

Ternary Phase Diagrams

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Crystallization in Ternary Systems

I. Equilibrium Crystallization Where all 2 Component Systems are Binary Eutectic Systems.

Figure 1 shows a three dimensional representation of the three component (ternary) system ABC. Note that composition is measured along the sides of the basal triangle and temperature (or pressure) is measured vertically. The top of the figure shows a surface with contour's representing lines of constant temperature. These contours are called *isotherms*. Note that the eutectic points in each of the binary systems project into the ternary systems as curves. These curves are called *boundary curves*, and any composition on one of these curves will crystallize the two phases on either side of the curve.

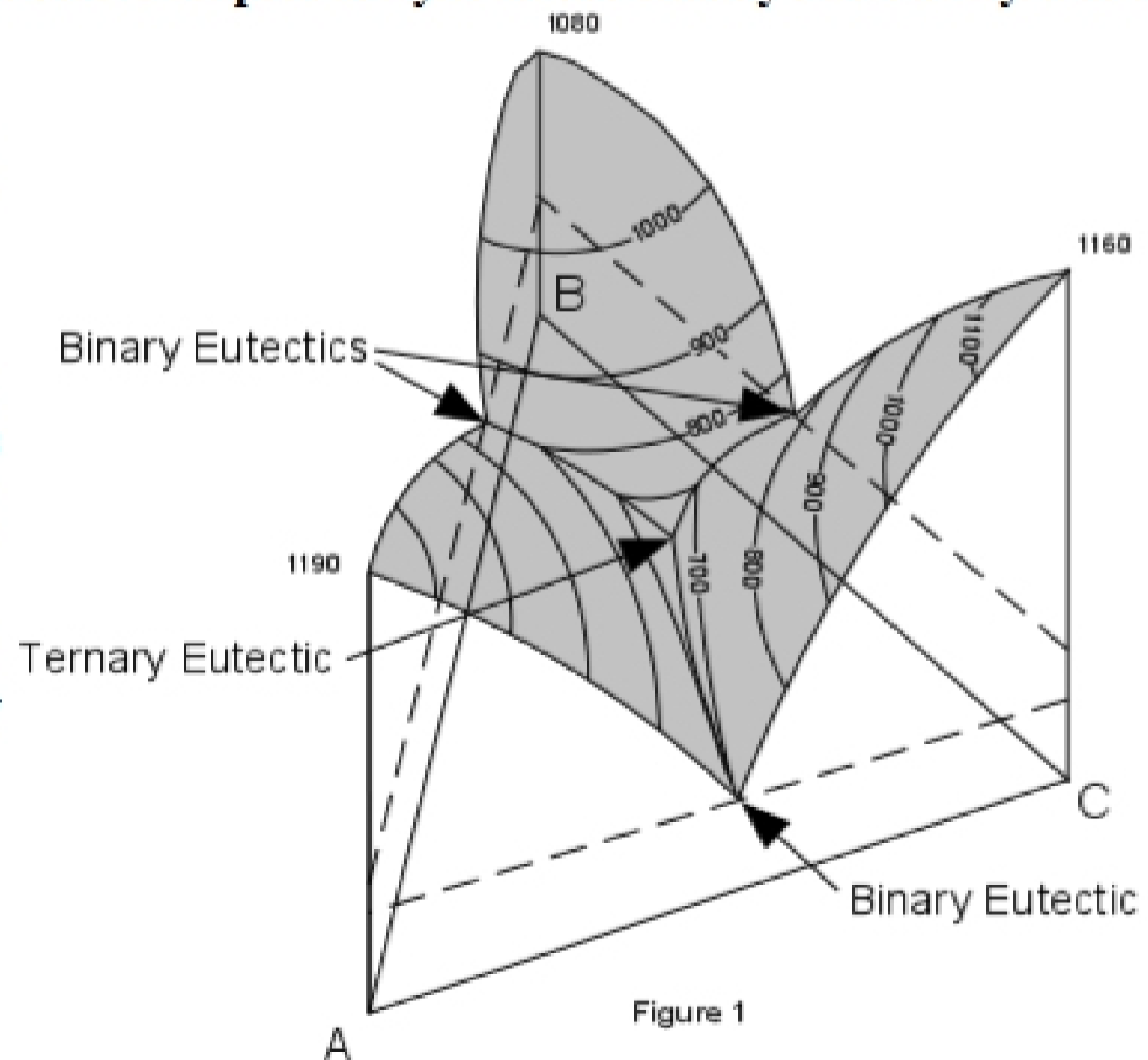


Figure 1

Figure 2 shows the same figure in two dimensions as seen from above. The boundary curves and isotherms are also shown projected onto the basal triangle. Note how the temperature decreases toward the center of the diagram

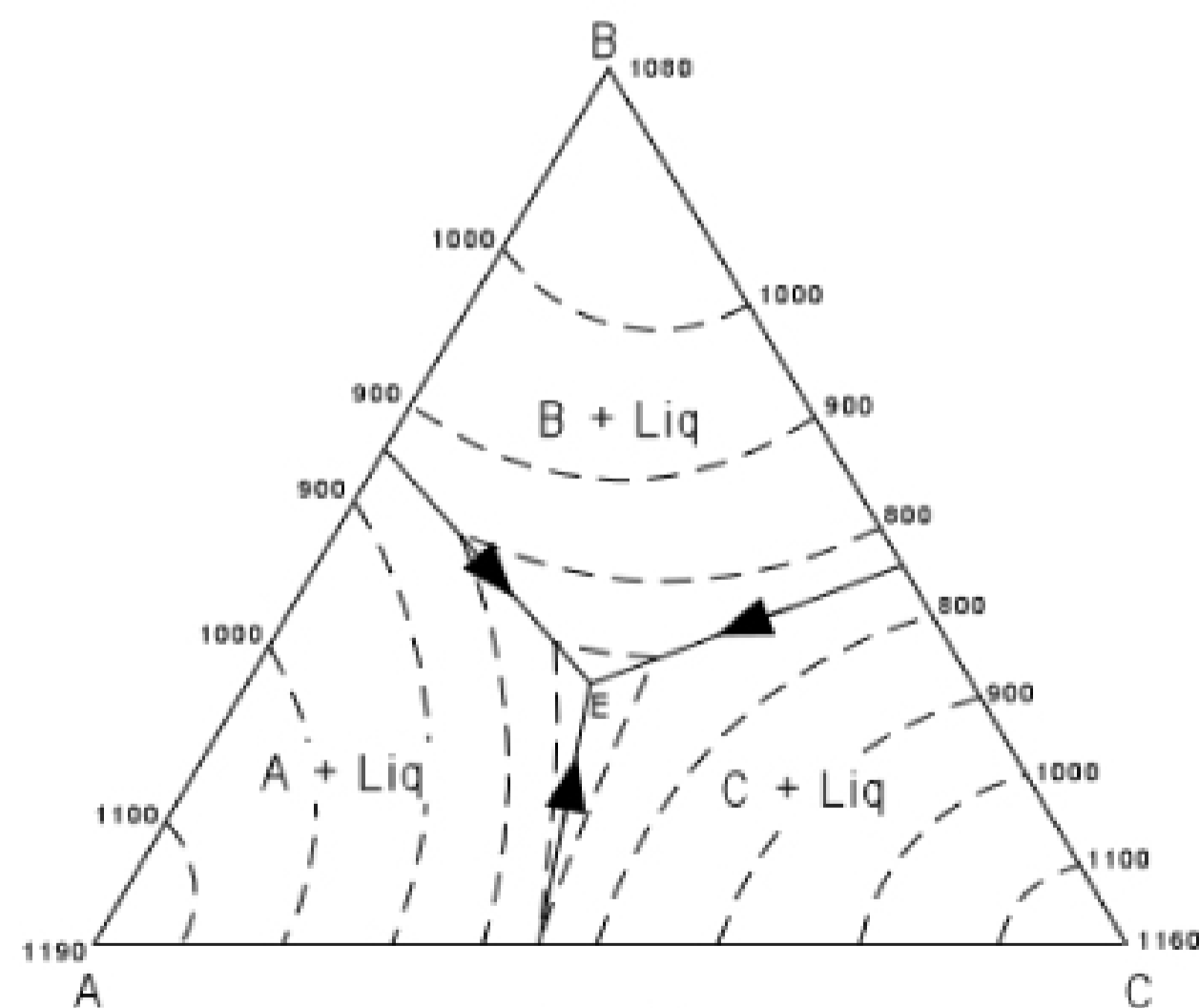


Figure 2

In Figure 3 we trace the crystallization of composition X. Figure 3 is the same as Figure 2, with the isotherms left off for greater clarity.

Note that the final solid must consist of crystals A + B + C since the initial composition is in the triangle ABC.

At a temperature of about 980° the liquid of composition X would intersect the liquidus surface. At this point it would begin to precipitate crystals of C. As temperature is lowered, crystals of C would continue to precipitate, and the composition of the liquid would move along a straight line away from C. This is because C is precipitating and the liquid is becoming impoverished in C and enriched in the components A + B.

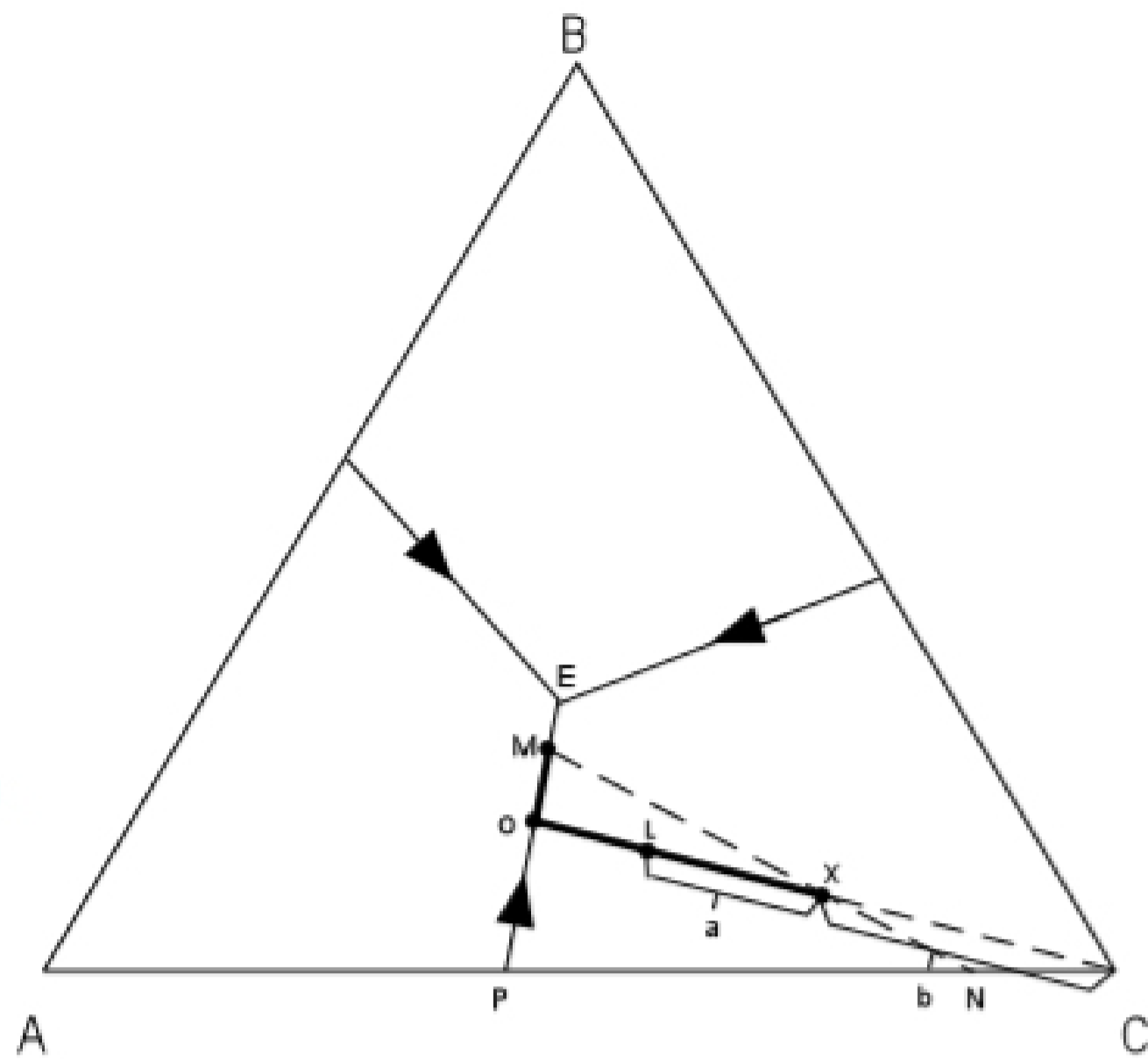


Figure 3

At a temperature of about 820° , point L in Figure 3, we can determine the relative proportion of crystals and liquid.

$$\% \text{ crystals} = a/(a+b)*100$$

$$\% \text{ liquid} = b/(a+b)*100$$

With further cooling, the path of the liquid composition will intersect the boundary curve at point O. At the boundary curve crystals of A will then precipitate. The liquid path will then follow the boundary curve towards point M. The bulk composition of the solid phase precipitated during this interval will be a mixture of A + C in the proportion shown by point P.

At point M, the bulk composition of the solid phases so far precipitated through the cooling history lies at point N (the extension of the straight line from M through the initial composition X). At this time the % solid will be given by the distances :

$$(\text{distanceMX}/\text{distanceMN})*100$$

and the % liquid by the distances:

$$(\text{distanceXN}/\text{distanceMN})*100$$

Note, however, that the solid at this point consists of crystals of A and crystals of C. So, we must further break down the percentages of the solid. This is done as follows: The percentage of the solid that is A will be given by the distance from C to N relative to the distance between A and C; i.e. by the formula:

$$\%A \text{ in solid} = (\text{distanceNC}/\text{distanceAC})*100$$

Similarly, the percentage of the solid consisting of crystals of C is given by the formula:

$$\%C \text{ in solid} = (\text{distanceAN}/\text{distanceAC}) * 100$$

We can now calculate the exact percentage of all phases present in composition X at a temperature of 660° (where the liquid composition is at point M). The following formulae apply:

$$\%A \text{ crystals} = \%A \text{ in the solid} * \% \text{ crystals}/100$$

or

$$\%A = (\text{distanceNC}/\text{distanceAC}) * 100 * (\text{distanceMX}/\text{distanceMN})$$

and

$$\%C \text{ crystals} = \%C \text{ in the solid} * \% \text{ crystals}/100$$

or

$$\%C = (\text{distanceNA}/\text{distanceAC}) * 100 * \text{distanceMX}/\text{distanceMN}$$

Note also that we can determine the **composition** of all phases present in the system at this point. The composition of the liquid is given by reading the composition of point M off the basal triangle. Since it is a mixture of A, B, and C, it will have a composition expressed in terms of the percentages of A, B, and C. The composition of the solids are 100%A and 100% C; i.e. they are pure solid phases (not mixtures).

With further cooling, the liquid composition will move to the ternary eutectic, E, at a Temperature of about 650°, at which point crystals of B will precipitate. The temperature will remain constant until all of the liquid is used up. The final crystalline product will consist of crystals of A + B + C in the proportions given by the initial composition X.

Crystallization will proceed in an analogous manner for all other compositions in the ternary system.

To summarize, we can express the path of crystallization for composition X in an abbreviated form as follows:

$$T > 980^\circ \text{ All Liquid}$$

$$980^\circ - 680^\circ \text{ Liq} + \text{C}$$

$$680^\circ - 650^\circ \text{ Liq} + \text{C} + \text{A}$$

$$T = 650^\circ \text{ Liq} + \text{C} + \text{A} + \text{B}$$

$$T < 650^\circ \text{ C} + \text{A} + \text{B} \text{ (all solid)}$$