Lecture 17: 11.07.05 Free Energy of Multi-phase Solutions at Equilibrium

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Reading: Lupis, *Chemical Thermodynamics of Materials*, Ch 8 'Binary Phase Diagrams,' pp. 196-203

Supplementary Reading: -

ANNOUNCEMENTS:

UPCOMING EXAM:

BONDING/STRUCTURE REVIEW: THURS. 11/10 7pm–9ish

THERMO REVIEW: TBD (DISCUSS AT RECITATION TOMORROW);
W OR SUNDAY

THERMO COVERAGE: LECTURES 9–16

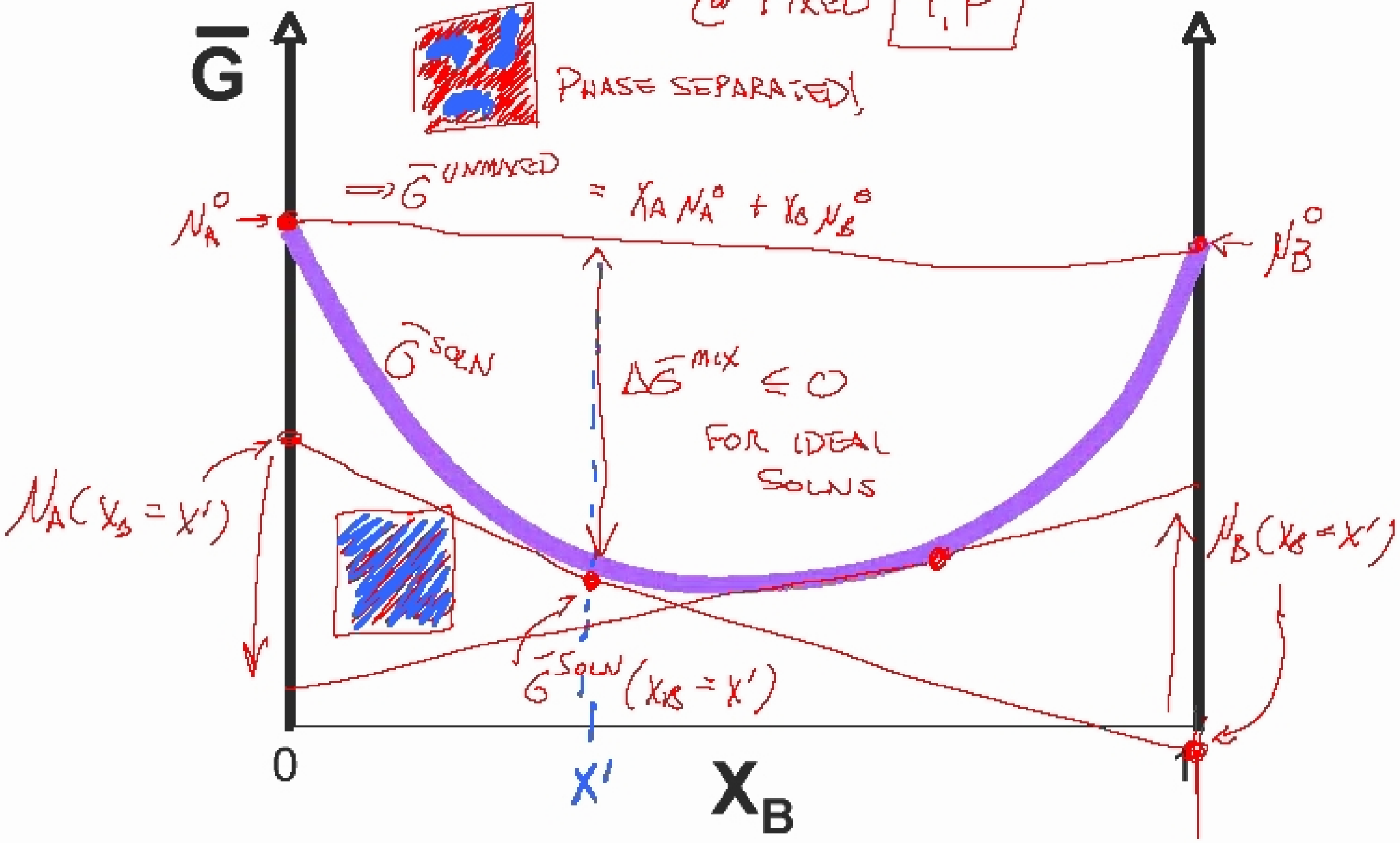
Last time

IDEAL SOLUTIONS:

$$\bar{G}^{\text{SOLUTION, ID}}(X_B, T) = (1-X_B)\left[\mu_A^\circ(T) + RT\ln(1-X_B)\right] + X_B\left[\mu_B^\circ(T) + RT\ln X_B\right]$$

$$\Delta\bar{G}^{\text{MIX}} = \bar{G}^{\text{SOLN, ID}} - \bar{G}^{\text{UNMIXED}} = RT\left[(1-X_B)\ln(1-X_B) + X_B\ln X_B\right]$$

@ FIXED $\boxed{T, P}$



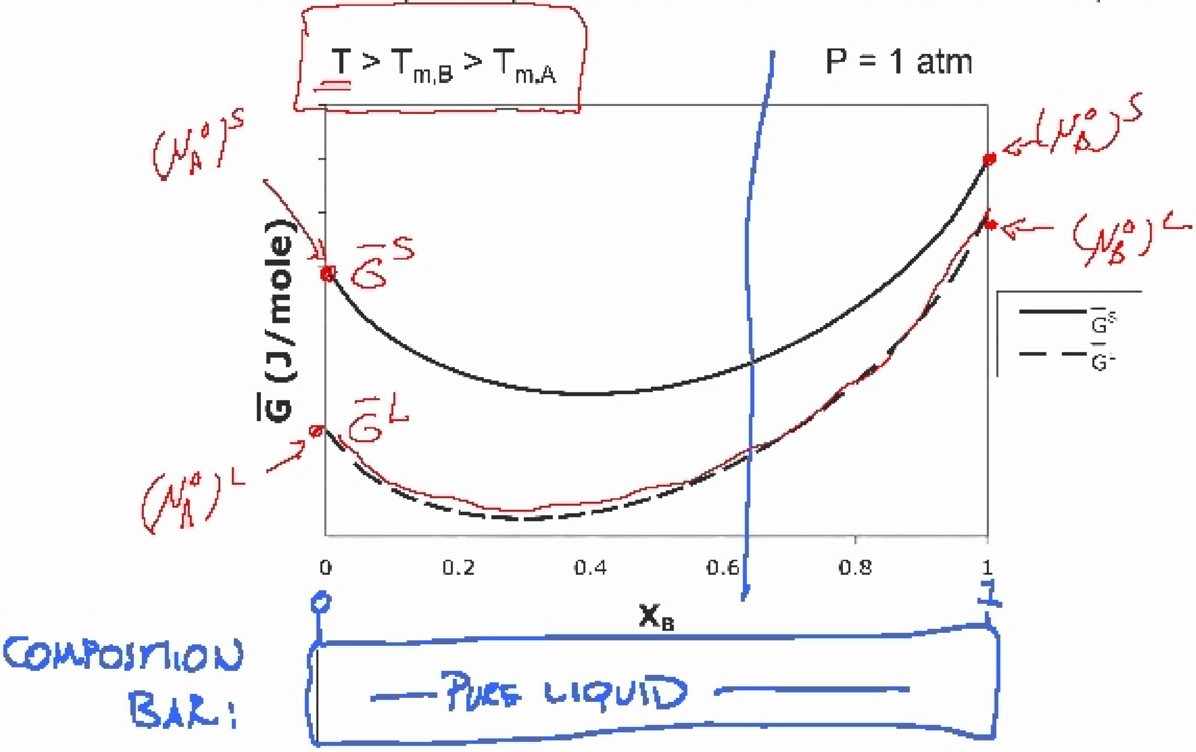
Free energy diagrams of multi-phase solutions[1]

- Last lecture we examined the structure and interpretation of free energy vs. composition diagrams for ideal binary (two-component) solutions. The free energy diagrams we introduced last time can conveniently be also used to analyze multiphase equilibria that allow us to graphically depict the requirements for equilibrium.

The common tangent construction and the lever rule

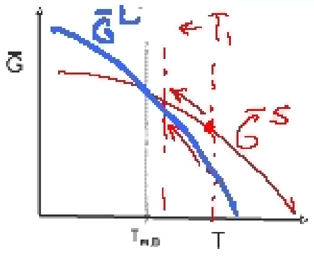
- **KEY CONCEPTS**: Free energy vs. composition diagrams are useful tools for graphically analyzing phase equilibria in binary systems at constant pressure. **Common tangents** between the free energy curves of different phases occur in regions where 2 phases are in equilibrium. The points where common tangents touch the free energy curves identify the compositions of the two phases in equilibrium. The **lever rule** is used to determine how much of each phase is present in two phase equilibrium regions.

- Suppose we have a binary *ideal* solution of *A* and *B*. We showed last time the shape of the free energy curve for such a solution. The molar free energy for the solution can be diagrammed for different phases of the solution- for example the liquid state and the solid state- as a function of composition:



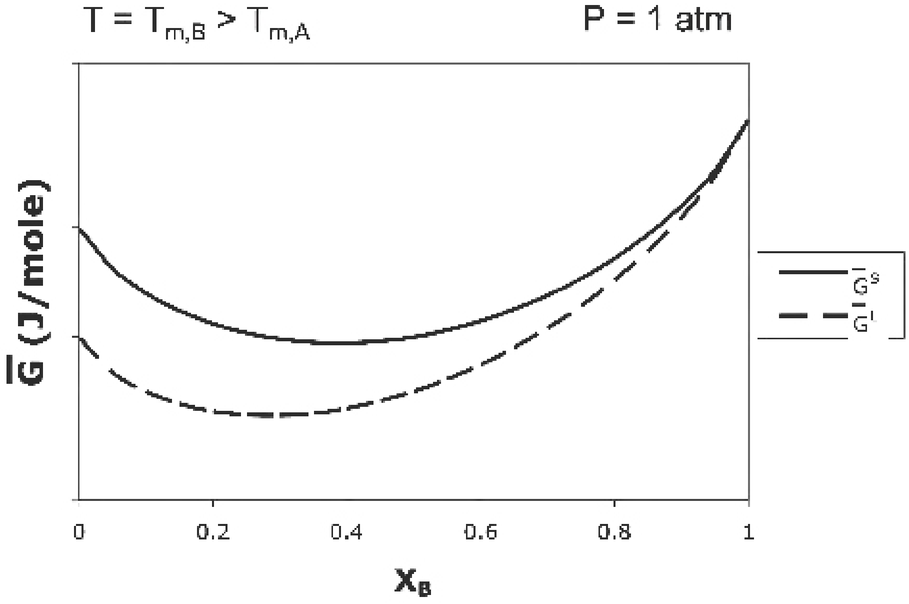
- Suppose we lowered the temperature from the above situation. How would the two free energy curves change? Which curve will move more, considering that:

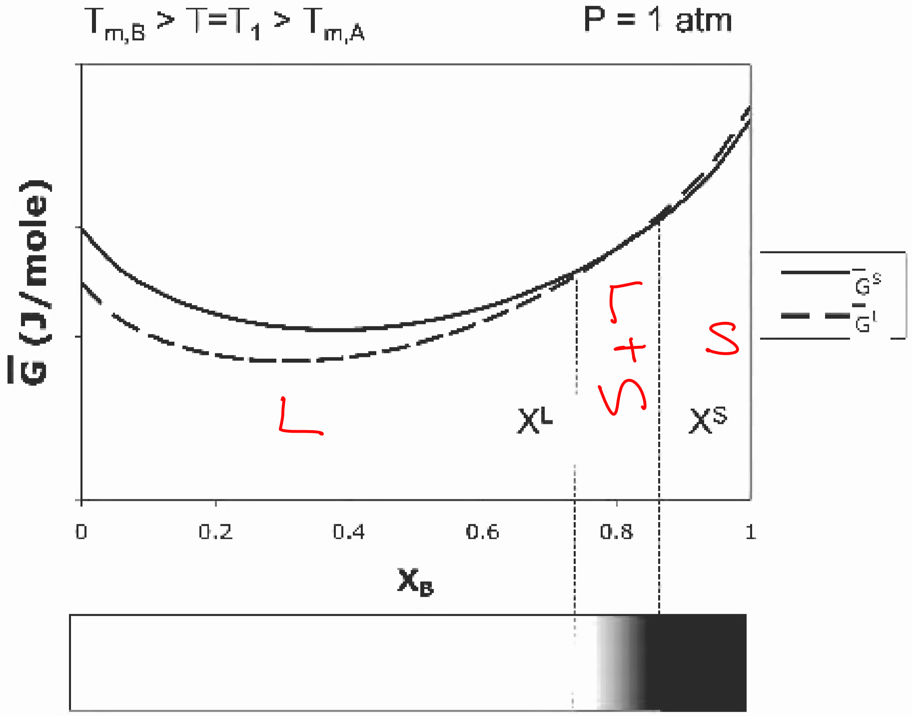
FIXED X_B, P



$\overline{G}^L$ GOING TO RISE FASTER THAN $\overline{G}^S$

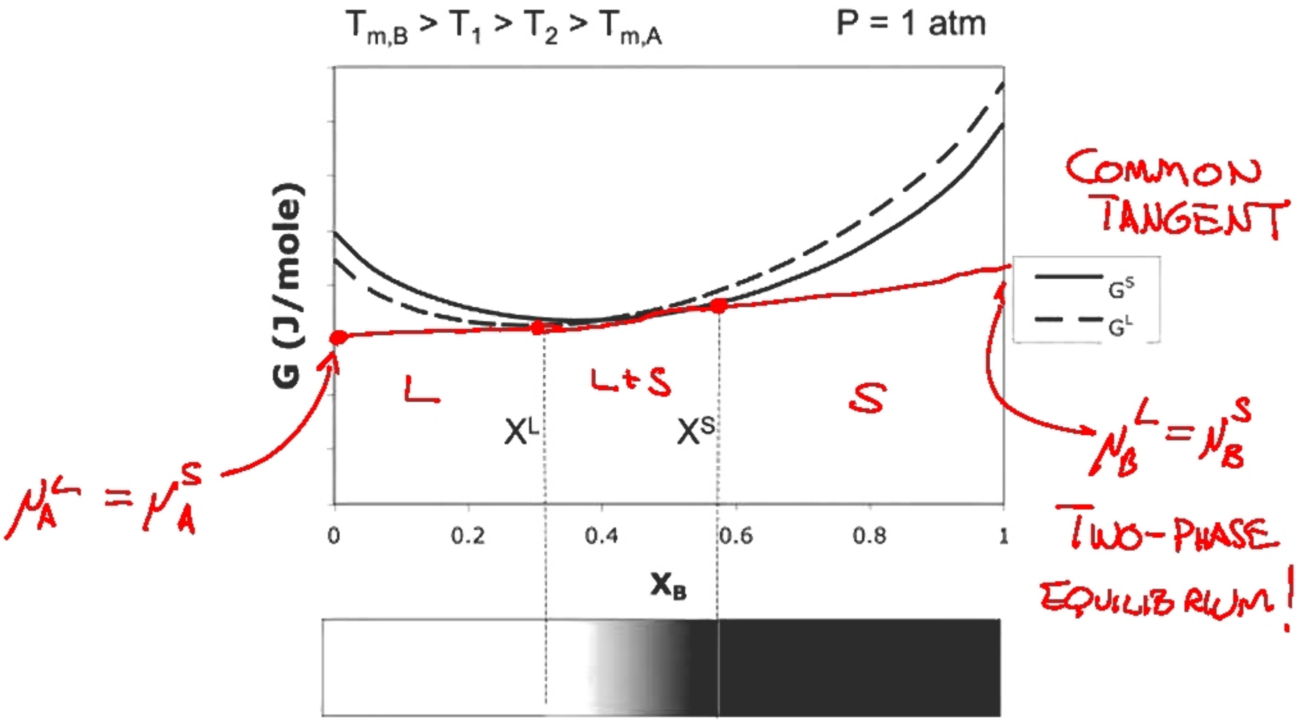
$$\overline{G} = \overline{H} - T\overline{S}$$



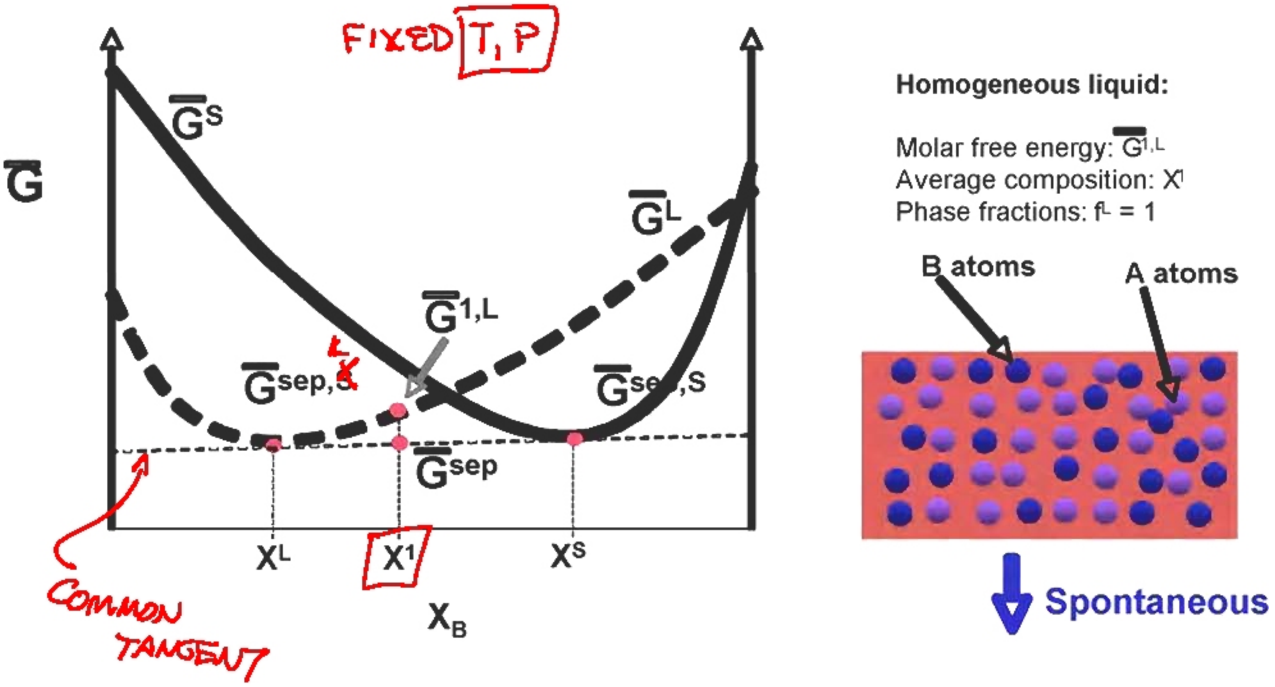


- What is happening in the second figure? We have reduced the temperature to the point where the stable state of pure B is a solid. Remember that the chemical potential is given by the end-points of the tangent to the free energy curve at a given composition. But we find that at T_1, a line can be drawn tangent to both free energy curves- a line that is tangent to the liquid curve at composition X^L, and the solid curve at X^S.

- Lowering the temperature slightly more:



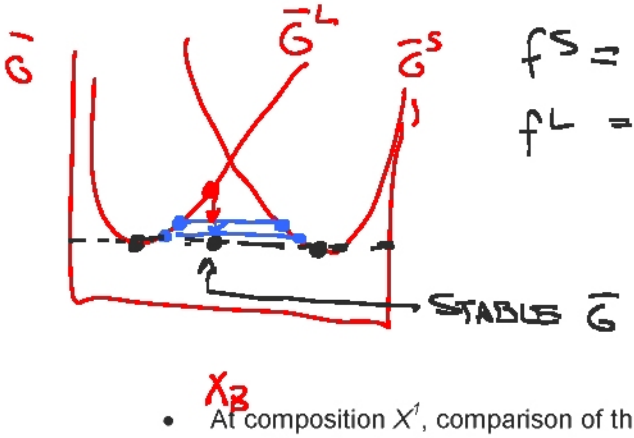
- We find that in the composition range from X^L to X^S, the chemical potentials of component *A* in the solid and liquid states are equal, and the chemical potentials of *B* in the solid and liquid states are equal …but this is the condition for two-phase equilibrium! *Thus for compositions between the common tangent points, two phases are present in the material,* solid and liquid. Why do two phases co-exist between X^S and X^L? Let's analyze the blown-up diagram below:

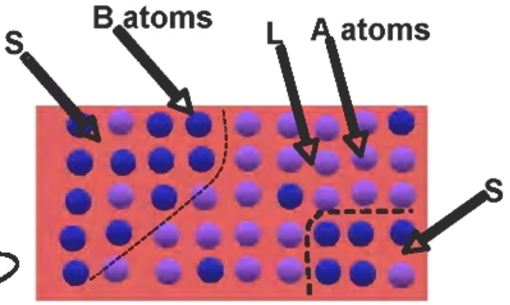


$$\bar{G}^{SEP} = \underline{\underline{f^S}}\,\bar{G}^{SEP,S} + \underline{\underline{f^L}}\,\bar{G}^{SEP,L}$$

f^S = MOLE FRACTION SOLID

f^L = " " LIQUID





Two-phase system: solid and liquid:

Molar free energy: $\bar{G}^{sep}$
Average composition: X^1
Composition of solid phase: X^S
Composition of liquid phase: X^L
Phase fractions: f^L = ?
f^S = ?

- At composition X^1, comparison of the solid state free energy with that of the liquid shows that the liquid would be the form with lowest free energy- thus the liquid solution would be more stable than the solid. However, the free energy of the liquid is not the lowest possible free energy state. If the A and B atoms in the homogenous liquid solution re-arrange, a portion transforming to a solid with composition X^S and a portion remaining in a liquid solution with composition altered to X^L, the heterogeneous solid/liquid mixture takes on the free energy $\bar{G}^{sep}$, which is lower than that of the homogeneous liquid solution at X^1. f^L and f^S are the phase fractions of liquid and solid phases, respectively. Note that because a heterogeneous (2-phase) mixture is being formed, the free energy is determined in a manner similar to that discussed earlier for heterogeneous mixtures (e.g. our block of Si in contact with a block of Ge)- simply a weighted average of the molar free energies of the liquid phase (composition X^L) and the solid phase (composition X^S).

  - How much solid phase forms? How much liquid is present?

    - The composition of the liquid phase is X^L, and the composition of the solid phase is X^S. Therefore, the amount of each phase present can be determined simply by requiring that the average composition of the system remains X^1:

PHASE FRACTIONS MUST BE CONSISTENT W/OVERALL COMPOSITION OF SYSTEM:

$$\text{(i)}\ f^S X^S + f^L X^L = X^1 \qquad \text{(ii)}\ f^S = 1 - f^L$$

$$f^S + f^L = 1$$

MULTIPLY BY $\left(\frac{-1}{-1}\right)$

USING (i)+(ii): $$f^L = \frac{(X^1 - X^S)}{(X^L - X^S)} \overset{\downarrow}{=} \frac{(X^S - X^1)}{(X^S - X^L)} = \frac{\overline{BC}}{\overline{AC}}$$

    - Similarly, if we write X_1 in terms of f^S we obtain:

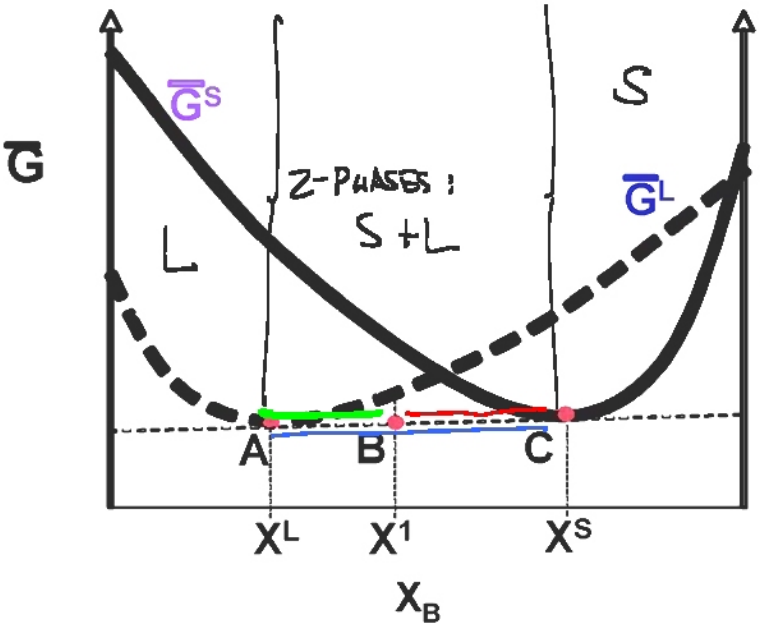
$$f^S = \frac{(x^1 - x^L)}{(x^S - x^L)} = \frac{\overline{AB}}{\overline{AC}}$$

LEVER RULE

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

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

- These two equations for the fraction of solid and liquid formed have a graphical equivalent:



$X^S - X^1 = \overline{BC}$

$X^S - X^L = \overline{AB}$

  - The mathematical and graphical construction to identify the fraction of each phase is known as the ***lever rule***.

Practical sources of free energy data

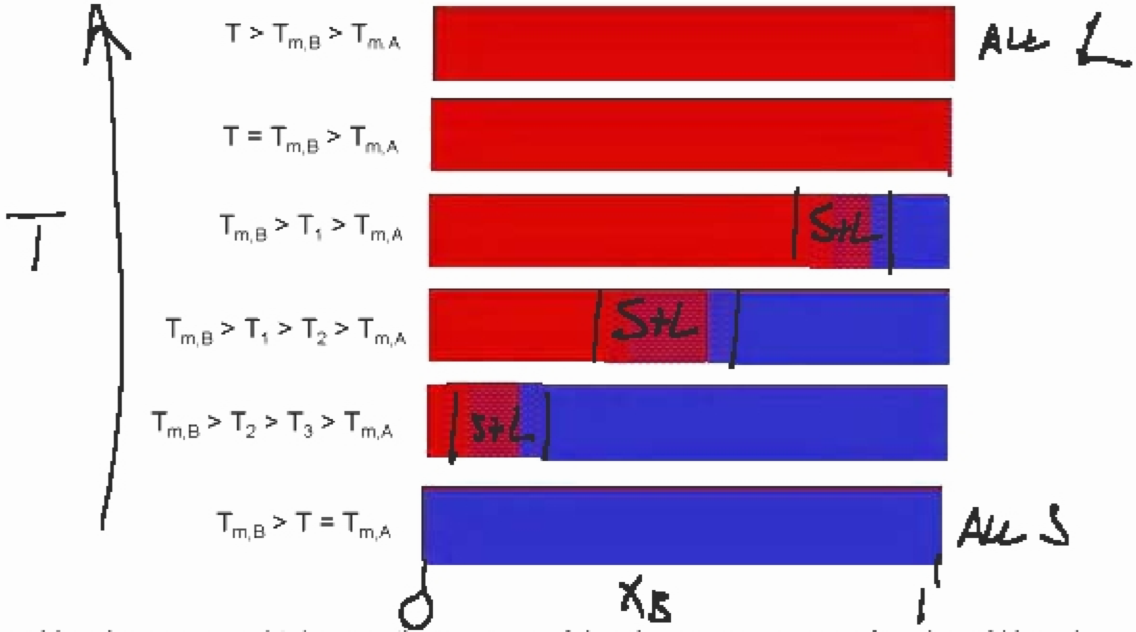
- Where do we get the information for these diagrams?
  - **National Institute of Standards and Technology Chemistry WebBook**
    - http://webbook.nist.gov/chemistry
    - heat capacity, enthalpy, and entropy data
  - **JANAF Tables**
    - Joint Army Navy Air Force database of thermochemical data
    - Exhaustive Cp, entropy, enthalpy, free energy data
    - QD511.J74. 1986
  - **Selected Values of Thermodynamic Properties of Metals and Alloys**
    - R. Hultgren, R.L. Orr, P.D. Anderson, and K.K. Kelley
    - John Wiley, NY 1963
    - QD171.S44
  - **Thermo-Calc**
    - Software available on Athena for performing many thermodynamic calculations, building phase diagrams, etc.

Introduction to binary phase diagrams

- **KEY CONCEPTS**: The phase equilibria as a function of composition for a fixed temperature (and fixed pressure) predicted by Free energy vs. composition diagrams can be collated to create a binary phase diagram, which maps out stable phases in T vs. composition space (pressure assume fixed)—the binary system analog of single component phase diagrams. The Gibbs phase rule can be applied to these diagrams, accounting for the fixed pressure (D + P = C + 1). Tie lines allow the lever rule to be directly applied to phase diagrams in order to calculate the amount of each phase present in multiphase equilibria.

Phase diagram of an ideal solution

- From an examination of free energy vs. composition diagrams, we found that phase separation (induced for example by reducing the temperature and freezing a liquid solution) proceeds by the following progression across the composition window of an ideal binary solution (For a system where $T_{m,B} > T_{m,A}$):



- It would make sense to obtain a continuous map of the phases present as a function of X_B and temperature for a binary system: such a map is a key tool in materials science & engineering and is known as a **binary phase diagram**. For the ideal binary solution we have been analyzing, the phase diagram looks like this:

TYPICAL IDEAL SOLN PHASE DIAGRAM ('LENS')

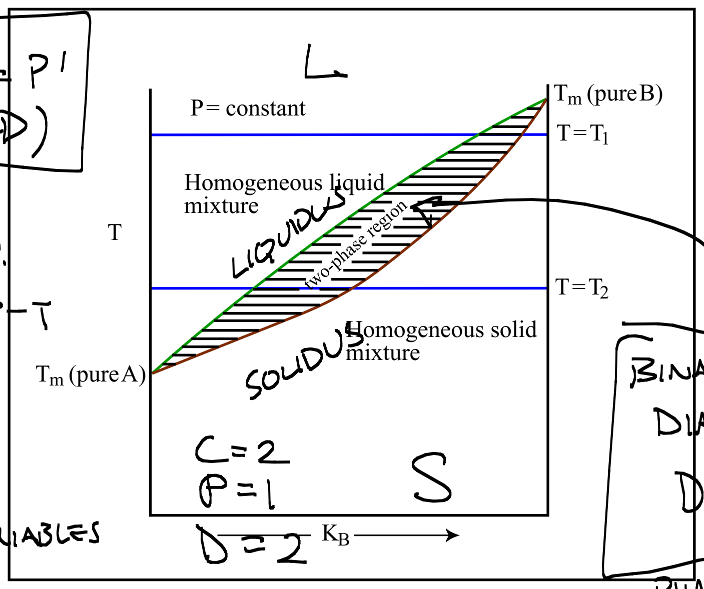
@P = P' (FIXED)

GIBBS PHASE RULE:

SINGLE COMPONENT P-T DIAGRAM:

$D + P = C + 2$

↑ T, P AS VARIABLES



C=2
P=2
D=1

S+L

BINARY PHASE DIAGRAM:

$D + P = C + 1$

PHASE RULE @ FIXED P

Figure by MIT OCW.

- This is the simplest form a binary phase diagram can take.

Tie lines and the lever rule on a binary phase diagram

- The lever rule that we developed using free energy vs. composition diagrams can be directly applied to a binary phase diagram (T vs. composition). This is done using **tie lines**—horizontal isotherms connecting the boundaries of a two-phase region:

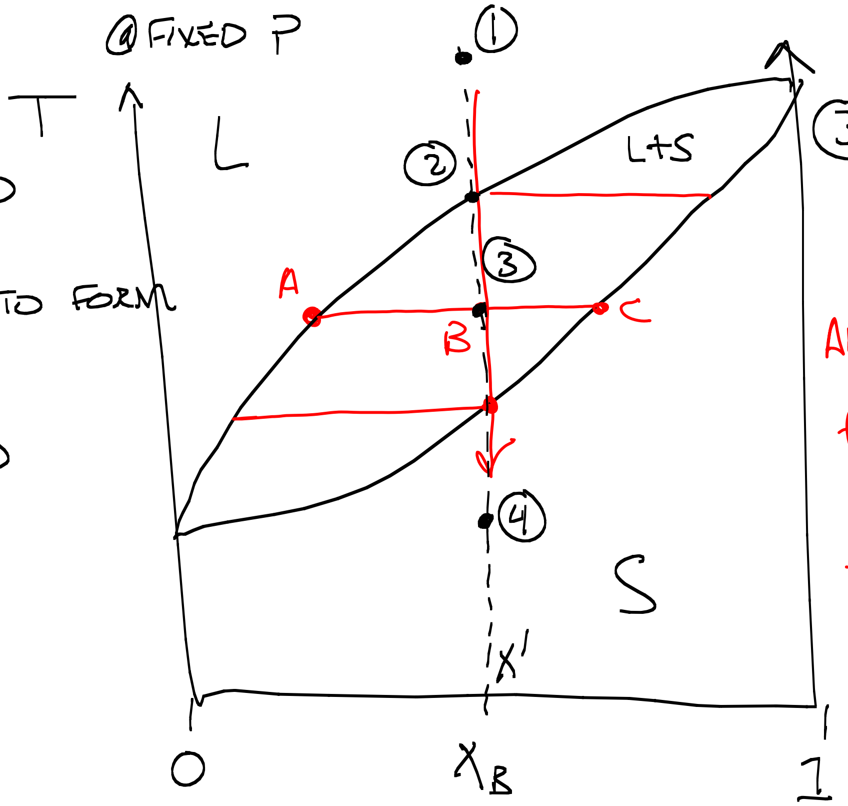
@ FIXED P

① PURE LIQUID

② FIRST SOLID STARTING TO FORM

③ ?

④ PURE SOLID



③ 2-PHASE EQUILIBRIUM: S/L

APPLY LEVER RULE:

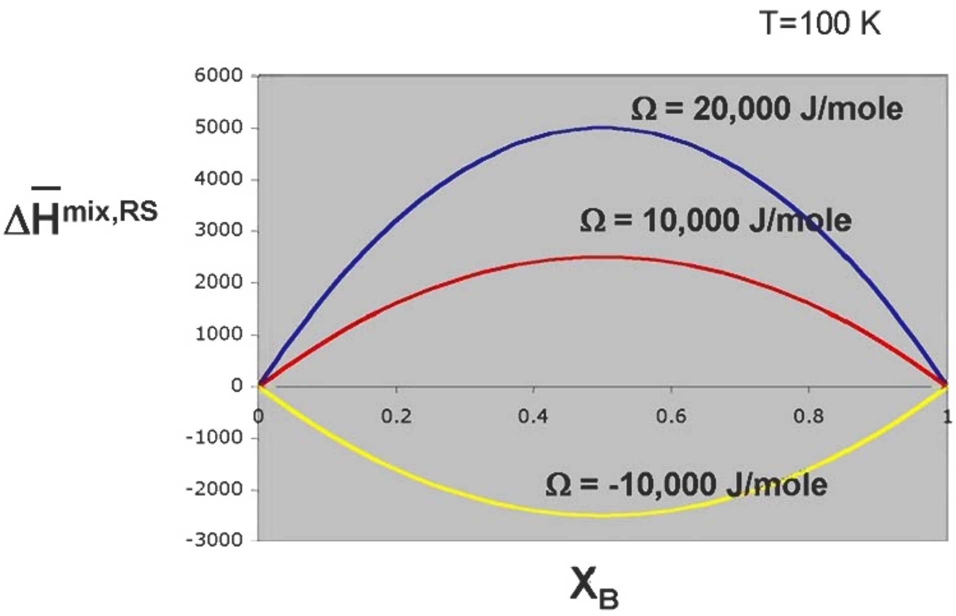
$$f^S = \frac{\overline{AB}}{\overline{AC}}$$

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

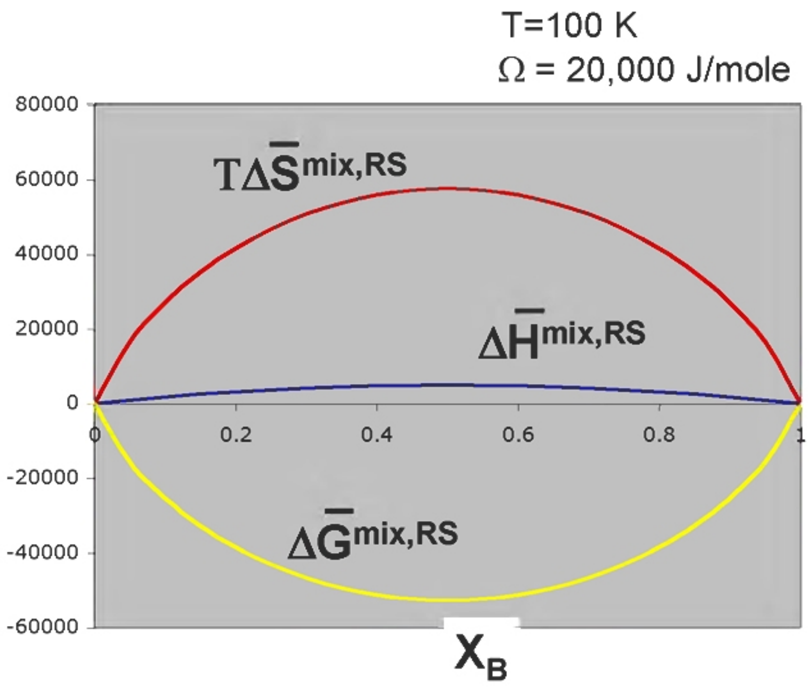
Binary solutions with limited miscibility: Miscibility gaps

The Regular Solution Model, part I

- What happens if the molecules in the solution interact with a finite energy? The enthalpy of mixing will now have a finite value, either favoring ($\Delta \overline{H}^{mix} < 0$) or disfavoring ($\Delta \overline{H}^{mix} > 0$) mixing of the two components. The simplest model of a solution with finite interactions is called the **regular solution model**:
    - Let the enthalpy of mixing take on a finite value given by:
    - We take the entropy of mixing to be the same as in the ideal solution. This gives a total free energy of mixing which is:
    - The regular solution model describes the liquid phase of many real systems such as Pb-Sn, Ga-Sb, and Tl-Sn, and some solid solutions. Today we will analyze the behavior of a system with this free energy function; in a few lectures we will show how the given forms of the enthalpy and entropy of mixing arise from consideration of molecular states (using statistical mechanics).



- The overall free energy of mixing arises from the balance between favorable mixing entropy and unfavorable enthalpy contributions:



- The free energy of the system varies with the value of Ω and with temperature:
    - As a function of temperature at a fixed positive value of Ω:

References

1. Carter, W. C. *3.00 Thermodynamics of Materials Lecture Notes* http://pruffle.mit.edu/3.00/ (2002).