
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**.

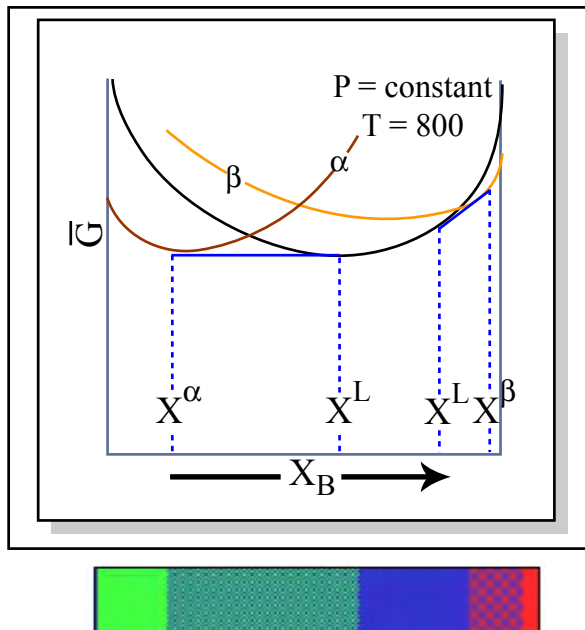
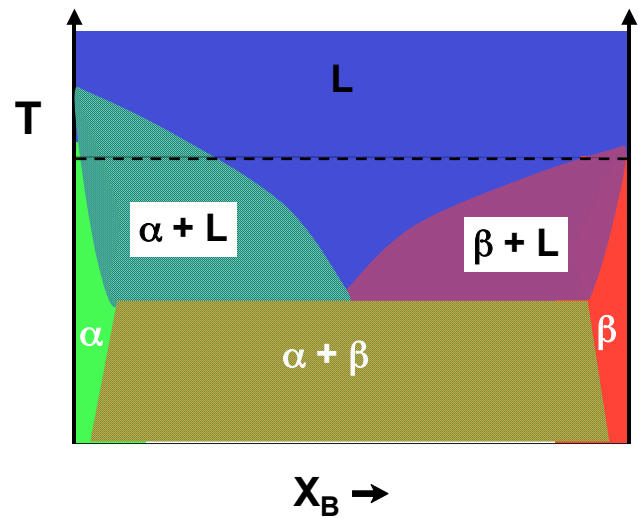


Figure by MIT OCW.



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:

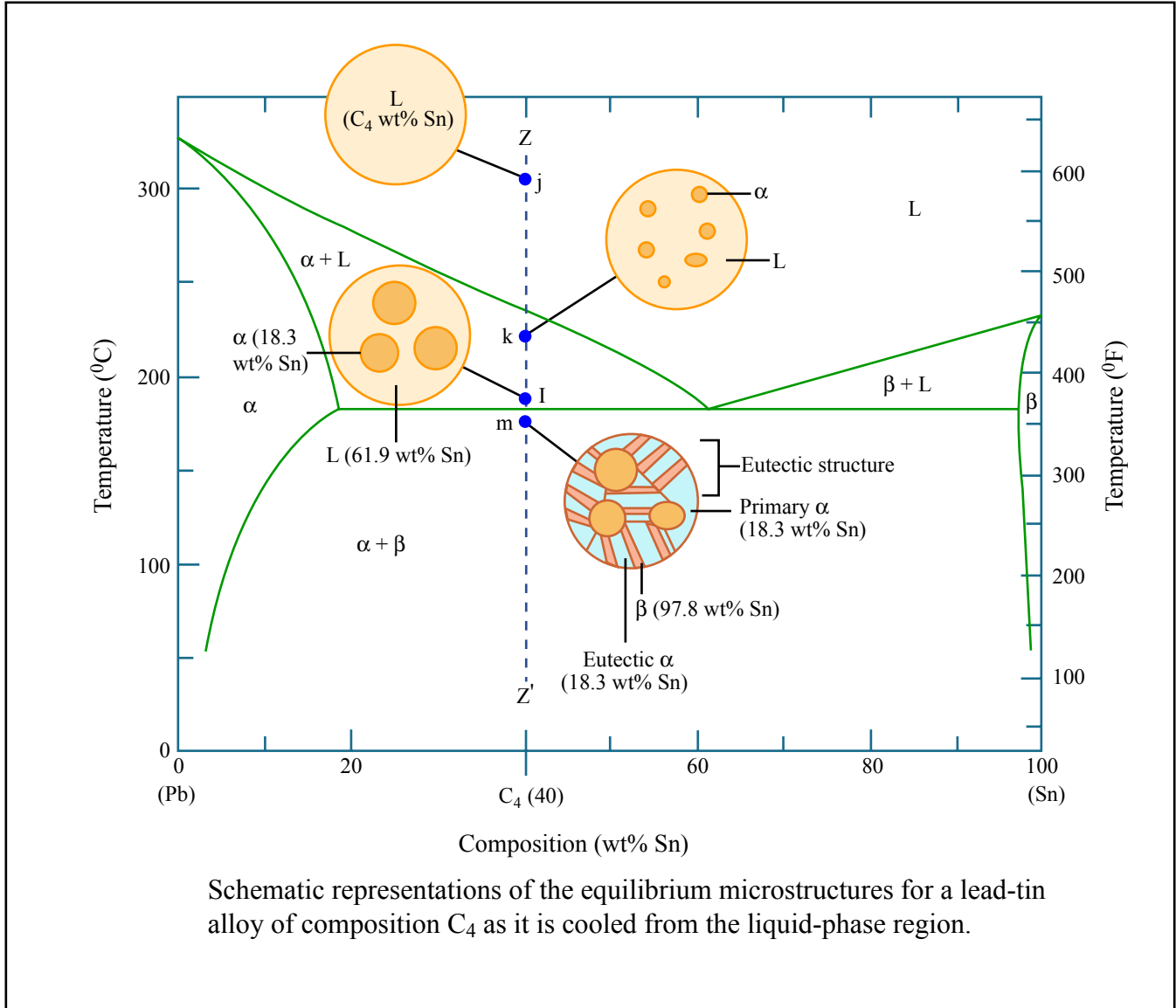


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Example eutectic systems

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

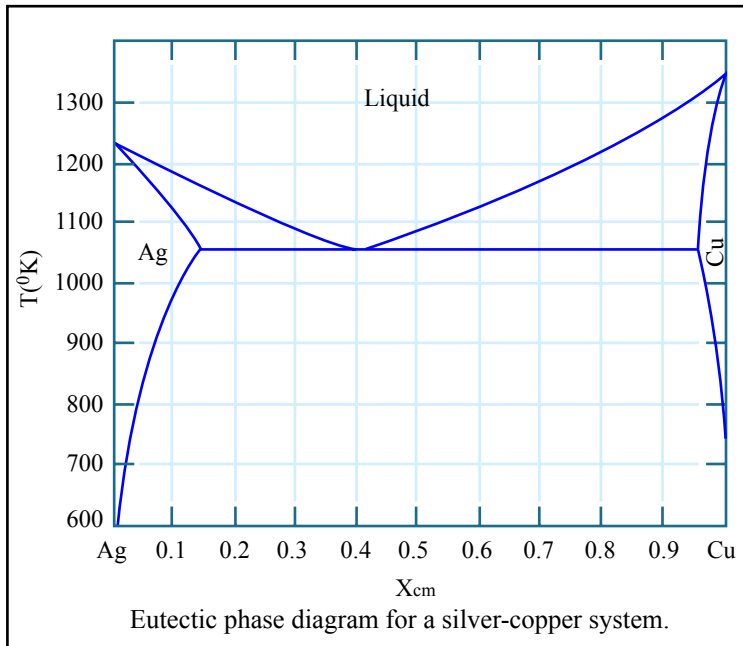


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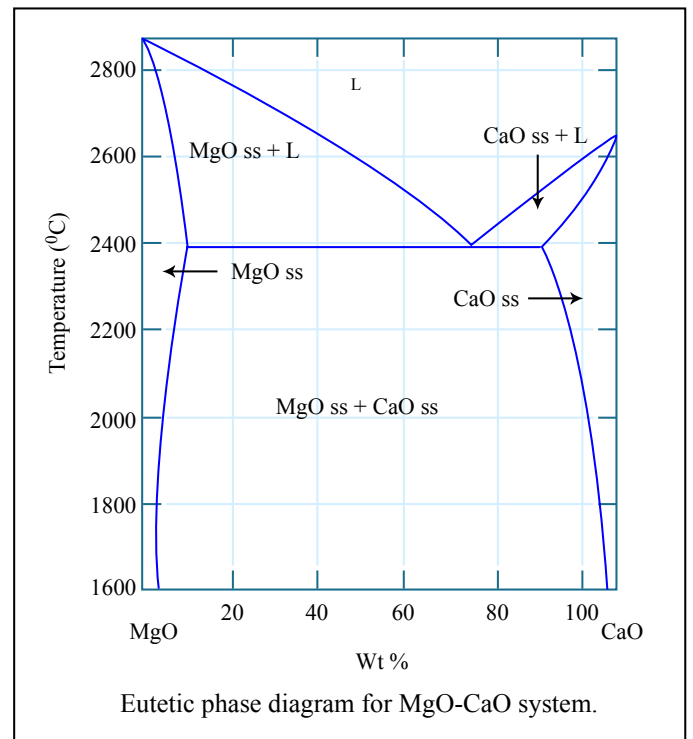


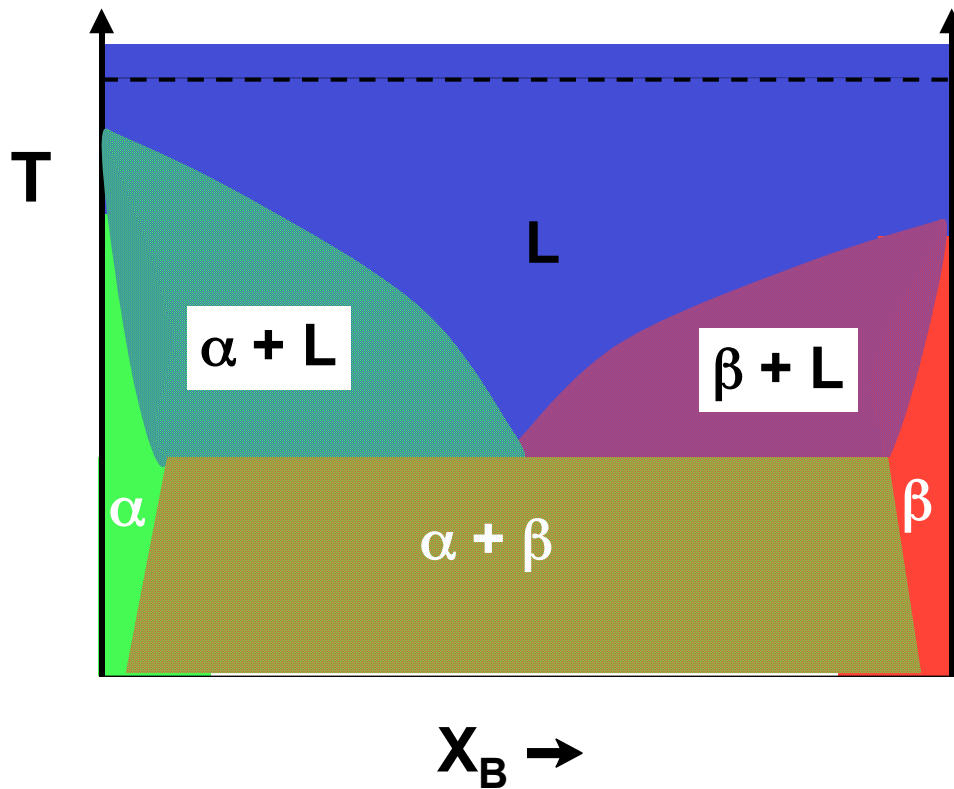
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- Eutectic phase diagrams are also obtained when the solid state of a solution has regular solution behavior (can you show this?)

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?



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: $L \leftrightarrow (\alpha + \beta)$ (upper two region is liquid)
 - Eutectoid: $\gamma \leftrightarrow (\alpha + \beta)$ (upper region is solid)
 - *One* 2-phase region splits into *two* 2-phase regions:
 - Peritectic: $(\alpha + L) \leftrightarrow \beta$ (upper two-phase region is solid + liquid)
 - Peritectoid: $(\alpha + \gamma) \leftrightarrow \beta$ (upper two-phase region is solid + solid)

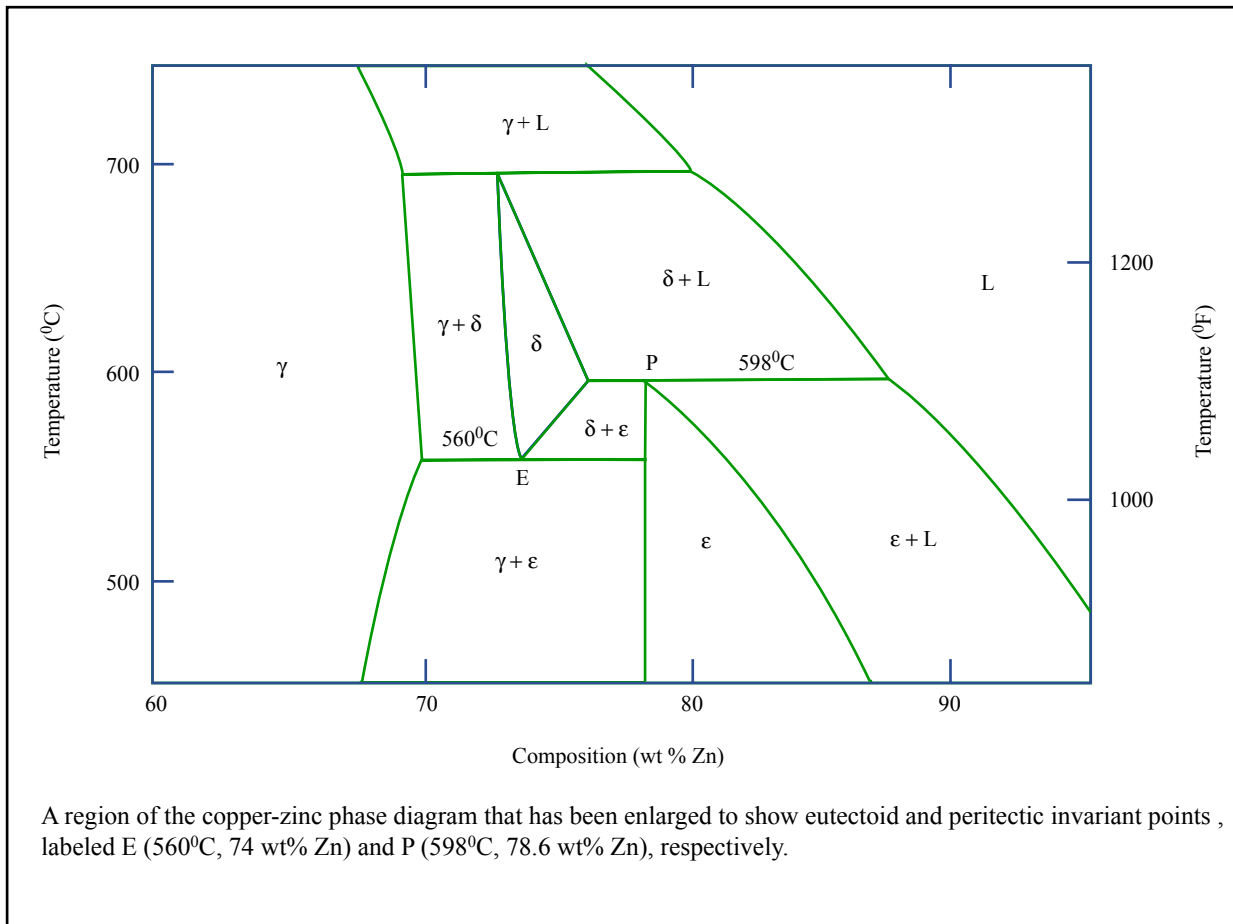
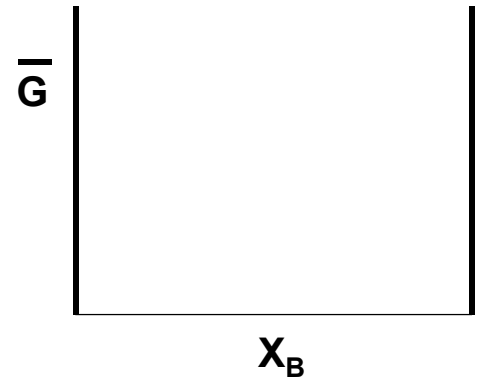
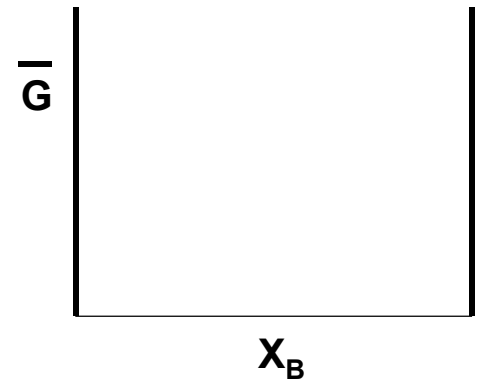
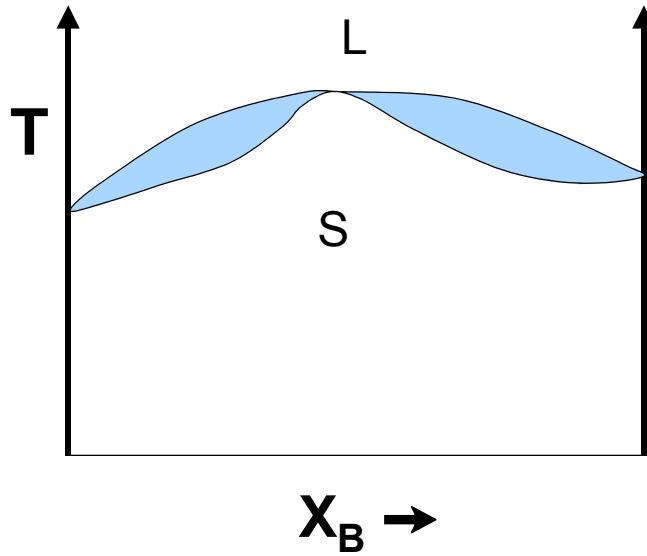


Figure by MIT OCW.

- 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 diagrams³

- 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**.

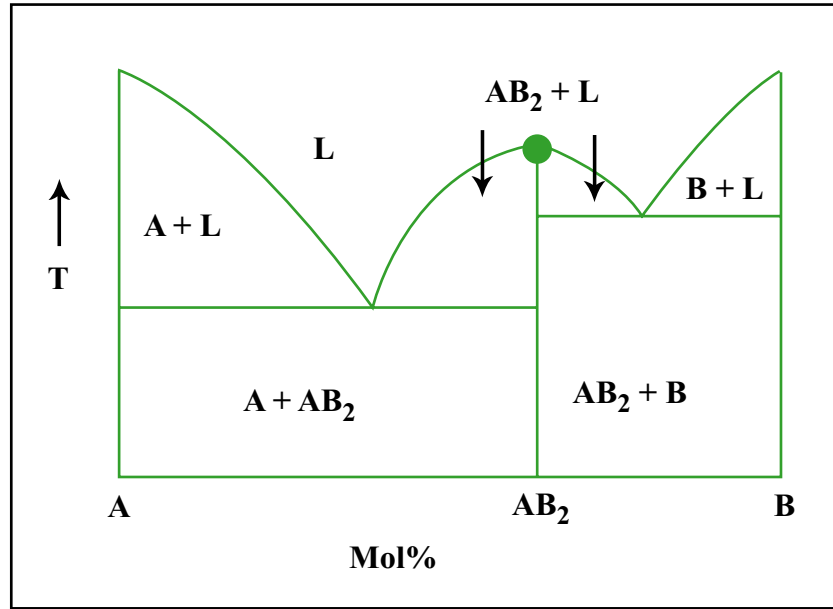


Figure by MIT OCW.

- 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-Al₂O₃:

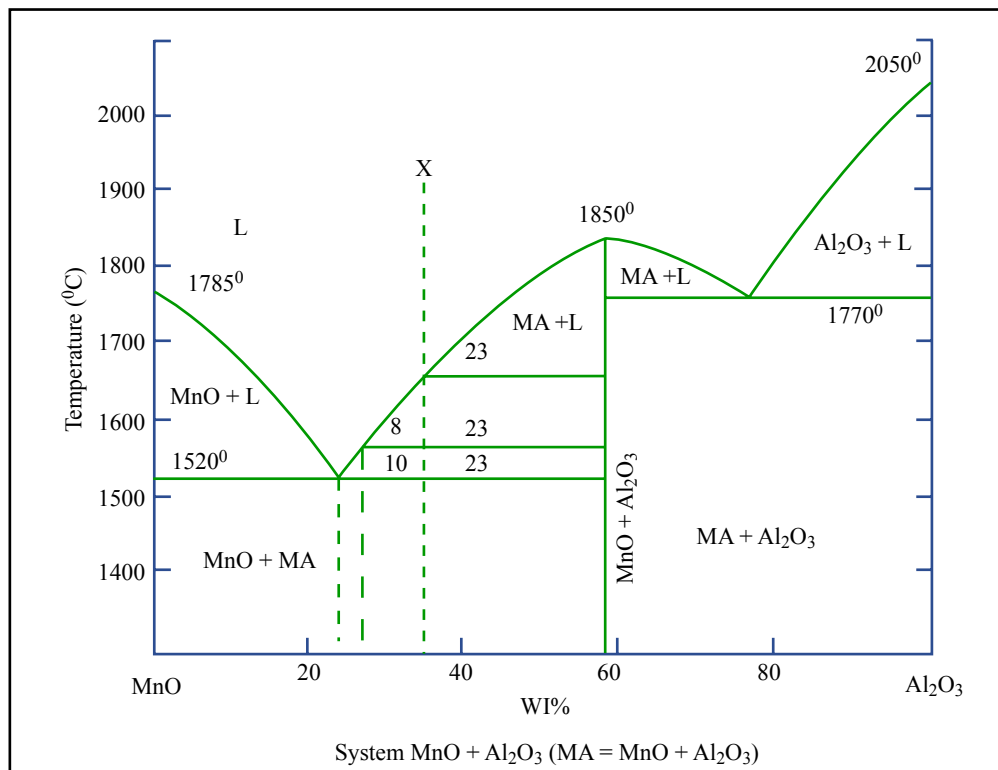


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Example binary phase diagrams

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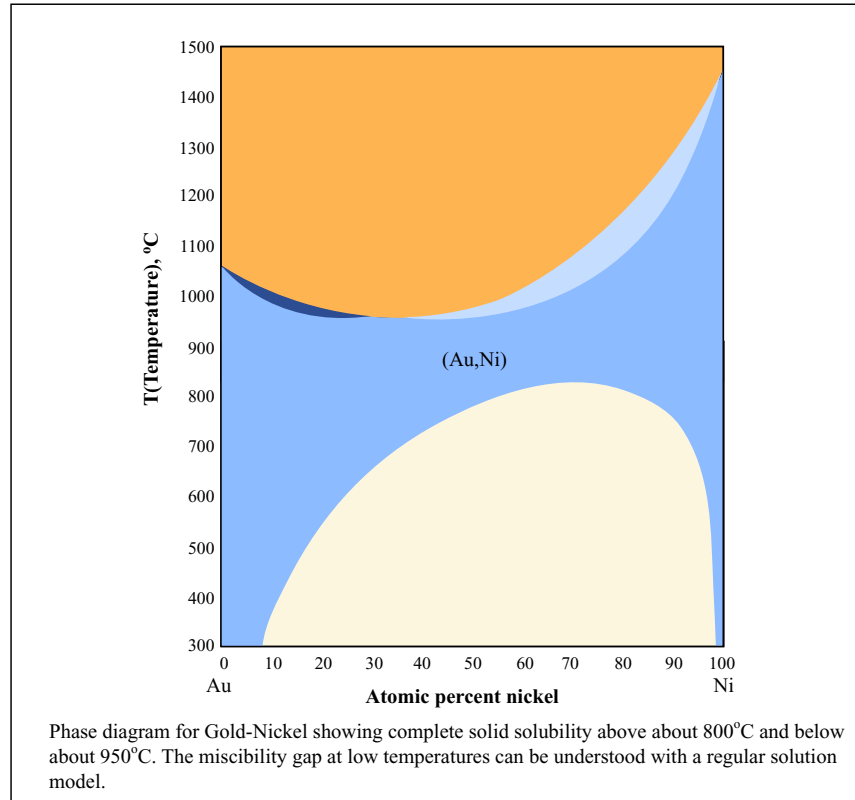
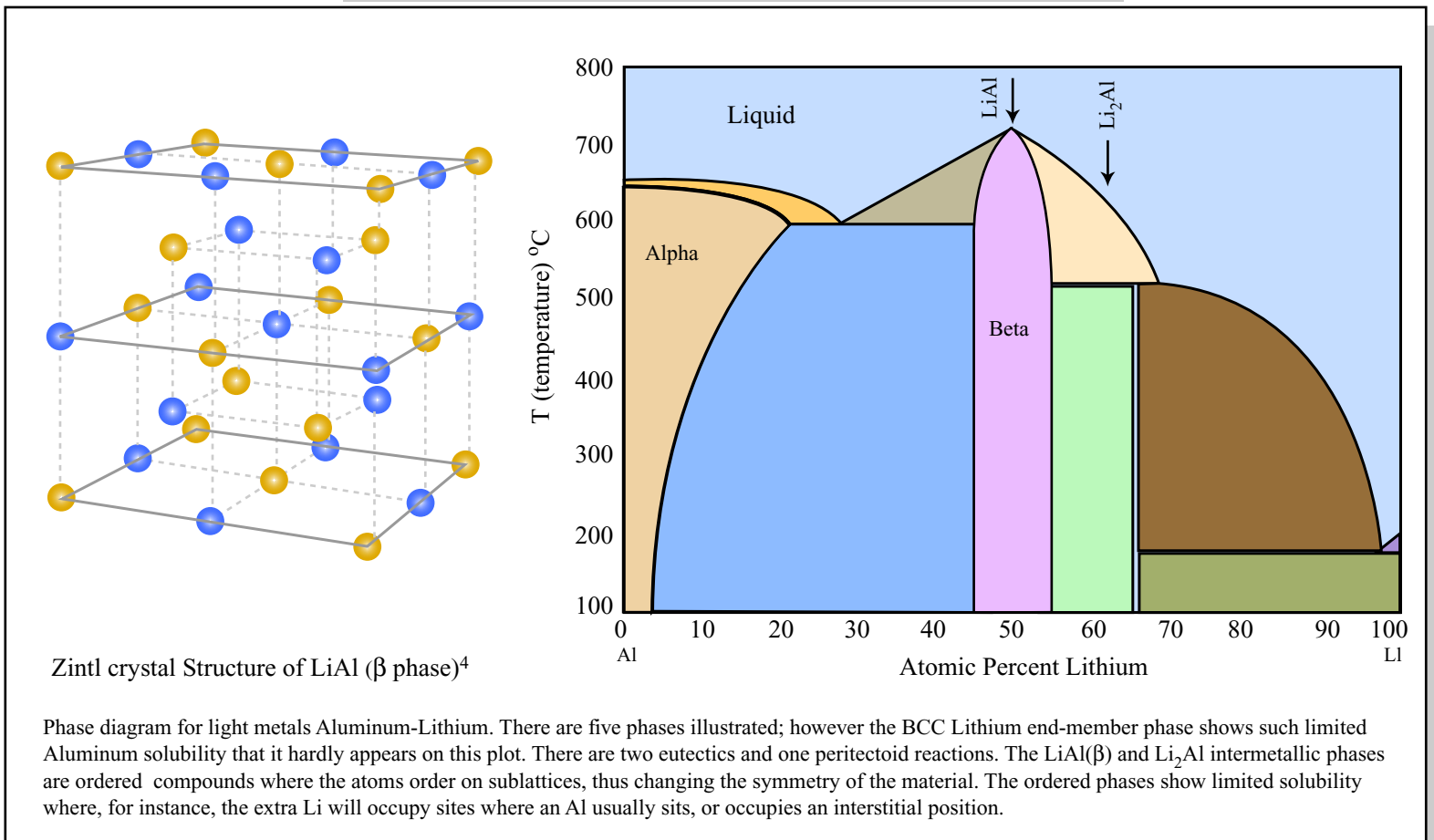


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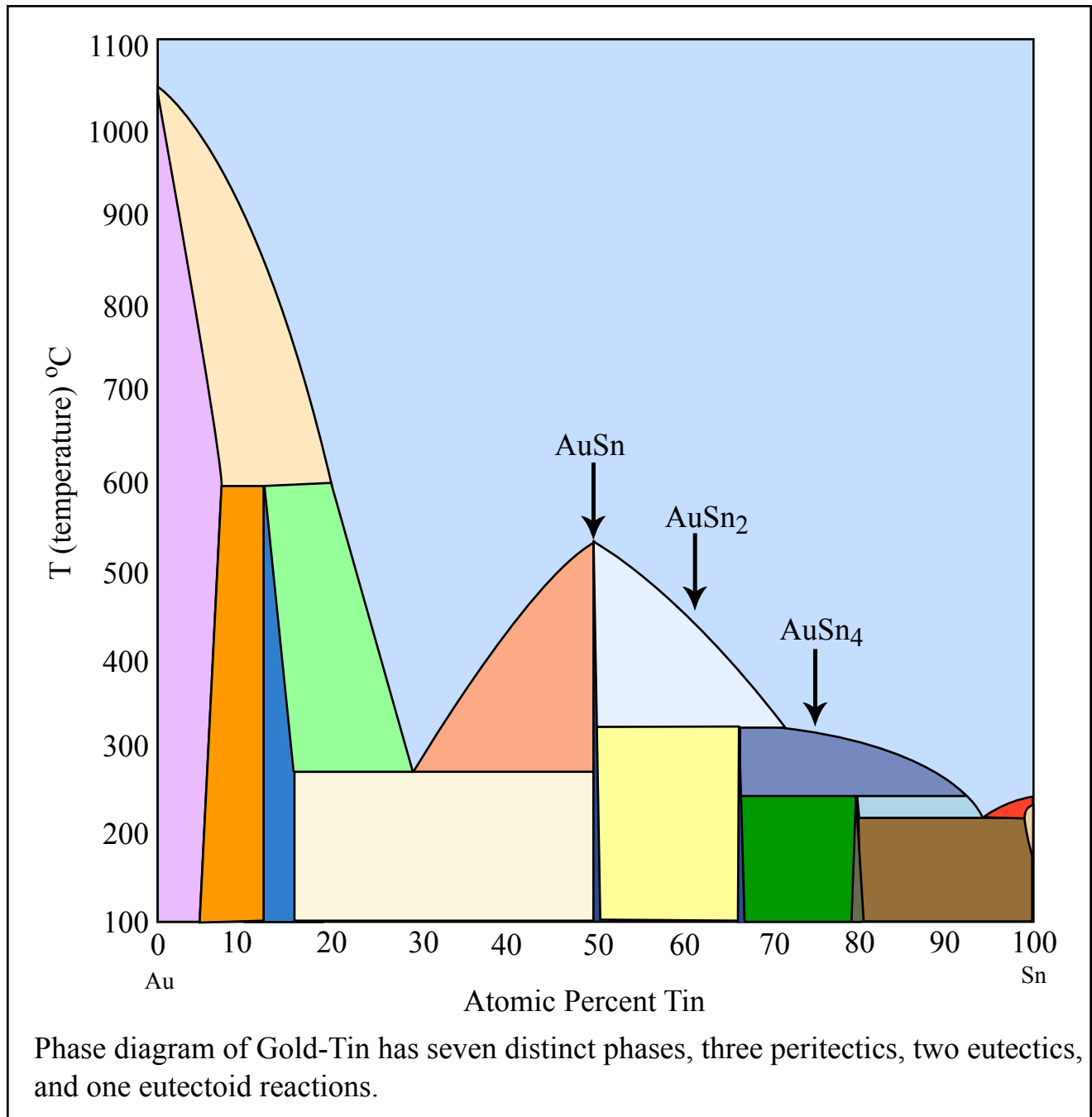


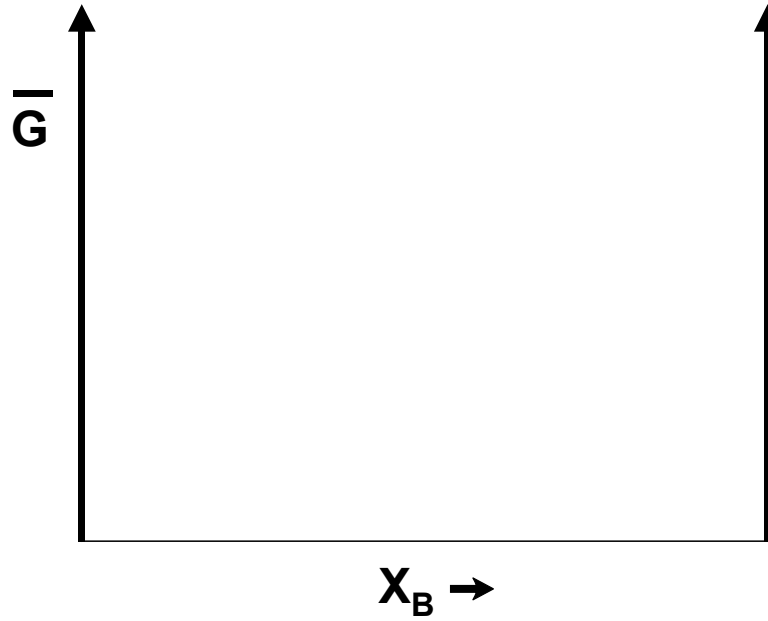
Figure by MIT OCW.

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



INSIDE SPINODAL: SYSTEM UNSTABLE
TO SMALL COMPOSITION
FLUCTUATIONS

OUTSIDE SPINODAL: SYSTEM STABLE
TO *SMALL* COMPOSITION
FLUCTUATIONS

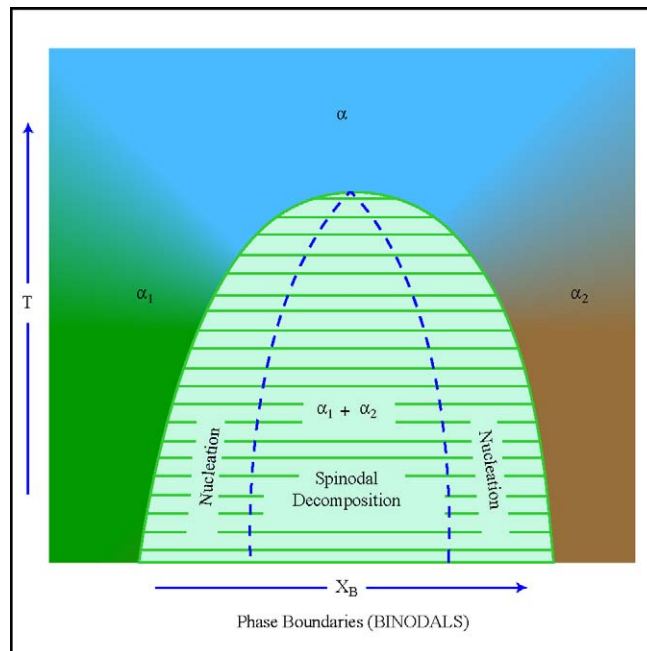
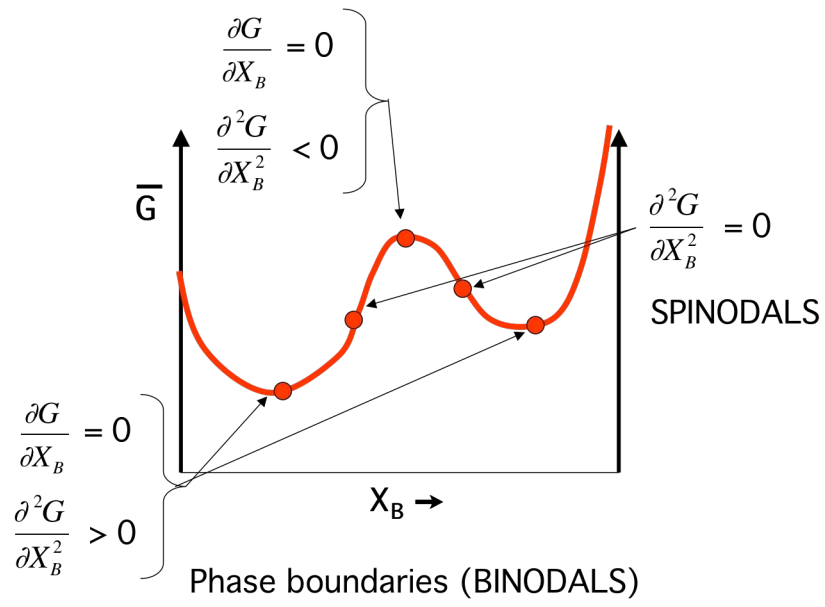


Figure by MIT OCW.

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:

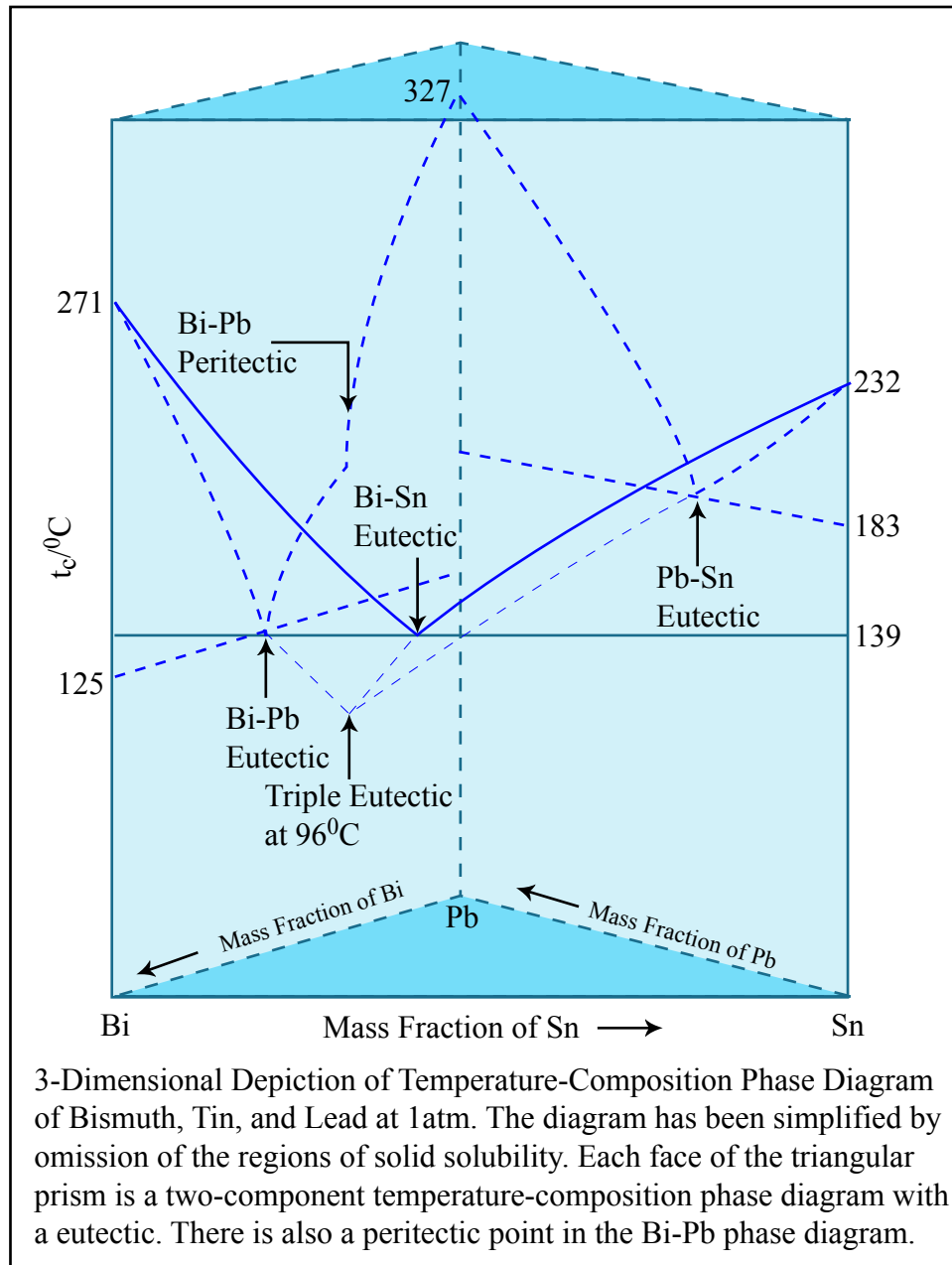
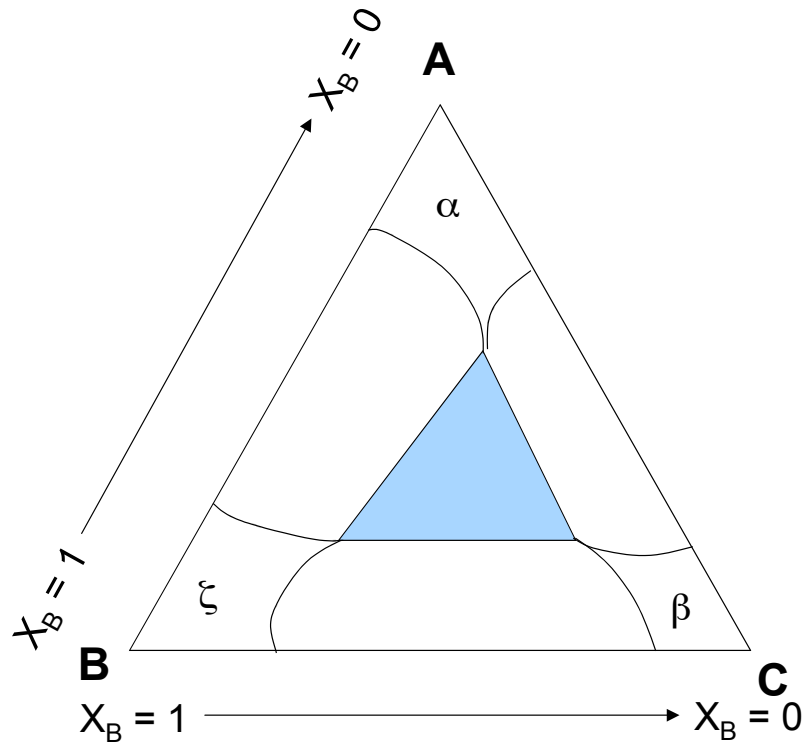


Figure by MIT OCW.

- 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:

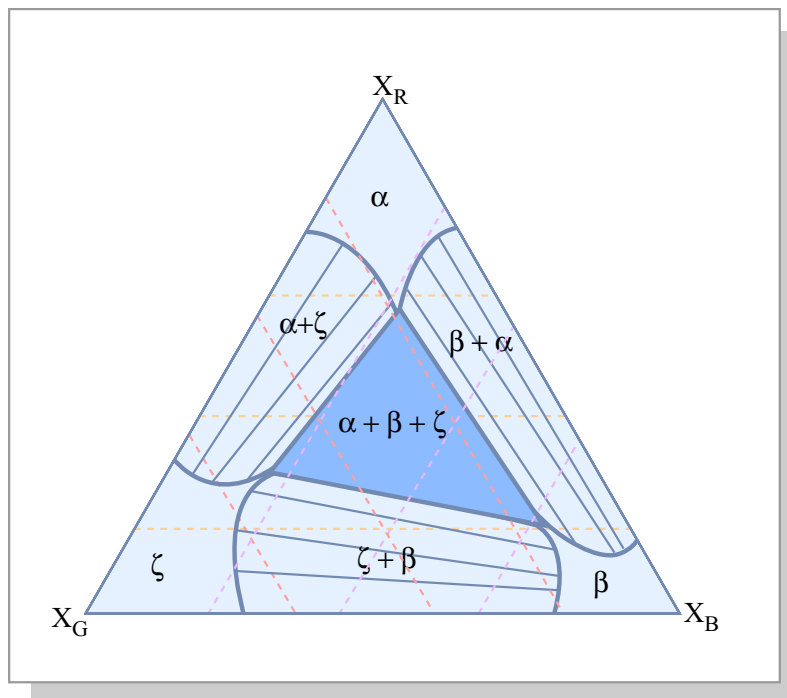


Figure by MIT OCW.

- 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

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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 Physical Chemistry*, 1471-1481 (1983).
5. Carter, W. C. (2002).
6. Mortimer, R. G. *Physical Chemistry* (Academic Press, New York, 2000).