

COMPOSITION

Phase Diagrams 1

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A major principle of materials science is that “PROPERTIES are related to STRUCTURE.” A material’s structure is only partly described by reporting the composition. You must also report the phases, composition of the phases, and amounts of phases. To understand how to do this, we will introduce PHASE DIAGRAMS, practice with their use, and then take advantage of them to discuss the topic of METALS in a few more modules. Phase diagrams are extremely useful in summarizing a large quantity of information about a materials structure.

Please be aware that the topic of PHASE DIAGRAMS represents the some of the most difficult content encountered for students in a dental materials science course -- because this topic was never previewed to you as an undergraduate coming from a biological science background.

INTRODUCTION

Systems, components, and phases.

Reasons for constructing phase diagrams (phase maps):

1. Summarize phases that exist at different temperatures.
2. Track changes that occur as the temperature changes.

Important definitions:

1. **SYSTEM:** The quantity of matter being considered.
2. **COMPONENTS:** Ingredients making up the system. (A mixture of NaCl and H₂O has 2 components and not 4.)
3. **PHASE:** Homogeneous, discrete portion of matter that cannot be separated by physical means alone.

Systems:

1. Water and Ethanol
2. Water and Salt
3. Water and Excess Salt
4. Water and Oil
5. Gold and Copper
6. Copper and Tin

Components:

- 2 (water, ethanol)
- 2 (water, salt)
- 2 (water, salt)
- 2 (water, oil)
- 2 (gold, copper)
- 2 (copper, tin)

Phases:

- 1 (solution of water and ethanol)
- 1 (solution of water and salt)
- 2 (solution of water and salt, excess salt)
- 2 (oil in water, water in oil)
- 1 (solution of gold and copper)
- 2 (copper in tin, tin in copper)



Most of the important events for dental materials occur in solid and liquid states and can be determined and tracked with phase diagrams. These are maps that indicate which phases exist for any component or combination of components at any temperature. We really should be tracking pressure as well, but for all practical purposes, we are usually operating at 1 atmosphere of pressure and so we ignore that variable. We often call these phase maps. You use phase diagrams to track what changes in phases are occurring as the temperature changes.

[CLICK] Now let's look at 3 key definitions. **[CLICK]** A SYSTEM is a quantity of matter under consideration. It could simply be the material in a beaker or it could be all material that represents a chemical combination of 60% of gold with 40% of silver. **[CLICK]** COMPONENTS are the ingredients making up the system. In the case of Au and Ag, there are two elements being intimately mixed and so we have 2 components. However, components can be compounds as well. If NaCl and H₂O are being mixed then they are the 2 components. There are not 4 components (Na, Cl, H, O). **[CLICK]** Finally, a PHASE is a homogeneous, discrete portion of matter that cannot be separated by physical means alone. A phase may be one or more than one component.

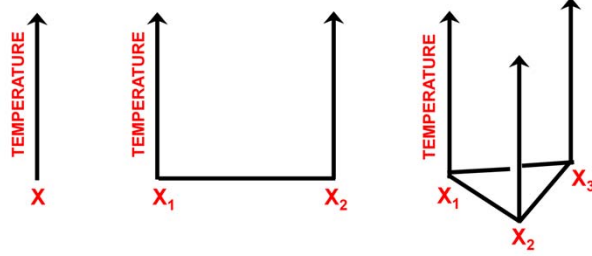
[CLICK] Let's try to use these terms, and they make more sense. **[CLICK]** Consider system 1 of water and ethanol. It has 2 components (water and ethanol) and forms a single phase that is solution of water and ethanol. **[CLICK]** In system 2 of water and salt, there are 2 components (water and salt) that dissolve together to form a single solution of salt water. **[CLICK]** System 3 involves water with excess salt, so that it will not all dissolve into the water. There are 2 components. It forms 2 phases. One is a liquid solution of salt water and the other is excess solid salt. **[CLICK]** System 4 is a combination of water and oil. There are 2 components, water and oil. They are only sparsely soluble in each. Nothing is totally insoluble in something else. Therefore, you end up with 2 phases, an oil-rich one with small amounts of dissolved water, and a water-rich one with small amounts of dissolved oil. **[CLICK]** System 5 is a combination of gold and copper formed by melting the two elements together. There are two components that form a single complete single solution. **[CLICK]** System 6 is similar to system 5. There are 2 components, copper and tin. However, they are not completely soluble in each and form 2 phases, a copper-rich one with some tin, and a tin-rich one with some copper. This is analogous to the oil and water system except there is more affinity to dissolve into one and other.

CLASSIFICATION OF SYSTEMS

By numbers of components and/or by phases present.

Classification of phase diagrams by “number of components”

1. **Unary** = 1 component = T vs X (constant P)
2. **Binary** = 2 components = T vs X_1, X_2 (constant P)
3. **Ternary** = 3 components = T vs X_1, X_2, X_3 (constant P)
4. **Quaternary** = 4 components = T vs X_1, X_2, X_3, X_4 (constant P)



Classification of 2-component diagrams based on the “phases present”

1. **Complete solid solution**
2. **Eutectic, Peritectic, Syntectic, Monotectic (and others)**

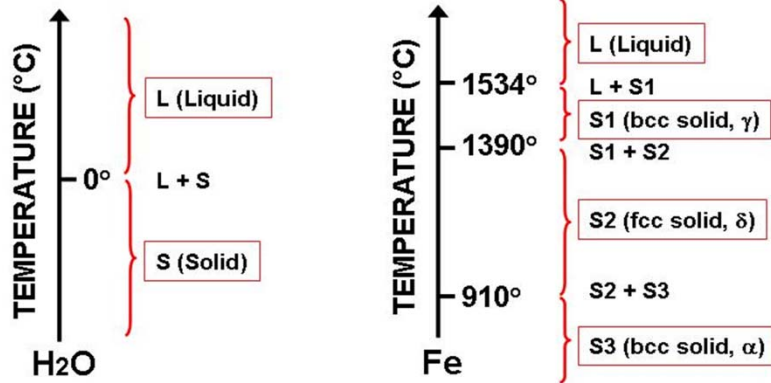


Systems are normally described first in terms of the actual components involved, such as oil-and-water or gold-and-copper. However, you can also classify systems in terms of the number of components involved. One components systems (e.g., H_2O ; Au) will be map that is simply a **[CLICK]** vertical temperature line with the starting and ending temperatures indicated for the phases or states of matter. We will explore these shortly. **[CLICK]** A binary phase diagram is two-dimensional and includes the temperature lines for all the combinations of X_1 being mixed with X_2 . **[CLICK]** A ternary diagram is actually three-dimensional and includes the temperature lines for all the combinations of X_1 , X_2 and X_3 being mixed together. There is no convenient way to represent quaternary or more complex phase diagrams.

[CLICK] For two-dimensional phase diagrams, one can also name the diagrams based on the phases present. We will discuss these details in the next module. In a moment we will discuss examples of a complete solid solution diagram and a eutectic diagram.

PHASE DIAGRAM EXAMPLES

Unary phase diagram.



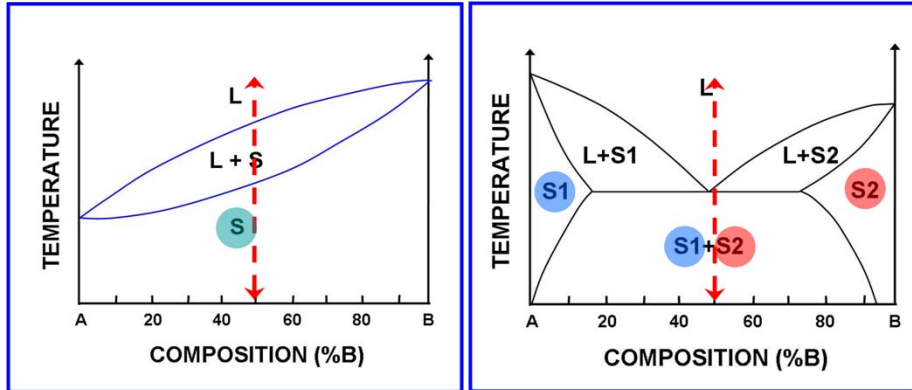
Two unary phase diagram examples are presented. Let's examine each carefully.

For the unary diagram for H₂O, in the range around the freezing point, there is only one phase (liquid) above the freezing point, one phase (solid) below the freezing point, and two phases at the freezing point (liquid plus solid) while freezing is taking place.

For iron (Fe), the situation is similar surrounding its freezing temperature of 1534C. However the first solid phase which forms is stable only down to 1390C where it wants to transform into a new phase. You can think of this as it is changing its crystal structure to allow the atoms to pack more efficiently together while it is shrinking as the temperature drops. Different crystal structures or solid state phases can be labeled S₁, S₂, etc. or given a Greek letter codes. The code generally is associated with the type of crystal structure involved but not always. As cooling continues, Fe changes its phase (or crystal structure) one more time at 910C creating S₃ which is bcc and abbreviated as alpha. Iron has 3 different possible equilibrium phases (but one at a time) in the solid state depending on the temperature. These are called ALLOTROPES.

PHASE DIAGRAM EXAMPLES

Binary phase diagram.



Binary = Complete Solid Solution

Binary = Eutectic



Let's look at two examples of possible binary phase diagrams. Both diagrams have a y-axis of temperature and an x-axis of composition (which includes all the possible combinations of mixtures of A and B). A and B represent hypothetical components. We could have called the components C1 and C2, or X1 and X2, or any other letters. The x-axis is read as %B but the composition is reported as %A-%B. **[CLICK]** A composition of 50A-50B is located in the center of the diagrams and indicated as a vertical line for all temperatures. The information on the diagram describes what phases will be present along that particular composition line at different temperatures. It looks like a unary diagram for an alloy.

[CLICK] On the left is a COMPLETE SOLID SOLUTION binary diagram. It is called that because for all combinations of A mixed with B in the solid state, **[CLICK]** the two components are miscible and form a solid solution. The solid state has single phase. All the crystals are the same phase. Combinations of A and B melt over a range rather than at a distinct point like the pure A and B components.

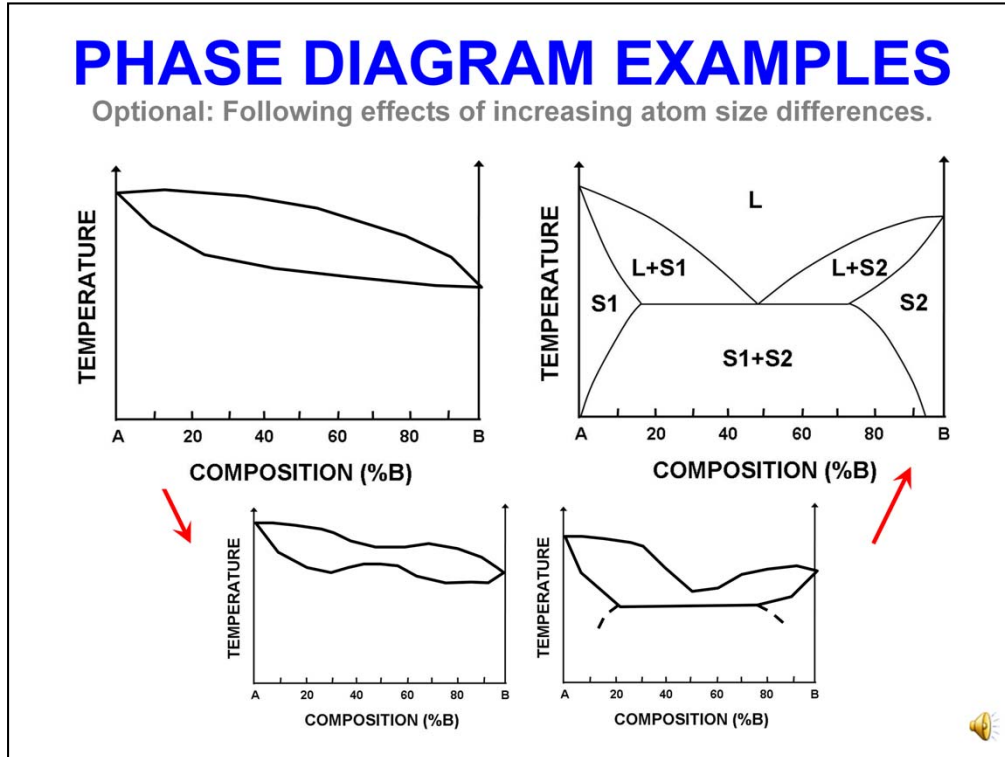
[CLICK] For the diagram on the right, there is only partial solubility of A and B. **[CLICK]** There are two phases. There are two types of crystals. One represents a solution of B in A that is rich in A. The other represents a solution of A in B that is rich in B. The compositions of the two crystal types and the amounts of the crystals will vary depending on the temperature. Shortly we will explain how you can use the diagram to actually calculate the compositions of phases and amounts of phases.

[CLICK] There are no solid phases that actually have the overall composition of 50A-50B.

Note that if the composition were at the far edges of the range (e.g., **[CLICK]** 98A-2B or **[CLICK]** 5A-95B) that there are regions where there is so little A in B or B in A that the combination produces a solid solution that is only one phase.

PHASE DIAGRAM EXAMPLES

Optional: Following effects of increasing atom size differences.



The following discussion is optional. It simply helps to explain the origins of the shapes of the diagrams.

The complete solid solution and partial solid solution diagrams depend on the ability of A and B to dissolve into each other. As atom sizes get bigger or their chemistry becomes more different, there is less and less chance to get them to mix well. Let's focus on their sizes. HUME-ROTHERRY RULES in its simplest translation states that if the size varies by more than 14-15% for metal atoms or ions, then the system will become two phases.

Let's follow this by starting with the complete solid solution (far left) with the assumption that atom sizes differ by 5%. **[CLICK]** Now let's make them differ by 10% and examine the effect on the L+S phase boundaries. **[CLICK]** Next increase the size differences to 13% and notice the distortion. As this difference gets to perhaps 20% we end up with the binary diagram on the right. There are just a limited number of binary boundary patterns that are possible and we will introduce those in a future module.

DETERMINING PHASES

How do you know how many phases are present?

Identification of the phases present at equilibrium:

1. **INSPECTION:** The solid is usually not clear and the phases are very small (usually crystals) so the solid is viewed under a microscope and often etched to provide relief between the phases.
2. **PHASE DIAGRAM:** If the phase diagram is present, then you can simply look up the number of phases by locating the correct composition and temperature intersection on the phase map.
3. **GIBBS PHASE RULE:** The total variables are related and involve the thermodynamic variables (temperature, pressure from $PV=nRT$), number of phases (P , which we want to know), the number of components (C), and degrees of freedom (F , variations in composition/temperature that produce the same phases).

$$F = C - P + 2$$



F = number of degrees of freedom

C = number of components

P = number of phases

2 = number of thermodynamic variables



Now let's ask the question, "how do you know how many phases are present for any composition at any temperature?" **[CLICK]**

Most phases are microscopic. **[CLICK]** For a solid, you can magnify and image and inspect it to distinguish different phases by their appearance and boundaries. Generally, the surface is polished and then etched to help in this process.

[CLICK] If you know the components and temperature – and have the phase diagram – you can simply look up the number of phases that should exist at equilibrium. Many phase diagrams are published. Almost all simple unary, binary, and ternary ones are known for METALS -- and many are known for CERAMICS.

[CLICK] As the number of components increases, it becomes much more difficult to visually produce a map of the components or else there is no information published. In these cases, one can use the GIBBS PHASE RULE. **[CLICK]** This is an equation relating all the variables of the system. **[CLICK]** If you know the components, degrees of freedom, and thermodynamic variables (T , P), then you can calculate the number of phases (P). **[CLICK]** If the pressure is assumed to be constant, then the 2 becomes a 1 in the equation. You are NOT responsible for this equation but you should know that a RULE exists to allow you to do this.

QUICK REVIEW

Review of systems, components, phases, and phase diagrams.

- **What are the AXES on a phase diagram?**
COMPONENTS are the x-axis; TEMPERATURE is the y-axis.
- **What is the definition of a PHASE?**
HOMOGENEOUS, DISCRETE PORTION OF MATTER THAT CANNOT BE SEPARATED BY PHYSICAL MEANS ALONE.
- **What CLASSIFICATION is given to a 2-component phase diagram?**
BINARY
- **What is an example of a phase diagram type in which the 2 components are only PARTIALLY SOLUBLE in each other?**
EUTECTIC
- **How do you know the NUMBER of equilibrium phases that exist in any system at a specific temperature?**
(1) INSPECTION, (2) GIBBS PHASE RULE, or (3) PHASE DIAGRAM.



Here is a quick review of the concepts from this module.

[CLICK] (1) What are the AXES on a phase diagram?

[CLICK]

[CLICK] (2) What is the definition of a PHASE?

[CLICK]

[CLICK] (3) What CLASSIFICATION is given to a 2-component phase diagram?

[CLICK]

[CLICK] (4) What is an example of a phase diagram type in which the 2 components are only PARTIALLY SOLUBLE in each other?

[CLICK]

[CLICK] (5) How do you know the NUMBER of equilibrium phases that exist in any system at a specific temperature?

[CLICK]



THANK YOU



THANK YOU.