



Analytical Methods for Materials

Laboratory Module #4

Phase Diagram Determination

Suggested Reading

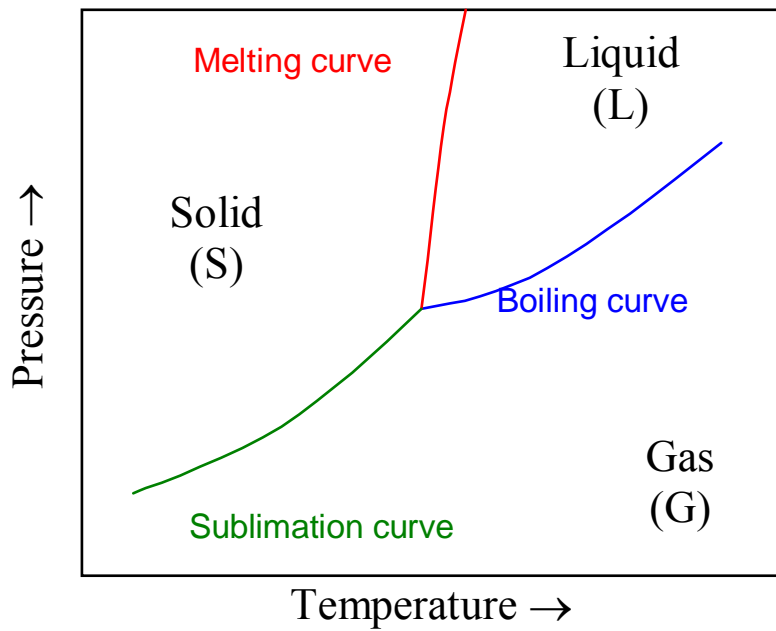
- C. Suryanarayana and M.G. Norton, *X-ray Diffraction A Practical Approach*, (Plenum Press, New York, 1998), pages 167-192.
- B.D. Cullity and S.R. Stock, *Elements of X-ray Diffraction, 3rd Edition*, (Prentice-Hall, Upper Saddle River, NJ, 2001), Ch. 11, pages 331-346.
- F.N. Rhines, *Phase Diagrams In Metallurgy*, (McGraw-Hill, New York, NY, 1956).

Objectives

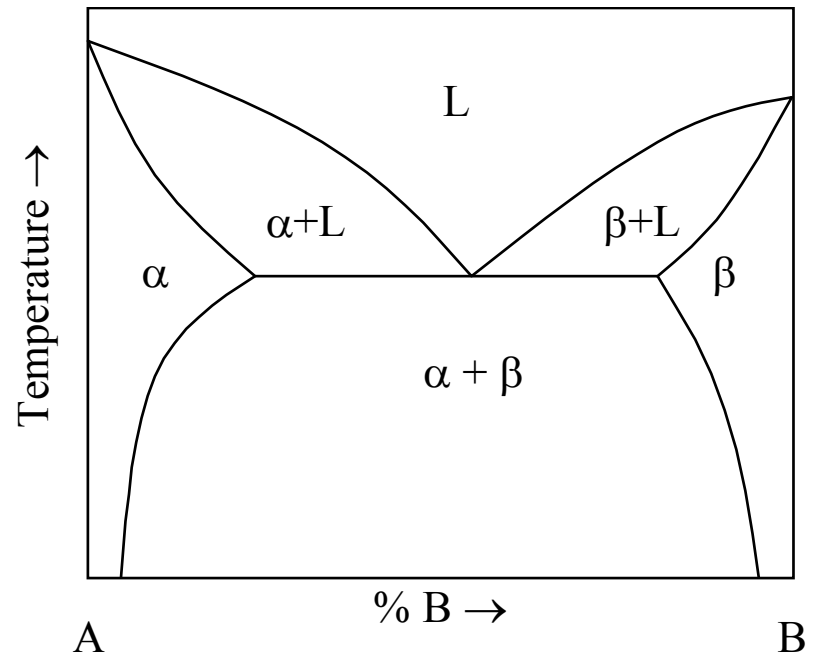
- Upon completion of this module you will be able to use the lattice parameter determination techniques to determine the solid solubility of one element/compound into another and to construct experimental phase diagrams.

Background

- Phase diagrams:
 - Used to establish what phases are present at different temperatures, pressures and compositions within an alloy system.
- Maps of phases that are present under specific conditions.
- Pressure – Temperature – Composition
 - P - T - x diagrams



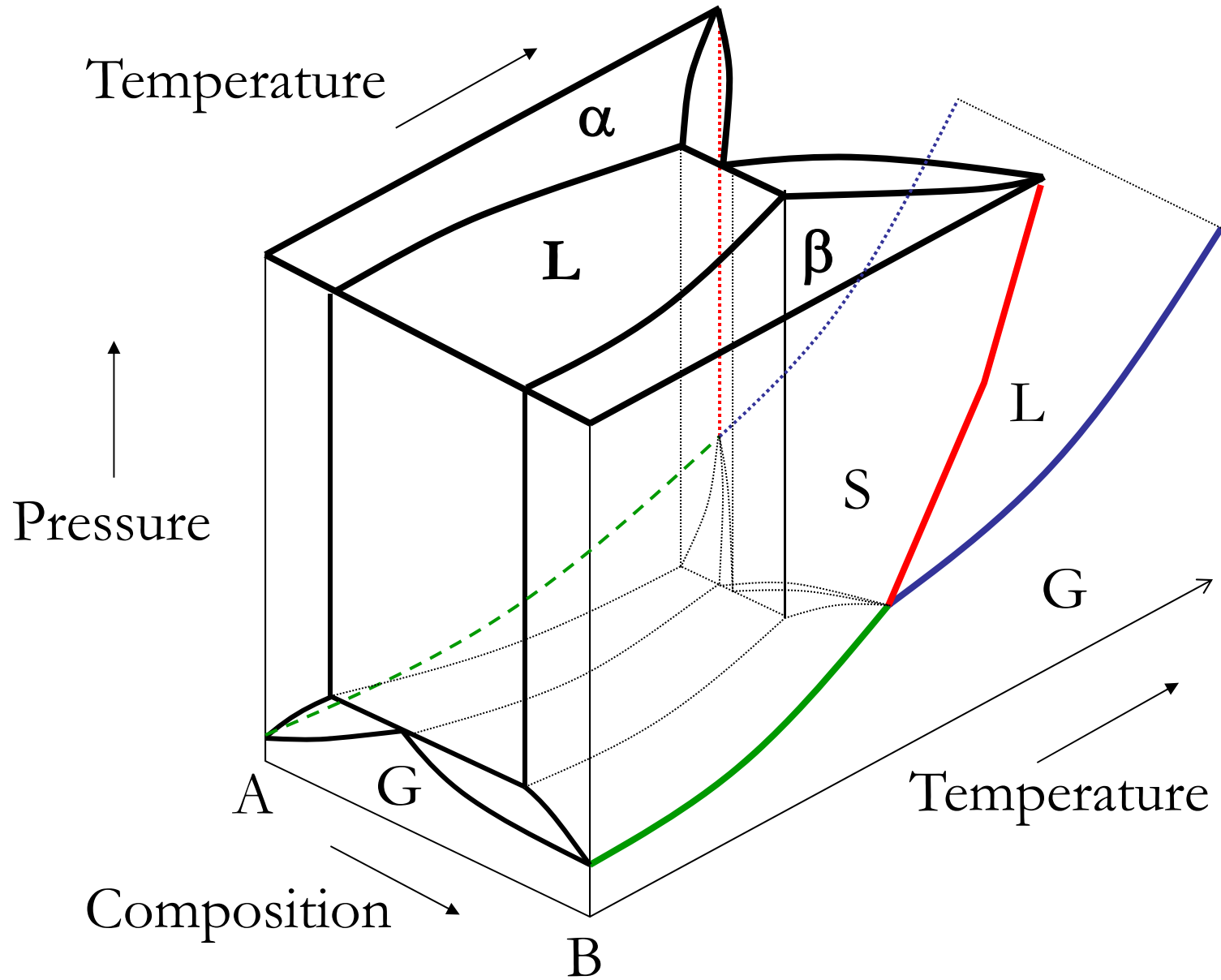
P-T diagrams



T-x diagrams

PHASE DIAGRAMS AS
YOUR'RE PROBABLY USED
TO SEEING THEM

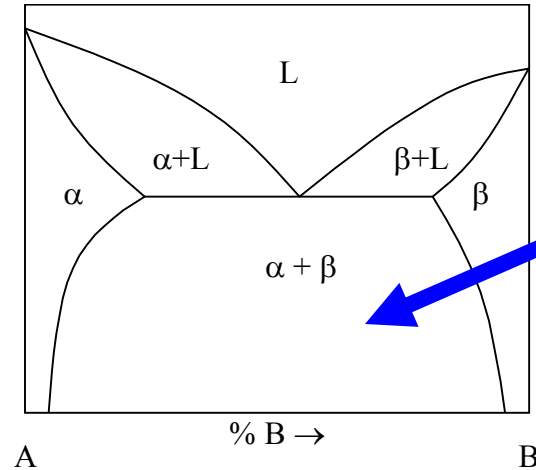
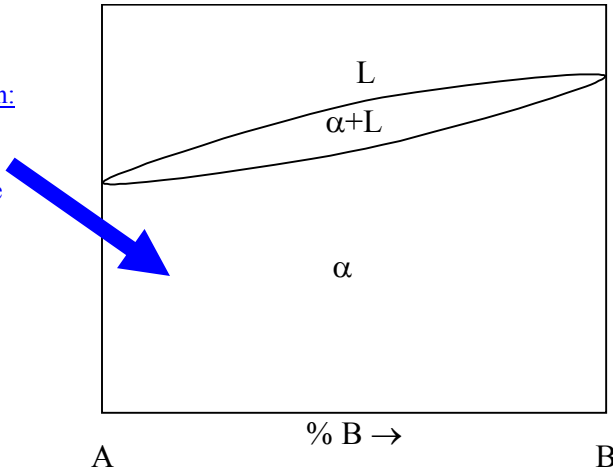
NOT AT ALL TO SCALE



Typical Binary Phase Diagrams

Continuous Solid Solution:

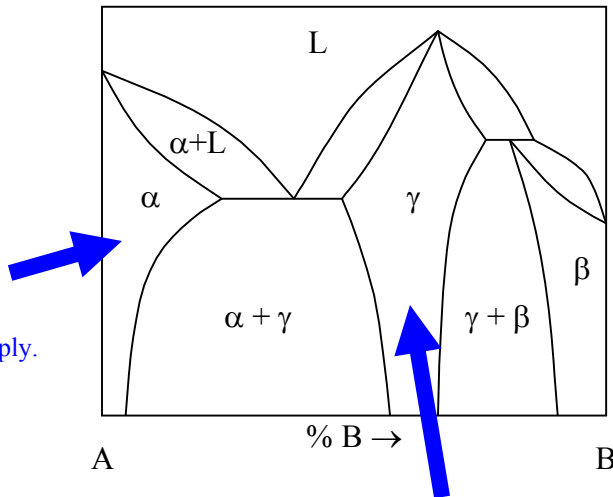
- Complete mixing of components.
- Components have same crystal structure.



Two Phase Equilibrium

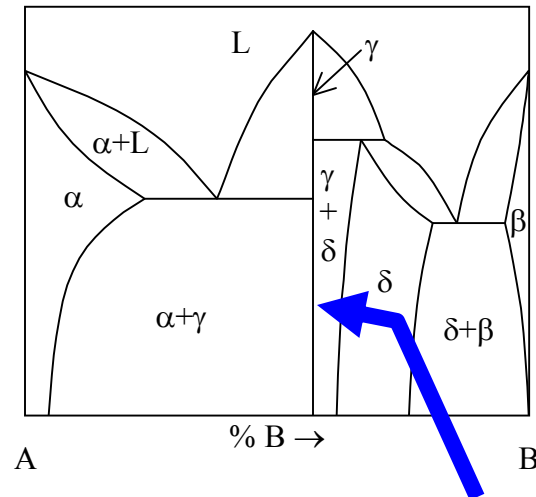
Primary (terminal) Solid Solution:

- Partial solubility of components.
- Hume Rothery rules apply.



Intermediate Solid Solution:

- Almost always has a different crystal structure than the phases on either side.



Intermediate Compound:

- Almost always has a different crystal structure than the phases on either side.

Types of Systems/Reactions

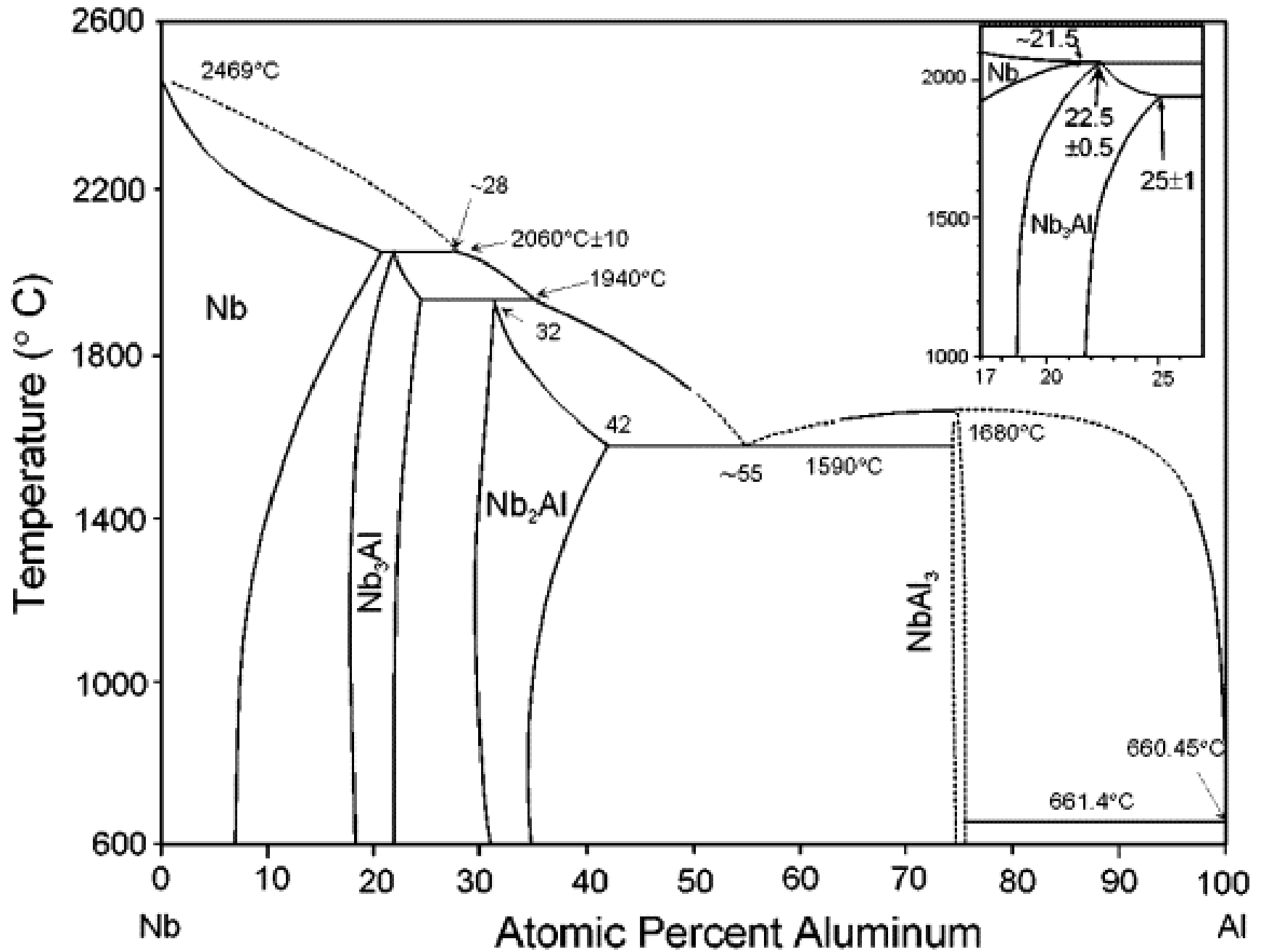
- **Isomorphous**
 - Constituents are mutually soluble in all proportions and in all states.
- **Eutectic**
 - $L \rightarrow S_1 + S_2$
- **Eutectoid**
 - $S_1 \rightarrow S_2 + S_3$
- **Peritectic**
 - $L + S_1 \rightarrow S_2$
- **Peritectoid**
 - $S_1 + S_2 \rightarrow S_3$
- **Monotectic**
 - $L_1 \rightarrow S + L_2$
- **Syntectic**
 - $L_1 + L_2 \rightarrow S$

Most phase diagrams are very complex. Most include many of these reactions.

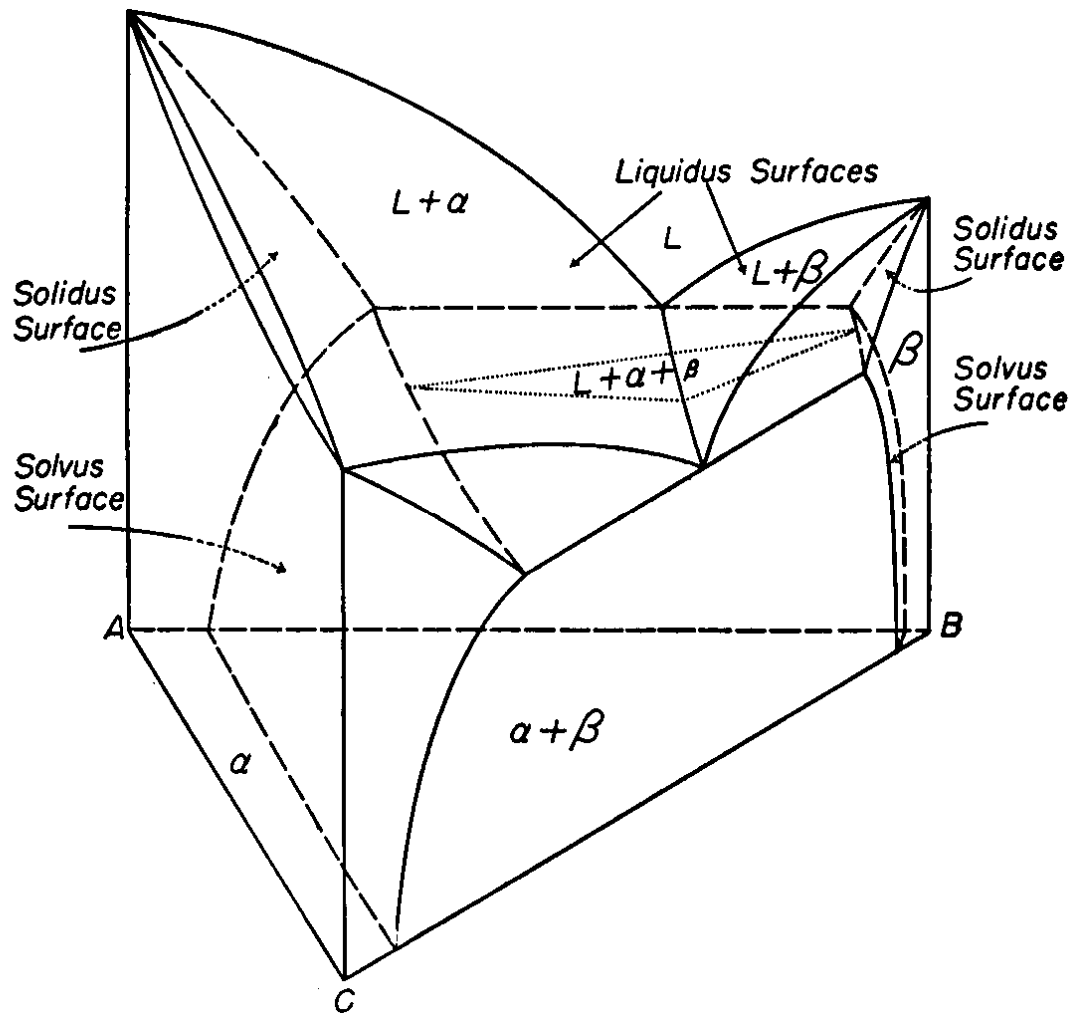
THIS IS WHY MATERIALS SCIENCE IS SO COMPLICATED AND FUN!

This is also why we get good jobs.





Typical Ternary Phase Diagram



The same rules apply for ternary and higher order systems.

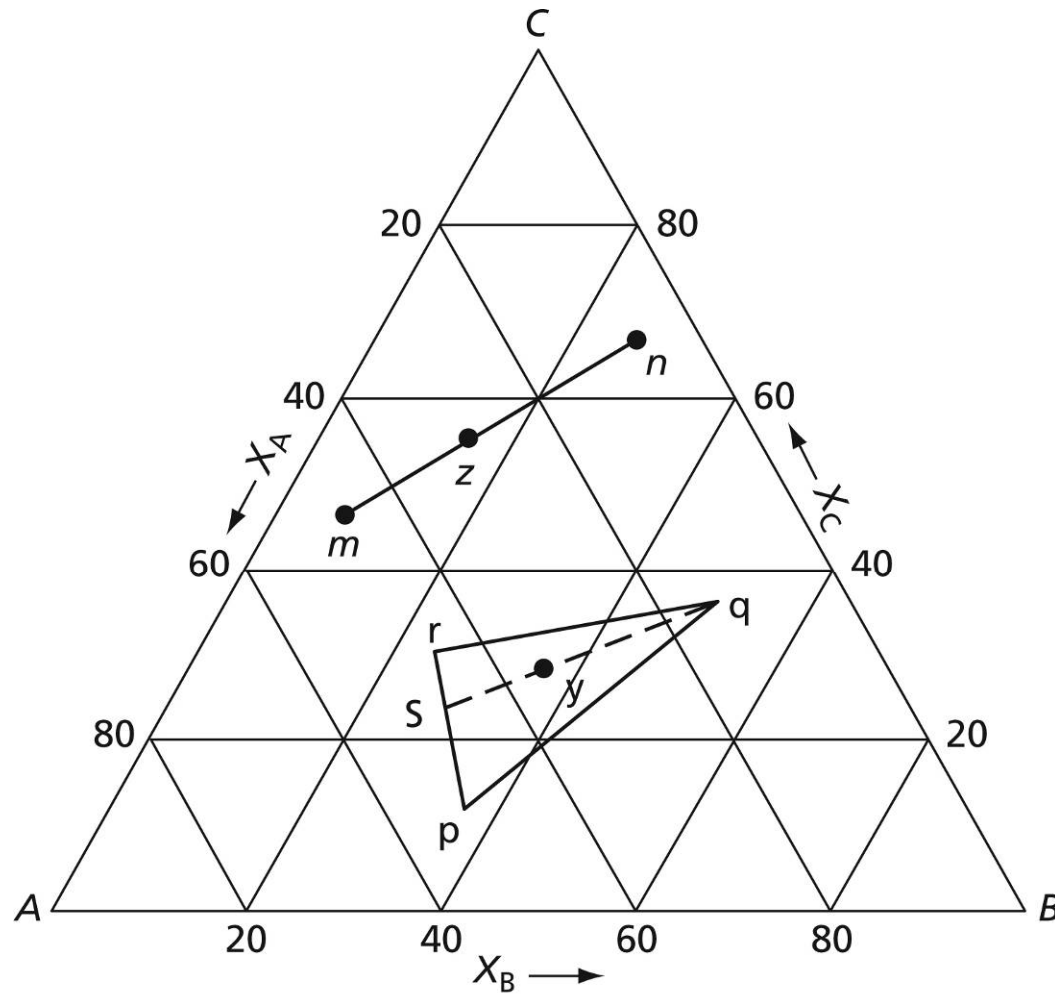


FIG. 11.25 Gibbs triangle for ternary alloy compositions



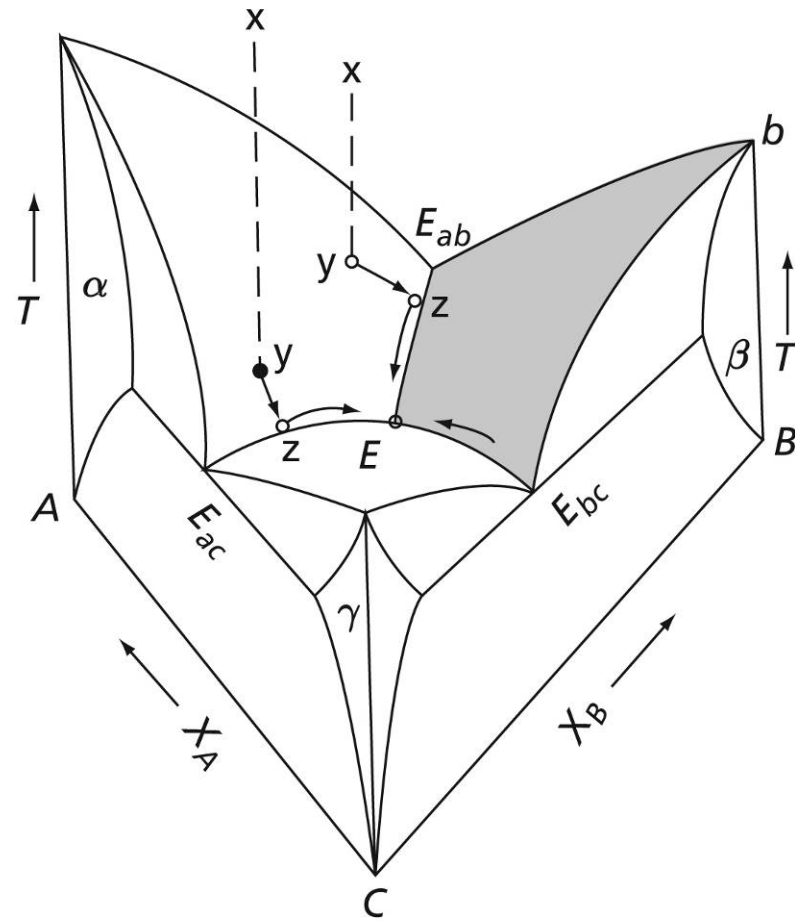


FIG. 11.26 A ternary phase diagram with three eutectic binaries between *A*, *B*, and *C*

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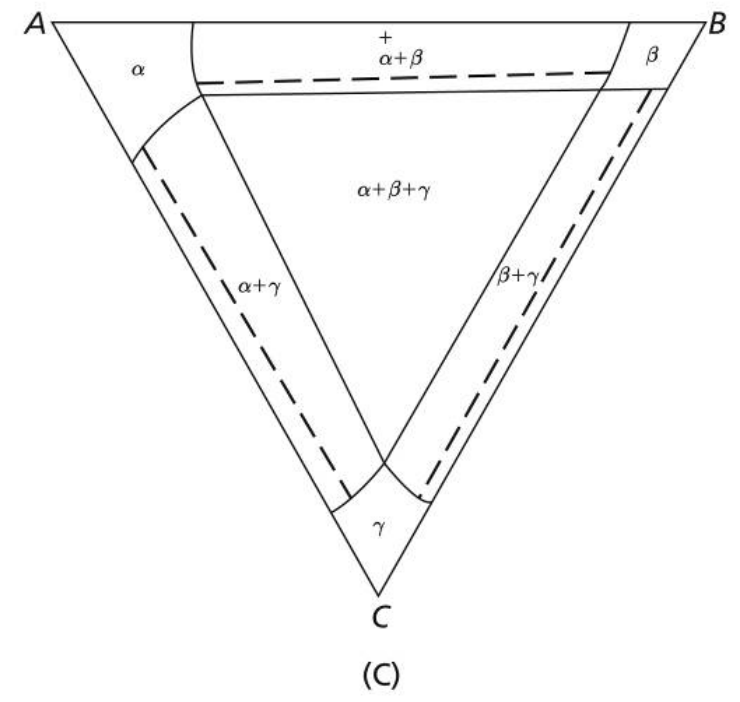
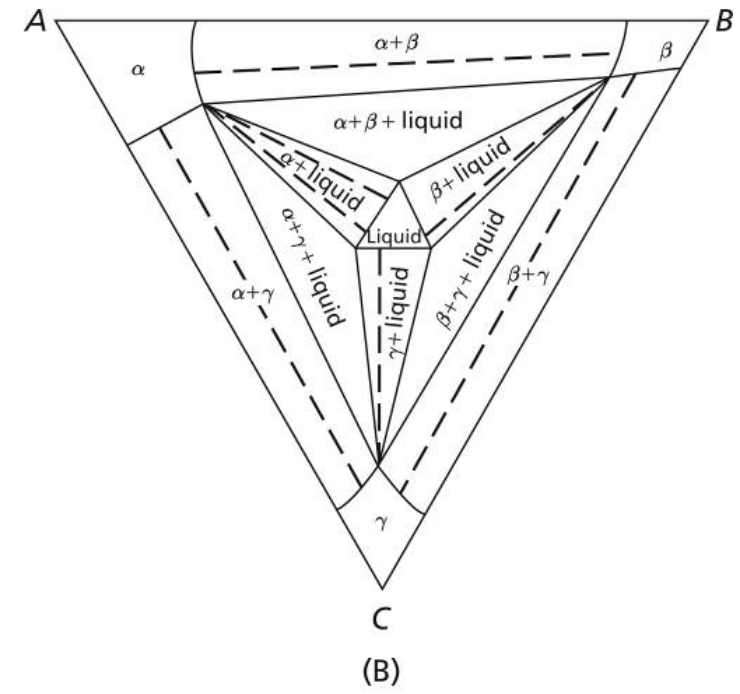
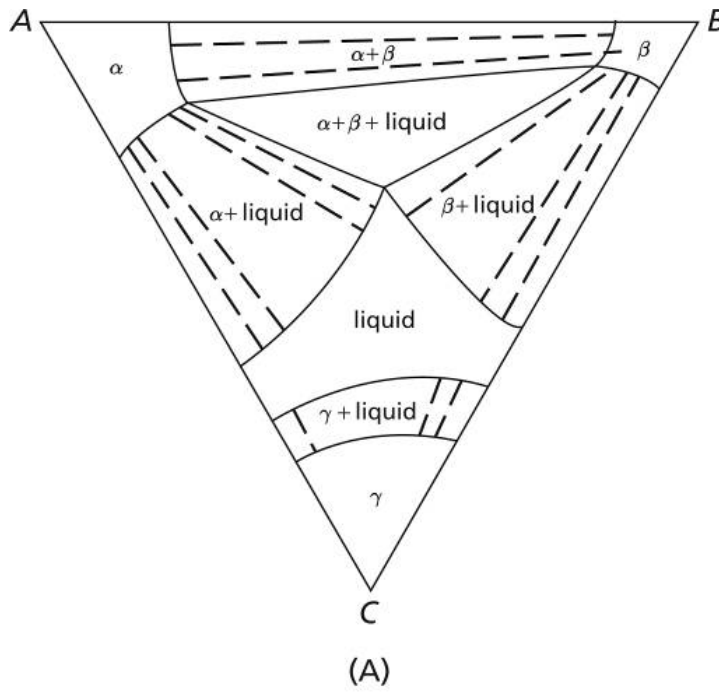


Fig. 11.27 Three isothermal sections for the ternary diagram shown in Fig. 11.26. A few of the tie lines are shown by dotted lines. (a) at a temperature below $A-B$ eutectic temperature but above eutectic temperatures of the ternary, $A-C$ and $B-C$; (b) at a temperature below the three binary eutectics but above the ternary eutectic, and (c) at a temperature below the ternary eutectic temperature. Adapted from Abbaschian, Reed-Hill, and Abbaschian, © 2009. Cengage Learning, Engineering. All Rights Reserved.

What is the composition at a given point?

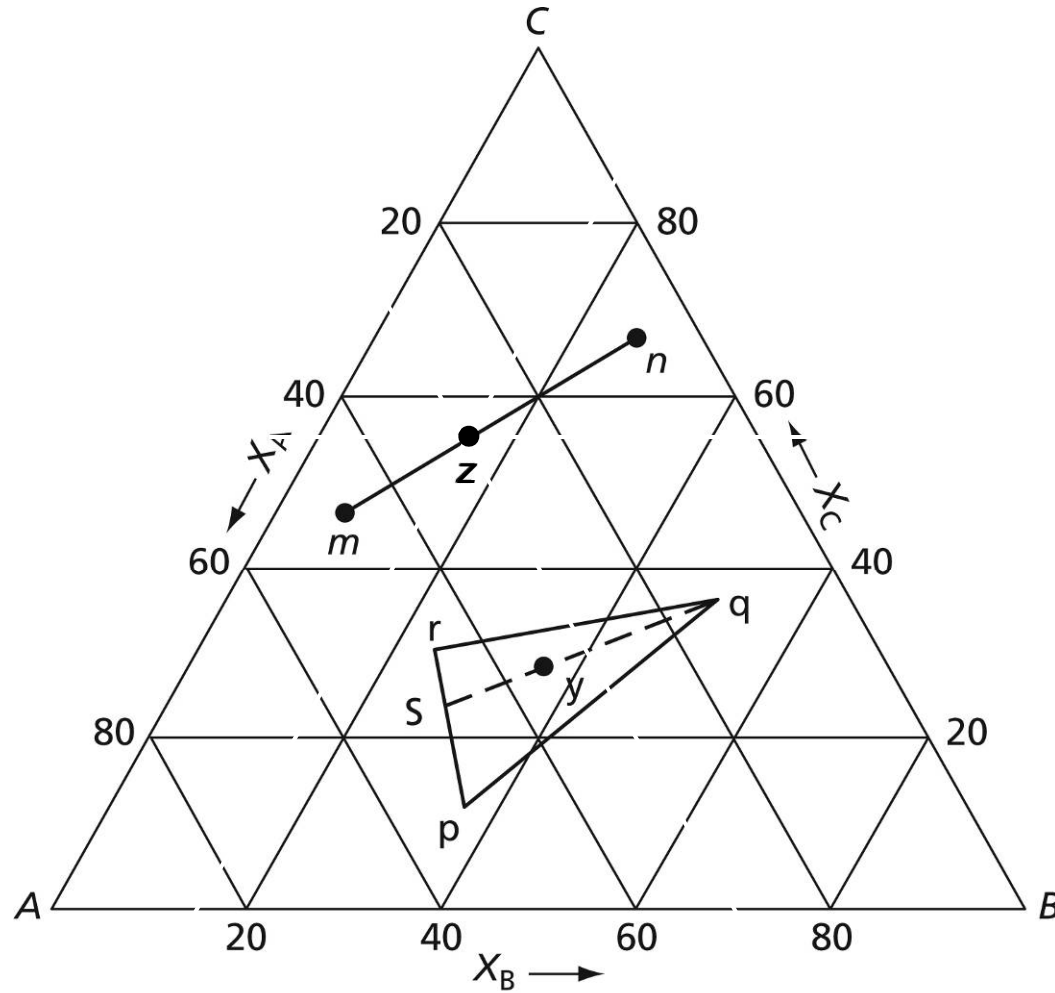
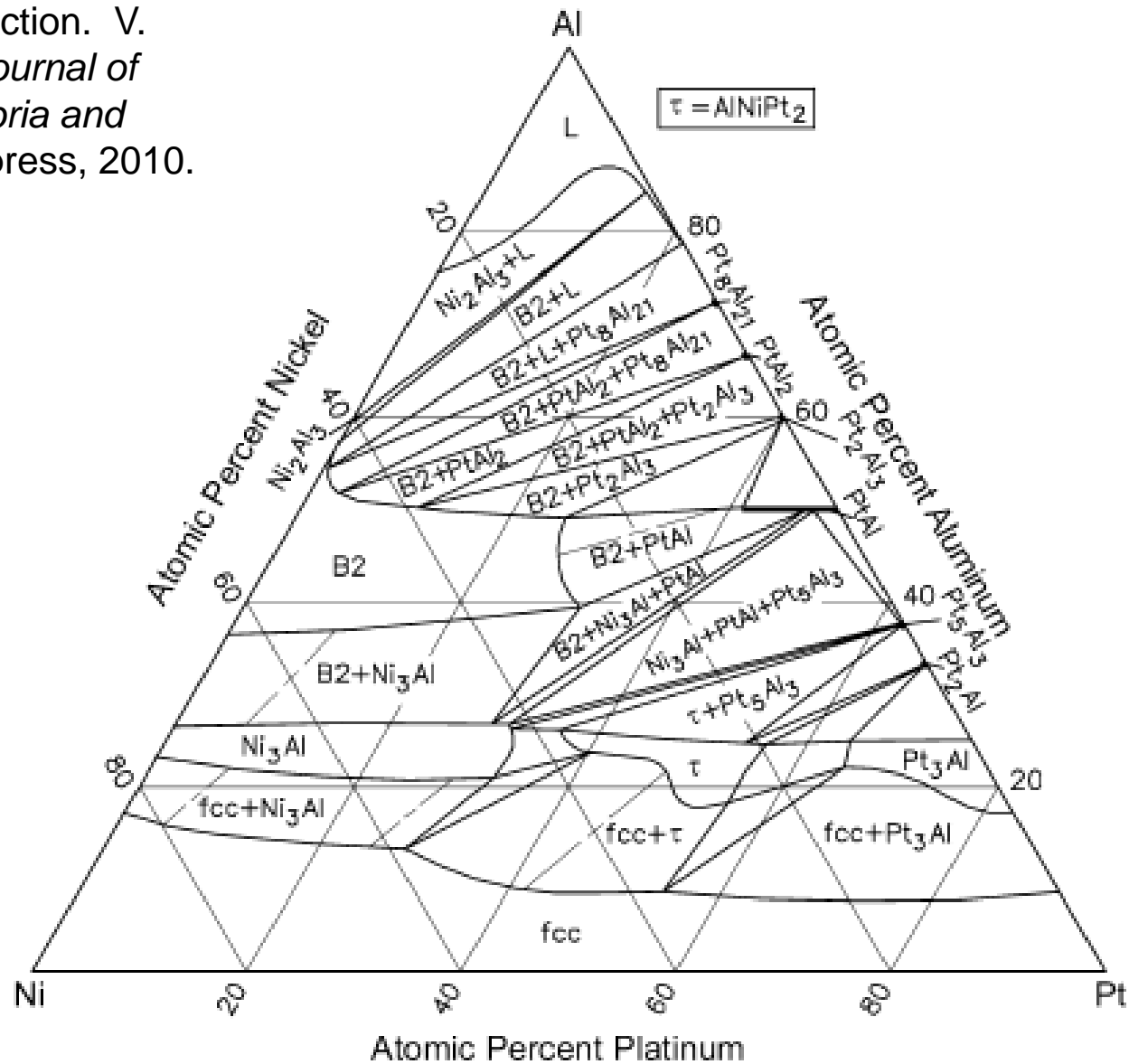


FIG. 11.25 Gibbs triangle for ternary alloy compositions



From Abbaschian, Reed-Hill, and Abbaschian, © 2009. Cengage Learning, Engineering. All Rights Reserved.

Computed 1100°C Al-Ni-Pt
 isothermal section. V.
 Raghavan, *Journal of
 Phase Equilibria and
 Diffusion*, in press, 2010.



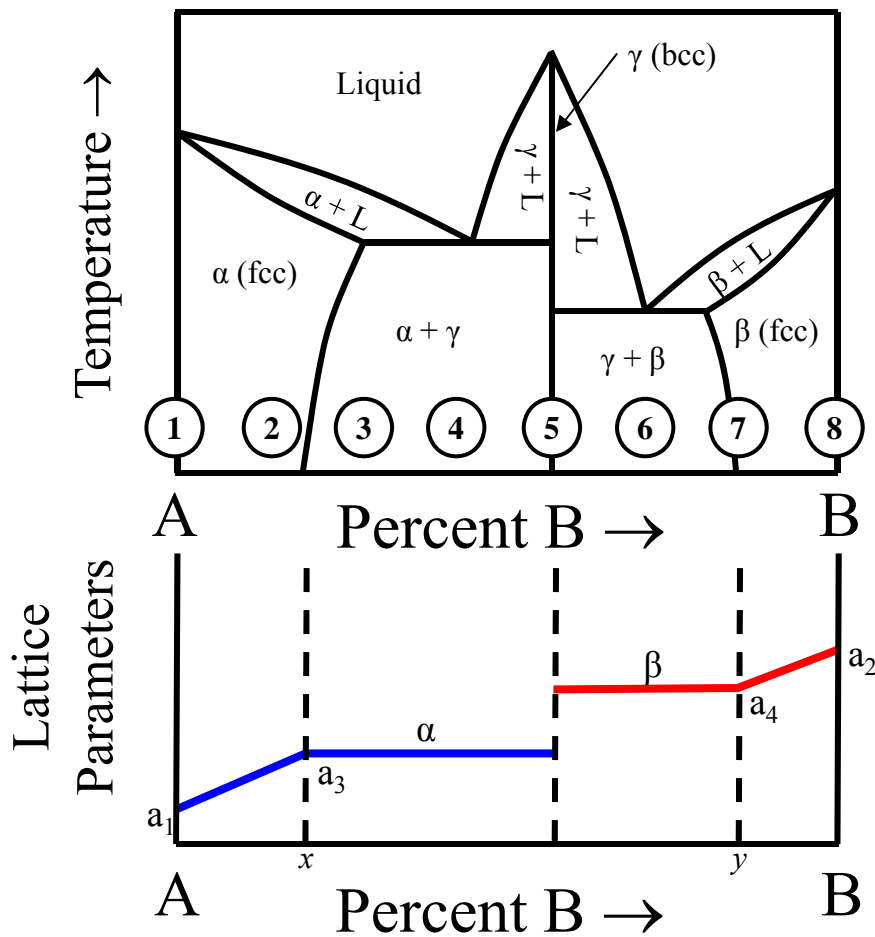


Figure 2

Phase diagram and lattice constants of a hypothetical alloy system. Adapted from Cullity and Stock, [Elements of X-ray Diffraction](#), 3rd Edition (Prentice Hall, Upper Saddle River, NJ) p. 334.

Lattice parameters change when composition changes.

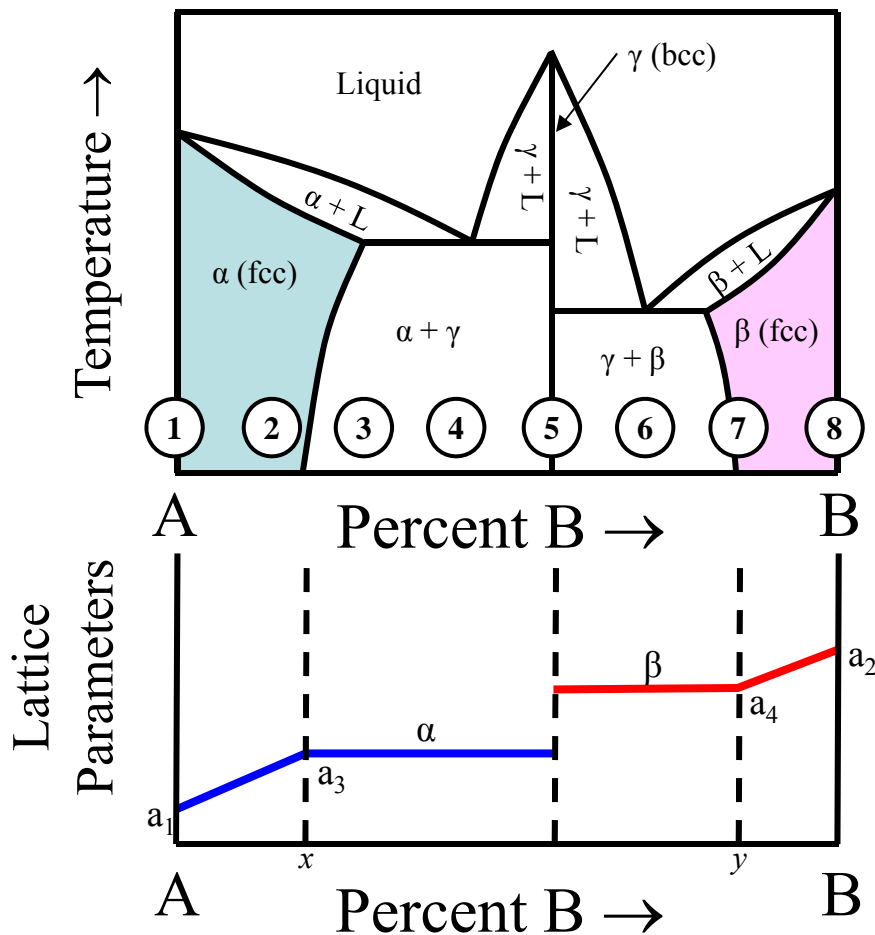


Figure 2

Phase diagram and lattice constants of a hypothetical alloy system. Adapted from Cullity and Stock, Elements of X-ray Diffraction, 3rd Edition (Prentice Hall, Upper Saddle River, NJ) p. 334.

In this system there are two terminal solid solutions

α and β

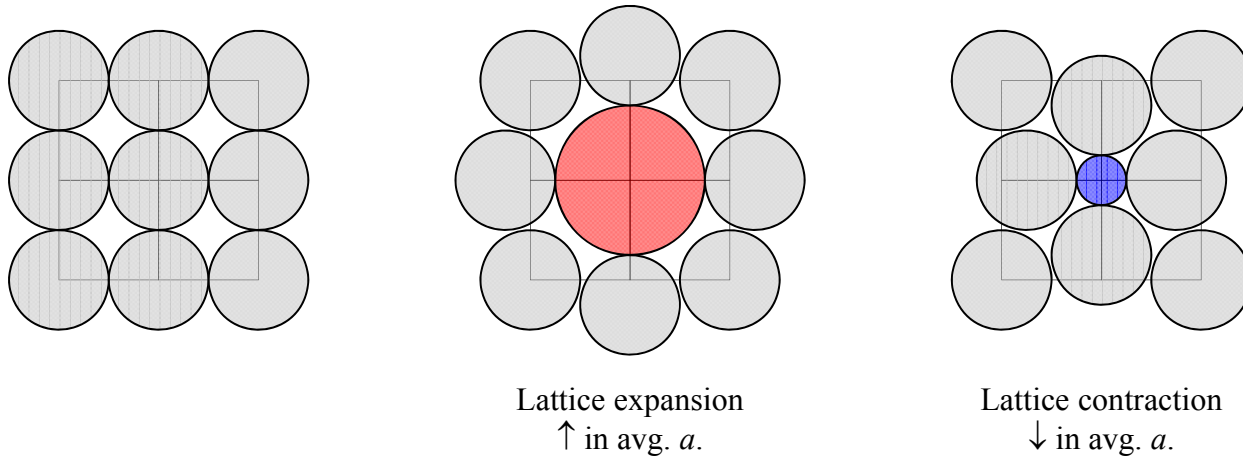
There is one intermediate phase

γ

which is a line compound



Implications of solid solubility



- Solutes often expand or contract the crystal lattice.

What happens to your XRD pattern?

The colored lines represent the relative locations of the XRD peaks for each phase

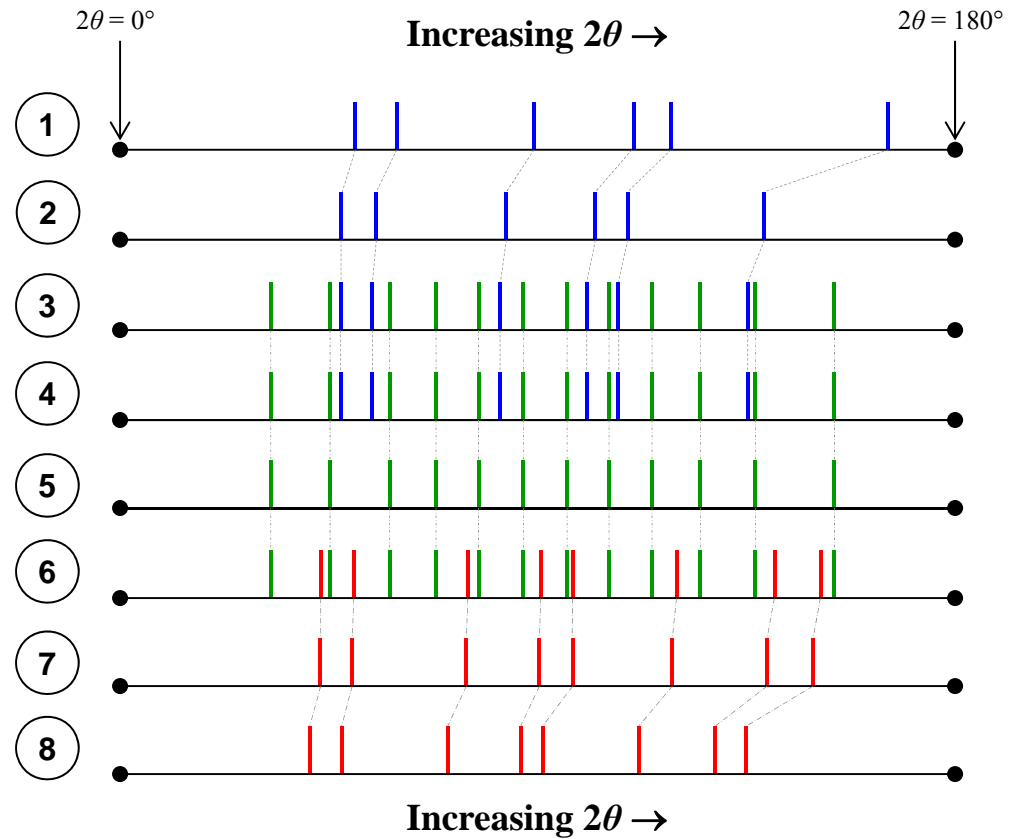
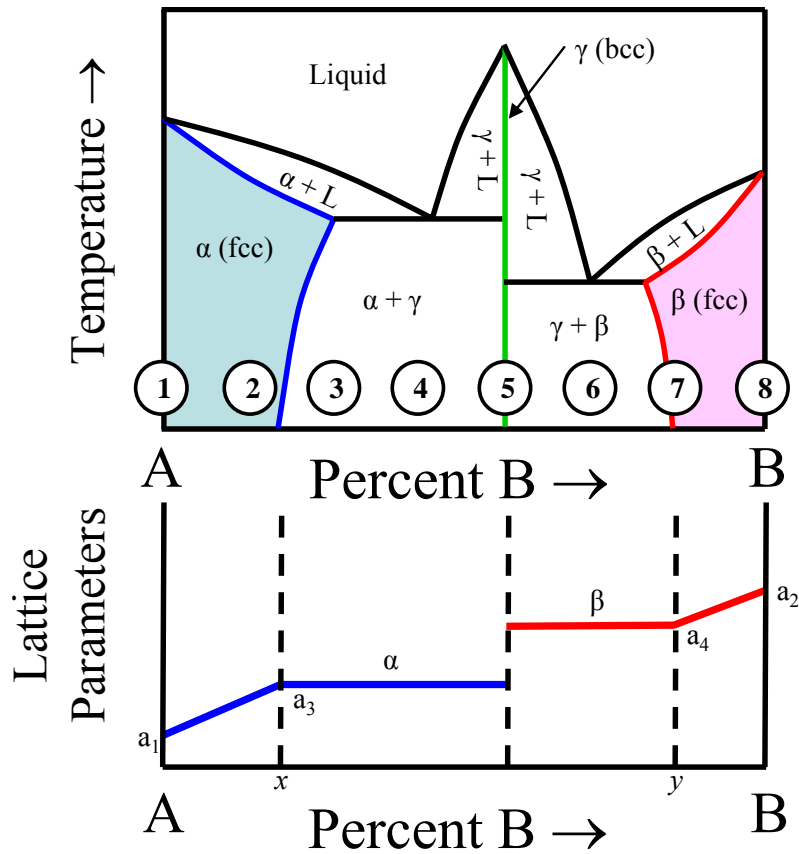


Figure 3: Calculated powder diffraction patterns for alloys 1 to 8 in the alloys system presented in Figure 2. Adapted from Cullity and Stock, *Elements of X-ray Diffraction*, 3rd Edition (Prentice Hall, Upper Saddle River, NJ) p. 335.

Key thing about XRD patterns

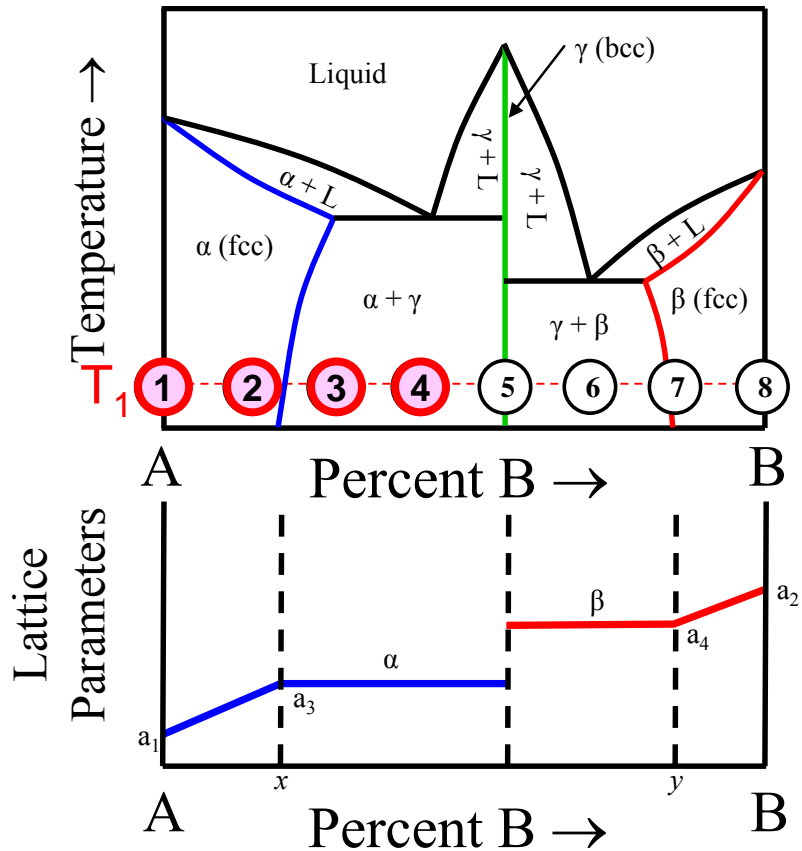
- Each phase has its own distinct XRD pattern which is just like a fingerprint for the phase.
- Peak locations for each phase in an XRD pattern are based upon unit cell dimensions.
- Thus each pattern will depend upon composition.

Summary of results for phase diagram

1. Pattern for pure A. FCC crystal structure. Calculated lattice parameter a_A .
2. Pattern of α -phase. Solid solution of A and B. In terms of atomic size $a_B > a_A$. Lattice expands. Thus a increases up to the solubility limit.
3. Beyond α phase boundary. Precipitation of γ -phase. Superimposed XRD patterns. Solubility of A in B does not change. Thus, lattice parameter of α -phase does not change. Peak locations for α -phase do not change.
4. Same pattern as (3). Only difference will be change in peak intensities (peak heights). This is due to a variation in the amounts of the α -phase and γ -phase that are present. Remember the lever rule?
5. Only pure γ -phase is present. BCC crystal structure. Distinct from other patterns.
6. Superimposed patterns of γ -phase and β -phase. The β -phase is solid solution of A in B. $a_B < a_A$. Lattice contracts as more A is added to B.
7. Pattern of pure β -phase. FCC crystal structure. Lattice parameter of β is greater than it was in (6) because there is less A in solid solution.
8. Pattern of pure B. FCC crystal structure. No A in solution. Largest lattice parameter.

This viewgraph is too busy!!!

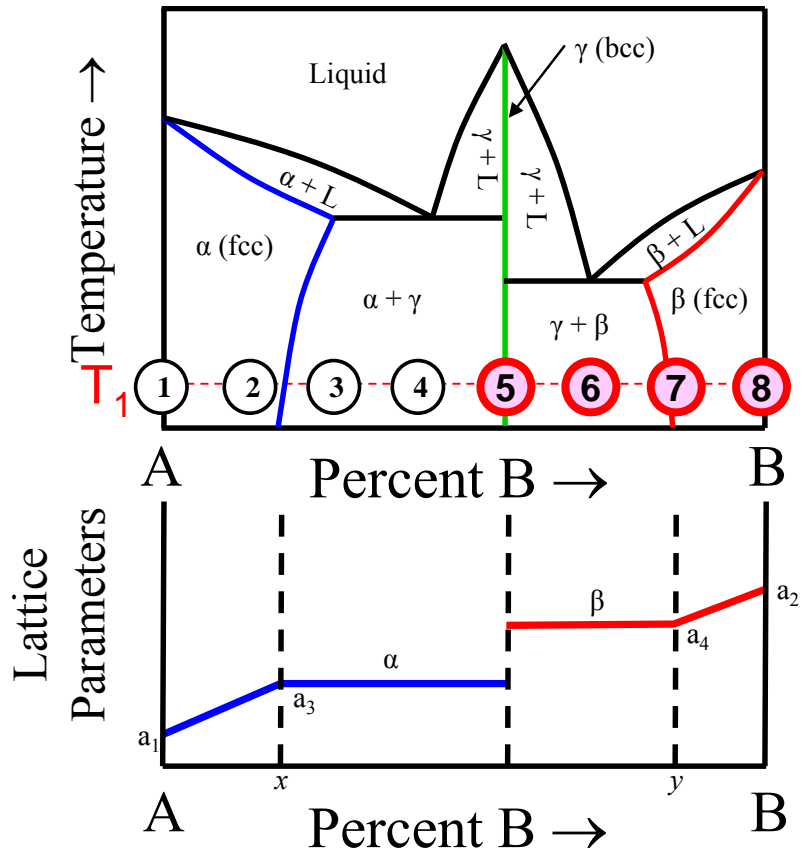
On the next two viewgraphs we will consider them one by one.



1. Pattern for pure A. FCC crystal structure. Calculated lattice parameter a_A .
2. Pattern of α -phase. Solid solution of A and B. In terms of atomic size $a_B > a_A$. Lattice expands. Thus a increases up to the solubility limit.
3. Beyond α phase boundary. Precipitation of γ -phase. Superimposed XRD patterns. Solubility of A in B does not change. Thus, lattice parameter of α -phase does not change. Peak locations for α -phase do not change.
4. Same pattern as (3). Only difference will be change in peak intensities (peak heights). This is due to a variation in the amounts of the α -phase and γ -phase that are present. Remember the lever rule?

Results from Hypothetical XRD Patterns at temperature T_1





Results from Hypothetical XRD
Patterns at temperature T_1

5. Only pure γ -phase is present. BCC crystal structure. Distinct from other patterns. Different crystal structure.
6. Superimposed patterns of γ -phase and β -phase. The β -phase is solid solution of A in B. $a_B < a_A$. Lattice contracts as more A is added to B.
7. Pattern of pure β -phase. FCC crystal structure. Lattice parameter of β is greater than it was in (6) because there is less A in solid solution.
8. Pattern of pure B. FCC crystal structure. No A in solution. Largest lattice parameter.



Determination of Phase Boundaries

- Isolate the exact locations where phases appear and disappear from a series of alloys of known composition.
- We must know something about composition.

Methods

1. Disappearing-phase method

2. Parametric method

- One method relies on intensity measurements for 2-phase alloys
- Other method relies on lattice parameter measurements for individual phases.

Which method is more accurate?

Why?

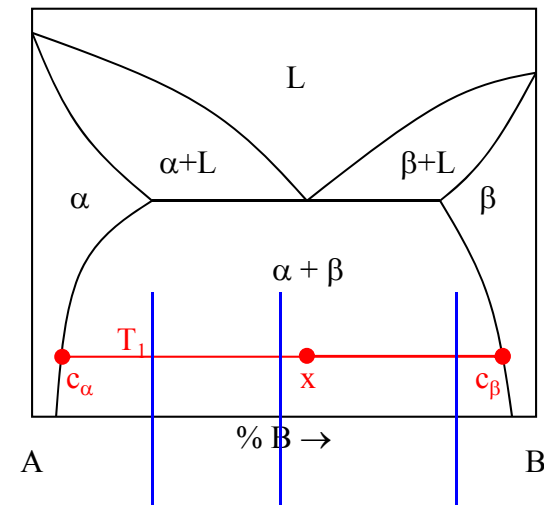
Disappearing-Phase Method

1. Equilibrate a series of two-phase alloys at a given temperature.
2. Quench them to room temperature and collect their XRD patterns.
3. Identify the two phases (*i.e.*, index the XRD patterns).
4. Locate one intense XRD peak from each phase. Peaks should be close to one another but should not overlap.
5. Plot the ratio of relative intensities for each phase, *e.g.*, I_{β}/I_{α} as a function of composition. Peak intensities will vary with composition.
6. Recall the lever rule. At the $\alpha/\alpha+\beta$ solvus line, the amount of β is zero. If you are beyond the solvus line, say at position x , the amount of β will decrease as you move toward the A-rich side of the phase diagram.
7. Since the intensity ratio scales with composition, extrapolation of I_{β}/I_{α} back to the solvus (*i.e.* $I_{\beta}/I_{\alpha} = 0$) yields the composition at the solvus.
8. Repeat for several temperatures and you generate the phase boundary.

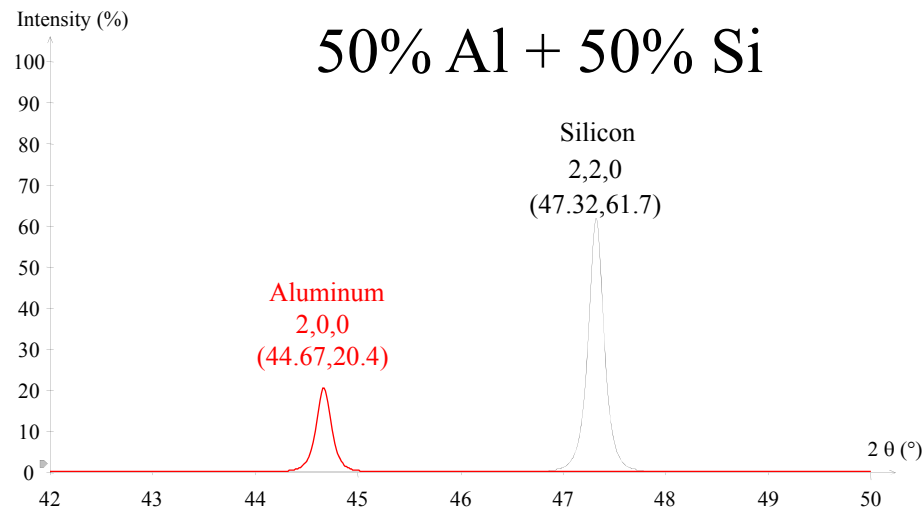
This viewgraph is too busy!!!
On the next few viewgraphs we will consider them one by one.

Disappearing-Phase Method

1. Equilibrate a series of two-phase alloys (w/ different compositions) at a given temperature.
2. Quench them to room temperature and collect their XRD patterns.
3. Identify the two phases (*i.e.*, index the XRD patterns).



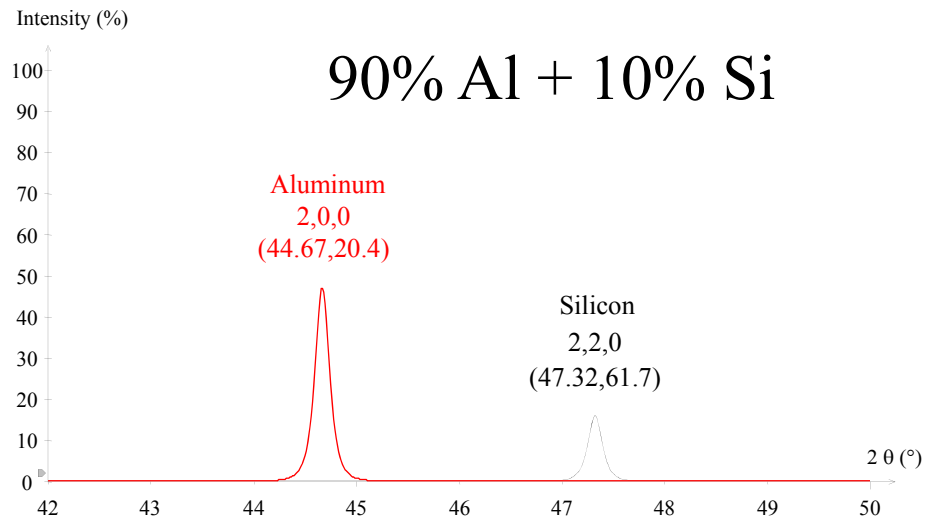
This viewgraph is too busy!!!
On the next few viewgraphs we will consider them one by one.



4. Locate one intense XRD peak from each phase. Peaks should be close to one another but should not overlap.

Note the change in peak intensity as composition changes.

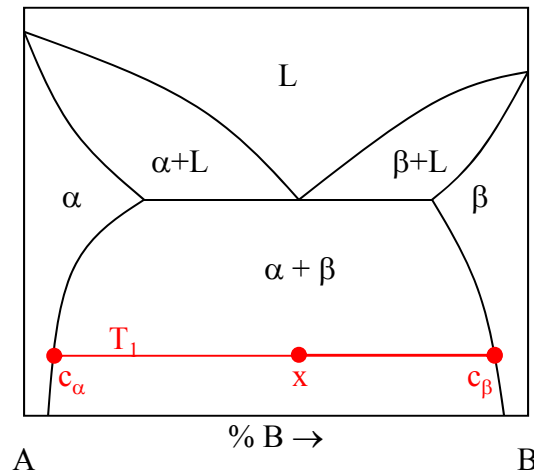
Why is there a change?



Disappearing-phase method

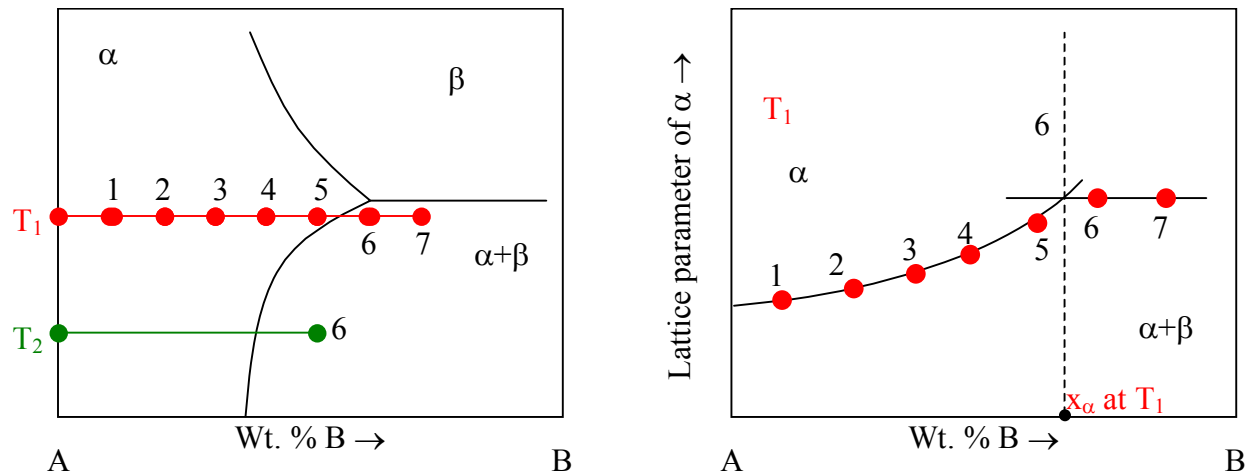
$$W_{\alpha} = \frac{c_{\beta} - x}{c_{\beta} - c_{\alpha}}$$

$$W_{\beta} = \frac{x - c_{\alpha}}{c_{\beta} - c_{\alpha}}$$



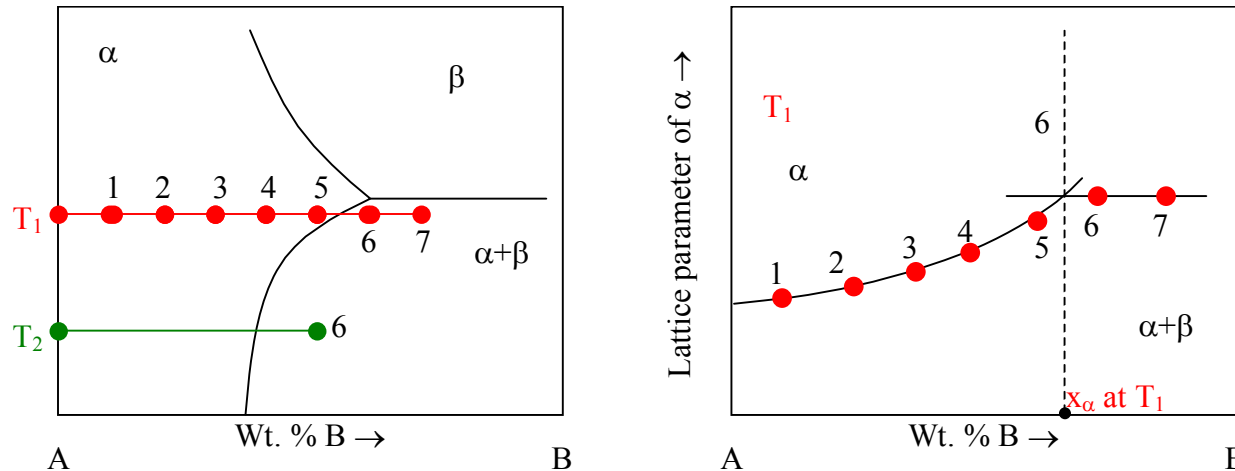
6. Recall the lever rule. At the $\alpha/\alpha+\beta$ solvus line, the amount of β is zero. If you are beyond the solvus line, say at position x , the amount of β will decrease as you move toward the A-rich side of the phase diagram.
7. Since the intensity ratio scales with composition, extrapolation of I_{β}/I_{α} back to the solvus (i.e. $I_{\beta}/I_{\alpha} = 0$) yields the composition at the solvus.
8. Repeat for several temperatures and you generate the phase boundary.

Parametric Method



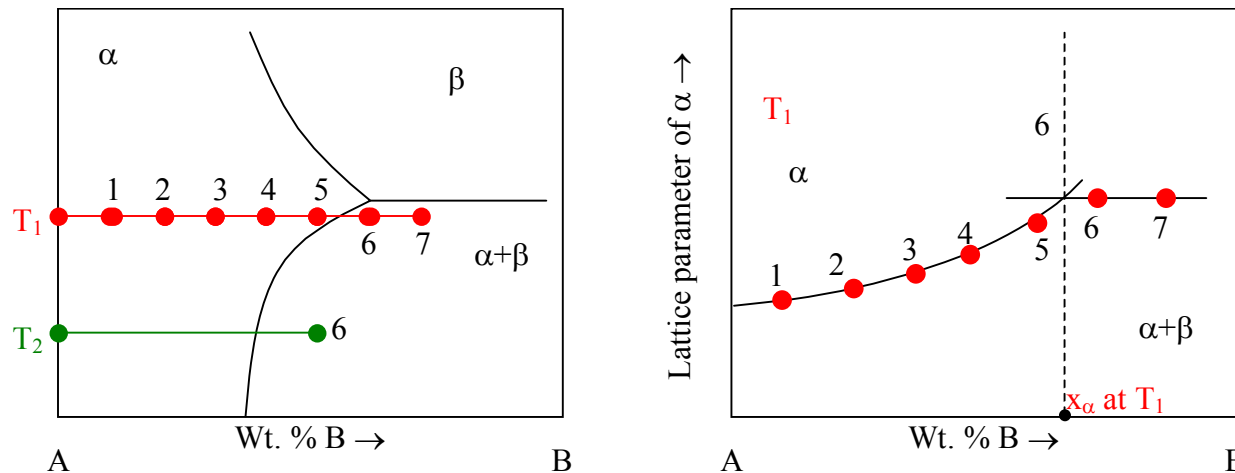
- Depends on lattice parameter measurements for individual phases.

Parametric Method – cont'd



1. Prepare a series of alloys with varying compositions.
2. Equilibrate them at a fixed temperatures (e.g., T_1 and T_2) as is schematically illustrated in the Figure above.
3. Determine the lattice parameter of α for each composition.

Parametric Method – cont'd



4. Plot a_{α} versus composition for each alloys as illustrated above.
5. The curve has two branches. They reflect the fact that the lattice parameter will no longer change once the solubility limit is exceeded. The two branches cross at the location (i.e., composition) of the solvus.
6. Repeat this procedure at different temperatures. This will yield the locations of the lines that you see on a phase diagram.

Final Note

- The parametric method yields more accurate results.
- Why?

Required Assignment

- Complete experimental module #4 from S&N. Turn in a hard copy of your results and a floppy disk or CD containing your original work.
- Do all of your work in MS EXCEL.
- WORK INDEPENDENTLY!

NEXT!

Determination of Crystallite Size and
Lattice Strain