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Rules for Interpretation of Ternary Phase Diagrams

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Fundamentals

A. *Lines.* There are three kinds of lines on a ternary phase diagram.
   i. <u>Alkemade</u> lines are straight and connect stoichiometric compositions. These lines form a series of Alkemade triangles that comprise the entire ternary triangle. (In the case of solid solution, dotted Alkemade lines connect to solid solution compositions.)
   ii. <u>Isothermal</u> are light, curved lines labelled with temperature values.
   iii. <u>Boundary</u> lines are heavy, curved lines that are positioned in the valleys of the isothermal surface
   iv. Composition grid lines may be drawn showing the composition grid.

B. *Alkemade triangles.* The ternary diagram is one big Alkemade triangle divided into smaller Alkemade triangles. Every point on the ternary is bounded by an Alkemade triangle.

C. *Area of primary crystallization.* Each compound has a high point surrounded by an area surrounded by valleys demarcated by Boundary Lines.

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

2. **<u>First Crystal</u>**
   Determine the area of primary crystallization in which the batch composition occurs. This is the <u>FIRST CRYSTAL</u> 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. **<u>Second Crystal (and amount of the 1st Xtal and liquid at T's before the 2nd Xtal appears)</u>**
   Draw a line from the composition of the first crystal through the batch composition until it hits a boundary line. This intersection shows the <u>SECOND CRYSTAL</u> 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. **<u>Third Crystal (and amount of the 1st & 2nd Xtals and liquid at T's before the 3rd Xtal appears)</u>**
   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 reacts 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 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.

Teaching notes

Begin teaching this subject using a ternary system with no significant solid solution such as the CaO-SiO_2-Al_2O_3 system. Nice diagrams of this system may be found in Phase Diagrams for Ceramists (Levin, E. M., Robbins, C. R., McMurdie, H. F. and American Ceramic Society (1964) Phase diagrams for ceramists. Columbus, Ohio: American Ceramic Society.) This is a multiple volume set in which figures are numbered sequentially. Use Figure # 630 or updated reditions.

Suggest each student colors all boundary lines blue, isothermal lines red, and Alkemade lines green.

Three sets of very light composition grid lines from 90% to 10% may be drawn at every 10% of the way across the diagram parallel to the 0% line opposite each vertex composition.

When locating compositions on the ternary, discourage students from using the confusing % labels drawn along the outer edges. Rather, encourage them to start by identifying the three vertices where each vertex compound is 100%. Then pick one compound, say “CaO”, and ask, “Where it is 0%?”. (Answer: At the SiO_2 and the Al_2O_3 vertices and all points on a straight line between those two points.) Therefore, 10% CaO will be a line parallel to this 0% line but 10% of the way towards CaO, etc.

Us the following abbreviations for the three oxides: C = CaO, S = SiO_2, A = Al_2O_3

Unless stoichiometric compounds fall on the expected stoichiometric ratios, the diagram is in wt. % (i.e. – compound CS should fall at 50% C to be atomic percent).

The word *characterize* means to determine all phases present and their amounts (percent) and the composition of each phase present. This is useful to have firmly established for use on exams, which should be conducted using a complete ternary phase diagram with a marked bulk composition so as to avoid partial credit grading difficulties arising from the student’s incorrect bulk composition placement.

The following informal expressions and visual cues are employed by the author when teaching students how to navigate a ternary diagram to determine the crystallization order and to be able to characterize the system at any temperature.

1. Locate and circle the bulk composition (given) on the diagram.
2. Pretend you are flying over the ternary surface where everything is 100% liquid. Then parachute down to the bulk composition. The elevation of the isothermal surface where you land is the temperature at which the first crystal appears. Determine what mountain you are on (i.e. - what area of primary crystallization). The crystal whose area of primary crystallization you are on is the first crystal to appear. For this explanation, call it crystal A.
3. Identify the location of the first crystal, A, and turn your back to it and walk directly away from the peak where it is located. As you walk downhill (down in temperature), your location is the composition of the liquid. A line from your location to peak A, through the bulk composition, defines two line segments from which the lever rule may be applied to determine amount of A [$y/(x + y)$] and amount of liquid [$x/(x + y)$]. Remember that the use of the lever law is like a child’s mobile hanging from the bulk composition point as shown in Figure 1.
4. Continue to walk away from A until you encounter the valley (boundary line). One might think of it as a river. The area of primary crystallization on the far side of the boundary line is the second crystal. The name of the mountain encountered (across the boundary line) is the second crystal,

called B, first appears at the temperature where the boundary line was encountered as shown on Figure 2.

5. Walk down the valley or river (boundary line). Your position in the boundary line represents the liquid composition. At any temperature (elevation), a tie line may be drawn through the bulk composition to the Alkemade line connecting the first and second crystals. This establishes two tie lines from which the amount of liquid A [x/(x + y)] and mixed crystals [y/(x + y)] be determined. The distribution of A and B within the mixed crystals is determined from the lever composed of line segments u and w. [A = w/(u +w) and B = u/(u +w)]. Note that u increases from 0 as one moves along the boundary line after the appearance of the second crystal.
6. Continue to walk down the river (boundary) until a second (tributary) boundary line is encountered. The mountain encountered, across that boundary line, is the third crystal, C, to form at the temperature where the second boundary line was encountered as shown in Figure 3.
7. If the three crystals are the final three, the system solidifies at the tributary point encountered. If not, continue to walk downstream (along the boundary) until the next tributary is encountered and a fourth crystal, D. As described in the Interpretation Rules, the mixed crystal, the end of the tie line moves from the A-B Alkemade line to the A-C or B-C Alkemade line (depending on whether the first or second crystal goes back into solution) at the tributary temperature. Once this peritectic reaction is completed at the tributary temperature, continue to move *down* in temperature on the second encountered boundary line the fourth crystal.

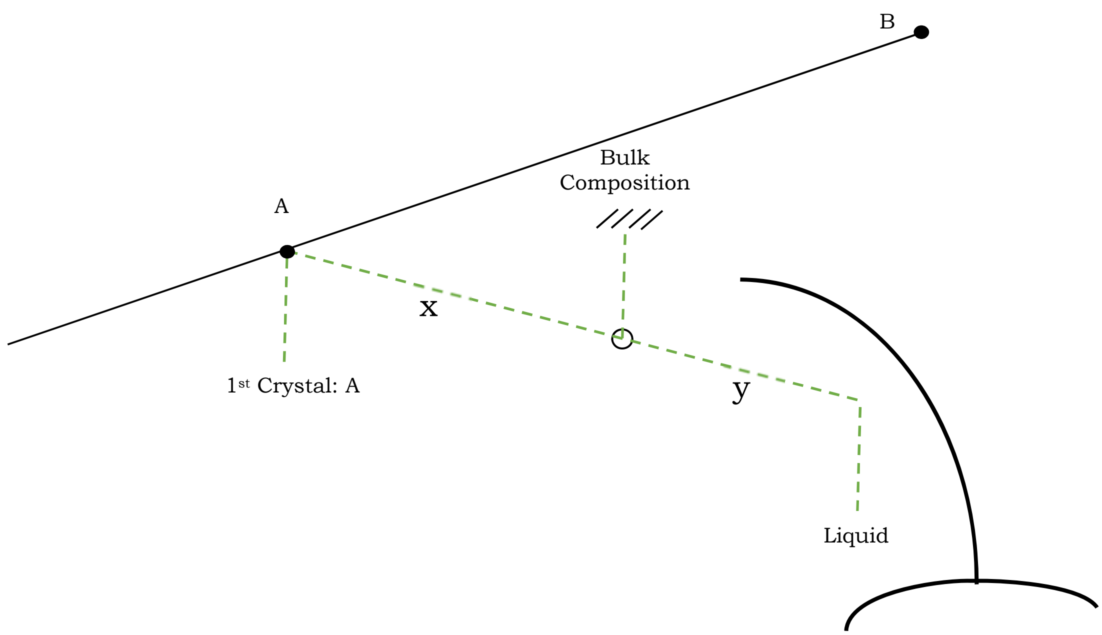

Figure 1. Lever Law for first crystal and liquid

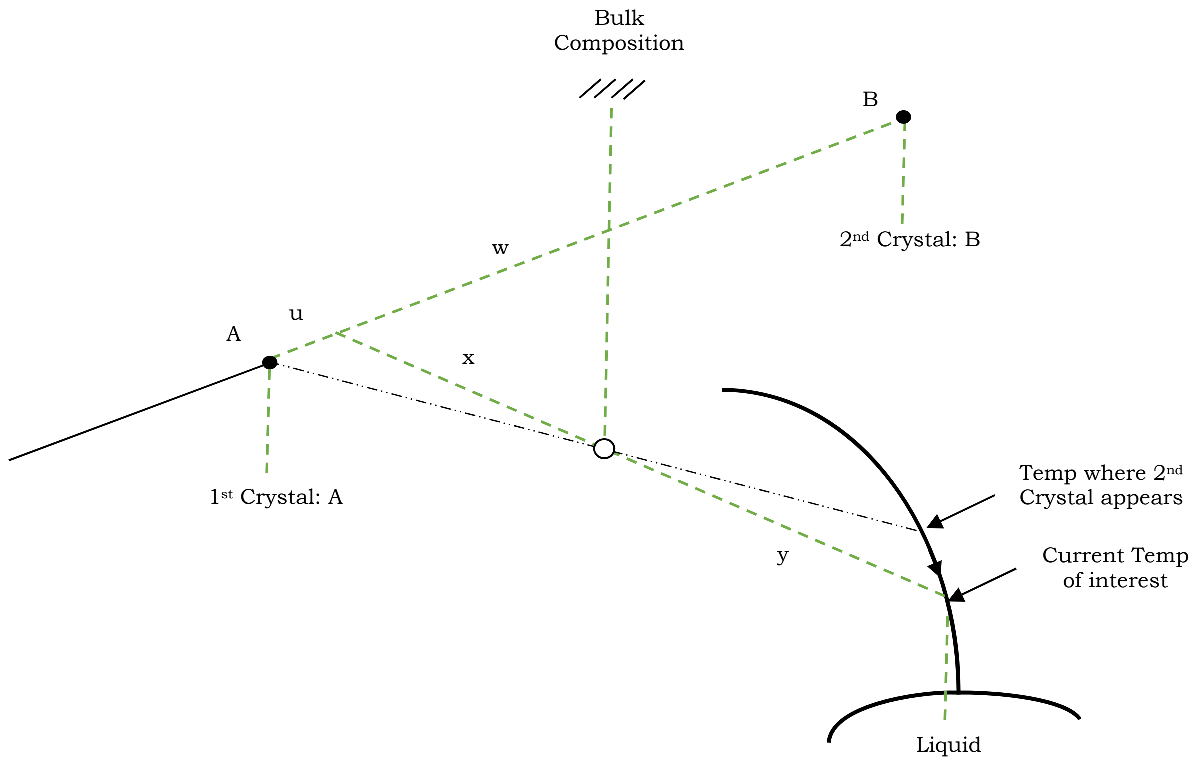

Figure 2. Lever Law for mixed crystals (first and second) and liquid

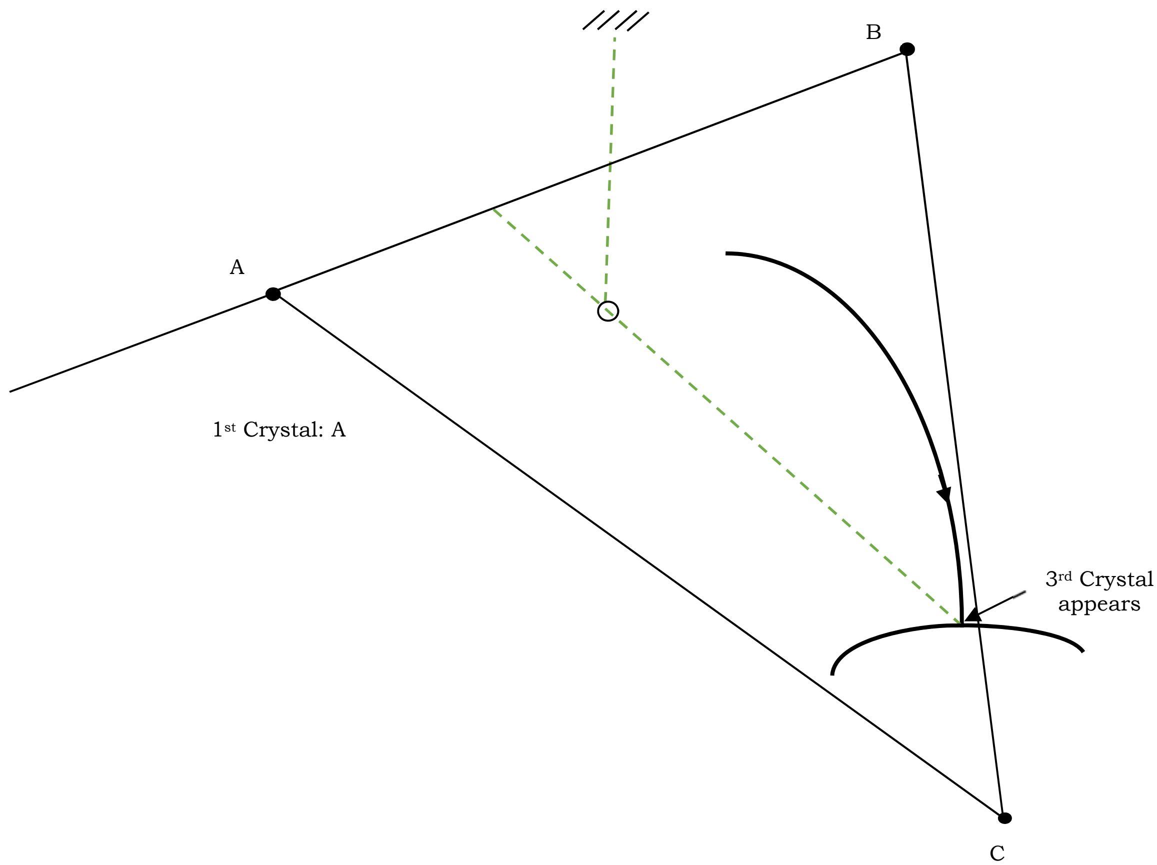

Figure 3. Third crystal

Updated and modified by s. Howard: July 8, 2018: