South Dakota School of Mines and Technology
Department of Materials and Metallurgical Engineering

Rules for Interpretation of Ternary Phase Diagrams

Stanley M. Howard

1. **Final Three Crystals**
   Place the batch composition on the equilateral triangle. The vertices of the Alkemade triangle enclosing the batch composition indicate the FINAL THREE CRYSTALS that will comprise the completely solidified batch.

2. **First Crystal**
   Determine the area of primary crystallization in which the batch composition occurs. This is the FIRST CRYSTAL which precipitates out of solution upon cooling. If the first crystal is not one of the final three crystals, a fourth crystal will be formed and the final crystals will be the second, third, and fourth crystals formed. If the first crystal is one of the final three crystals, the temperature at which the system finally becomes completely solid is the temperature at the point where these three crystals' primary crystallization areas intersect. This point is the ternary equivalent of a binary eutectic.

3. **Second Crystal (and amount of the 1st Xtal and liquid at T's before the 2nd Xtal appears)**
   Draw a line from the composition of the first crystal through the batch composition until it hits a boundary line. This intersection shows the SECOND CRYSTAL to precipitate. The temperature for the formation of the second crystal may be determined from the temperature at the intersection. At any temperature before the boundary line is reached, a tie line may be drawn from the first crystal through the batch composition to this temperature thereby establishing a lever from which the amounts of liquid and first crystal may be calculated. The composition of the liquid is always the composition at end of the tie line moving away from the crystal composition.

4. **Third Crystal (and amount of the 1st & 2nd Xtals and liquid at T's before the 3rd Xtal appears)**
   After the second crystal appears, the melt composition moves along the boundary line shared by the first and second crystals. From any point of lower temperature along this boundary line, a line may be drawn through the batch composition until it intersects the Alkemade line between the two crystals present. This sets up two levers which are used to calculate the amount of liquid, the amount of mixed crystals, and the composition of the mixed crystals. As the temperature falls, the point on this boundary line will eventually encounter another boundary line and, thus, another area of primary crystallization. This determines the THIRD CRYSTAL to form.

5. **If First Crystal is Not One of the Final Three Crystals**
   The tie line from the intersections of the three areas of primary crystallization through the batch composition to the Alkemade line connecting the first two crystals undergoes an interesting transformation. The end of the tie line on the Alkemade line connecting the first two crystals moves towards the batch composition stopping when it reaches the Alkemade line connecting the second and third crystals. This later Alkemade line always occurs before the batch composition is encountered. The lever rule cannot be applied during this transformation. It represents the peritectic-like phase transformation in which the liquid phase and all of the first crystal react to form more second and third crystals. This is called the tributary reaction in a ternary phase diagram.

6. **In the case where the First Crystal is Consumed leaving only the 2nd and 3rd Crystals**
   Once the first crystal is consumed by the tributary reaction, the liquid composition moves down the boundary line between the second and third crystals. From any point along this line, a tie line may be drawn through the batch composition to the Alkemade connecting the second and third crystals. This

sets up two levers that may be used as before to determine the amount of all phases present. The fourth and final crystal is formed when the next area of primary crystallization is encountered. The entire system solidifies at that temperature.

7. **If the Second Crystal is Not One of the Final Three Crystal**,
The second crystal is consumed by the tributary reaction. Initially the liquid composition moves down the boundary line between the first and second crystals (the only two present). From any point along this line, a tie line may be drawn as usual through the batch composition to the Alkemade connecting the first and second crystals. This sets up two levers which may be used as before to determine the amount of all phases present. When the first tributary point is reached, the third crystal is formed and there are no degrees of freedom. The second crystal is consumed leaving the first and third crystal and the liquid. Once the second crystal is gone, the liquid composition moves down the boundary line between the first and third crystals (the only two crystals present). A tie line from any such point on this boundary line may be drawn through the bulk composition to the Alkemade line connecting the first and third crystals (rather than the second and third crystals as when the first crystal is consumed). This intersection of the Alkemade line determines the amounts of first and third crystals in the mixed crystals. The fourth and final crystal is formed when the next area of primary crystallization is encountered. If the first, third and fourth crystals are the final three crystals, then the entire system solidifies at that temperature.

8. **Significance of the Boundary Tangent Intersection**
At any point along the boundary line shared by the first and second crystals, draw a tangent to the boundary line. If this tangent intersects the Alkemade line between the two crystals, both crystals are precipitating from solution at this temperature. If the tangent does not intersect the Alkemade line, the first crystal has become soluble and is going back into solution. (A mass balance using the lever rule would reflect this behavior.)

9. F**inal Three Crystal Amounts**
The amount of each crystal in the final solid can be found by constructing a regular grid over the Alkemade triangle bounding the batch composition.

10. **Gibbs Phase Rule Applies**
The Phase Rule is helpful in describing when the temperature is fixed such as during tributary reactions. For example, at the tributary point there are three solid phases and one liquid phase. According to the phase rule, C = 3(the ternary components)-0(no reactions)-1(P_T fixed) = 2; P = 4; F = C – P – 2 = 0. Therefore, the temperature is fixed until one of the phases is consumed. When the first crystal is a final crystal, the liquid is consumed; otherwise, the first crystal disappears. The extinction of one phase allows further cooling.

Acknowledgment

A similar *Rules for Interpreting Ternary Phase Diagrams* was presented to the author by Dr. Paul Herold, Professor, Department of Metallurgical Engineering, Colorado School of Mines (circa 1966). That text has been extensively edited over the years to arrive at this document, but some of the text used here may be remain direct quotes from Dr. Herold's valued original resource.

References

Ehlers, Ernest G., The Interpretation of Geologic Phase Diagrams, W. H. Freeman, San Francisco, 1972.

