THERMODYNAMICS

1. **Building a binary phase diagram**. Given below are data for a binary system of two materials A and B. The two components form three phases: an ideal liquid solution, and two solid phases α and β that exhibit regular solution behavior. Use the given thermodynamic data to answer the questions below.

LIQUID PHASE: ALPHA PHASE:

$$\left(\mu_A^o\right)^L = -500 - 4.8T\,\frac{J}{mole}$$ $$\left(\mu_A^o\right)^\alpha = -6000\,\frac{J}{mole}$$

$$\left(\mu_B^o\right)^L = -1,000 - 10T\,\frac{J}{mole}$$ $$\left(\mu_B^o\right)^\alpha = -1,000\,\frac{J}{mole}$$

(T is temperature in K) Ω = 8,368 J/mole

BETA PHASE:

$$\left(\mu_A^o\right)^\beta = -4,000 - 1.09T\,\frac{J}{mole}$$

$$\left(\mu_B^o\right)^\beta = -13,552 - 2.09T\,\frac{J}{mole}$$

(T is temperature in K)

Ω = 7,000 J/mole

a. Plot the free energy of L, alpha, and beta phases (overlaid on one plot) vs. X_B at the following temperatures: 2000K, 1500K, 1000K, 925K, and 800K. For each plot, denote common tangents and drop vertical lines below the plot to a 'composition bar', as illustrated in the example plot below. For each graph, mark the stable phases as a function of X_B in the composition bar below the graph, as illustrated in the example.

EXAMPLE:

T=2000 K

T=1000 K

T=1500 K

T=925 K

T=800 K
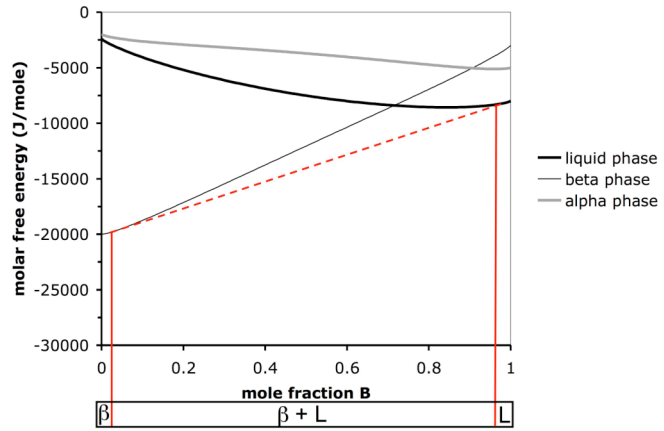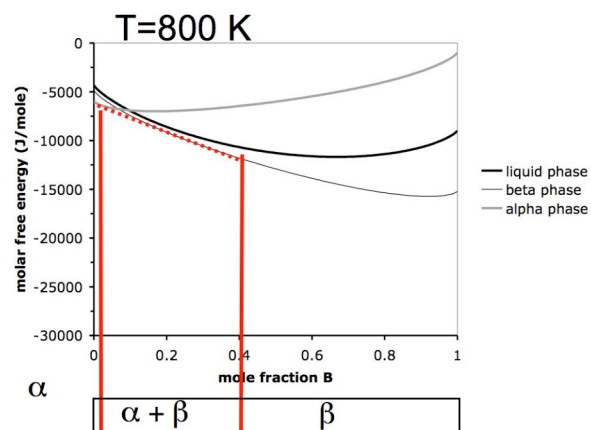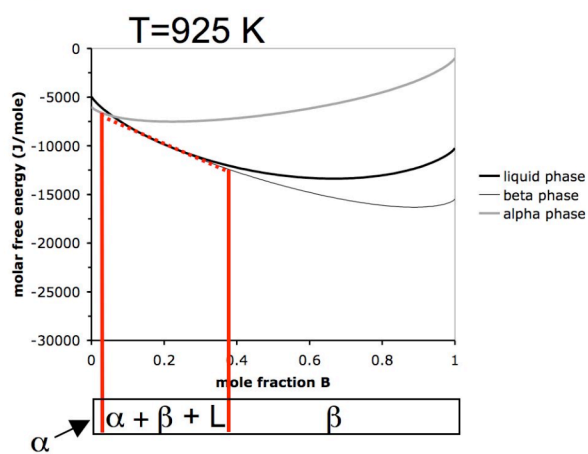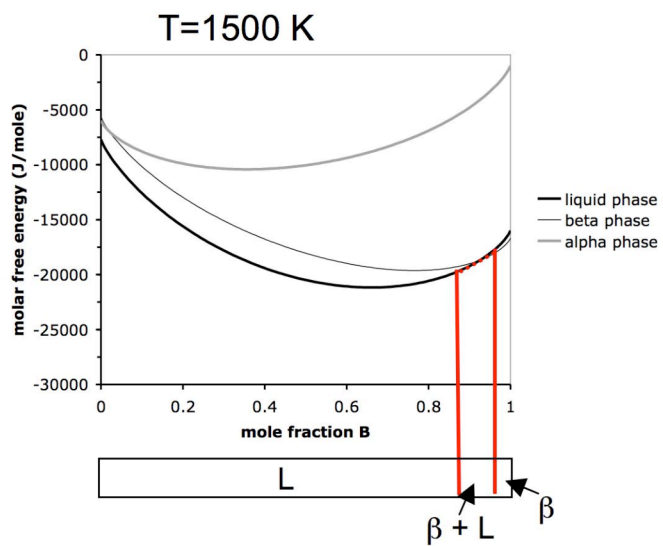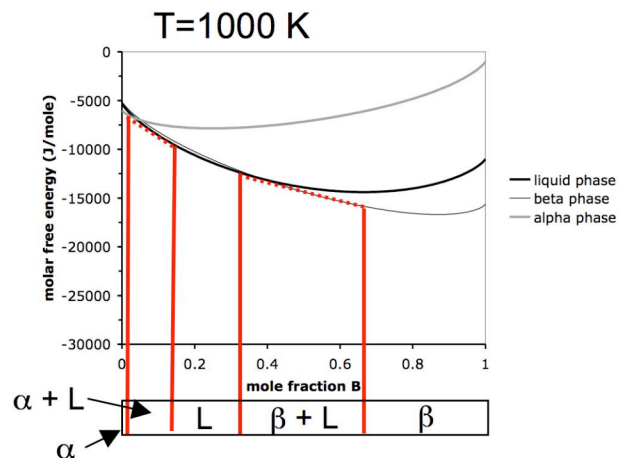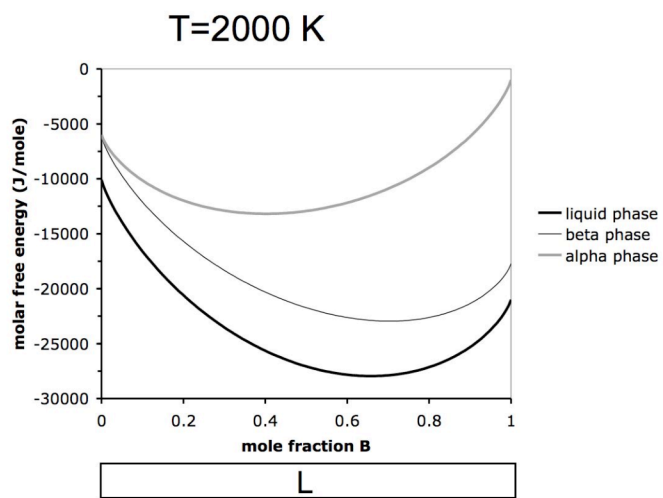
b. Using the free energy curves prepared in part (a), construct a qualitatively correct phase diagram for this system in the temperature range 800K – 2000K. Mark the invariant points on the diagram with a filled circle.
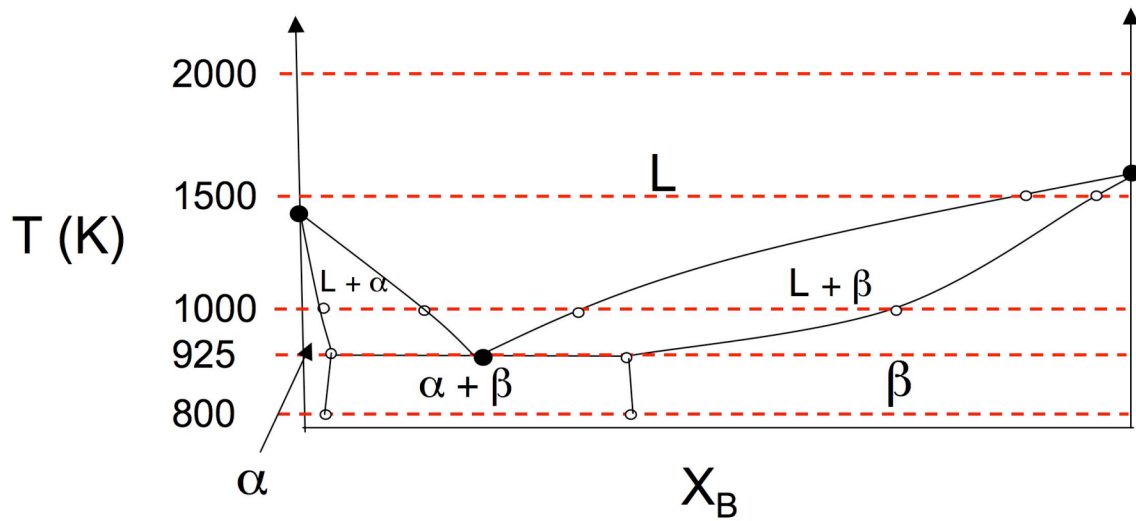
2. **Analyzing stable equilibria with binary phase diagrams.** Shown below is the phase diagram for the binary system MgO-Al$_2$O$_3$ at P = 1 atm. Use the diagram to answer the questions below.

   a. At T = 1750°C (broken line marked on diagram), what is the makeup of the system (what phases are present, what is the phase fraction of each phase, and what is the composition for each phase) at X_{Al2O3} = 0.2 and X_{Al2O3} = 0.6?

At : X_{Al2O3} = 0.2:

Phases present: periclase SS and spinel solid phases (determined by the location on the phase diagram)

Compositions: periclase: X_{Al2O3} = X^A ~ 0.05
                  Spinel: X_{Al2O3} = X^C ~ 0.45

Phase fractions: periclase: $f^{periclase} = \dfrac{X^C - X^B}{X^C - X^A} \approx \dfrac{0.45 - 0.2}{0.45 - 0.05} = 0.625$

                     Spinel: $f^{spinel} = \dfrac{X^B - X^A}{X^C - X^A} \approx \dfrac{0.2 - 0.05}{0.45 - 0.05} = 0.375$

At : X_{Al2O3} = 0.6:

Phases present: spinel solid phase (determined by the location on the phase diagram)
Compositions: Spinel: X_{Al2O3} = 0.6
Phase fractions: Spinel: $f^{spinel} = 1$

   b. Mark the invariant points on the diagram and label the type of each.

There are 5 invariant points on the diagram, as marked below- 2 eutectics and 3 congruent melting points (including the melting points of the pure compounds).

   c. Draw a qualitatively reasonable diagram of the molar free energy of each phase vs. X_{Al2O3} for T = 1750°C (overlay all of the curves on the same diagram). Mark the common tangents with a dashed line.
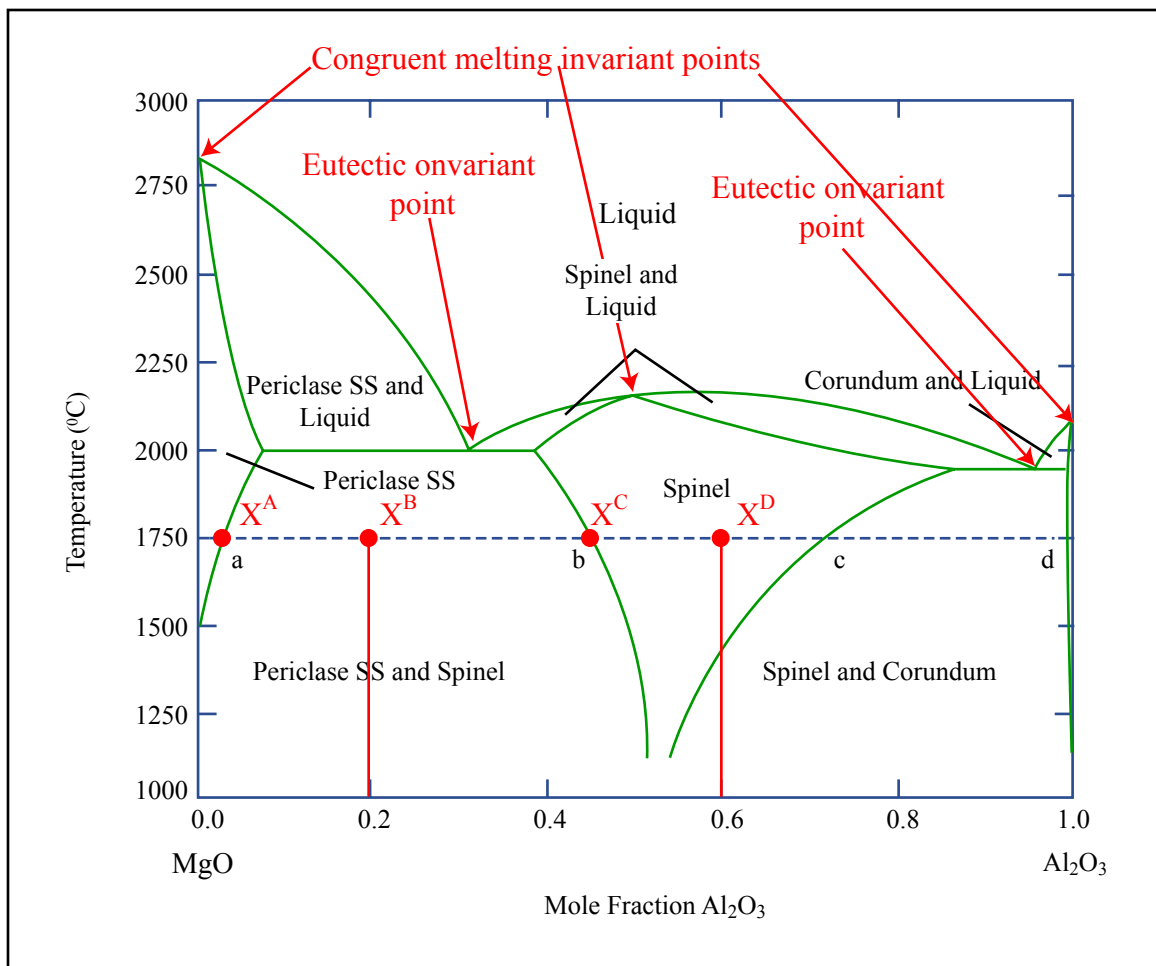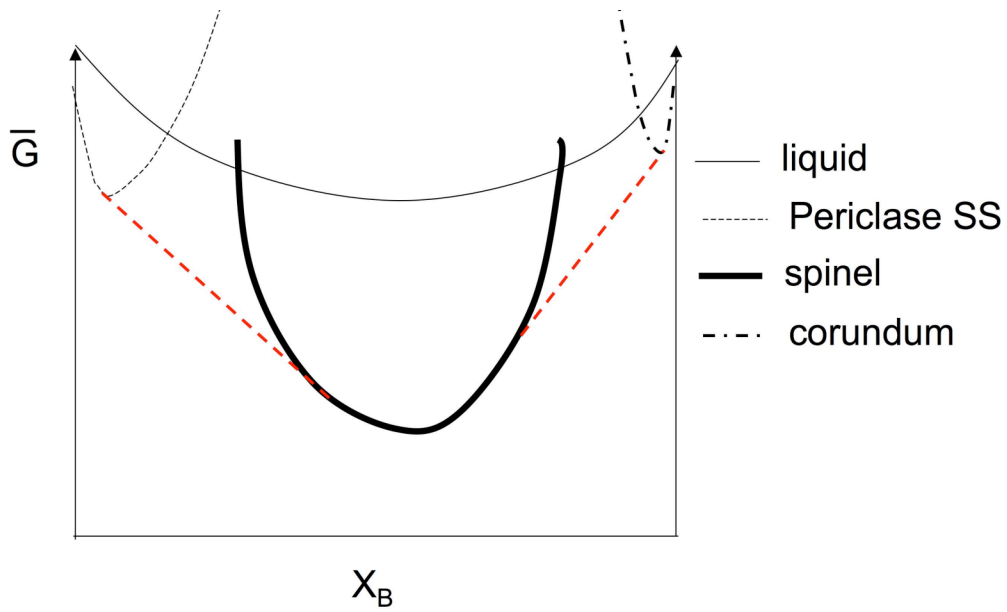
Figure by MIT OCW.

(Kingery, W. D., Bowen, H. K. & Uhlmann, D. R. Introduction to Ceramics (John Wiley, New York, 1976).)

3. **The structure of phase diagrams is not arbitrary**. Given below are two hypothetical structures for binary phase diagrams. Using sketches of Gibbs free energy curves vs. composition and/or a few brief sentences, explain why each of the proposed phase diagram structures is impossible.

   a. A solid phase alpha has a continuous boundary with liquid and no intervening two-phase (α + L) region:
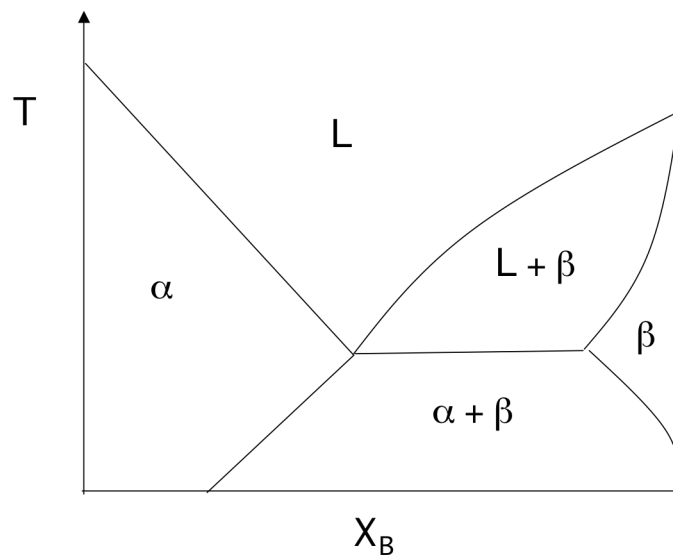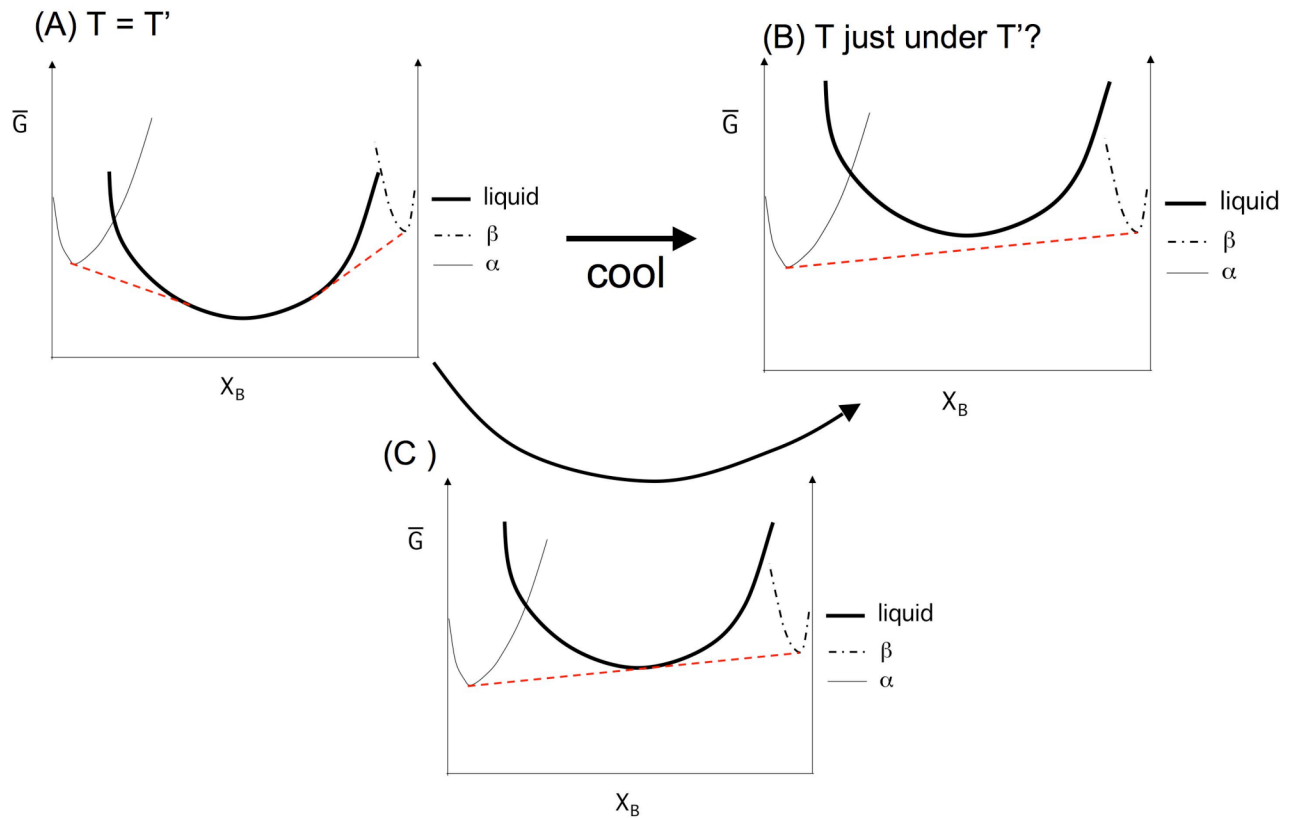

This phase diagram asks the question: why can't a congruent phase transition occur across a range of compositions in a binary system? Why must congruent transitions occur at a single point in composition space? As shown in the qualitative diagrams below, a congruent transition requires that the free energy curves of alpha phase and liquid have a single point in common and no common tangent; further, they must have a single point in common with no common tangent across a range of temperatures. Thus, as illustrated below, the free energy curves would have to shift with temperature perfectly in sync with one another. This is impossible since the liquid (high temperature stable phase) must have a greater entropy than the alpha phase (the low temperature stable phase)-- and thus the liquid curve must shift more rapidly with temperature than the alpha phase.
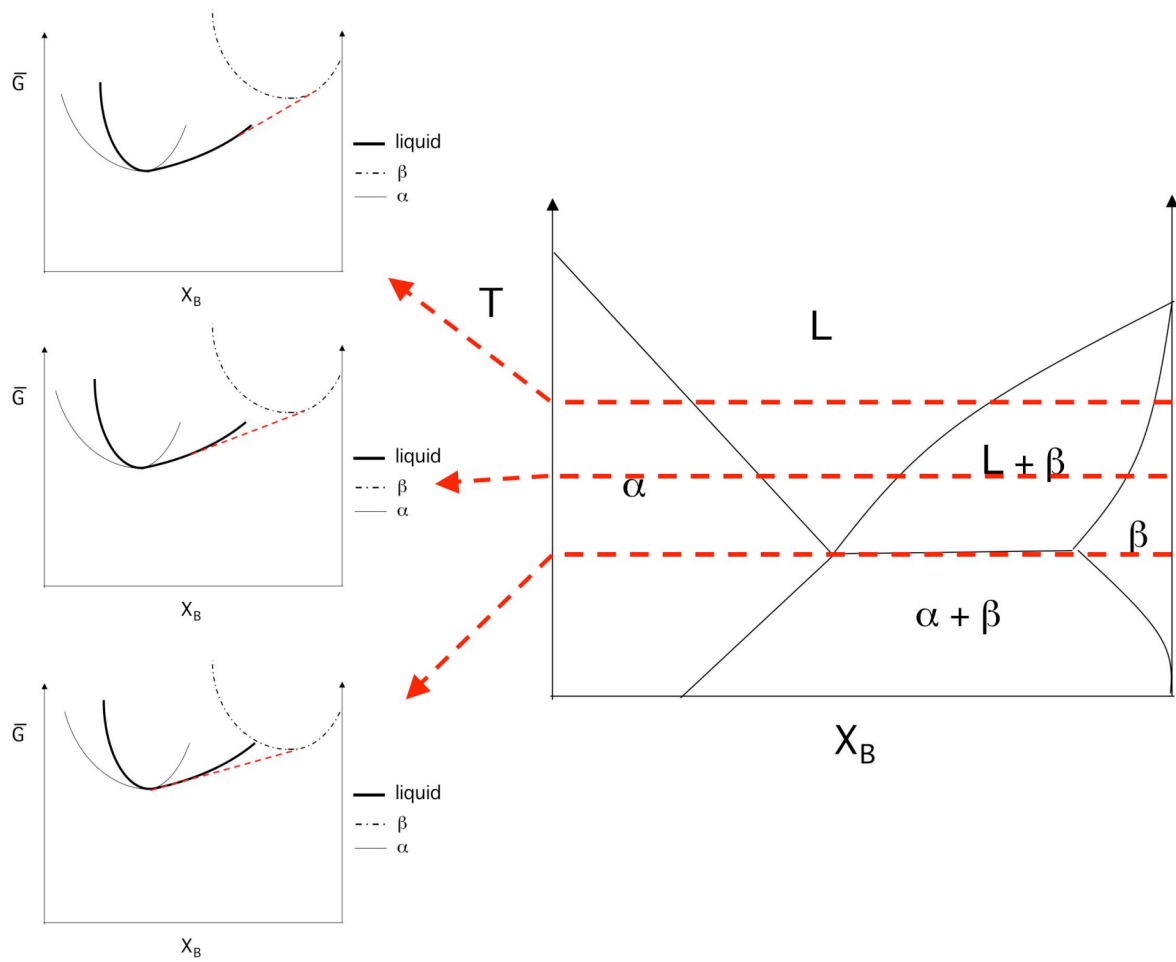
b. A diagram with a broad boundary between liquid and phase-separated α/β solids:
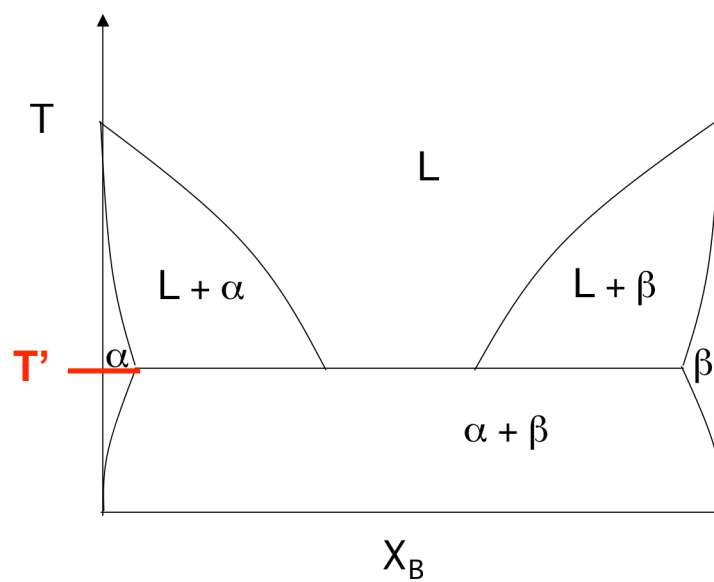
The phase diagram shown, where at one temperature (T') α + L and β + L flank a liquid-only region, and immediately below T' the equilibrium across this same region transforms to α + β only, requires free energy curves as illustrated below (A) and (B). However, because the free energies must move in a continuous manner (recall the shape of G vs. T), the curves cannot move from (A) to (B) without passing through an intermediate temperature where a common tangent across all three phases occurs at a single point (C)— a eutectic point.

(A) T = T'

$\overline{G}$

— liquid
-·- β
— α

X_B

cool

(B) T just under T'?

$\overline{G}$

— liquid
-·- β
— α

X_B

(C)

$\overline{G}$

— liquid
-·- β
— α

X_B

4. **Metastable and unstable systems**. Consider a regular solution with the following thermodynamic parameters:

$$\mu_A^o = -2,000 \frac{J}{mole}$$

$$\mu_B^o = -3,000 \frac{J}{mole}$$

$$\Omega = 8,500 \frac{J}{mole}$$

(Assume the standard state chemical potentials are approximately constant for this calculation.)

a. For a solution with a mole fraction B of 0.3 being cooled from elevated temperatures, at what temperature would phase separation first be observed (supposing the system is constantly re-equilibrating as the temperature is dropped)? *Hint: Your calculation is simplified by the fact that miscibility gap of simple regular solutions is symmetric about X_B = 0.5.*

Phase separation first occurs when the binodal (phase boundary) of the miscibility gap is crossed. Qualitatively:
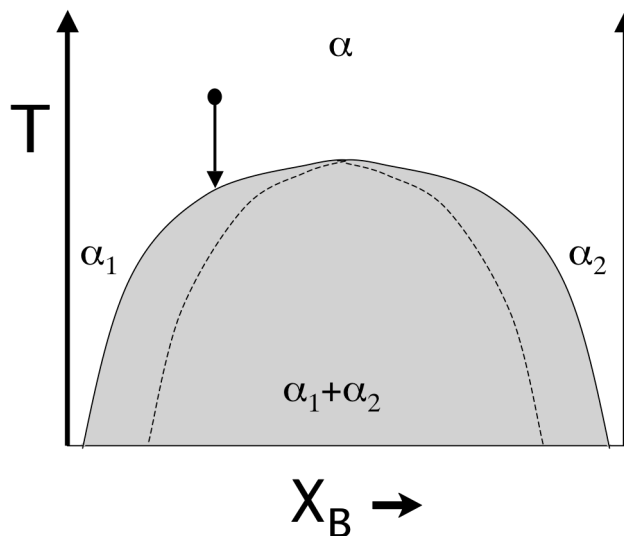
How do we identify the temperature at which this boundary sits for a solution with mole fraction B of 0.3? Because the system is a regular solution, the miscibility gap forms when the free energy assumes a common tangent with itself. The binodal lies at the compositions found at either end of the common tangent:
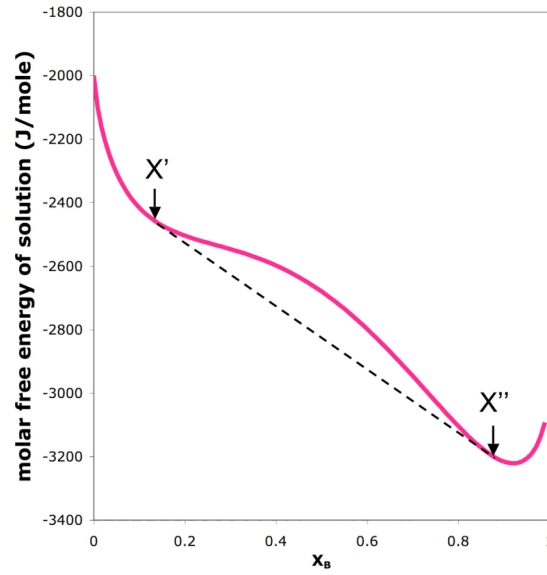
Thus, to find the binodal, we want to solve for the temperature at which the regular solution has a common tangent with itself, where one end of the common tangent is located at $X_B = 0.3$. Because, as hinted in the problem, the regular solution's shape is symmetric, the other end of the common tangent must lie at a composition symmetric to 0.3 about the central composition of $X_B = 0.5$—$X_B = 0.7$. Knowing the compositions we want, the common tangent is identified as the point where the slope of the free energy curve is the same at $X_B = 0.3$ and $X_B = 0.7$:

$$\left(\frac{\partial \overline{G}}{\partial X_B}\right)\Bigg|_{X_B=0.3} = \left(\frac{\partial \overline{G}}{\partial X_B}\right)\Bigg|_{X_B=0.7}$$

From lecture, we know that the regular solution free energy in terms of X_B is given by:

$$\overline{G}^{RS} = \mu_A^o X_B + \mu_A^o(1 - X_B) + \Omega X_B(1 - X_B) + RT\left[X_B \ln X_B + (1 - X_B)\ln(1 - X_B)\right]$$

Taking the first derivative with respect to X_B:

$$\left(\frac{\partial \overline{G}}{\partial X_B}\right) = \mu_B^o - \mu_A^o + \Omega - 2\Omega X_B + RT \ln \frac{X_B}{(1 - X_B)}$$

$$\left(\frac{\partial \overline{G}}{\partial X_B}\right)\Bigg|_{X_B=0.3} = \left(\frac{\partial \overline{G}}{\partial X_B}\right)\Bigg|_{X_B=0.7}$$

$$\mu_B^o - \mu_A^o + \Omega - 2\Omega(0.3) + RT \ln \frac{0.3}{(1 - 0.3)} = \mu_B^o - \mu_A^o + \Omega - 2\Omega(0.7) + RT \ln \frac{0.7}{(1 - 0.7)}$$

$$-2\Omega(0.3) + RT \ln \frac{0.3}{(1 - 0.3)} = -2\Omega(0.7) + RT \ln \frac{0.7}{(1 - 0.7)}$$

Simplifying the expression and solving for T, we find $T_{binodal}$ = 482 K. A plot of the free energy of the solution and the common tangent are shown below.
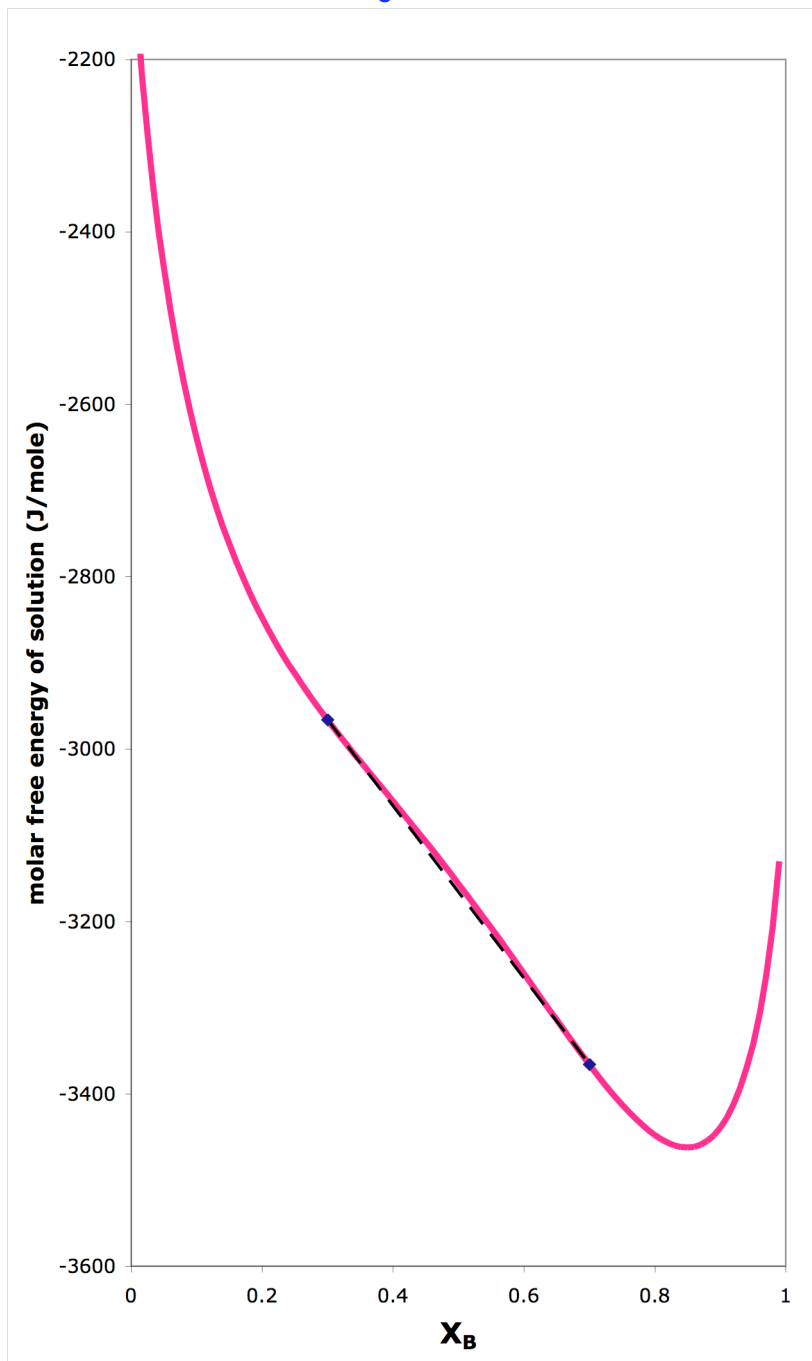
Note that as seen in the graphical view above, the common tangent formed for the regular solution free energy curve here does **not** connect two global (or even local) minima in the free energy-- i.e., the first derivative $\left(\dfrac{\partial \overline{G}}{\partial X_B}\right)\Big|_{X_B = 0.3} \neq 0$. We **are** however forming a common tangent between two

minima in the free energy **of mixing**: $\left(\dfrac{\partial \Delta \overline{G}^{mix}}{\partial X_B}\right)\bigg|_{X_B=0.3} = \left(\dfrac{\partial \Delta \overline{G}^{mix}}{\partial X_B}\right)\bigg|_{X_B=0.7} = 0$. This is illustrated in the free energy of mixing plot shown below for the same system shown above. Why are the two plots different? The free energy of mixing does not contain the contribution to the free energy from the standard state conditions, μ_A^o and μ_B^o, while these two terms provide the 'cant' to the free energy of solution curve. Why would an equilibrium phase separated state (identified by the common tangent on the free energy plot above) be comprised of two phases with free energies that are **not** local or global minima with respect to composition? Answer: **Because the composition is not free to move arbitrarily in a closed system**. For a sample with a composition between the ends of the common tangent (e.g., $X_B = 0.5$), if the system phase separates to lower its free energy, it must do so while maintaining a total composition of $X_B = 0.5$—because the only physical event occurring in this process is rearrangement of A and B molecules into the two separate phases. The **net** amount of A and B in the whole system must remain constant. Under this constraint, the lowest free energy achievable derives from a linear mixture of two phases with compositions denoted by the ends of the common tangent. Note that the common tangent satisfies the requirement that the chemical potentials of A and B are the same in each phase.
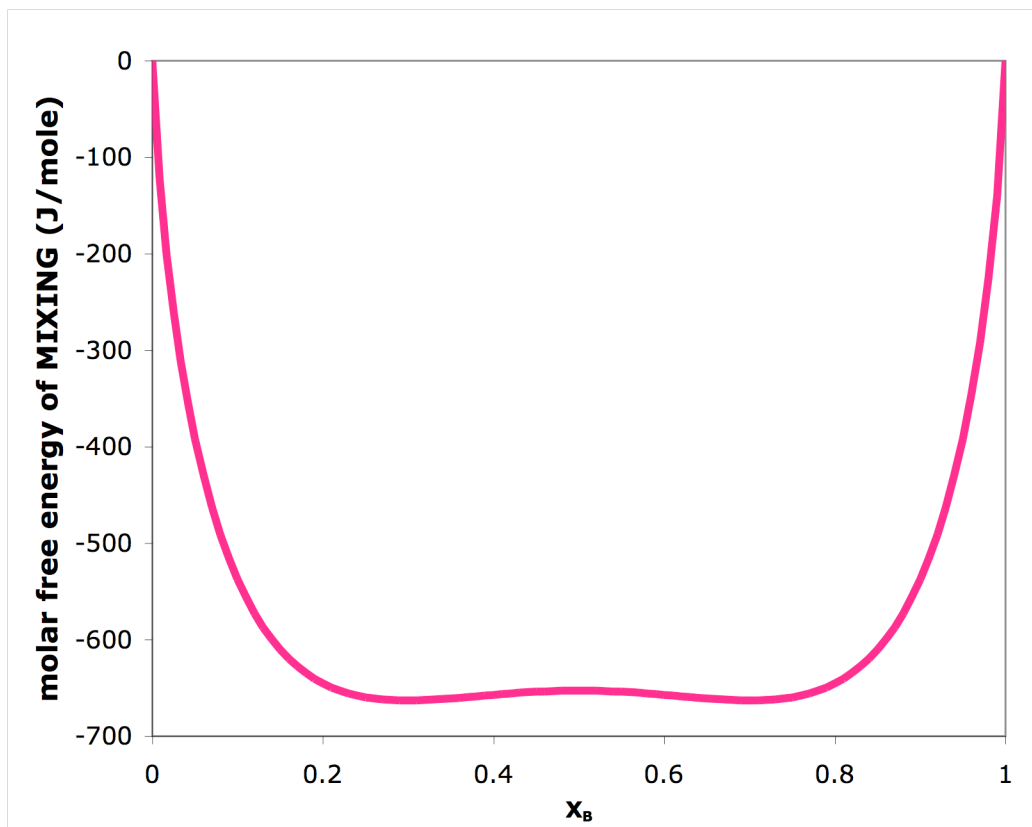
b. The mode of phase separation in a system (nucleation and growth vs. spinodal decomposition) can be controlled by quenching (rapidly cooling) a system from a homogeneous high-temperature state to a temperature where one mode of phase separation or the other will be operable. What is the lowest temperature that this solution with a mole fraction B of 0.3 could be quenched to and still phase separate by a nucleation and growth mechanism?

The nucleation and growth mechanism of phase separation occurs in the region of the phase diagram between the binodal and spinodal boundaries:
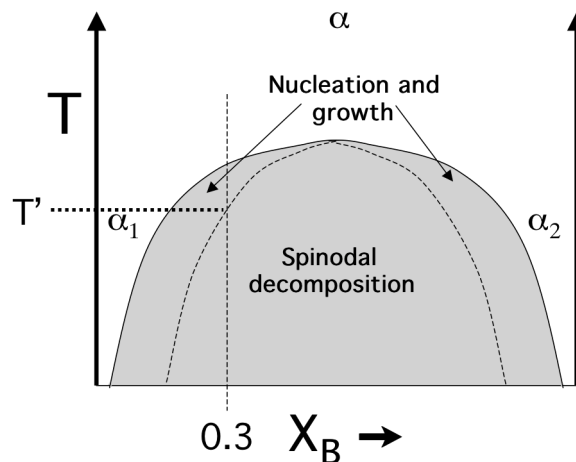
At X_B = 0.3, T' in the above diagram is the minimum temperature where the system can be quenched to obtain nucleation and growth; below this temperature spinodal decomposition will be favored. This minimum temperature coincides with the location of the spinodal boundary. To determine T' for this particular composition, we solve for the location of the spinodal: the temperature where the second derivative of the free energy goes to zero. The spinodals are defined by the saddle points in the 'hump' of the regular solution free energy curve. We determined the first derivative of G with respect to X_B above. The second derivative is:

$$\left(\frac{\partial^2 \overline{G}}{\partial X_B^2}\right) = -2\Omega + RT\left[\frac{1}{X_B} + \frac{1}{(1-X_B)}\right] = 0$$

$$-2(8500) + (8.3144)T\left[\frac{1}{0.3} + \frac{1}{(1-0.3)}\right] = 0$$

$$T_{spinodal} = 429K$$

5. **Peritectic phase diagrams**. Use the given phase diagram for the binary system of copper and cobalt to answer the questions below.
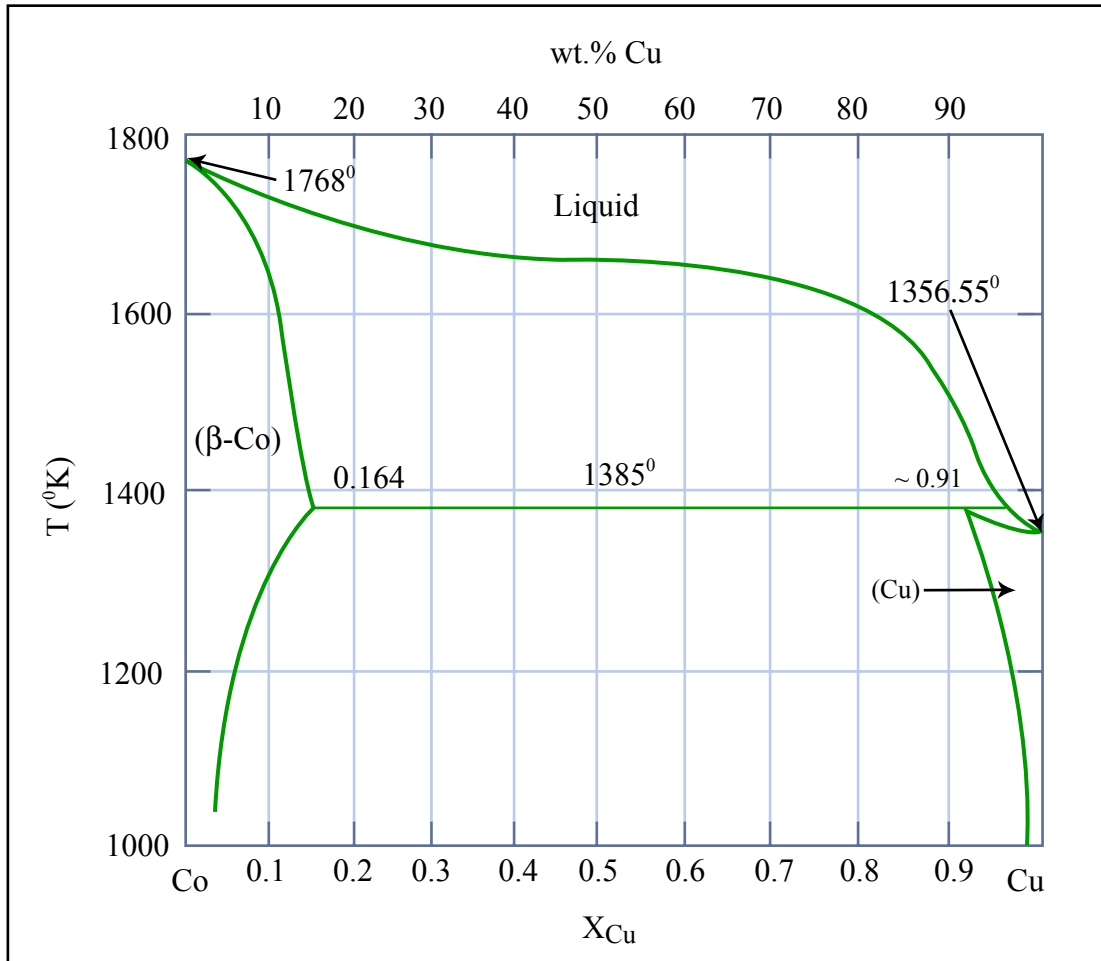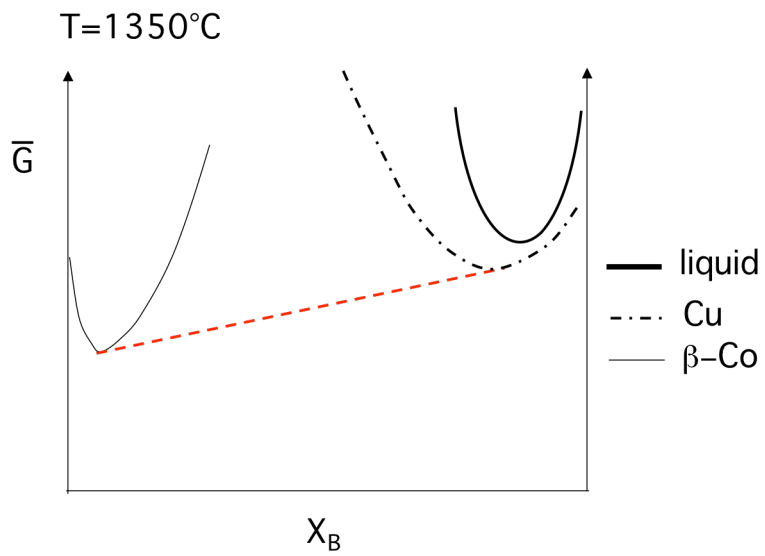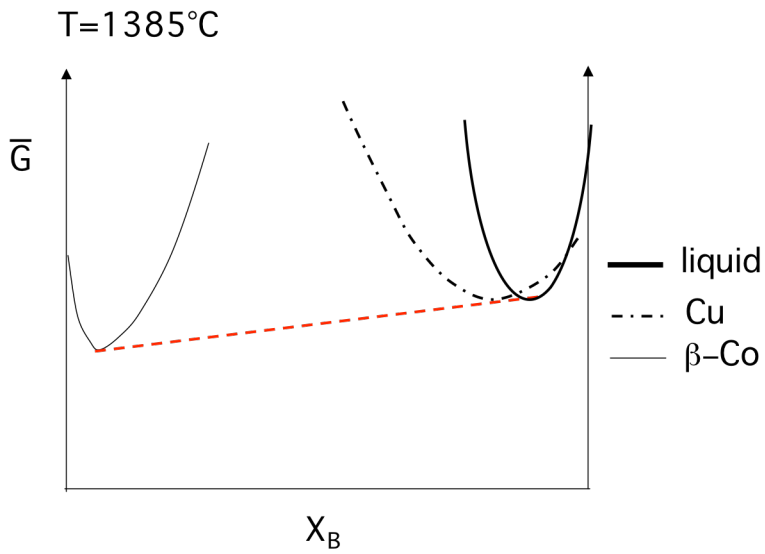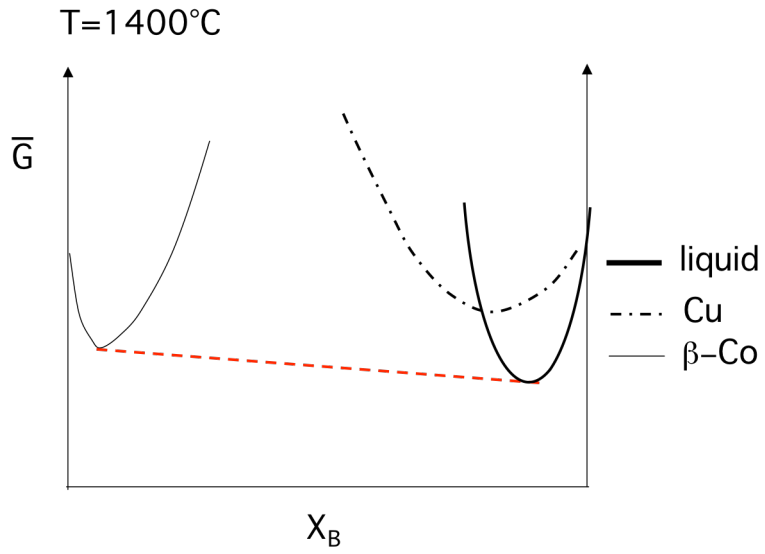

Figure by MIT OCW.

(Lupis, C. H. P. Chemical Thermodynamics of Materials (Prentice-Hall, New York, 1983)

a. Draw a reasonable set of free energy curves for each phase of the Cu-Co system at 1400°C, the peritectic temperature of 1385°C, and just below the peritectic at 1350°C.

T=1400°C

$\overline{G}$

X_B

liquid
Cu
β−Co

T=1385°C

$\overline{G}$

X_B

liquid
Cu
β−Co

T=1350°C

$\overline{G}$

X_B

liquid
Cu
β−Co

Note that the highly off-center shapes of the minima in these free energy curves often occur because the phases of the system exhibit regular solution behavior (i.e., the minima are one of the two 'wells' of the free energy of a regular solution below its critical temperature)—examples of such free energy curves are shown in your reading from the text by Lupis on binary phase diagrams.

      b. Suppose a solution with 50 mole% Cu were cooled to 1400°C and equilibrated, then further cooled to 1200°C. How much "primary" β-Co phase would be present in the final sample (mole fraction)? How much *total* β-Co phase would be present in the final sample (mole fraction)?

The total amount of β-Co phase present at 1200°C Is determined from applying the lever rule to a tie line connecting the phase boundaries at this temperature:
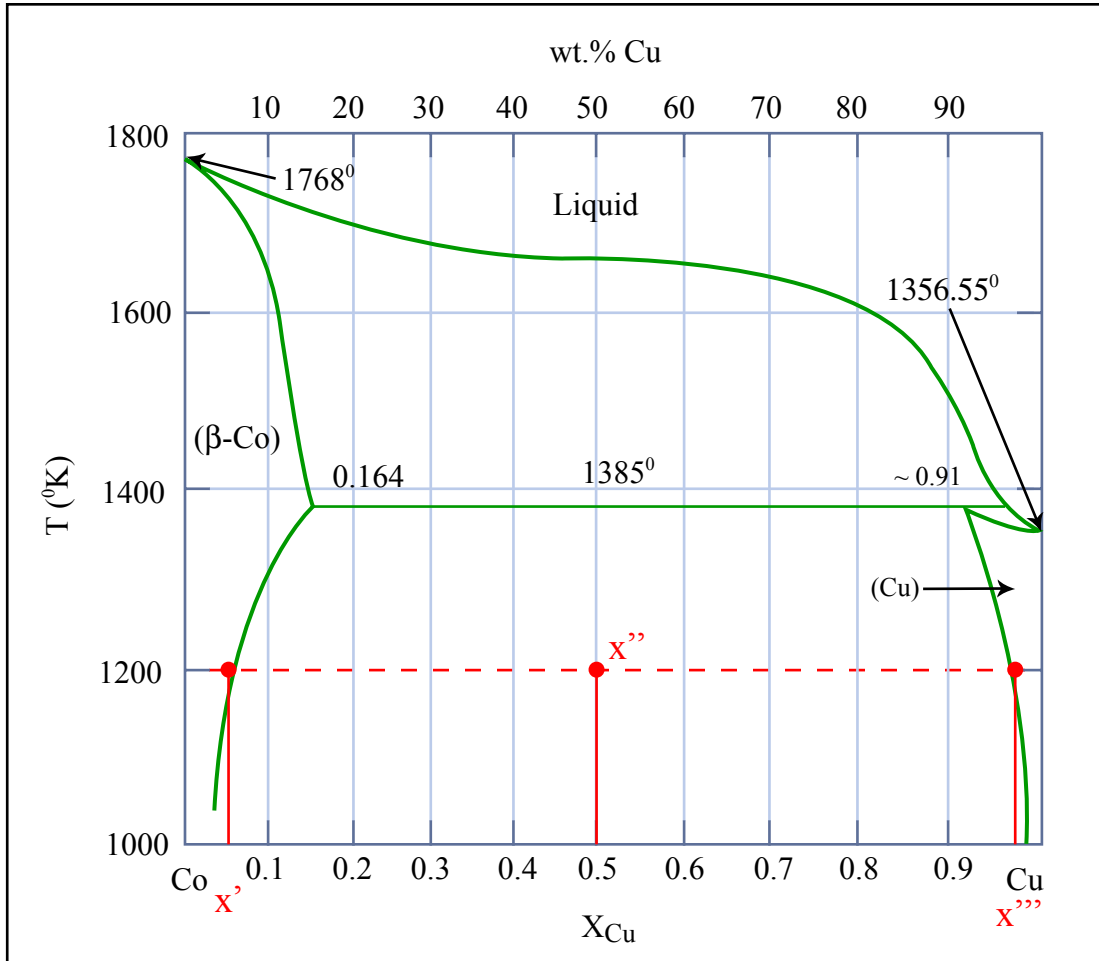

Figure by MIT OCW.

$$f^{\beta - Co} = \frac{X''' - X''}{X''' - X'} \cong \frac{0.98 - 0.5}{0.98 - 0.05} = 0.52$$

The amount of 'primary' β-Co is a more subtle question: Note that as the sample is cooled from high temperature to the peritectic temperature, the amount of 'primary' β-Co—that portion which formed during the first solidification in the L + β-Co two-phase field is actually reduced: part of the primary β-Co is consumed (along with all of the liquid) to form the solid Cu phase at the peritectic temperature. Once cooled past the peritectic, the amount of β-Co only changes very slowly and slightly (according to the gently sloping boundaries on either side of the two-phase β-Co + Cu field. Thus to

first order, we could consider **all** of the β-Co remaining at 1200°C to be 'primary' material originally formed during the initial solidification above the peritectic temperature.