

## 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

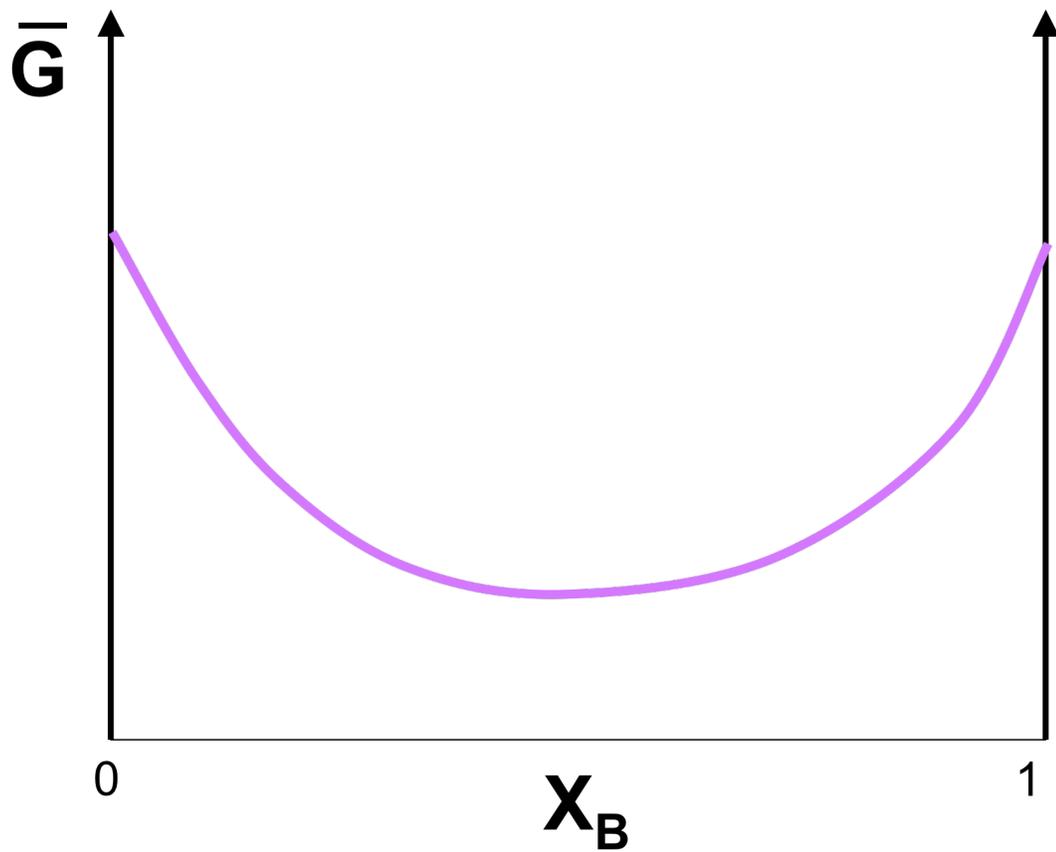
**Supplementary Reading:** -

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**Last time**

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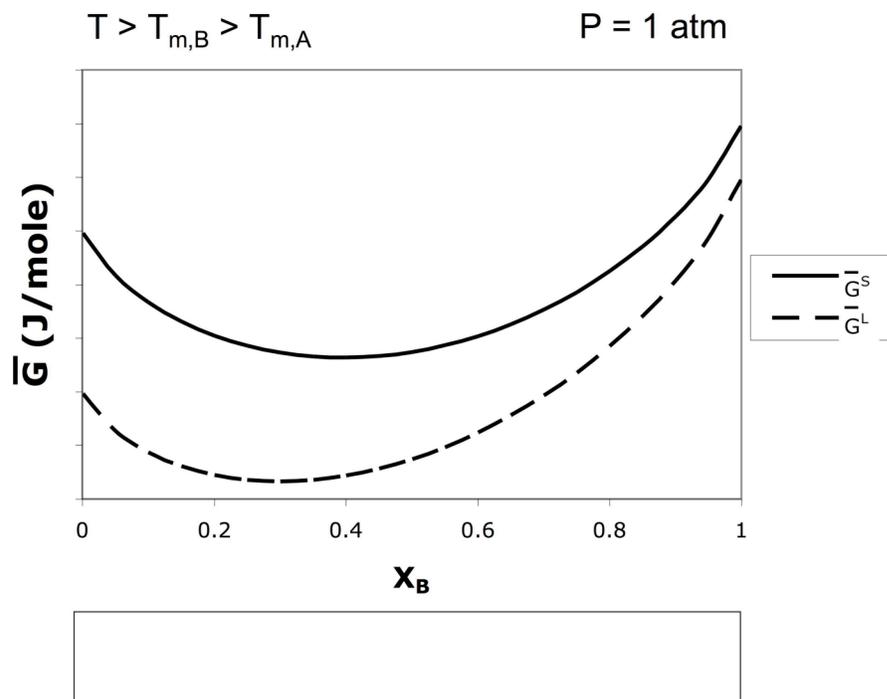
## Free energy diagrams of multi-phase solutions<sup>1</sup>

- 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.

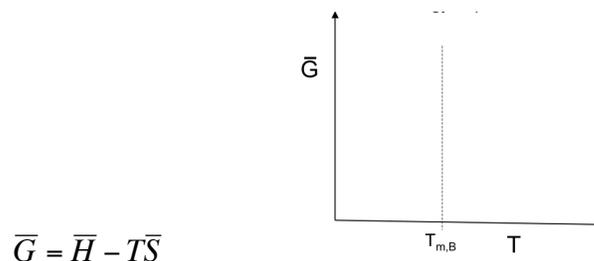
### The common tangent construction and the lever rule

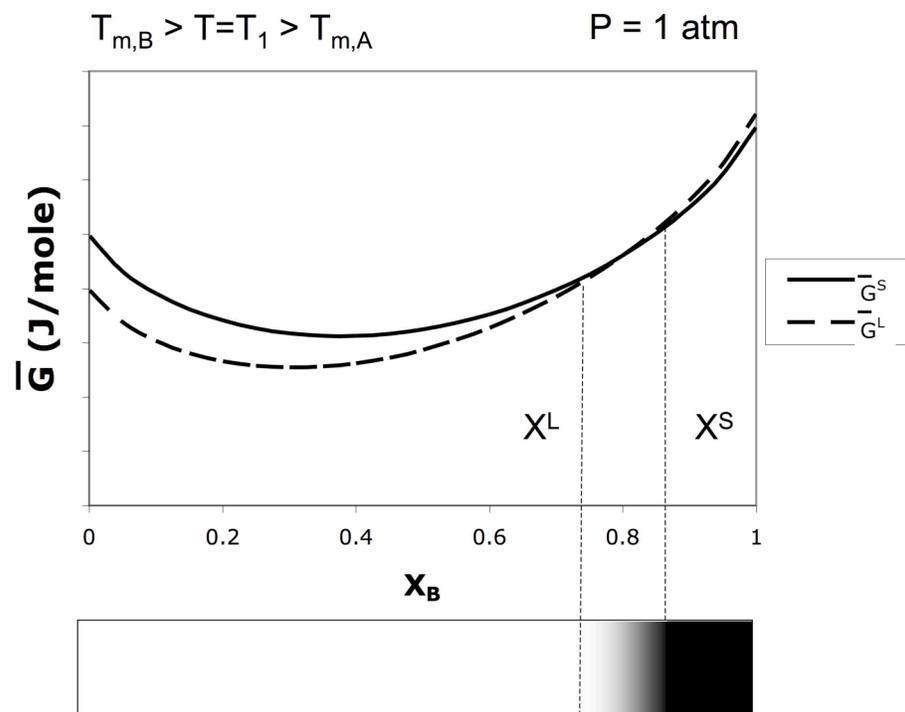
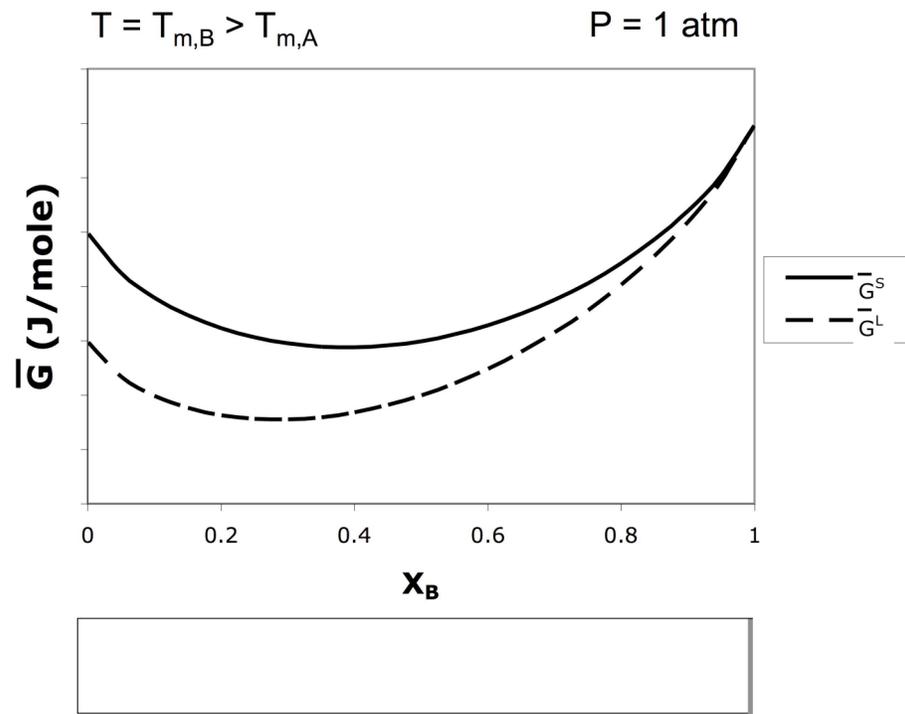
- KEY CONCEPTS:** Free energy vs. composition diagrams are useful tools for graphically analyzing phase equilibria in binary systems at constant pressure. **Common tangents** between the free energy curves of different phases occur in regions where 2 phases are in equilibrium. The points where common 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:

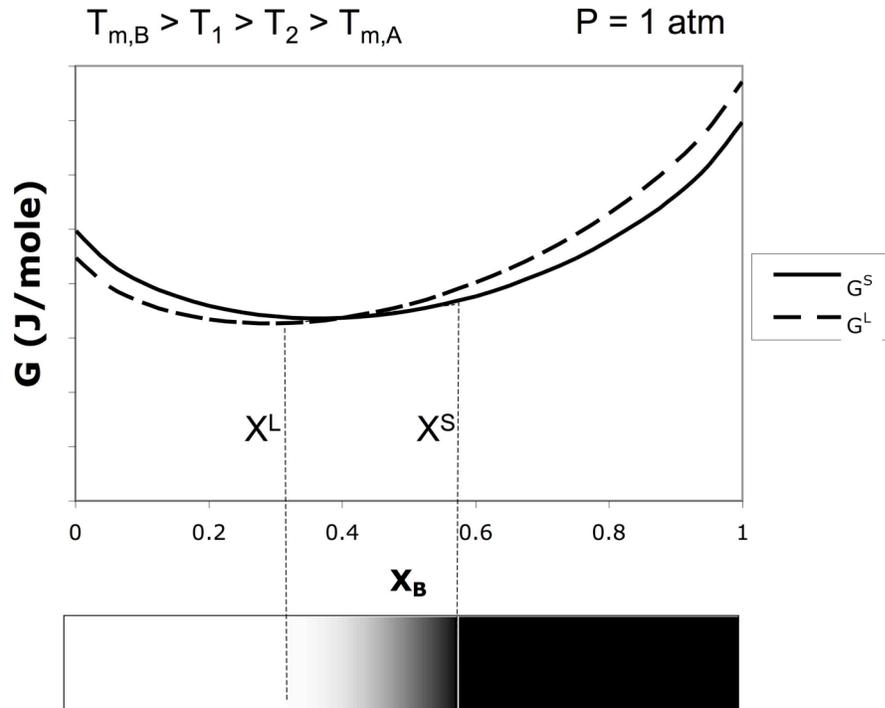




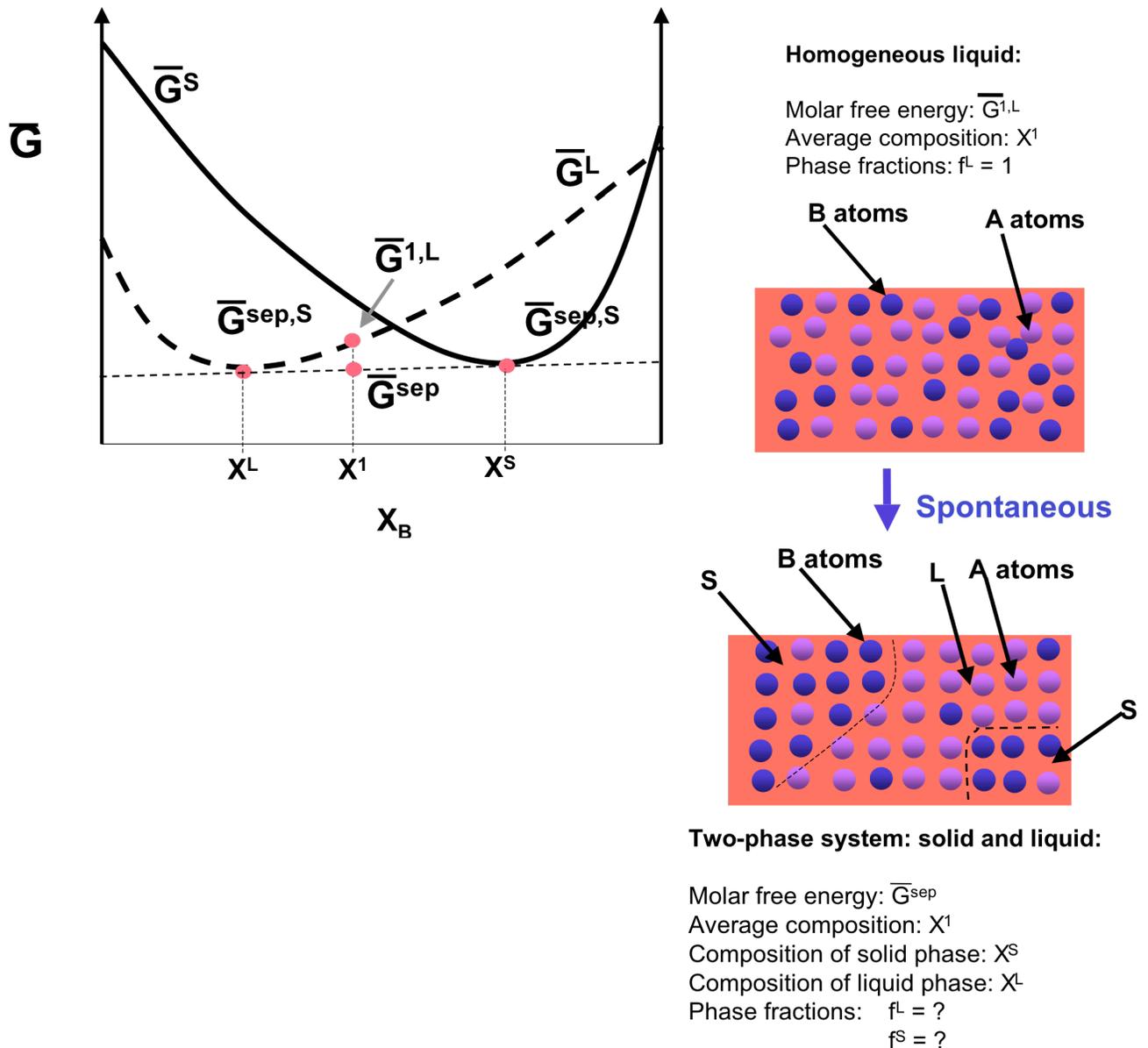
- □ What is happening in the second figure? We have reduced the temperature to the point where the stable state of pure B is a solid. Remember that the chemical potential is given by the end-

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:*

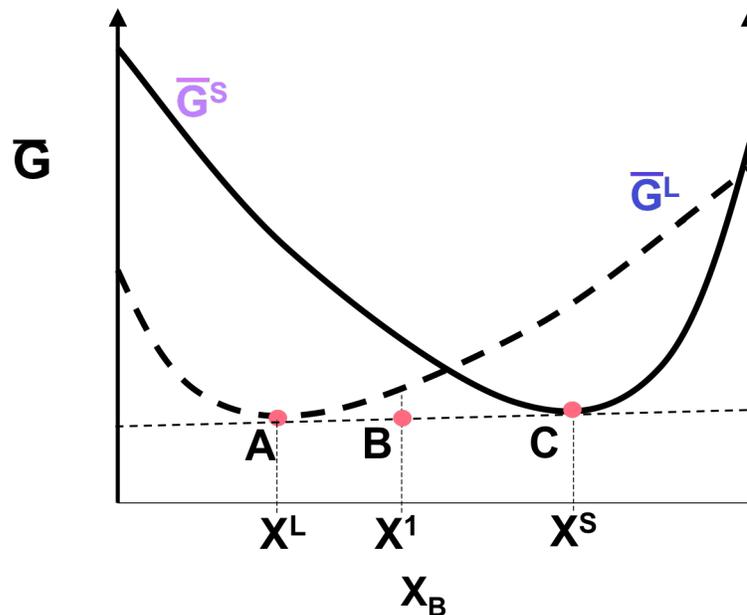


- At composition  $X^1$ , comparison of the solid state free energy with that of the liquid shows that the liquid would be the form with lowest free energy- thus the liquid solution would be more stable than the solid. However, the free energy of the liquid is not the lowest possible free energy state. 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  $X^1$ :

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

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



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

**Practical sources of free energy data**

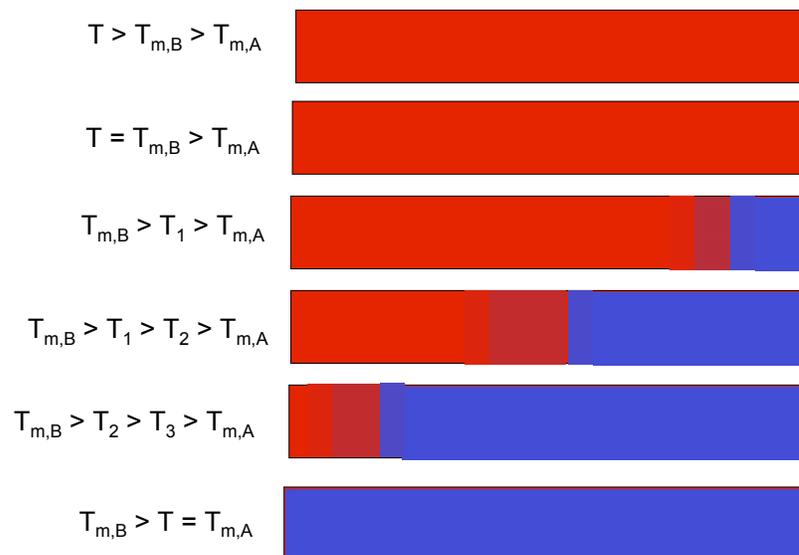
- Where do we get the information for these diagrams?
  - **National Institute of Standards and Technology Chemistry WebBook**
    - <http://webbook.nist.gov/chemistry>
    - heat capacity, enthalpy, and entropy data
  - **JANAF Tables**
    - Joint Army Navy Air Force database of thermochemical data
    - 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:

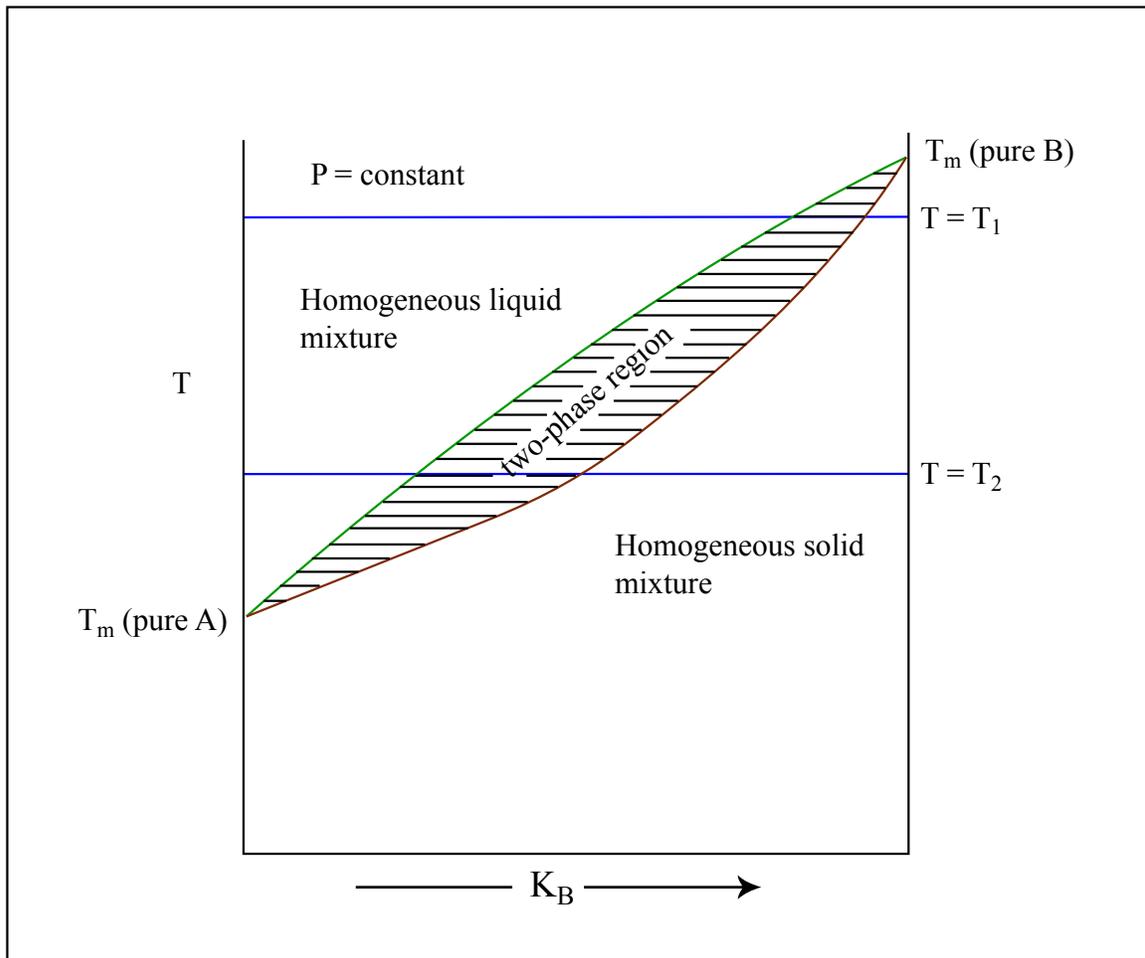


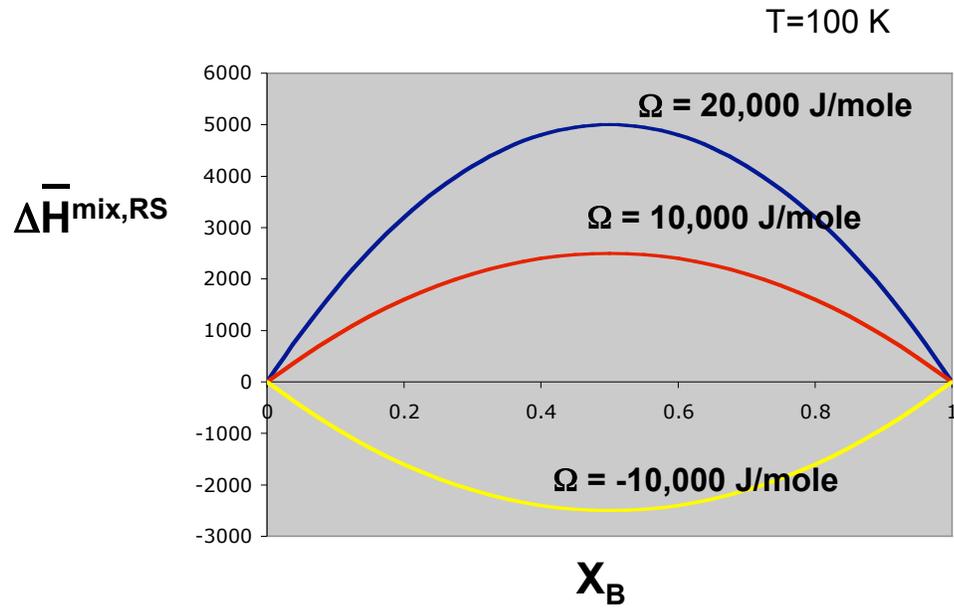
Figure by MIT OCW.

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

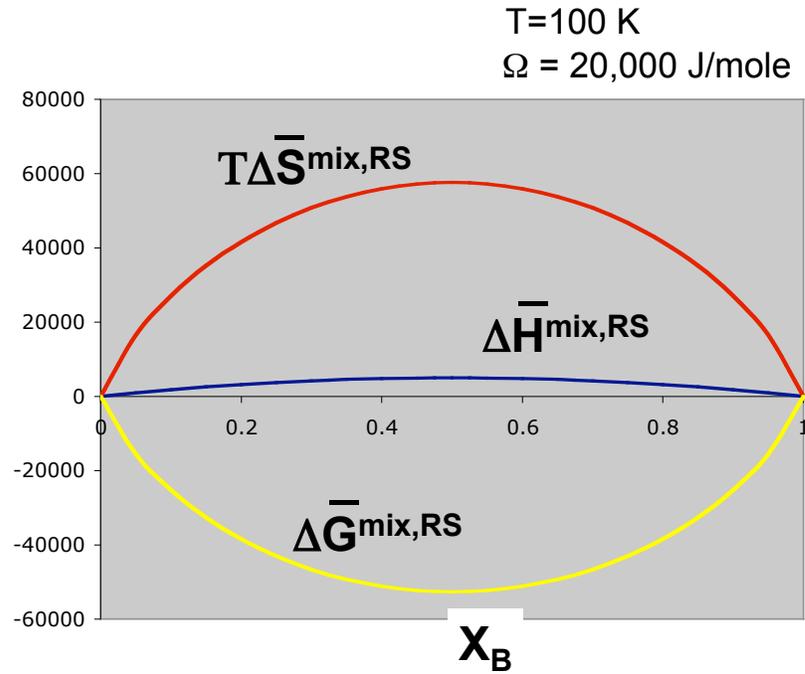
### Tie lines and the lever rule on a binary phase diagram

- 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:





- 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  $\Omega$  and with temperature:
  - As a function of temperature at a fixed positive value of  $\Omega$ :

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## References

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