the microstructures of these alloys (at room temperature) differ from that produced by complete transformation?

2. Draw the space diagram of a ternary system made up of two binary peritectic-type systems and one eutectic-type system and having a class II four-phase equilibrium below the two binary peritectic temperatures but above the temperature of the binary eutectic. Develop isothermal sections sufficient to display the internal structure of this diagram.