Tutorial Modules for the Study of Phase Equilibrium Diagrams

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Abstract

Understanding and interpreting phase equilibrium diagrams is an essential skill for materials engineers. Extensive collections of diagrams are available, making this a resource that can be used to design process cycles, determine reaction paths, and predict thermodynamic compatibility. Hence, courses in phase equilibria are ubiquitous in materials programs. The most difficult skills to master in these classes involve the visualization of the response of complex systems to changes in temperature and composition.

At the University of Missouri-Rolla (UMR), students have developed a series of computer-based tutorial modules that cover topics from the undergraduate course in phase equilibria. Students designed the modules to help future classes understand difficult concepts. Each student selected a subject, outlined the approach, prepared a detailed plan, and then constructed the presentation. Students were also required to present their modules to the class. Individual modules cover one, narrow topic that is important when studying one, two, or three component phase diagrams. Topics range from the use of the lever rule to the construction of vertical sections in ternary systems. With student permission, the modules were posted on the class web page.[1]

This past year, students prepared twenty-two tutorial modules. Because the tutorials are graphics-intensive, they provide the greatest help when they cover topics that require visualization skills. After posting on-line, the modules are a source of help that supplements material covered in lectures and in the text. The modules are available for students in future classes and for anyone else that needs to learn to interpret or analyze phase diagrams.

I. Introduction

Phase diagrams provide fundamental information on the equilibrium relations among different elements and compounds.[2] All materials scientists and engineers, particularly those that deal with high temperature materials, must understand how temperature, pressure, and concentration affect the kind and amount of different phases present at equilibrium.[3,4] The discipline of ceramic engineering is uniquely focussed on the development and utilization of materials that are used at high temperatures or that undergo high temperature processing.[5]

Most often, ceramists deal with "condensed" phases, i.e., liquids and solids. Pressure is generally assumed to be one atmosphere, although many diagrams exist for higher and lower pressures. The assumption of constant pressure simplifies diagrams by one dimension, shown by the example of a two component system. To fully describe the stable phases for two different chemical constituents present in different ratios and at various temperatures and pressures, a three dimensional diagram is required. If pressure is held constant, a two-dimensional composition-temperature diagram can fully describe the system, Figure 1. Similarly, a three component composition-temperature diagram must be three-dimensional, Figure 2. Understanding and interpreting these diagrams is aided by strong visualization skills.

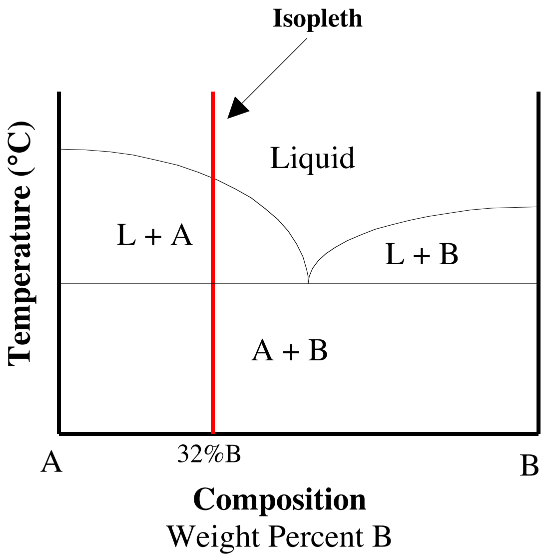

Figure 1. A hypothetical binary phase diagram with an isopleth at 32 weight percent B.

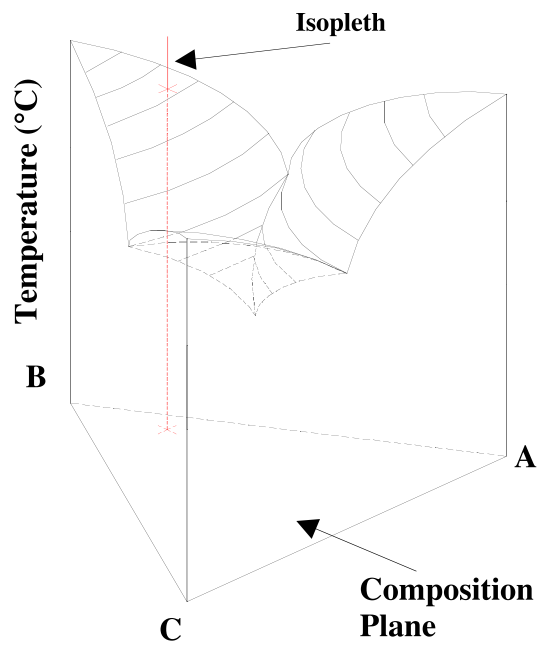

Figure 2. A hypothetical ternary phase diagram with an isopleth at 20% A, 70%B, 10%C.

When studying phase diagrams, the most common exercise is an isoplethal analysis. An *isopleth*[*] is a line of constant composition, shown in Figures 1 and 2. Isopleths are parallel to the temperature axis in a temperature-composition diagram. In a two-dimensional projection of a three component system, isopleths are points, like the dot labeled T_1 in Figure 3. For analysis, the amount and composition of each phase are calculated at several temperatures. With practice, a few specific temperatures can be selected that completely describe the changes that occur as a particular composition is heated or cooled. Typically, the important temperatures are an infinitesimal amount above and below the temperature of each phase change. Examples of phase changes during cooling include formation of the first solid at the *liquidus*, *polymorphic* phase transitions, *peritectic* reactions, association or dissociation reactions, and *eutectic* reactions. The phenomenon of resorption must also be described if it occurs, but it is difficult to identify because it happens over a range of temperatures. Resorption proceeds during cooling when the crystallization rate of a compound that formed at higher temperatures becomes negative, causing the first compound to dissolve back into the melt as a second solid forms.

[*] Terms in italics are defined at the end of the paper.

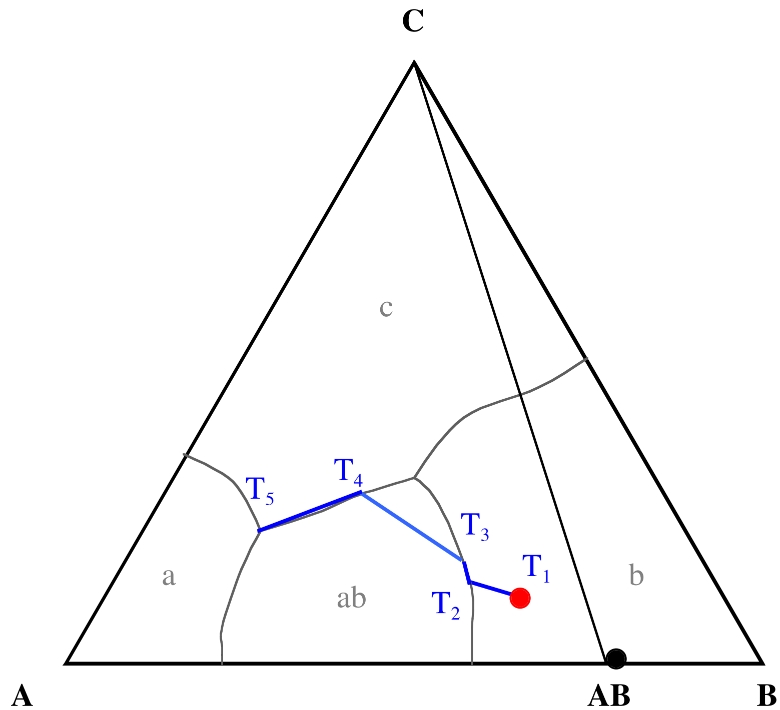

Figure 3. A two dimensional projection of a three component phase diagram with an incongruently melting binary compound, AB. The composition of the isopleth is 29%A, 60%B, and 11%C (dot at T_1) and its crystallization path proceeds from T_1 to T_2 to T_3 to T_4 and ends at T_5.

The purpose of this paper is to describe and promote a series of tutorial modules that were developed by the Phase Equilibria class in the Ceramic Engineering department at UMR. This paper outlines the assignment and summarizes two of the tutorials prepared by students. Holly Bentley prepared a module on the construction of phase analysis diagrams. Roger Smith designed a presentation to help students visualize the different phase volumes within a three-dimensional ternary phase diagram. The tutorials are designed to function as an on-line source of help for future classes. Some tutorials consist of worked examples. This type provides a step-by-step explanation of the solution to a typical homework or test problem, like the phase analysis diagram tutorial. Other tutorials provide an alternate explanation of a difficult concept to supplement information from the text or from lectures, like the ternary visualization module.

II. Construction of Tutorials

The tutorial assignment required each student to produce a stand-alone (i.e., no further explanation needed) PowerPoint presentation that stepped through the solution of an example problem or that provided a detailed explanation of a difficult concept. Each presentation had to provide the necessary background, solve a problem or explain a concept, and then summarize the lesson. The project counted for 20% of the final grade in the course. For comparison, the two exams in the course were worth 15% each. In line with its value, it was expected that each student would spend several hours outside class completing the assignment. From the instructor's perspective, the objectives of the assignment were: 1) for each student to explore some part of phase equilibria in depth and independently; 2) to help the students develop better presentation skills; and 3) to compile a series of tutorials in a permanent form for use in future semesters. As juniors, it was assumed that the students had a working knowledge of Microsoft PowerPoint from other classes, since it is the campus standard for presentations. The initial assignment stressed that tutorials would be graded on format, content, clarity, and completeness, not the use of flashy graphics or advanced features in the software.

The project was broken down into several sub-assignments, forcing the students to make incremental progress rather than putting it off until the night before the project was due. A list of potential tutorial topics and a timetable for completing the assignment were distributed on the first day of class along with the course syllabus. The list of suggested topics included the disclaimer that, with instructor approval, any relevant topic could be selected, not just one from the list. At the end of the 6^{th} week of class, a homework assignment was made that required each student to select a topic. If multiple students selected one topic, or if a topic was not suitable, instructor-student meetings were arranged to resolve the problems. Two weeks after topic selection, students were asked to hand in a one page outline of their approach to the topic. Again, instructor feedback was given if the approach was too ambitious or not detailed enough. Two weeks before the final version was due, students were asked (not required) to hand in a preview of their final presentation. The assignment stated that the final version had to run in a specified version of PowerPoint on the instructor's computer (a Mac, while most students have Windows-based PCs) by the due date. For those who handed in a preview to test compatibility (most did), suggestions and comments were made using the criteria that would be used to grade the final product. After this round of revision, students submitted the final version of the tutorial by email. Tutorials were graded on format (organization, length, spelling, grammar), content (useful examples), clarity (logical idea development), and completeness (any unanswered questions). After the due date, each student gave a 5 minute presentation in class to discuss their topic, explain the approach that was taken, and show a few of their best slides.

III. Phase Analysis Diagram Tutorial

A complete isoplethal analysis gives an experienced ceramist a clear picture of how the phase assemblage in a system evolves as temperature changes. However, the analysis can be misleading because the changes occur continuously over a range of temperatures, not just at the discrete points where the calculations are performed. Construction of a phase analysis diagram is one method for visualizing the phase evolution when a particular composition is heated or cooled. Discrete data are converted to a continuous function that more completely describes the behavior of the system. Phase analysis diagrams are helpful for identifying reactions and other phase changes that occur during heating or cooing. Holly constructed a phase analysis diagram for an isoplethal analysis in a ternary system where resorption occurred. Her composition was the point labeled T_1 in Figure 3. Her first step in constructing the phase analysis diagram was to identify the crystallization path (i.e., the composition of the liquid as a function of temperature as the melt cooled). Then, she performed an isoplethal analysis, which is summarized in Table I.

Table I. Isoplethal analysis in the hypothetical ternary system A-B-C (Figure 3) at a composition of 29% A, 60%B, and 11%C.

Temperature	Proportions	% Phases	Composition of Phases	Analysis A	B	C
$T_1(+)$	-	100% liquid	29% A, 60% B, 11% C	29	60	11
$T_1(-)$	50 mm ε* mm	100% Liquid ε% Solid	29% A, 60% B, 11% C 100% B	29	60 0	11
$T_2(+)$	50 mm 11 mm	82% Liquid 18% Solid	35%A, 52% B, 13%C 100% B	29	42 18	11
$T_2(-)$	50 mm 11 mm	82% Liquid 18% Solid	35%A, 52% B, 13%C 100% B, ε% AB (AB = 22%A, 78%B)	29	42 18	11
$T_3(+)$	24 mm 14 mm	63% Liquid 37% Solid	34%A, 49% B, 17%C ε% B, 100% AB (AB = 22%A, 78%B)	21 8	31 29	11
$T_3(-)$	24 mm 14 mm	63% Liquid 37% Solid	34%A, 49% B, 17%C 100% AB (AB = 22%A, 78%B)	21 8	31 29	11
$T_4(+)$	24 mm 38 mm	39% Liquid 61% Solid	42%A, 30% B, 28%C 100% AB (AB = 22%A, 78%B)	16 13	12 48	11
$T_4(-)$	24 mm 38 mm	39% Liquid 61% Solid	42%A, 30% B, 28%C ε% C, 100% AB (AB = 22%A, 78%B)	16 13	12 48	11 0
$T_5(+)$	14 mm 54 mm	21% Liquid 79% Solid	61%A, 16% B, 23%C 8.7% C, 91.3% AB (AB = 22%A, 78%B)	16 13	12 48	11 0
$T_5(-)$	-	100% Solid	12%A, 11%C, 77%AB (AB = 22%A, 78%B)	12 17	60	11

A melt containing 29% of component A, 60% of component B, and 11% of component C was cooled. This composition lies in the primary crystallization field of B and the compatibility triangle of A-AB-C. The cooling path is shown in Figure 3. The melt/liquid composition is the same as the system composition above the liquidus temperature (T_1), and progresses along the line from T_1 to T_5 as the system is cooled. Above T_1, a homogeneous liquid phase exists. As the

* ε signifies that an infinitesimal amount of a particular phase is present.

melt cools, B begins to crystallize just below T_1, or at T_1(-) in the vernacular of the class. Compound B continues to precipitate until the temperature is just above T_2, or T_2(+). At T_2(-), the compound AB begins to precipitate, while B is resorbed. By T_3(+), resorption of B is complete, leaving AB as the only crystalline phase in equilibrium with the liquid phase. Further cooling of the system produces additional AB until T_4(+). At T_4(-), crystals of C begin to form along with AB until the system cools to T_5(+). At T_5, the system undergoes a eutectic reaction to form the final solid, a mixture of AB, C, and A. Below T_5, only solid phases are present.

Once the isoplethal analysis is complete, a phase analysis diagram can be constructed. Keeping the composition-temperature format of a binary phase diagram, the amount (0 to 100 percent) of each phase is plotted along the x-axis for each temperature of the isoplethal analysis, Figure 4. First, the total amount of solid present at each temperature (the "% Phases" column in Table I) is plotted as the black points in Figure 4. Note that multiple black dots can be plotted at temperatures where the percentage of solid changes abruptly due to a reaction like the eutectic reaction at T_5. At each temperature, the solid can be a single phase or multiple solid phases. For multiple solids, the total percentage of solid must be broken down into the individual crystalline compounds present. This is accomplished by multiplying the percent solid (the "% Phases" column in Table I) by the percent of each phase that makes up the solid (from the "Composition of Phases" column in Table I) at each temperature. For example, at T_5(+) the system is made up of 80% solid and 20% liquid, so a black dot is placed at 80% at T_5. The solid is composed of 9% C and 91% AB. The solid is then subdivided into the amount of AB (91% of the solid is AB times 80% solid in the system = 73% of the total system is solid AB) and C. Now, a gray dot representing the amount of AB is plotted at T_5. In this case, the remainder of the solid phase is C (7% of the total system), but for a more complex system the calculation is repeated for all of the solids at all of the temperatures of interest in the system. Below the solidus temperature, T_5, the system contains 100% solid and the proportions do not change. The finished phase analysis diagram provides a graphic representation of the isoplethal analysis that highlights changes in percentages of different phases during cooling. The diagram in Figure 4 shows resorption between T_2 and T_3 and a eutectic reaction at T_5.

IV. 3-D Visualization of Ternary Diagrams Tutorial

A skill that eludes most engineers is visualization of three dimensional objects from a written description or from a sketch in a textbook. Three component phase diagrams are an example where visualization of the parts of the diagram can help increase the understanding of how the composition and relative amounts of solid and liquid phases evolve as a melt is cooled. By following specific rules for interpretation, an isoplethal analysis can be performed using a two dimensional projection of three dimensional composition-temperature information in a ternary system, as was demonstrated above. While this provides a sufficient level of understanding for students who might only have to interpret diagrams as part of a class, those who will use ternary diagrams for problem solving or in research often must have a deeper understanding of the stable phase assemblage as a function of temperature and composition. Historically, poorly reproduced two-dimensional projections or expensive models were the visual aids used to discuss ternary diagrams.

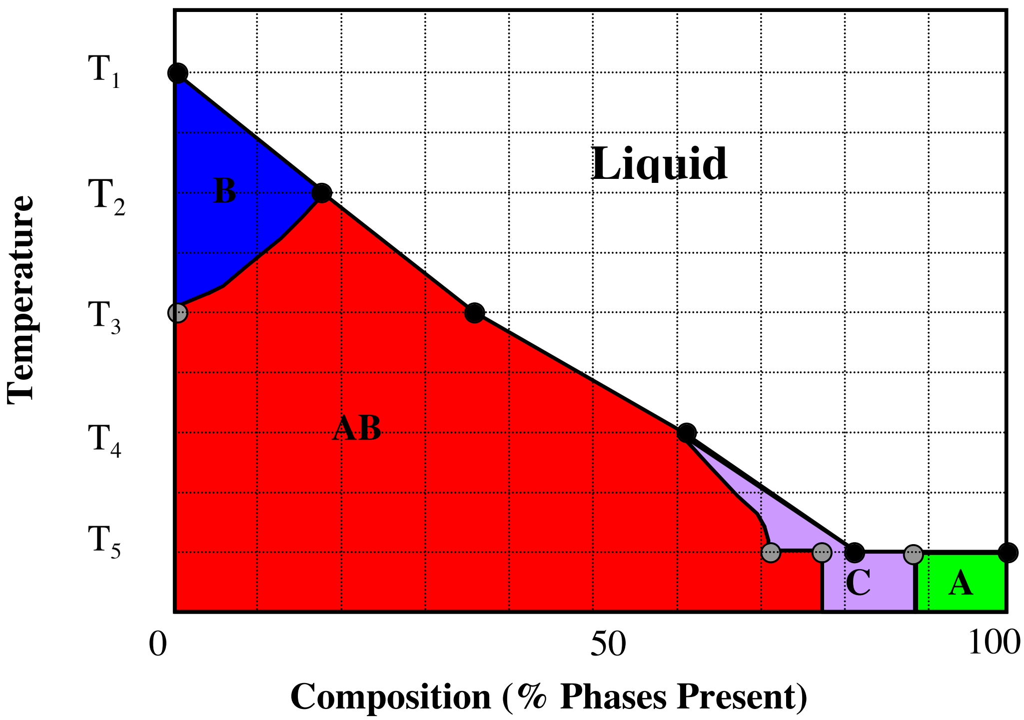

Figure 4. Phase analysis diagram for the A-B-C hypothetical system. The black dots represent the total amount of solid at each temperature and the gray dots divide the solid region into multiple phases.

In a ternary system, any mixture of the three components is a point within an equilateral triangle. The isopleth in Figure 3 is an example. It represents a composition of 29% of component A, 60% of B, and 11% of C. At any temperature, experiments or thermodynamic calculations define the solid and liquid phases that are stable at each composition. By examining multiple points at one temperature, regions within a triangle where the same phases are stable can be defined. Using a series of sections from different temperatures, a three-dimensional ternary phase diagram, like the one shown in Figure 2, can be assembled. Commonly, information from the ternary system is projected down onto a plane, shown in Figure 3, to facilitate isoplethal analysis. Features that are necessary for an accurate analysis include boundary lines between primary crystallization fields (gray lines/lettering), points representing the composition of compounds (black dot for AB), and isothermal contours that describe the shape of the liquidus surface (omitted in this projection). A three-dimensional diagram can be reconstructed from a two-dimensional projection, but this is not necessary for analysis. Due to the complexity of the three-dimensional diagram, most ternary isoplethal analyses are performed by rote, not by understanding the shapes of the regions of like crystalline make-up within the diagram.

Computer-aided design software offers a new, more interactive method for presenting three-dimensional information. The tutorial designed by Roger Smith uses images generated in AutoCad™ to show the complex shapes of the various volumes within the composition-temperature space in a ternary phase diagram. In his tutorial, Roger showed the whole diagram

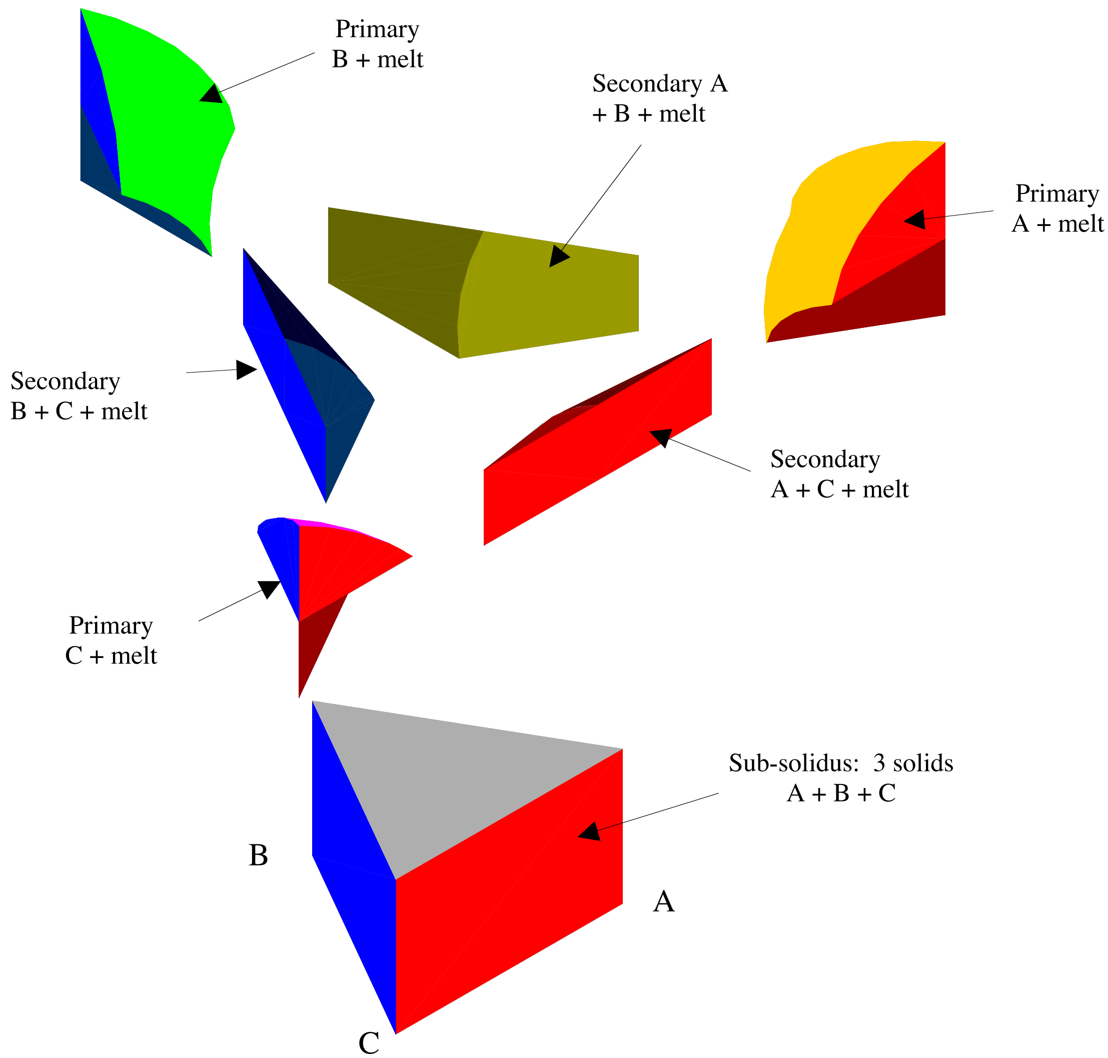

Figure 5. An exploded three-dimensional ternary phase diagram that shows the primary crystallization volumes (one solid in equilibrium with melt), secondary crystallization volumes (two solids in equilibrium with melt), and the sub-solidus region (three solids in equilibrium).

and then proceeded to explain how it could be dissected into regions of temperature-composition space that represented the primary crystallization volumes, the secondary crystallization volumes, and the sub-solidus region (Figure 5). He went on to show how these volumes were intersected by an isopleth similar to that shown in Figure 2. While a complete isoplethal analysis was not performed, the images set the stage for discussion of the changes that occur during cooling and the final assemblage of phases in a ternary system. This tutorial used a simple ternary eutectic system, but it provided a basis for understanding more complex diagrams.

V. Summary

Students prepared a series of computer tutorials as an assignment in an undergraduate course in phase equilibria. These computer-based modules serve as an on-line reference to help others understand difficult concepts in the class. The modules are graphics-intensive and help students visualize the evolution of the stable phase assemblage for a system as the overall composition and/or temperature changes. Examples of tutorials on the construction of phase analysis diagrams and the phase volumes within a three-dimensional, three component composition-temperature phase diagram were presented. The modules are particularly effective at helping students understand concepts that require strong visualization skills.

VI. Definitions

Isopleth:	A line of constant composition
Liquidus:	The temperature above which no solid is present (i.e., 100% liquid above)
Solidus:	The temperature below which no liquid is present (i.e., 100% solid below)
Polymorph:	Species with the same chemical composition, but different crystal structures
Peritectic:	A reaction of one solid with a melt to form a second solid
Eutectic:	The point where a melt solidifies directly to a solid of the same composition

VII. Acknowledgements

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VIII. References

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