Lecture 19: 11.23.05 Binary phase diagrams

Today:

Reading: W.D. Callister, Jr., "Fundamentals of Materials Science and Engineering," Ch. 10S Phase Diagrams, pp. S67-S84.

Supplementary Reading: Ternary phase diagrams (at end of today's lecture notes)

→ QUIZ 2 RESULTS: AVE: 76 ± 16

Last time

Eutectic Binary Systems

- It is commonly found that many materials are highly miscible in the liquid state, but have very limited mutual miscibility in the solid state. Thus much of the phase diagram at low temperatures is dominated by a 2-phase field of two different solid structures- one that is highly enriched in component A (the α phase) and one that is highly enriched in component B (the β phase). These binary systems, with unlimited liquid state miscibility and low or negligible solid state miscibility, are referred to as ***eutectic systems***.

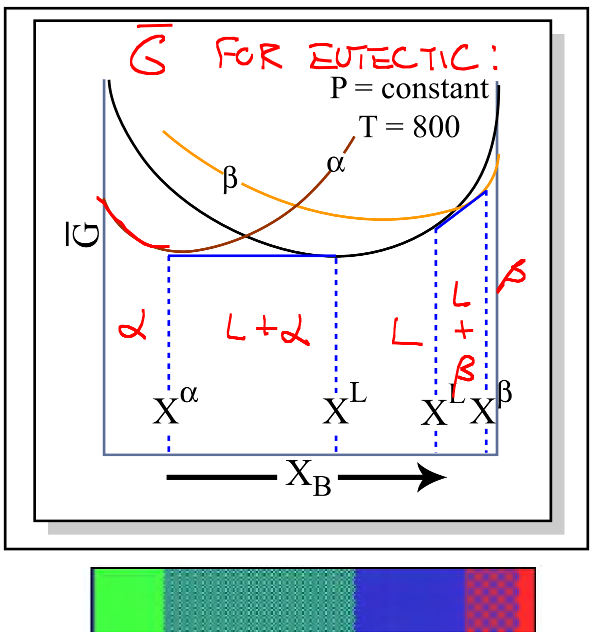
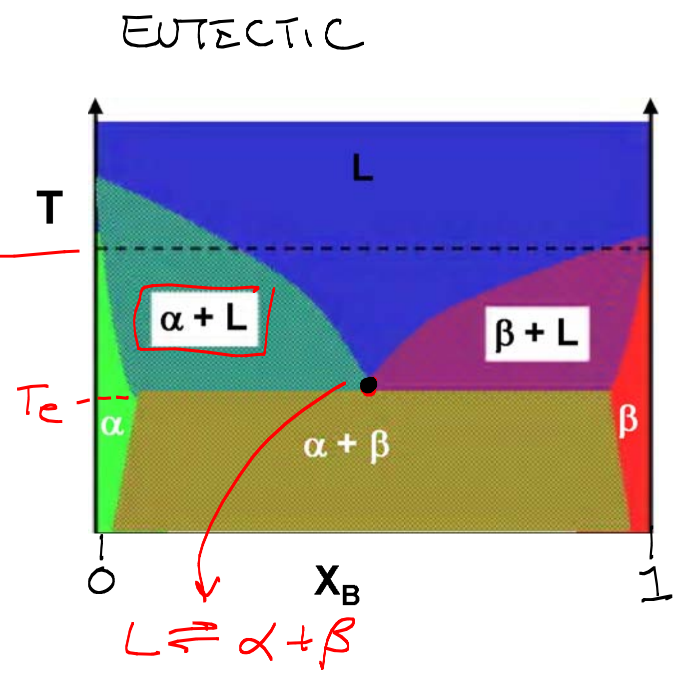


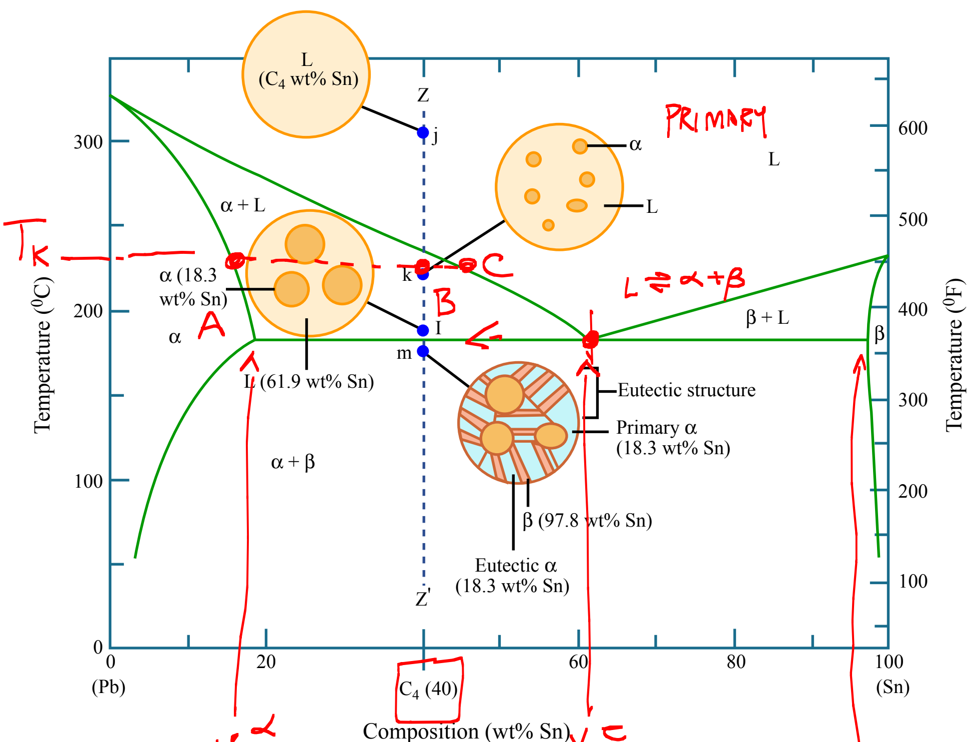
Figure by MIT OCW.



Analyzing phase equilibria on eutectic phase diagrams

- Next term, you will learn how these thermodynamic phase equilibria intersect with the development of **microstructure** in materials:

Pb - Sn



Schematic representations of the equilibrium microstructures for a lead-tin alloy of composition C_4 as it is cooled from the liquid-phase region.

Figure by MIT OCW.

$f^\alpha = \frac{\overline{BC}}{\overline{AC}}$

$f^L = \frac{\overline{AB}}{\overline{AC}}$

COMPOSITION
OF α: A
OF L: C

AT EUTECTIC, Te:

PHASES: PRIMARY α, EUTECTIC MIXTURE: L ⇌ α+β

PRIMARY α: COMPOSITION: X^α

PHASE FRACTION: $f^\alpha = \frac{X^e - C^4}{X^e - X^\alpha}$

EUTECTIC MIXTURE: → L: COMPOSITION X^e

COMPOSITION (OVERALL): X^e

$f^e = \frac{C^4 - X^\alpha}{X^e - X^\alpha}$

⇅

α : COMP. X^α $\quad f^{\alpha \text{ in } e} = \left(\frac{X^\beta - X^e}{X^\beta - X^\alpha}\right)$

+

β : COMP. X^β $\quad f^{\beta \text{ in } e} = \left(\frac{X^e - X^\alpha}{X^\beta - X^\alpha}\right)$

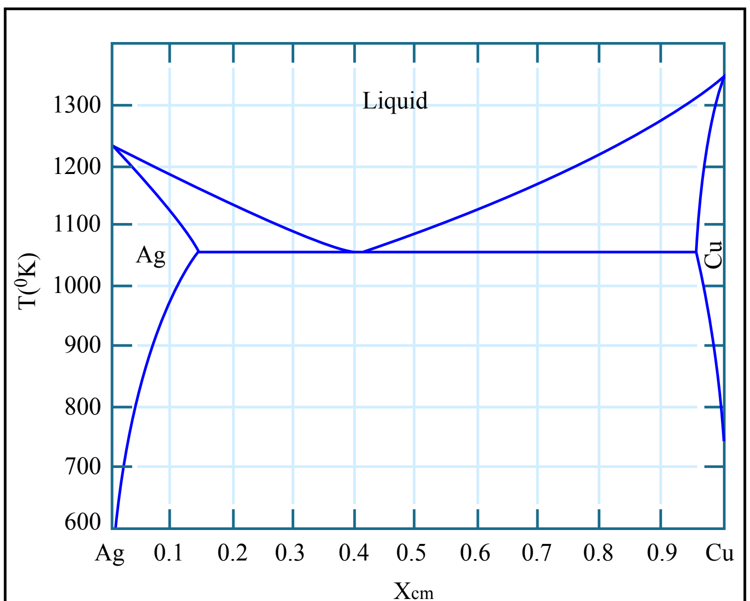
Example eutectic systems

Solid-state crystal structures of several eutectic systems

Component A	Solid-state crystal structure A	Component B	Solid-state crystal structure B
Bi	rhombohedral	Sn	tetragonal
Ag	FCC (lattice parameter: 4.09 Å at 298K)	Cu	FCC (lattice parameter: 3.61 Å at 298K)
Pb	FCC	Sn	tetragonal

← 10% DIFFERENCE →

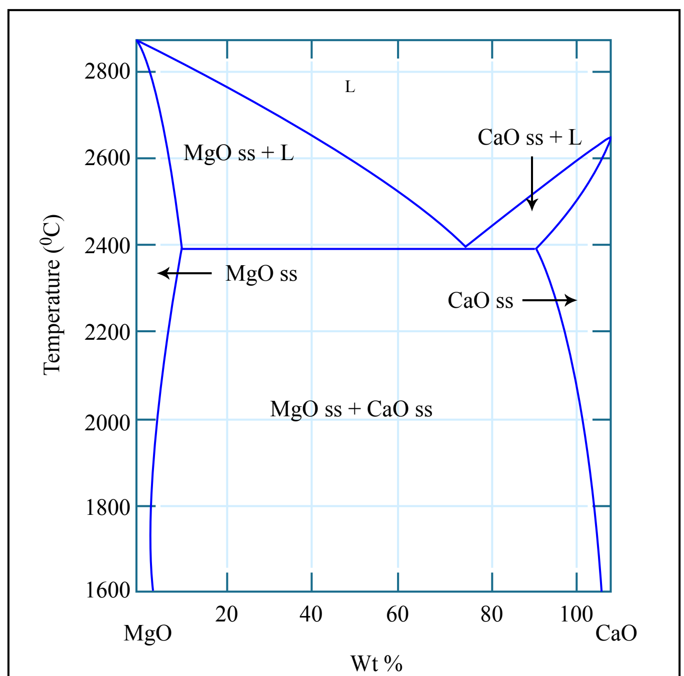
METAL SOLUTION



Eutectic phase diagram for a silver-copper system.

Figure by MIT OCW.

CERAMIC SOLUTION



Eutetic phase diagram for MgO-CaO system.

Figure by MIT OCW.

- Eutectic phase diagrams are also obtained when the solid state of a solution has regular solution behavior (can you show this?)

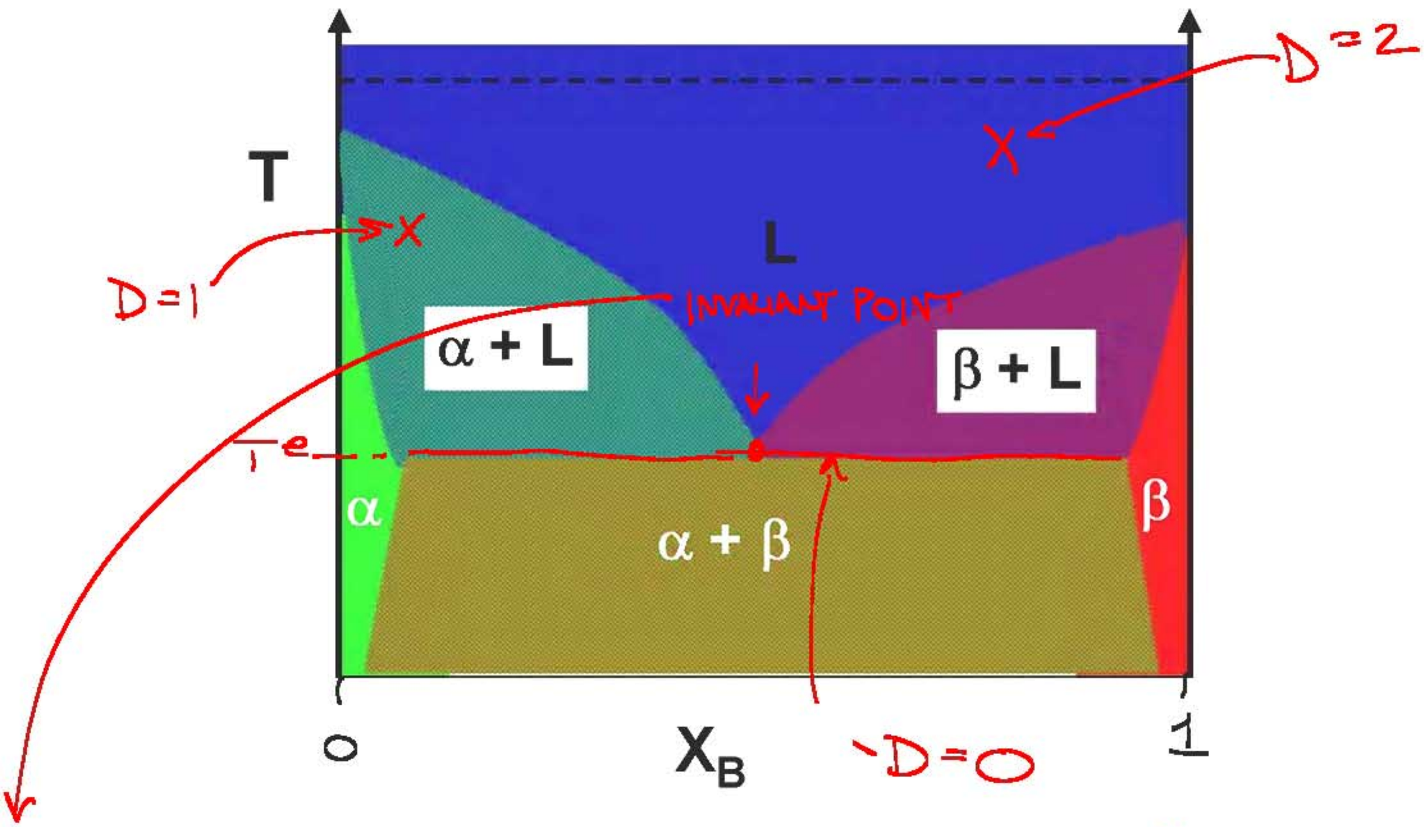
Invariant points in binary systems

The phase rule and eutectic diagrams: eutectic invariant points

- *All* phase diagrams must obey the phase rule. Does our eutectic diagram obey it?

$$D + \Phi = C + 1 \xrightarrow{C=2} D = 3 - \Phi$$

(PRESSURE IS FIXED)

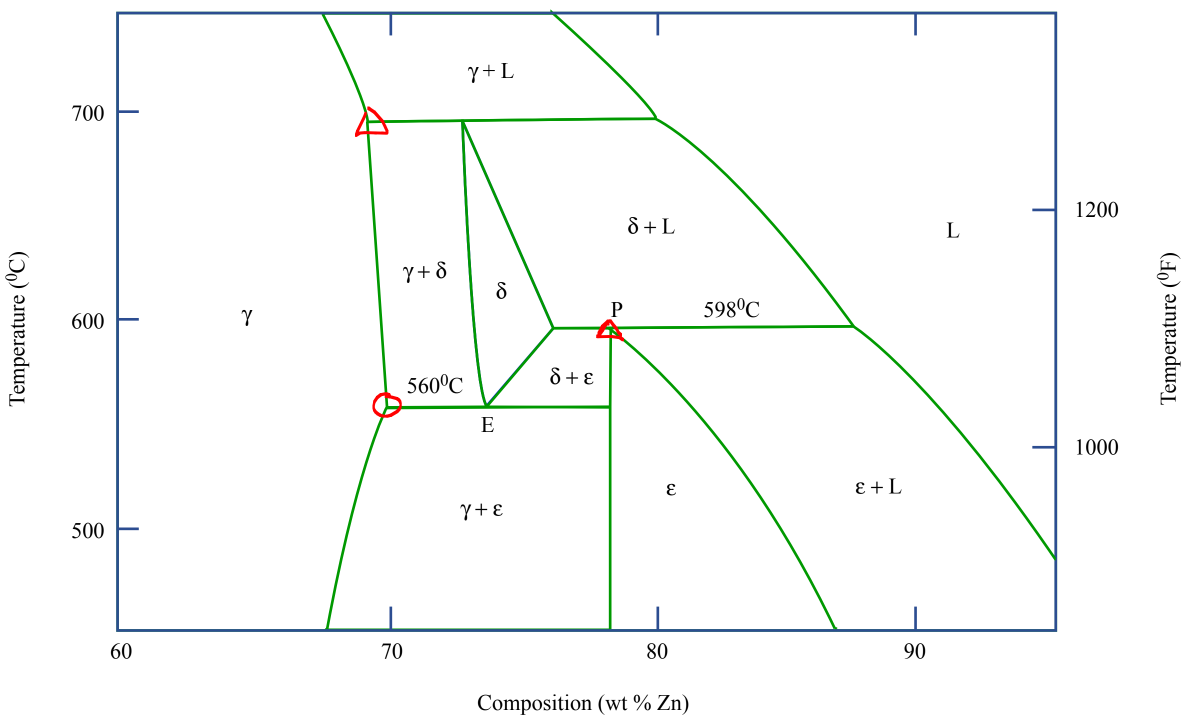


IN SOLUTIONS: COMPLETE TRANSFORMATION OF SYSTEM FROM ONE PHASE TO ANOTHER AT A SINGLE TEMP. CAN ONLY HAPPEN AT INVARIANT POINTS.

Other types of invariant points

- Other transformations that occur in binary systems at a fixed composition and temperature (for constant pressure) are given titles as well:
  - *Two* 2-phase regions join into *one* 2-phase region:
    - Eutectic: **L <-> (α + β)** (upper two region is liquid)
    - Eutectoid: **γ <-> (α + β)** (upper region is solid)
  - *One* 2-phase region splits into *two* 2-phase regions:
    - Peritectic: **(α + L) <-> β** (upper two-phase region is solid + liquid)
    - Peritectoid: **(α + γ) <-> β** (upper two-phase region is solid + solid)

Cu-Zn



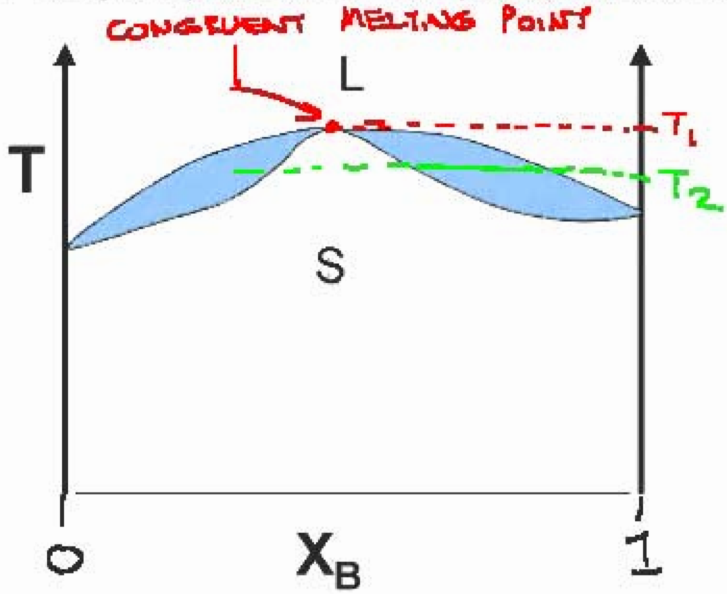
A region of the copper-zinc phase diagram that has been enlarged to show eutectoid and peritectic invariant points , labeled E (560⁰C, 74 wt% Zn) and P (598⁰C, 78.6 wt% Zn), respectively.

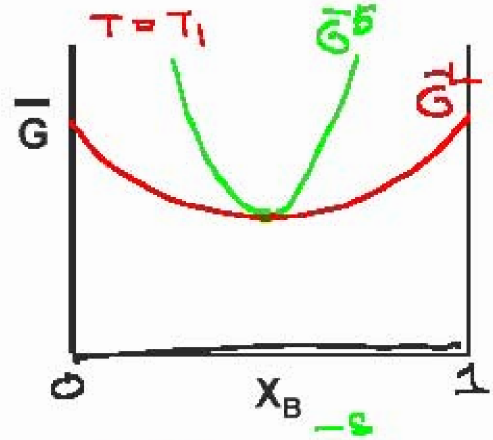
Figure by MIT OCW.

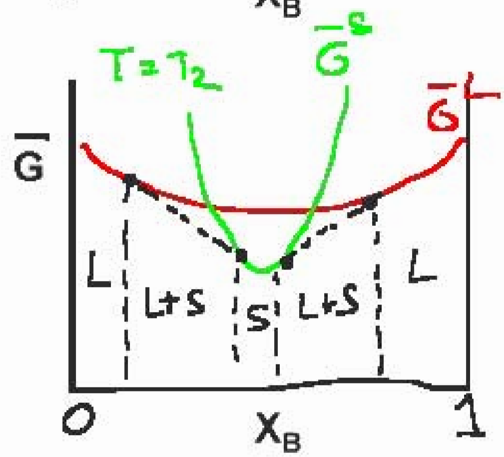
- Note that each single-phase field is separated from other single-phase fields by a two-phase field.

Congruent phase transitions

- **Congruent phase transition:** complete transformation from one phase to another at a fixed composition







Intermediate Compounds in phase diagrams[3]

- Stable compounds often form between the two extremes of pure component A and pure component B in binary systems- these are referred to as ***intermediate compounds***.

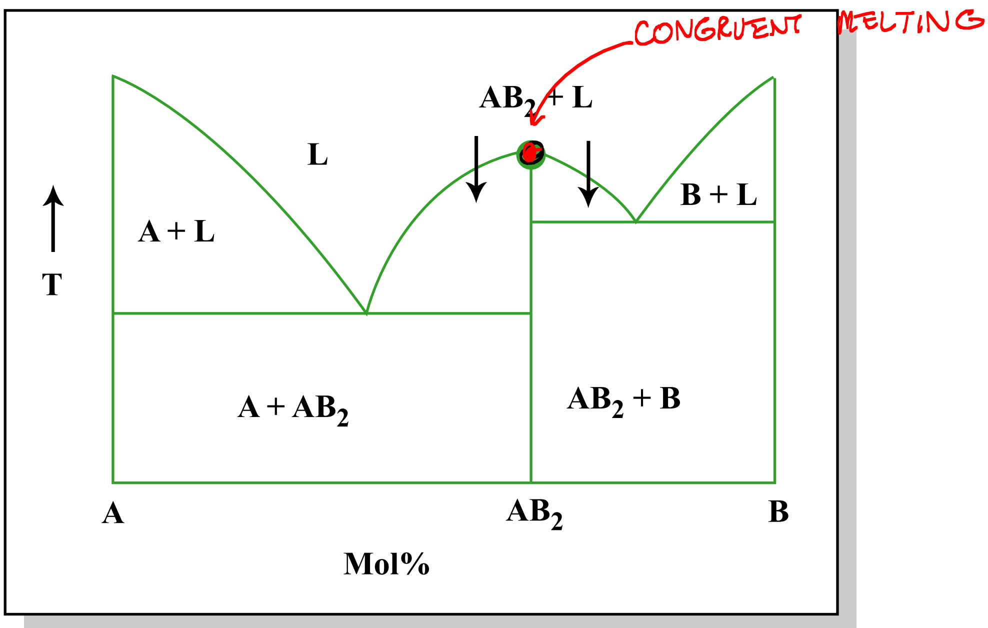


Figure by MIT OCW.

- When the intermediate compound melts to a liquid of the same composition as the solid, it is termed a ***congruently melting*** compound. Congruently melting intermediates subdivide the binary system into smaller binary systems with all the characteristics of typical binary systems.

- Intermediate compounds are especially common in ceramics, as the pure components may form unique molecules at intermediate ratios. Shown below is the example of the system MnO-Al_2O_3:

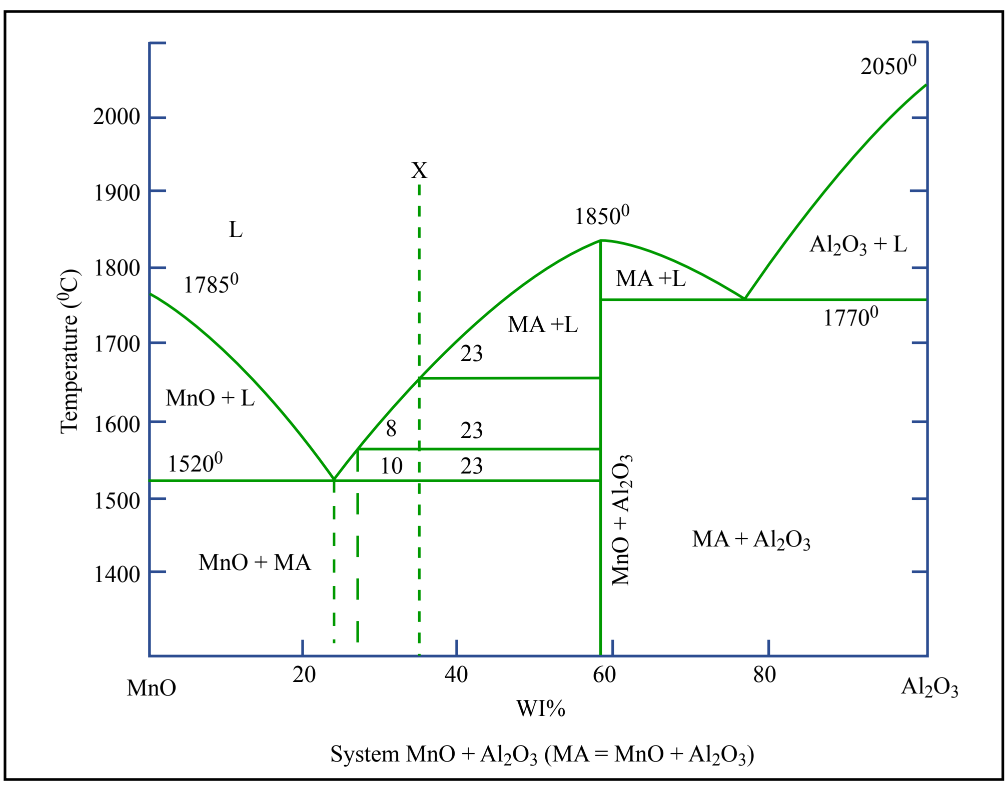
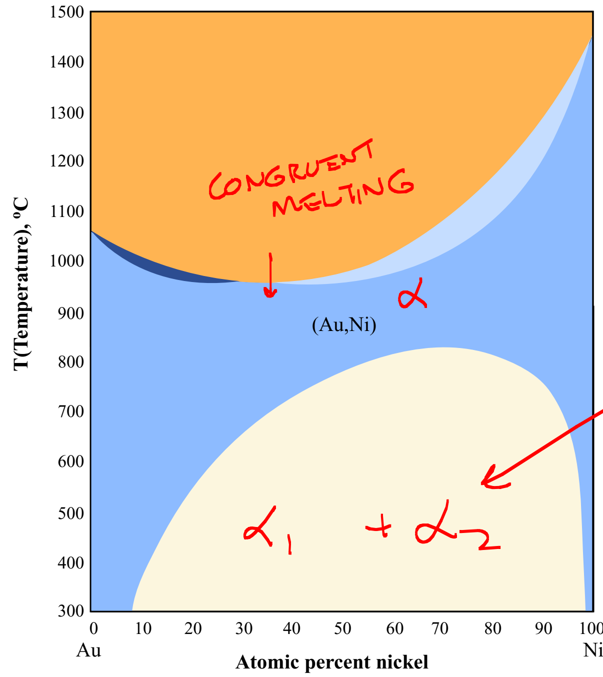


Figure by MIT OCW.

(Bergeron and Risbud[3])

Example binary phase diagrams

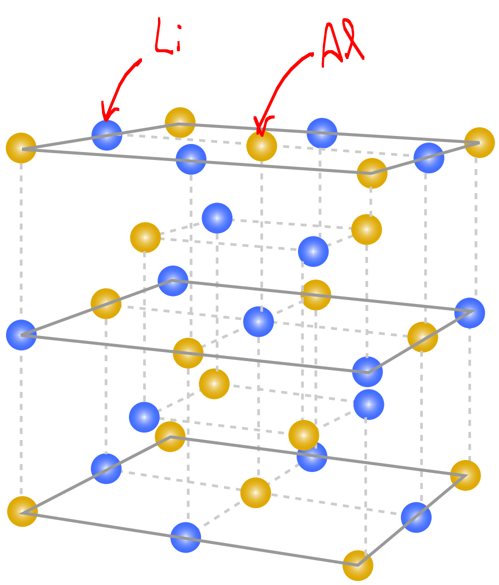
CAN YOU SHOW THAT CONGRUENT MELTING OFTEN OCCURS IN SYSTEMS W/ MISCIBILITY GAPS?



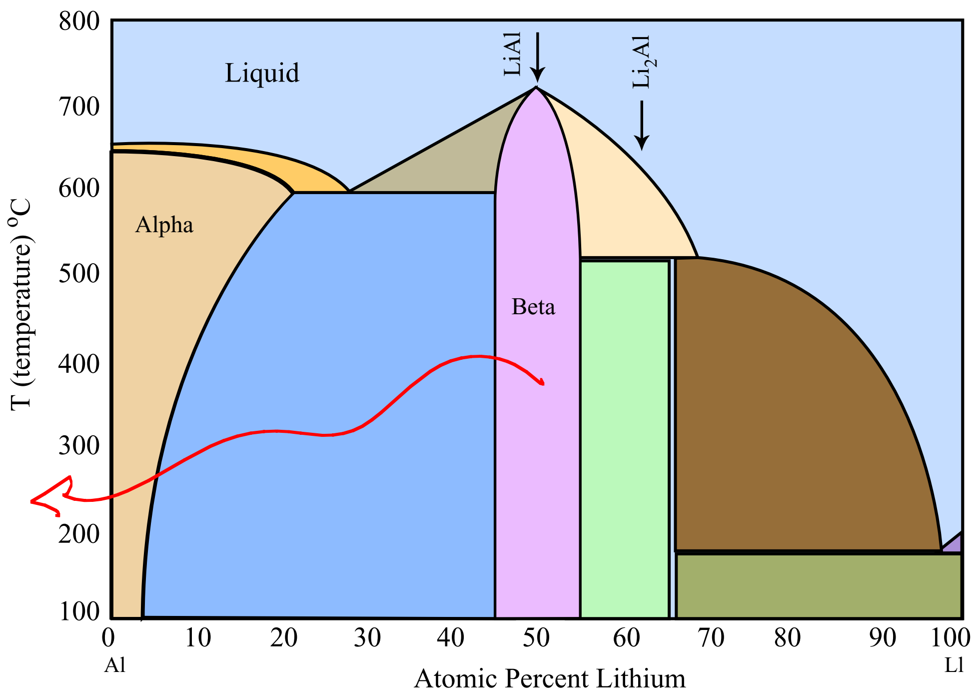
MISCIBILITY GAP (REGULAR SOLUTION MODEL)

Phase diagram for Gold-Nickel showing complete solid solubility above about 800°C and below about 950°C. The miscibility gap at low temperatures can be understood with a regular solution model.

Figure by MIT OCW.

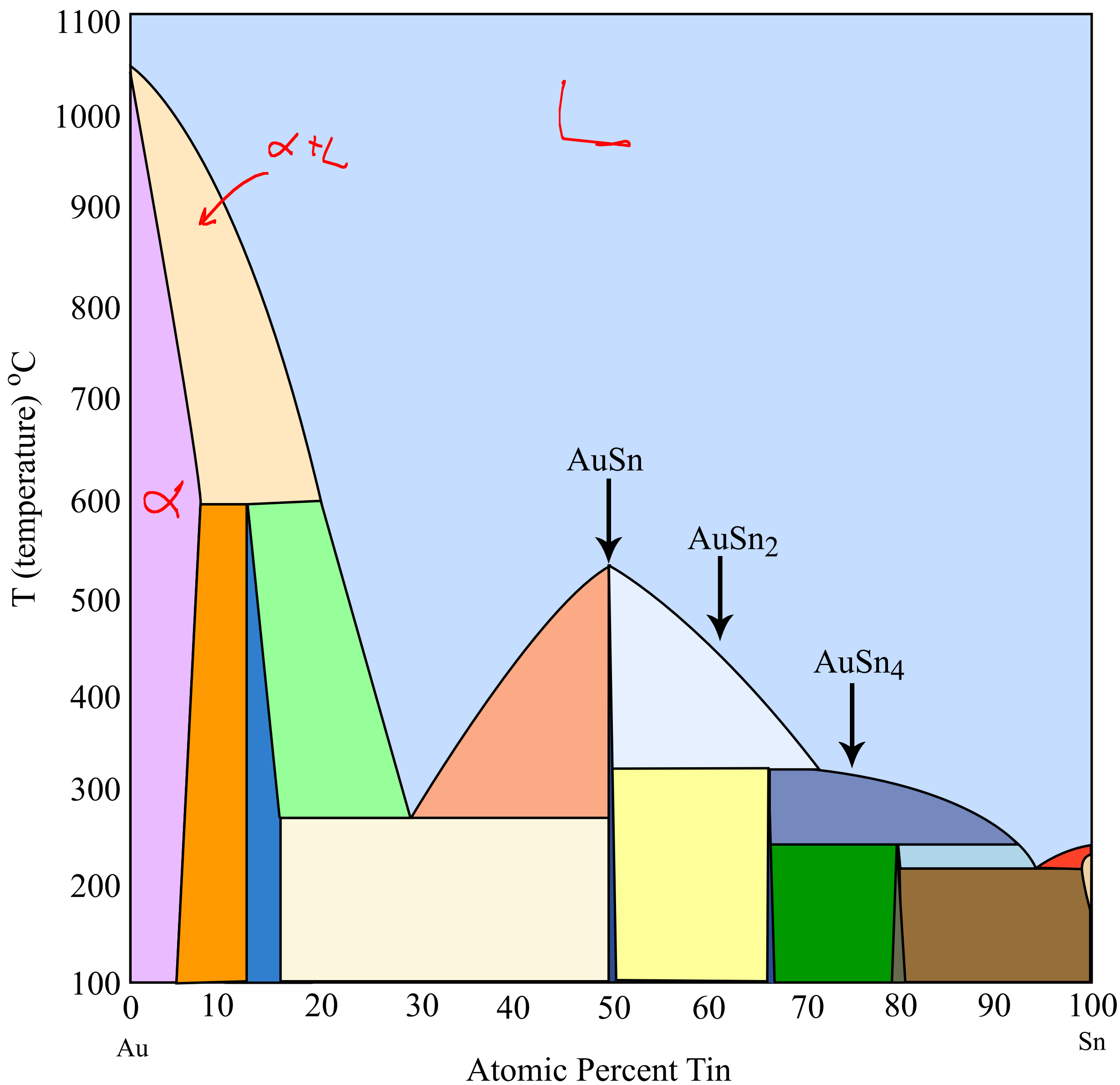


Zintl crystal Structure of LiAl (β phase)[4]



Phase diagram for light metals Aluminum-Lithium. There are five phases illustrated; however the BCC Lithium end-member phase shows such limited Aluminum solubility that it hardly appears on this plot. There are two eutectics and one peritectoid reactions. The LiAl(β) and Li_2Al intermetallic phases are ordered compounds where the atoms order on sublattices, thus changing the symmetry of the material. The ordered phases show limited solubility where, for instance, the extra Li will occupy sites where an Al usually sits, or occupies an interstitial position.

Figure by MIT OCW.



Phase diagram of Gold-Tin has seven distinct phases, three peritectics, two eutectics, and one eutectoid reactions.

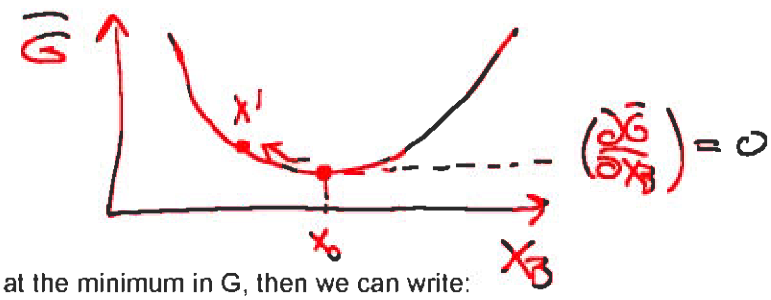
Figure by MIT OCW.

Delineating stable and metastable phase boundaries: spinodals and miscibility gaps

- We saw last time that a homogeneous solution can spontaneously decompose into phase-separated mixtures when interactions between the molecules are unfavorable. The example we started with was the regular solution model for the free energy, where the enthalpy of mixing two components might be positive (i.e., in terms of total free energy, unfavorable).

Conditions for stability as a function of composition

- For closed systems at constant temperature and pressure, the Gibbs free energy is minimized with respect to fluctuations in its other extensive variables. Thus, if we allow the composition of a binary system to vary, the system will move toward the minimum in the free energy vs. X_B curve:



- If the system is at the minimum in G, then we can write:

$$(d\bar{G})_{T,P,n} = \bar{G}(X_B = X') - \bar{G}(X_B = X_0) \geq 0$$

- We can perform a Taylor expansion for a fluctuation in Gibbs free energy, *assuming the only variable that can vary is composition* (X_B):

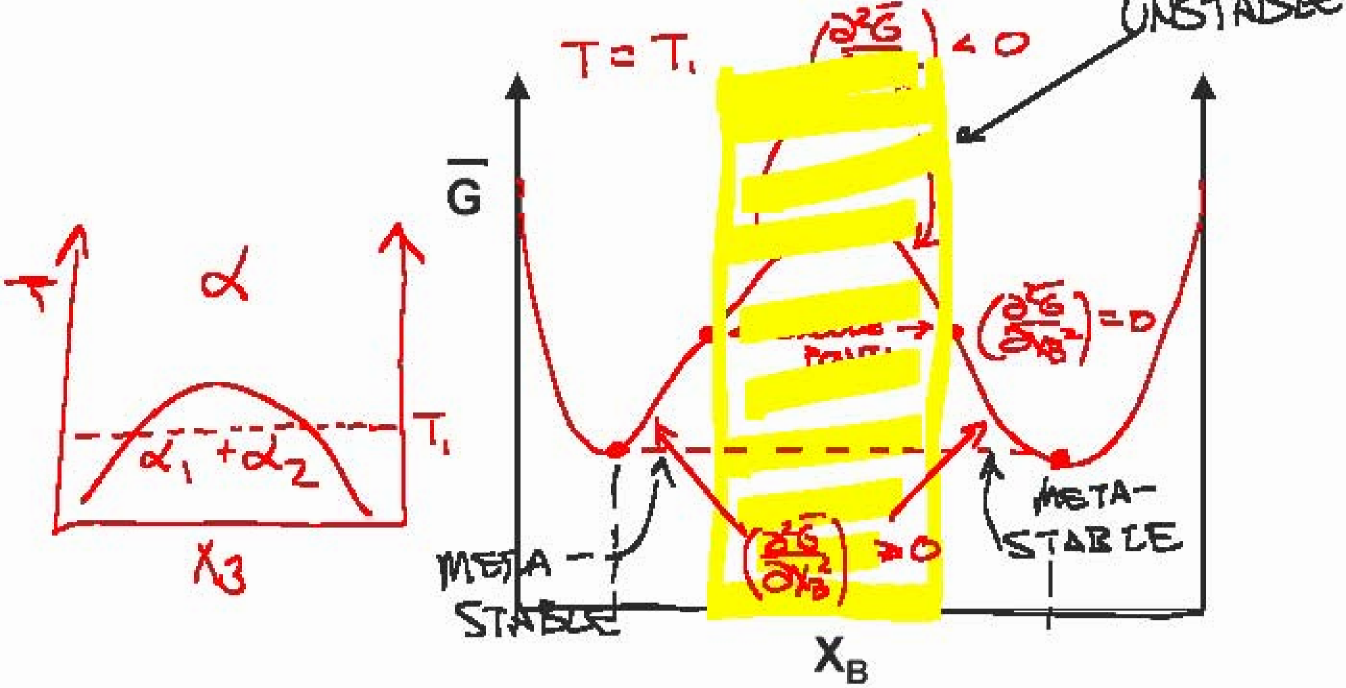
$$dG = \left(\frac{\partial \bar{G}}{\partial X_B}\right)_{T,P}\Bigg|_{X_B=X_0} dX_B + \frac{1}{2}\left(\frac{\partial^2 \bar{G}}{\partial X_B^2}\right)\Bigg|_{X_B=X_0} (dX_B)^2 + \frac{1}{3!}\left(\frac{\partial^3 \bar{G}}{\partial X_B^3}\right)\Bigg|_{X_B=X_0} (dX_B)^3 + \dots$$

First term: 0 AT X_0. Second term: ≥ 0 → STABLE! Third term: NEGLECT (SMALL)

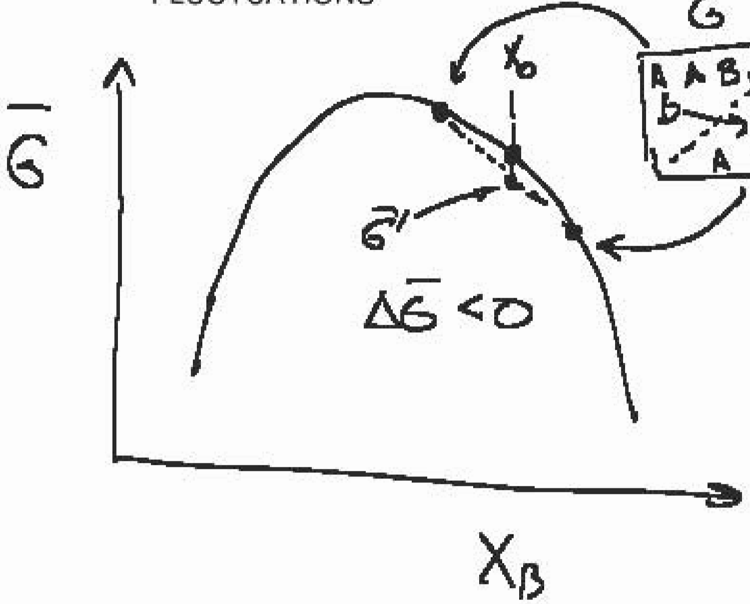
  - If we examine the consequence of a fluctuation in composition near the extremum point of the free energy curve, the first derivative of G is zero. If we assume the third-order (and higher) terms are negligible, then the condition for stable equilibrium is controlled by the value of the second derivative.

STABLE EQUILIBRIUM W/RESPECT TO COMPOSITION FLUCTUATIONS!

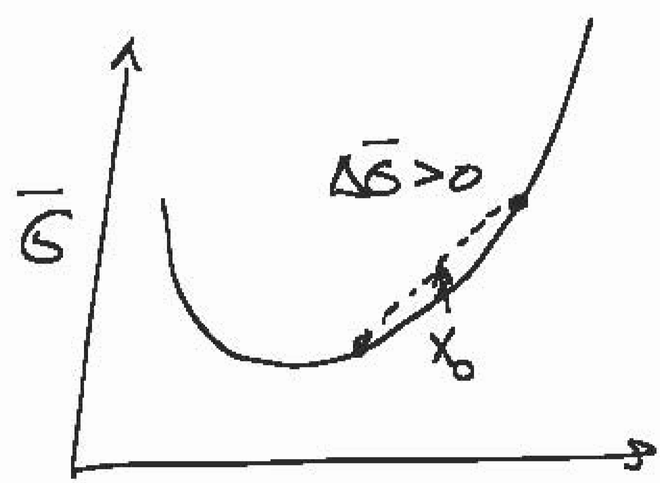
$$\left(\frac{\partial^2 \bar{G}}{\partial X_B^2}\right)\Bigg|_{X_B=X_0} \geq 0$$

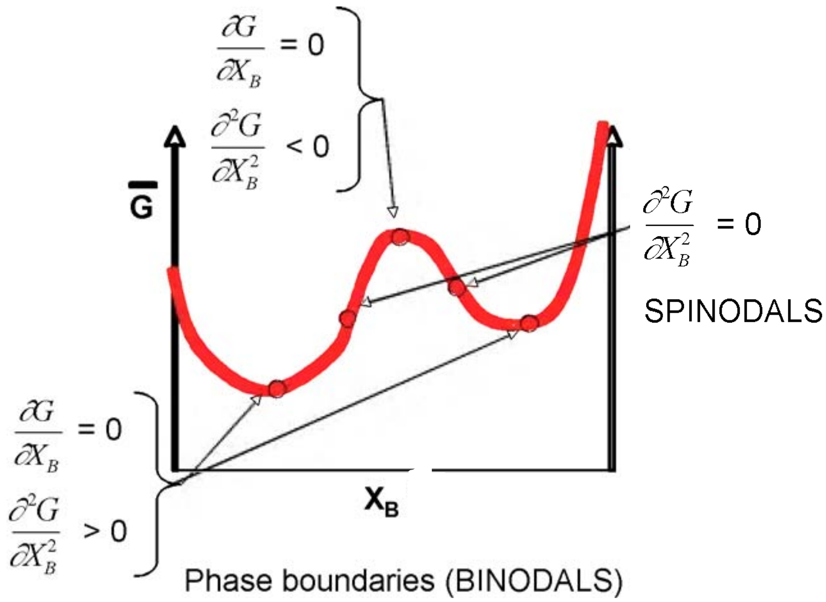


INSIDE SPINODAL: SYSTEM UNSTABLE TO SMALL COMPOSITION FLUCTUATIONS



OUTSIDE SPINODAL: SYSTEM STABLE TO *SMALL* COMPOSITION FLUCTUATIONS





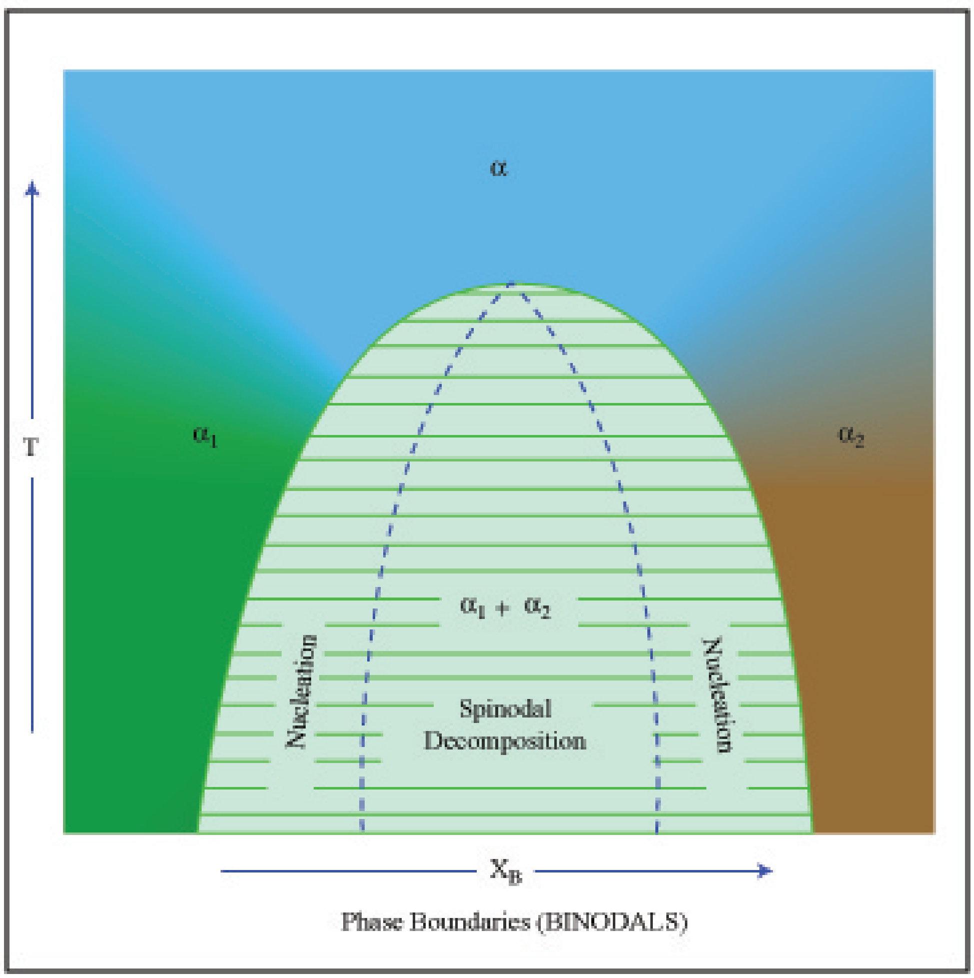
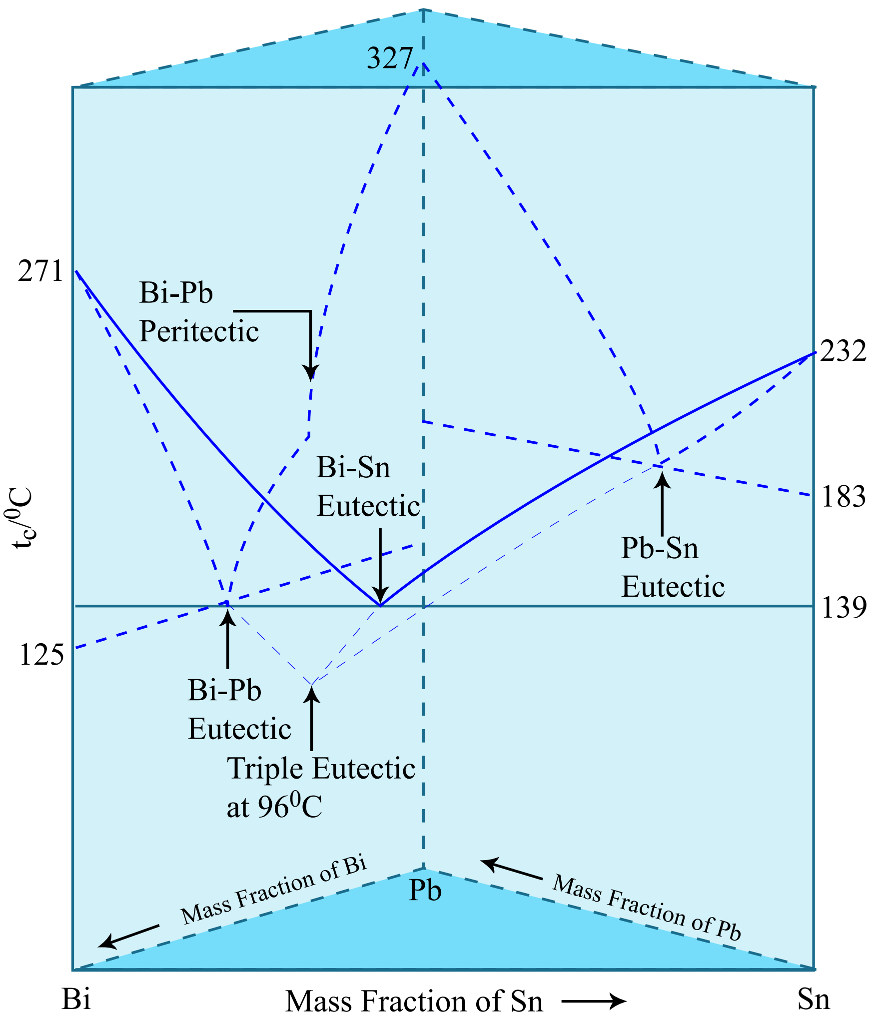


Figure by MIT OCW.

Supplementary Information (not to be tested): Ternary solution phase diagrams

- A 3-component analog to the binary phase diagram is also commonly encountered in materials science & engineering problems. For a 3 component system, a triangular 2D phase equilibrium map can be used to represent the stable phases as a function of composition in the 3-component ternary solution:

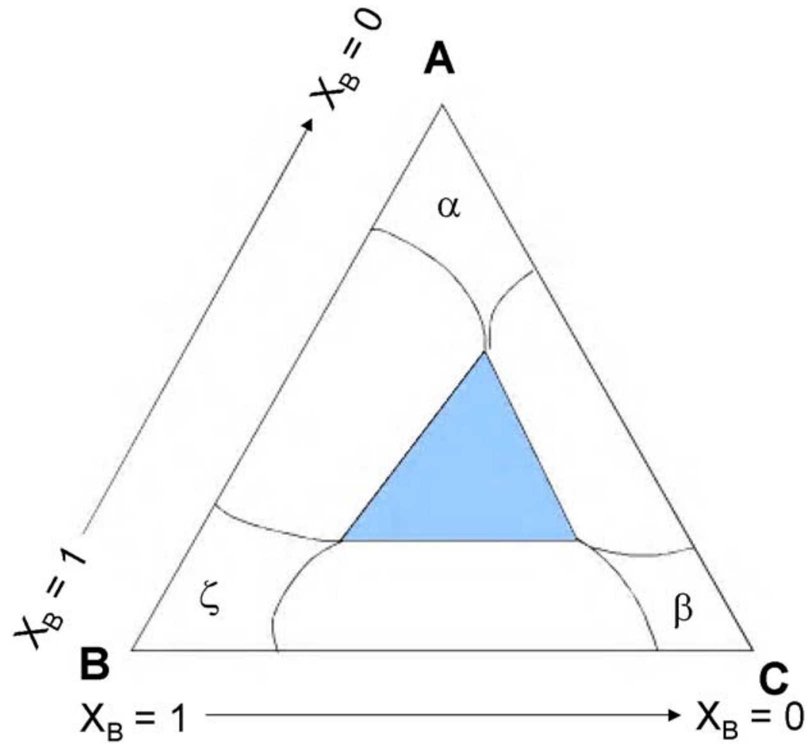


3-Dimensional Depiction of Temperature-Composition Phase Diagram of Bismuth, Tin, and Lead at 1atm. The diagram has been simplified by omission of the regions of solid solubility. Each face of the triangular prism is a two-component temperature-composition phase diagram with a eutectic. There is also a peritectic point in the Bi-Pb phase diagram.

Figure by MIT OCW.

- 3D depictions are necessary to show all 3 composition variables and temperature at fixed pressure (temperature is shown in the vertical axis)- in this arrangement, each face of the triangular column is the equivalent binary phase diagram (2 components present while 3rd component is not present).

- A single horizontal slice from the 3D ternary construction provides the phase equilibria as a function of composition for a fixed value of temperature and pressure:



- Similar to binary phase diagrams, tie lines are used to identify the compositions and phase fractions in multi-phase regions of the ternary diagram:

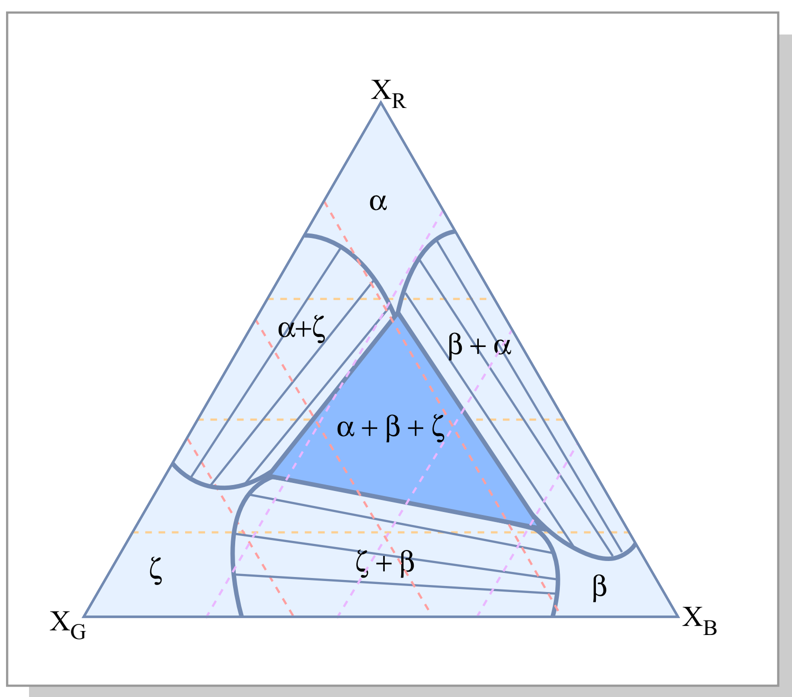


Figure by MIT OCW.

  - The phase rule allows 3-phase equilibria to lie within fields of the ternary diagram, unlike the binary systems, where 3-phase equilibria are confined to invariant points.

References

1. McCallister, W. D. *Materials Science and Engineering: An Introduction* (John Wiley & Sons, Inc., New York, 2003).
2. Lupis, C. H. P. *Chemical Thermodynamics of Materials* (Prentice-Hall, New York, 1983).
3. Bergeron, C. G. & Risbud, S. H. *Introduction to Phase Equilibria in Ceramics* (American Ceramic Society, Westerville, OH, 1984).
4. Lindgren, B. & Ellis, D. E. Molecular Cluster Studies of Lial with Different Vacancy Structures. *Journal of Physics F-Metal Physics* [illegible], 1471-1481 (1983).
5. Carter, W. C. (2002).
6. Mortimer, R. G. *Physical Chemistry* (Academic Press, New York, 2000).