Lecture 16: 11.04.05 Single-Component phase diagrams continued; Thermodynamics of solutions

Today:

Reading: Gaskell, *Introduction to Metallurgical Thermodynamics*, Ch. 11.5 'The free energy of solution,' pp. 328-338

$+$

Engel and Reid 9.6, 9.7

Supplementary Reading: -

ANNOUNCEMENTS:

EXAM 2 COVERAGE THROUGH TODAY

Last Time

Single-component phase diagrams and the Gibbs phase rule

$C = 1$

PHASE RULE : $D + \mathcal{P} = C + 2$

PHASE FIELD
$\mathcal{P} = 1 \quad D = 2$

TRIPLE POINT
$\mathcal{P} = 3$
$D = 0$

COEXISTENCE CURVE
$\mathcal{P} = 2 \quad D = 1$

THERE CAN BE NO 4-PHASE
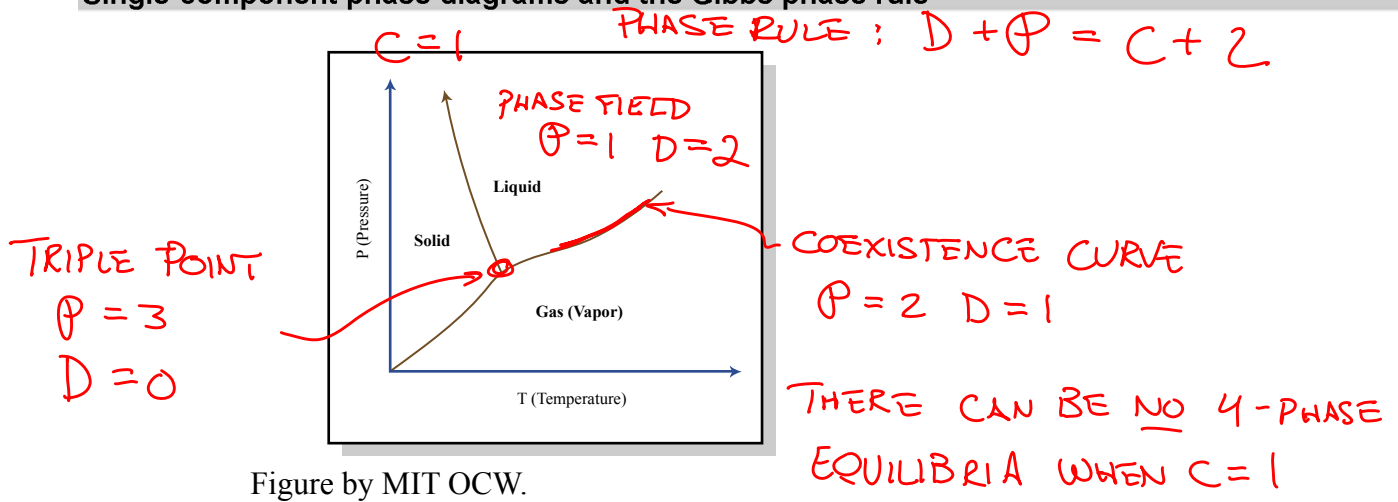EQUILIBRIA WHEN $C = 1$

Figure by MIT OCW.

- o There is one unique value of pressure and temperature, the **triple point**, that can allow the 3 phases to co-exist; any change in the variables of the system causes the equilibrium to shift to one between only 1 or 2 phases.

Constraints on the shape of phase boundaries (coexistence curves): The Clausius-Clapeyron equation

- For 2 phases in equilibrium (let's use the example of solid and liquid in equilibrium at the melting temperature):

@ $\boxed{A}$: $\mu^S = \mu^L$

- To find a nearby condition of T and P where the two phases are still in equilibrium, we must have:(1)
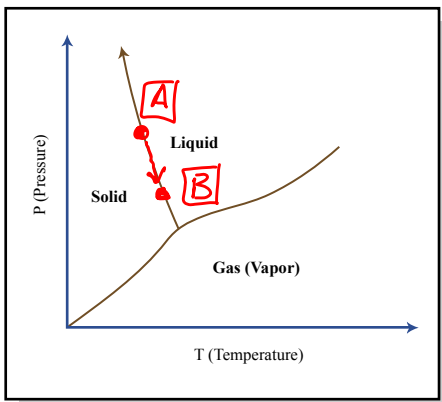
Figure by MIT OCW.

@ $\boxed{B}$: $\mu^S + d\mu^S = \mu^L + d\mu^L$

$\downarrow$ SINCE : $\mu^S = \mu^L$

$\therefore d\mu^S = d\mu^L$

GIBBS-DUHEM EQN FOR EACH PHASE :

$V^S dP - S^S dT - n^S d\mu^S = 0$

DIVIDE
BY n $\searrow$ $\overline{V}^S dP - \overline{S}^S dT - d\mu^S = 0$ (i)

FOR LIQUID :

$\overline{V}^L dP - \overline{S}^L dT - d\mu^L = 0$ (ii)

SET (i) = (ii) :

$$\bar{V}^S dP - \bar{S}^S dT - dN^S = \bar{V}^L dP - \bar{S}^L dT - dN^L$$

$$dN^S = dN^L$$

$$(\bar{S}^L - \bar{S}^S) dT = (\bar{V}^L - \bar{V}^S) dP$$

$$\underbrace{(\bar{S}^L - \bar{S}^S)}_{\Delta \bar{S}_m} \qquad \underbrace{(\bar{V}^L - \bar{V}^S)}_{\Delta \bar{V}_m}$$

$$\left. \frac{dP}{dT} \right|_{COEXIST \ curve} = \frac{\Delta \bar{S}_m}{\Delta \bar{V}_m} = \frac{\Delta \bar{H}_m}{T_m \Delta \bar{V}_m}$$

CLAUSIUS -
CLAPEYRON
EQ'N

- The Clausius-Clapeyron equation dictates the slope of the two-phase co-existence curve for single-component materials. We already know that the enthalpy change on melting is typically positive, therefore the sign of the change in volume on melting will usually dictate whether the slope of P vs. T is positive or negative.
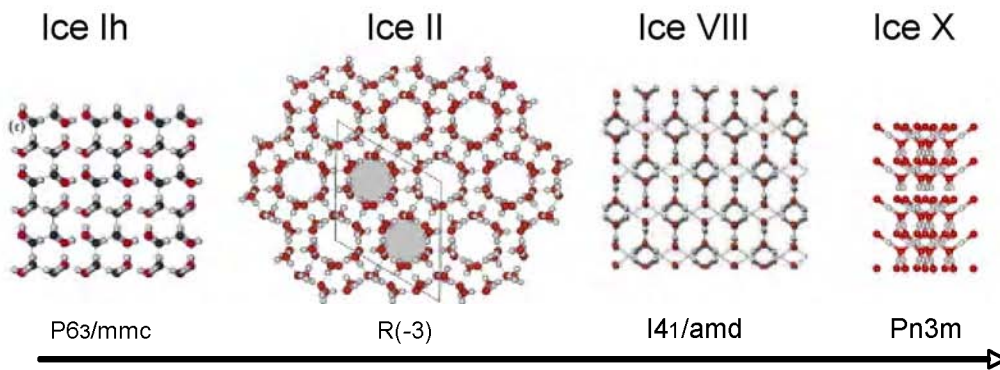
Example single-component phase diagrams

- The phase diagram of water:

$$\frac{dP}{dT}\bigg|_{COEX} = \frac{\Delta \bar{H}_m}{T_m \Delta \bar{V}_m}$$

$\Delta \bar{H}_m \geq 0$

$T_m \geq 0$

SIGN OF SLOPE IS SET BY VALUE $\Delta \bar{V}_m$

S L

ICE Ih

SLOPE < 0

$\Delta \bar{V}_m = \bar{V}^L - \bar{V}^S < 0$

$\bar{V}^L < \bar{V}^S$

FOR MOST S→L $\Delta \bar{V}_m$ IS SMALL;

∴ $\frac{dP}{dT}$ IS STEEP !

(source: http:www.lsbu.ac.uk/water/phase.html)
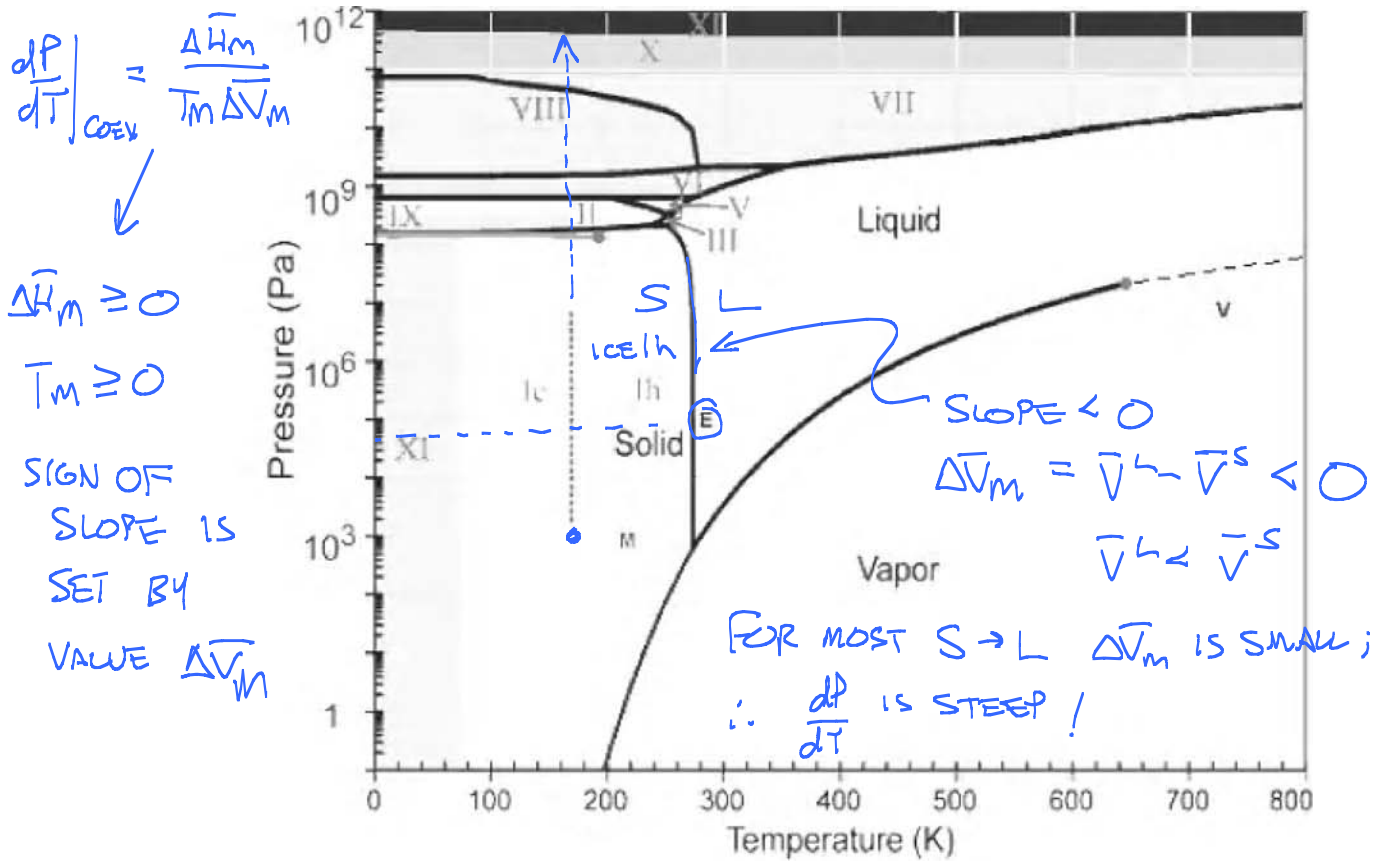
- Water transitions through increasingly dense crystal structures as pressure is increased:

Courtesy of London South Bank University. Used with permission.

Ice Ih	Ice II	Ice VIII	Ice X
P6₃/mmc	R(-3)	I4₁/amd	Pn3m

Source: http://www. lsbu.ac.uk/water/phase .html

$P\left(\frac{g}{cm^3}\right)$: 0.92   1.17   1.46   2.51

P

Courtesy of London South Bank University. Used with permission.
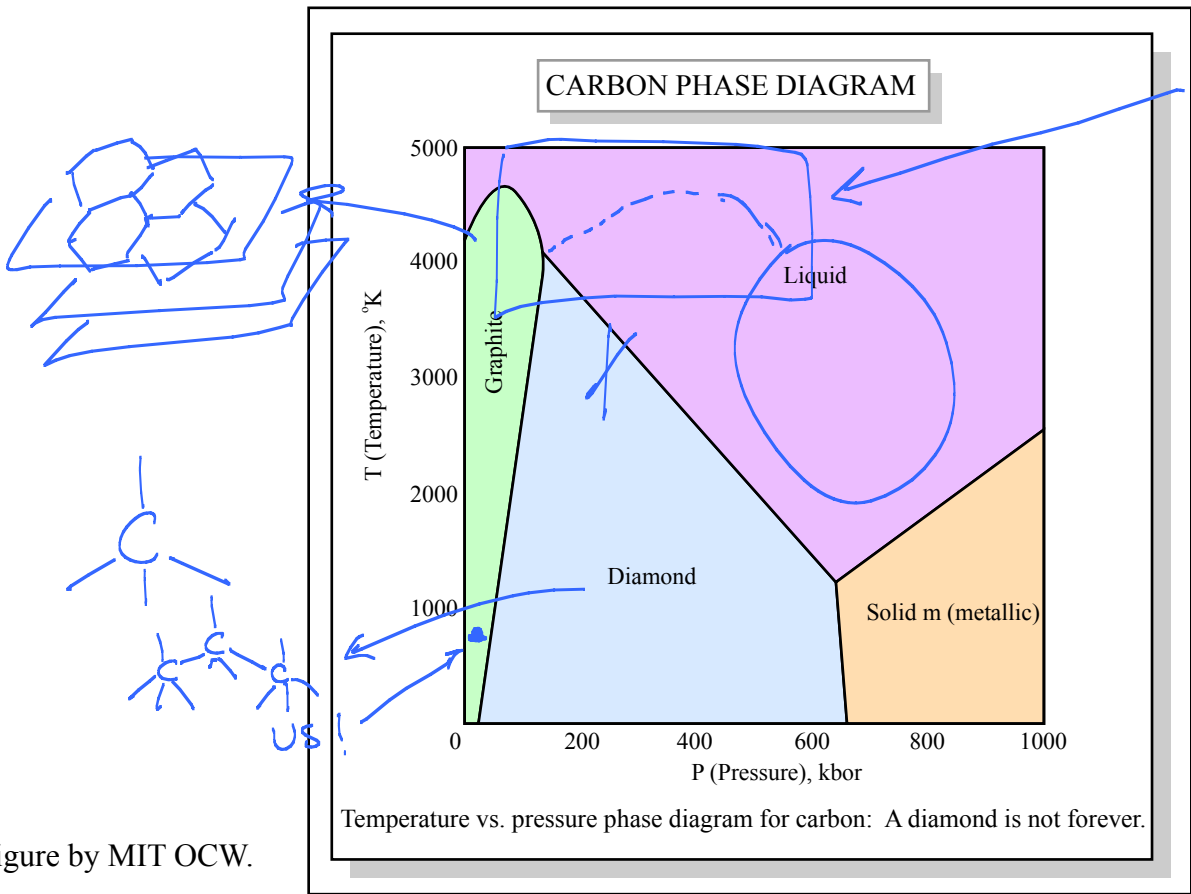
CARBON PHASE DIAGRAM

Temperature vs. pressure phase diagram for carbon: A diamond is not forever.

Figure by MIT OCW.

IRON PHASE DIAGRAM

Temperature vs. pressure phase diagram for iron.

Figure by MIT OCW.

$\Delta \bar{V}_M$ SMALL $\rightarrow$ $\frac{dP}{d\bar{T}}$ HAS A STEEP SLOPE!

Pressure (atm)

$\simeq 1$

Liquid

Cubic

Tetragonal

Vapor

Monoclinic

-273   0   1000   2000   3000   4000

Temperature (^{o}C)

Proposed diagram for system ZrO_2
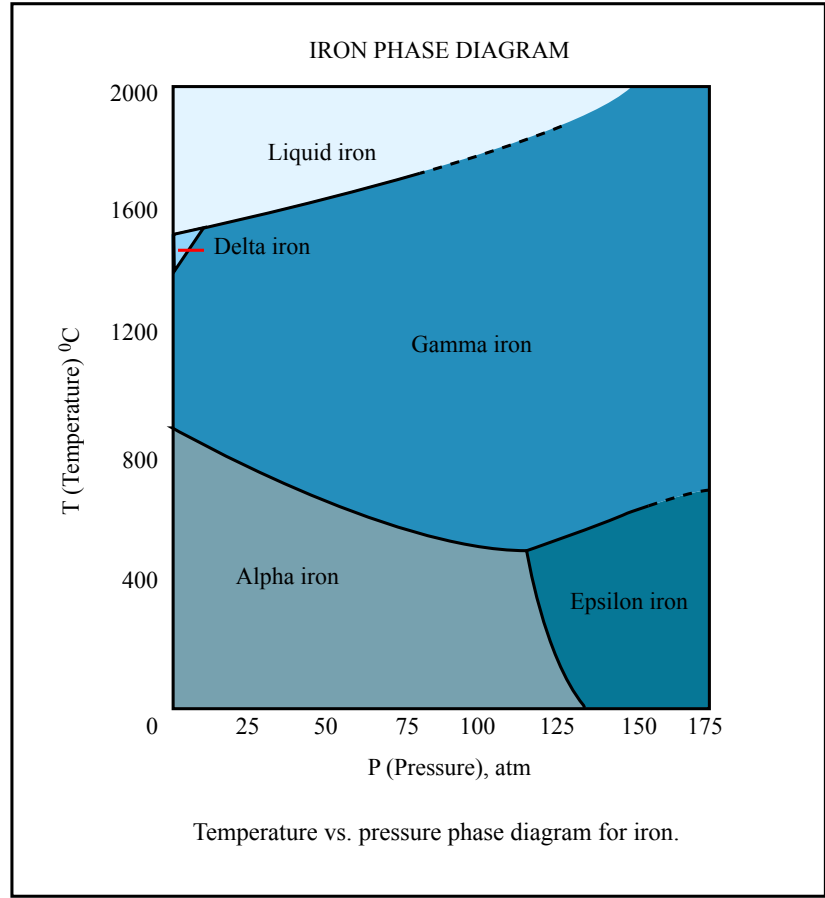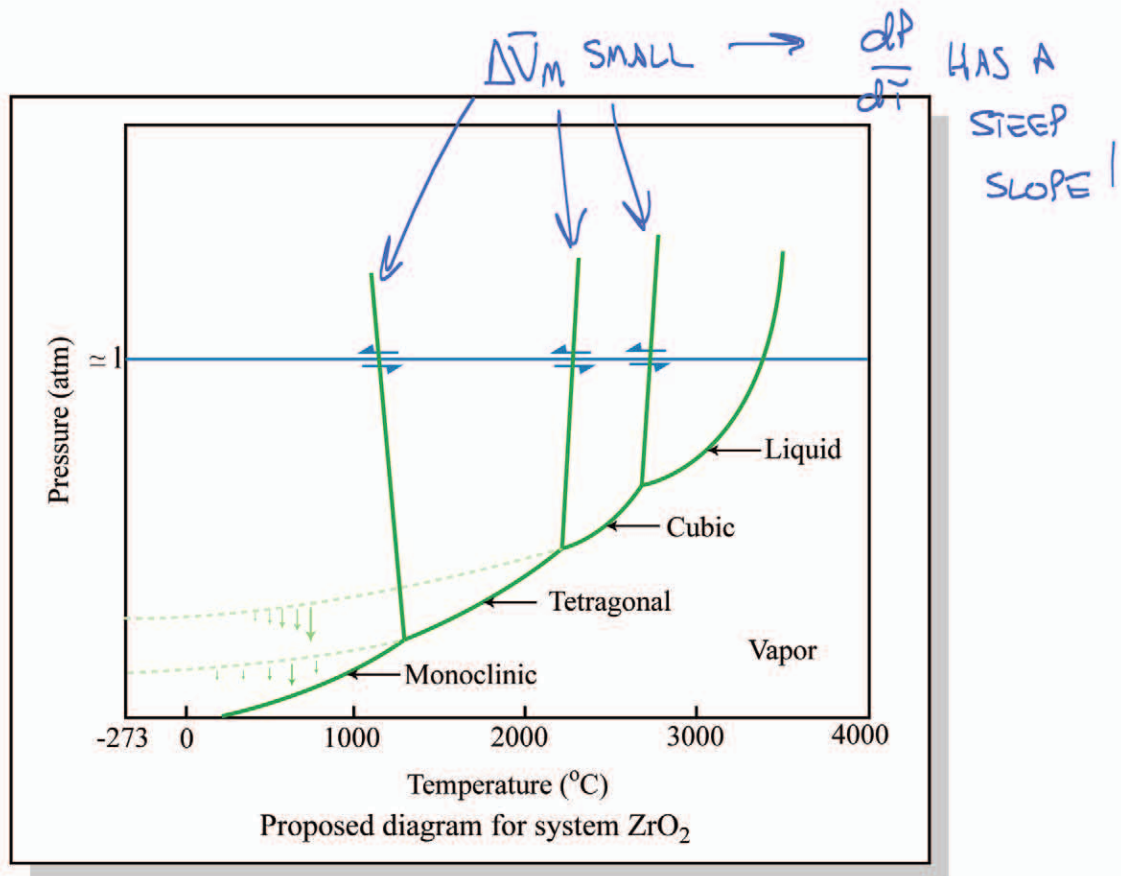
Figure by MIT OCW.

Walking along lines of constant temperature or pressure in a single-component phase diagram

- Consider now how the free energy varies as we move along a line of a single-component phase diagram at constant pressure or constant temperature:
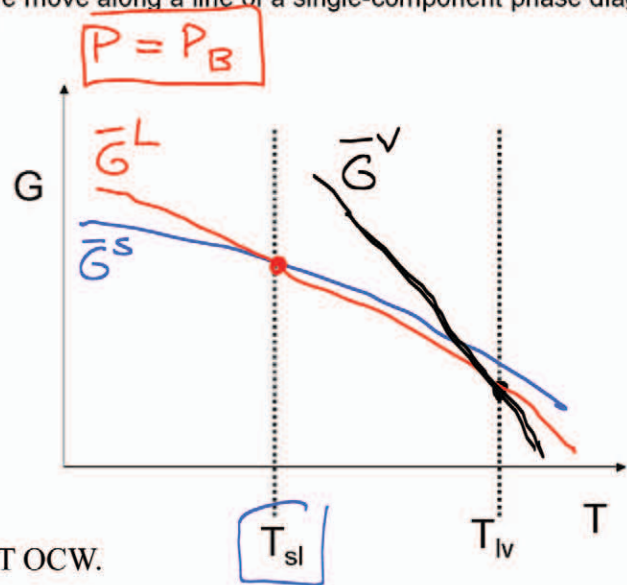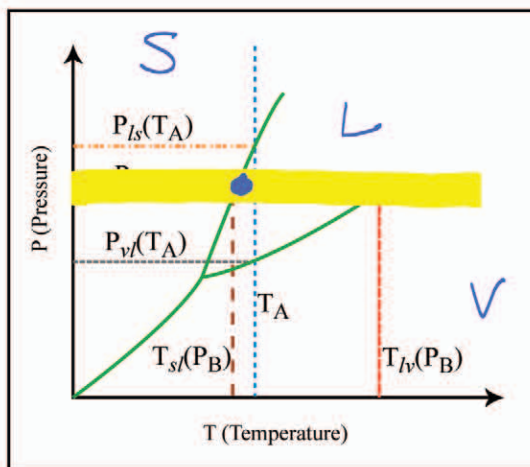
$\boxed{P = P_B}$

S

L

$P_{ls}(T_A)$

$P_{vl}(T_A)$

T_A

P (Pressure)

$T_{sl}(P_B)$ $T_{lv}(P_B)$

V

T (Temperature)

G

$\bar{G}^L$ $\bar{G}^V$

$\bar{G}^S$

$\boxed{T_{sl}}$ T_{lv} T

Figure by MIT OCW.

Graphical constructions of the free energy in mixtures and solutions

- **KEY CONCEPTS**: Ideal solutions are models for materials that have similar crystal structures and bonding. Formation of an ideal solution from its unmixed components is always spontaneous, because the free energy of mixing has no penalizing enthalpy term (there are no unfavorable bonding interactions) and the entropy gain on mixing is always positive.

- In addition to mapping out stable phases for single-component systems, phase diagrams can also be used to chart stable phases as a function of temperature (or pressure) vs. composition for binary (2-component) or ternary (3-component) systems. In order to understand how the phase boundaries in systems of more than one component arise, we will first discuss another useful graphical constructions: free energy vs. composition diagrams.

Free energy diagrams of ideal solutions

- Earlier we introduced the general solution model for the chemical potential:

$$\mu_i(T,P) = \mu_i^o(T) + RT \ln a_i$$

- When the activities of the components are equal to their compositions, the solution is *ideal*:

$$IDEAL: \quad a_i = X_i \quad \Rightarrow \quad \mu_i = \mu_i^o(T) + RT \ln X_i$$

- Knowing the chemical potentials of the components, we can determine the total free energy of the solution. What does a plot of the total free energy for a binary ideal solution of two components *A* and *B* look like vs. the composition X_B?

  - The total molar free energy for the solution is: $C = 2$

$$\overline{G}^{SOLUTION} = \sum_{i=1}^{C} X_i \overline{G}_i = \sum_{i=1}^{C} X_i \mu_i \overset{\downarrow}{=} X_A \overline{G}_A + X_B \overline{G}_B$$

$$= X_A \left[\mu_A^o + RT \ln X_A \right] + X_B \left[\mu_B^o + RT \ln X_B \right]$$

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

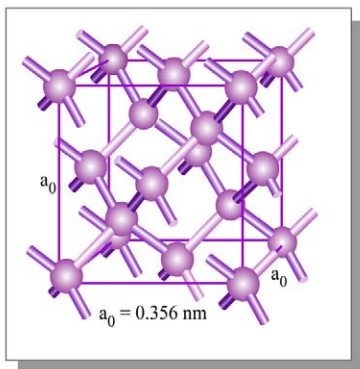$$\underbrace{\qquad}_{X_A + X_B = 1}$$

CONSTANTS FIXED BY T

o   All we need to plot the free energy for a given temperature and pressure is the standard state
        chemical potential of each component. (For many materials of interest, this data is available in
        databases and published tables).

- Let's look at what the free energy curve looks like for a hypothetical A/B solution at a
            fixed pressure that has the following parameters:
    - $\mu_{A,}^{0}$ = -3.0 KJ/mole
    - $\mu_{B,}^{0}$ = -1.0 KJ/mole
    - T = 300K

- Ideal solutions always give curves with this qualitative nature; the depth of the "smile"
        and its tilt are controlled by the specific values of *T* and the standard state chemical
        potentials of the pure components.

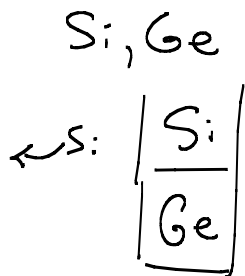**Mixing to form ideal solutions always occurs spontaneously**

o   The free energy diagram allows us to readily determine what a system gains (thermodynamically) by
        forming a solution. Nearly ideal solid solutions can form for materials that have compatible crystal
        structures, similar bonding, and similar elemental/molecular sizes. Suppose I have a Ge-Si solid
        solution (a useful semiconductor material), which behaves very nearly as an ideal solution.

Figure by MIT OCW.

Si, Ge

$\longleftarrow S: \left| \dfrac{Si}{Ge} \right|$

$a_{Si} = 5.43\ \text{Å}$ $\widehat{V}_{Si} = \dfrac{12.05}{cm^3/mole}$

$a_{Ge} = 5.65\ \text{Å}$ $\widehat{V}_{Ge} = 13.57\ \dfrac{cm^3}{mole}$

LATTICE PARAMETER a

SAME AS DIAMOND!

⇒ (diamond crystal structure(3))

Si   Ge   ➡   Si-Ge solid solution

$$\bar{G}^{SOLN} = (1-X_B)\left[\mu_A^\circ + RT\ln(1-X_B)\right] + X_B\left[\mu_B^\circ + RT\ln X_B\right]$$

- o Before formation of the solution, (i.e., imagine a crystal of pure Si bonded to a crystal of pure Ge) the molar free energy of the system is simply the sum of the free energies per mole of each pure component multiplied the total mole fraction:

$$\bar{G}^{UNMIXED} = X_A\bar{G}_A^\circ + X_B\bar{G}_B^\circ = (1-X_B)\mu_A^\circ + X_B\mu_B^\circ$$

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

≤ 0 $\bar{G}_B^\circ$ FOR ALL X_B!

IDEAL SOLNS FORM SPONTANEOUSLY!
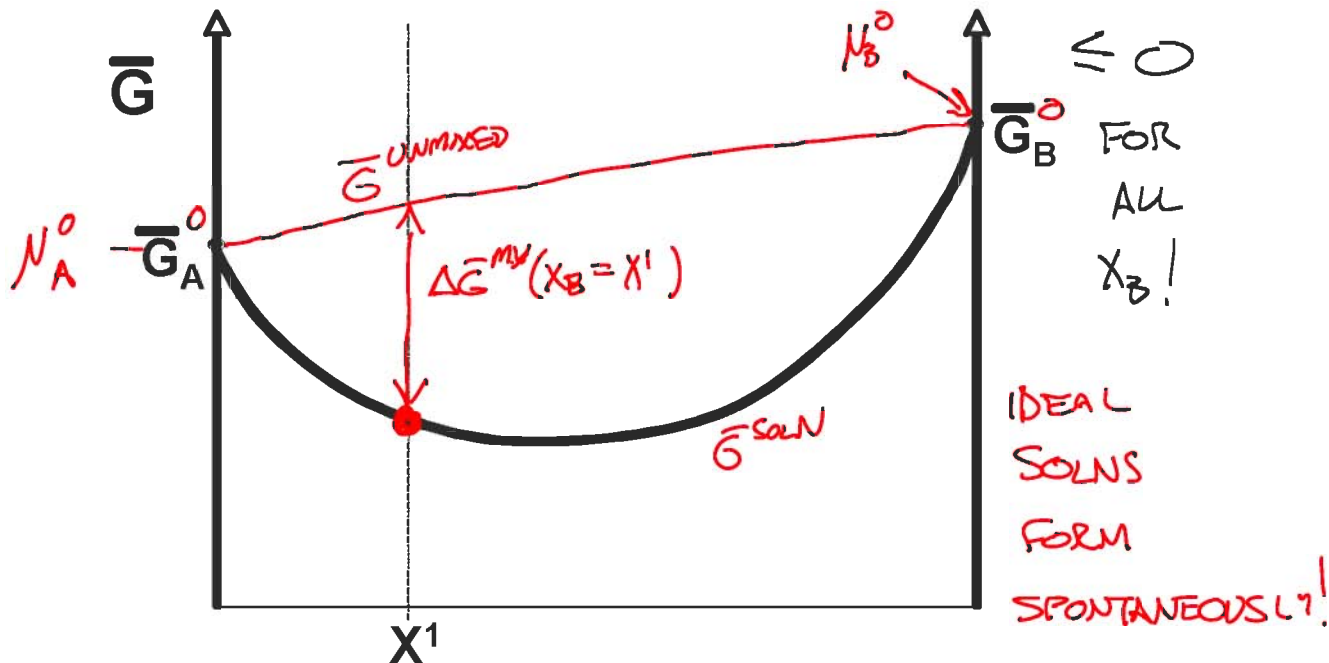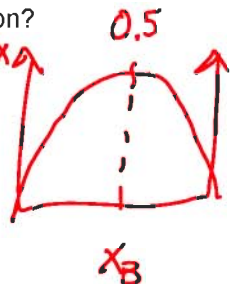
$$\Delta\bar{G} = \Delta\bar{H} - T\Delta\bar{S}$$

$$X_B \ddot{Y}$$

Ideal solutions have only an entropic contribution to the free energy of mixing: intermolecular interactions are presumed to be the same in the two components

- • What are the changes in enthalpy and entropy that occur on mixing to form an ideal solution?

$$\left(\frac{\partial\Delta\bar{G}^{MIX}}{\partial T}\right)_{P,n} = -\Delta\bar{S}^{MIX}$$

$$\therefore \Delta\bar{S}^{MIX} = -R\left[(1-X_B)\ln(1-X_B) + X_B\ln X_B\right]$$

$$\Delta\bar{H}^{MIX} = \Delta\bar{G}^{MIX} + T\Delta\bar{S}^{MIX} = 0$$

IDEAL SOLN : NO ENTHALPIC COMPONENT!
ALL ENTROPY!

Extracting chemical potentials from plots of the free energy

- We can learn more from free energy diagrams than the free energy change on mixing. The diagram also provides a convenient graphical means to determine chemical potentials/partial molar free energies of the components as a function of composition. To see how this is done, we start by writing the free energy of the solution:

$$G = \sum_{i=1}^{C} \mu_i n_i = \mu_A n_A + \mu_B n_B \qquad \overline{G} = \frac{G}{n} = \mu_A X_A + \mu_B X_B$$

  - What is the differential of the molar free energy?

GIBBS-DUHEM EQN (AGAIN!): $V dP - S dT - n_A d\mu_A - n_B d\mu_B = 0$

@ CONST. T, P: $n_A d\mu_A + n_B d\mu_B = 0$

↳ DIVIDE BY n: $X_A d\mu_A + X_B d\mu_B = 0$

$d\overline{G}? = \mu_A dX_A + X_A d\mu_A + X_B d\mu_B + \mu_B dX_B$

$\underbrace{\qquad\qquad}_{=0}$

$d\overline{G} = \mu_A dX_A + \mu_B dX_B = (\mu_A - \mu_B) dX_A$

↑

CLOSED SYSTEM: $dX_A = - dX_B$

$\dfrac{d\overline{G}}{dX_A} = \mu_A - \mu_B \xrightarrow[\substack{\text{MULTIPLY} \\ \text{BY} \\ X_B}]{} X_B \dfrac{d\overline{G}}{dX_A} = X_B(\mu_A - \mu_B)$

$$X_B \frac{d\overline{G}}{dX_A} = X_B(\mu_A - \mu_B)$$

$\downarrow$ ADD TO $\overline{G} = \mu_A X_A + \mu_B X_B$

$$\overline{G} + X_B \frac{d\overline{G}}{dX_A} = \mu_A \underbrace{(X_A + X_B)}_{=1}$$

$$\mu_A = \overline{G} + X_B \frac{d\overline{G}}{dX_A}$$

$$\mu_B = \overline{G} + X_A \frac{d\overline{G}}{dX_B}$$

- These two equations tell us how to determine the chemical potentials from free energy diagrams. Returning to our diagram:

$$\mu_B = \overline{G} + X_A \frac{d\overline{G}}{dX_B}$$

$$= \overline{G} + (1-X')\frac{(Y - \overline{G})}{(1-X')} = Y$$
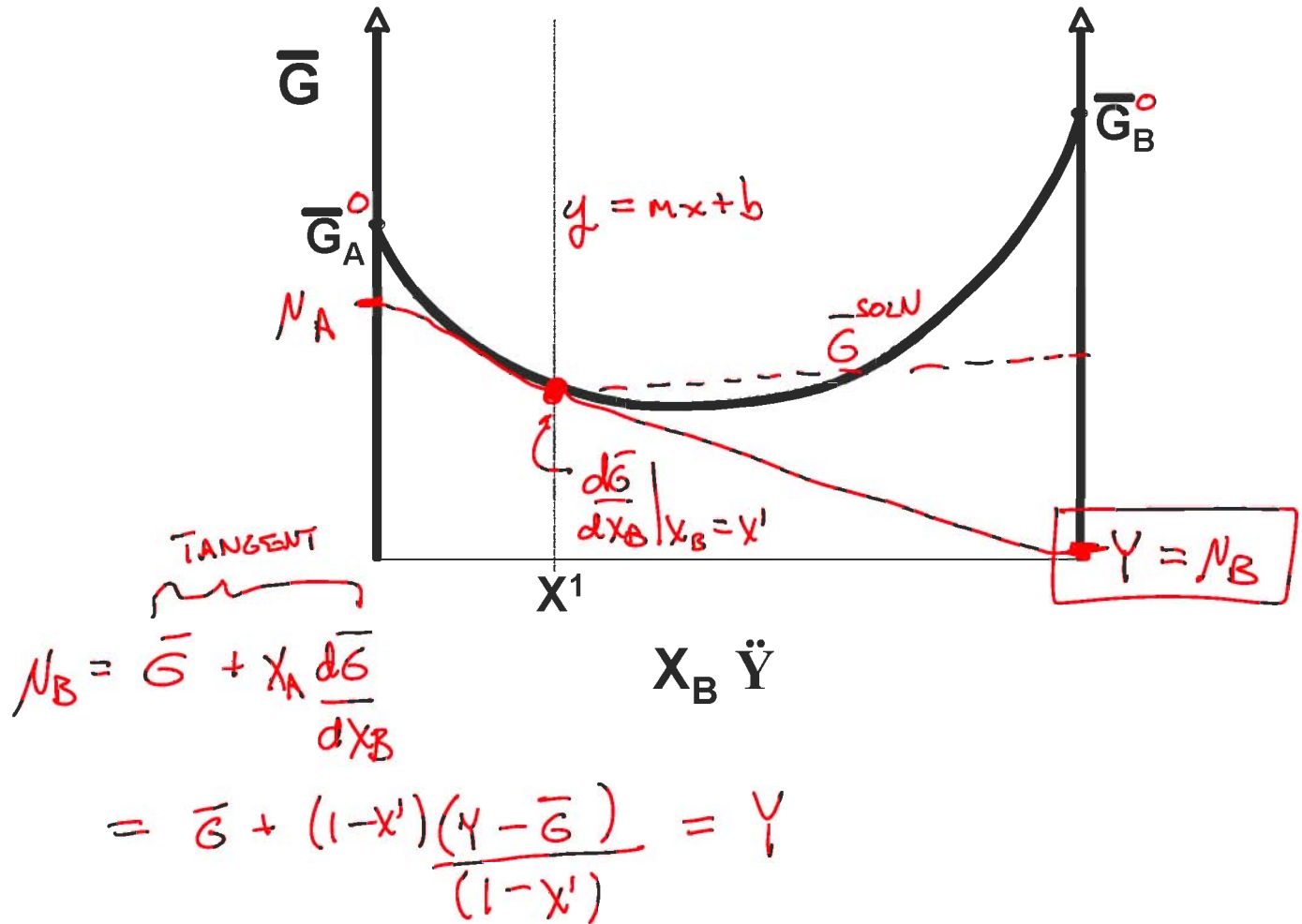
Application of solution free energy analysis: Melting point depression

- You probably know that roads and sidewalks are salted in winter to help prevent ice buildup and subsequent traffic accidents. Thermodynamics provides the explanation for this phenomenon.

(a) No Solute
$T = T_f$

(b) Solute Reduces μ_{water}
$T = T_f$

(c) Lower T reduces μ_{ice}
$T = T_2 < T_f$

$\mu_{water} = \mu_{ice}$ $\mu_{water} < \mu_{ice}$ $\mu_{water} = \mu_{ice}$

The freezing temperature is lowered by adding solute. (a) The freezing temperature of pure solvent is T_f. (b) Adding solute reduces the tendency of the water to escape from the liquid mixture to ice. At T_f, this melts the ice. (c) Lowering the temperature to $T < T_f$ lowers the tendency of water to escape from the ice, to reach a new freezing point.
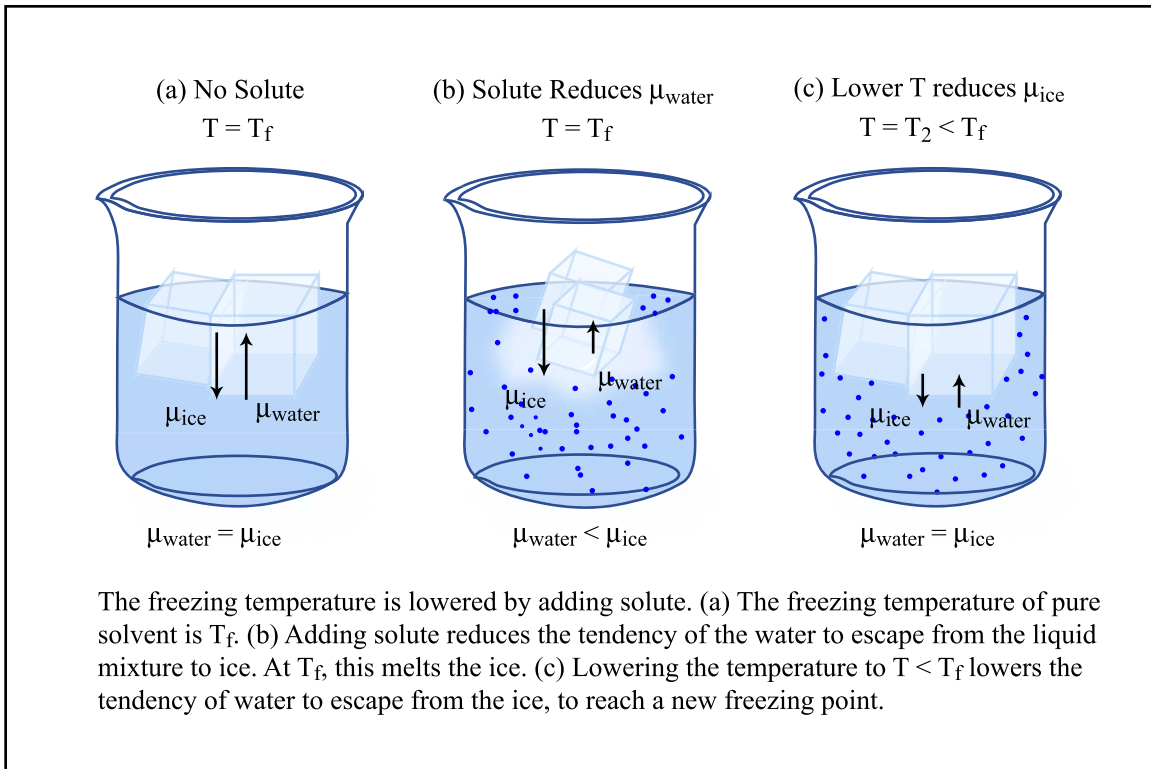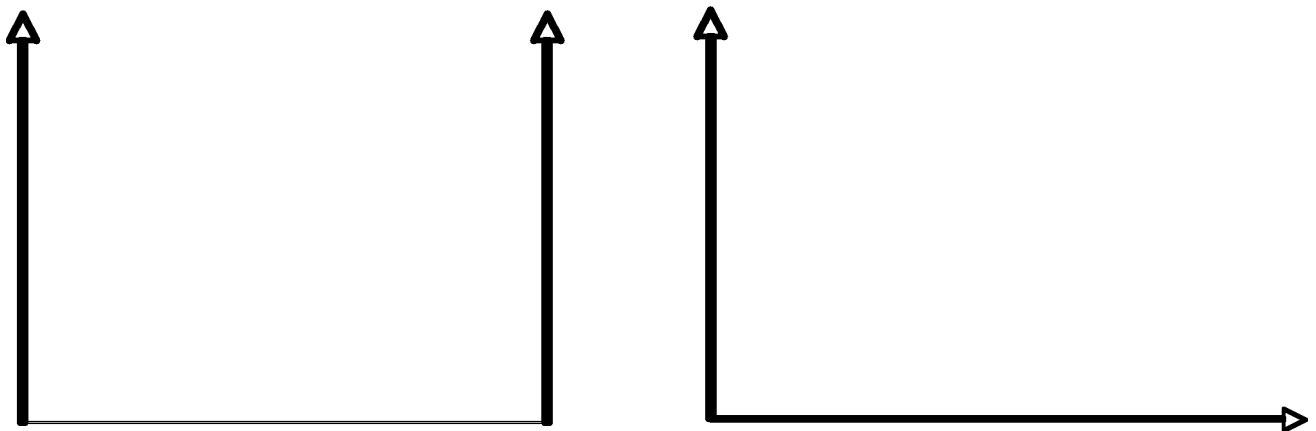
Figure by MIT OCW.

- Qualitatively:

Free energy diagrams of multi-phase solutions(5)

- We have already dealt at length with the criteria for equilibrium at constant temperature and pressure in closed systems: the Gibbs free energy must reach a minimum, and for multi-phase materials, this implies that the chemical potential of each component must be the same in every phase present. The free energy diagrams we introduced last time can conveniently be used to analyze multiphase equilibria that satisfy these conditions graphically.

The common tangent construction and the lever rule

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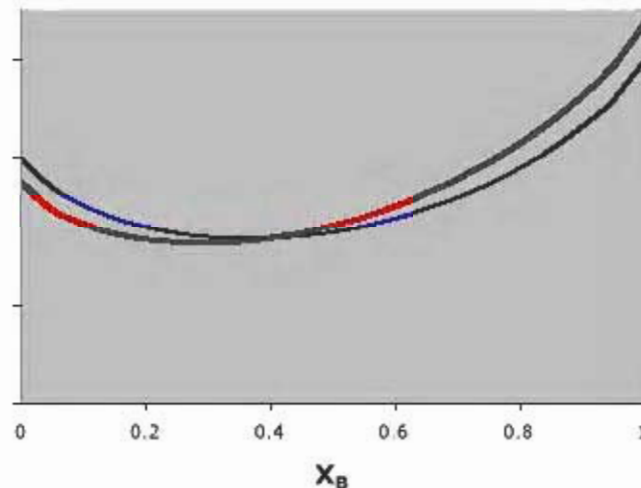

- o We can answer numerous questions about the thermodynamics of this system from such a diagram:

    - Which phase is thermodynamically stable at each value of X_B for this temperature?
    - What is the molar free energy change to melt pure A? to melt pure B?
    - What is the free energy change on forming a liquid solution from 0.5 moles of pure B and 0.5 moles of pure A?

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

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

    o   The answer is seen in the following two diagrams:
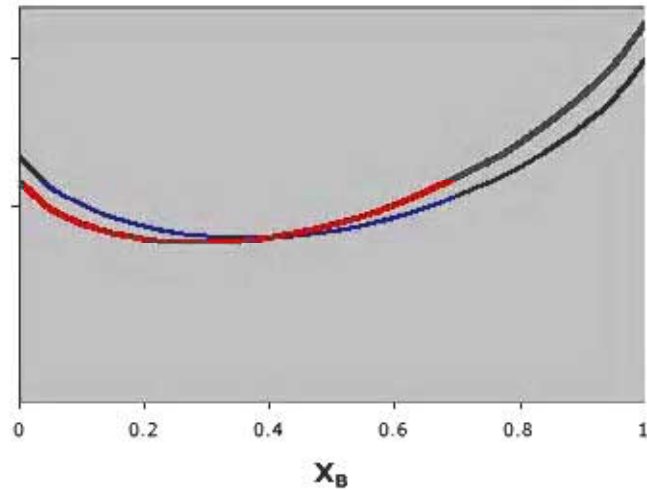
$$T_{m,B} > T=T_1 > T_{m,A}$$
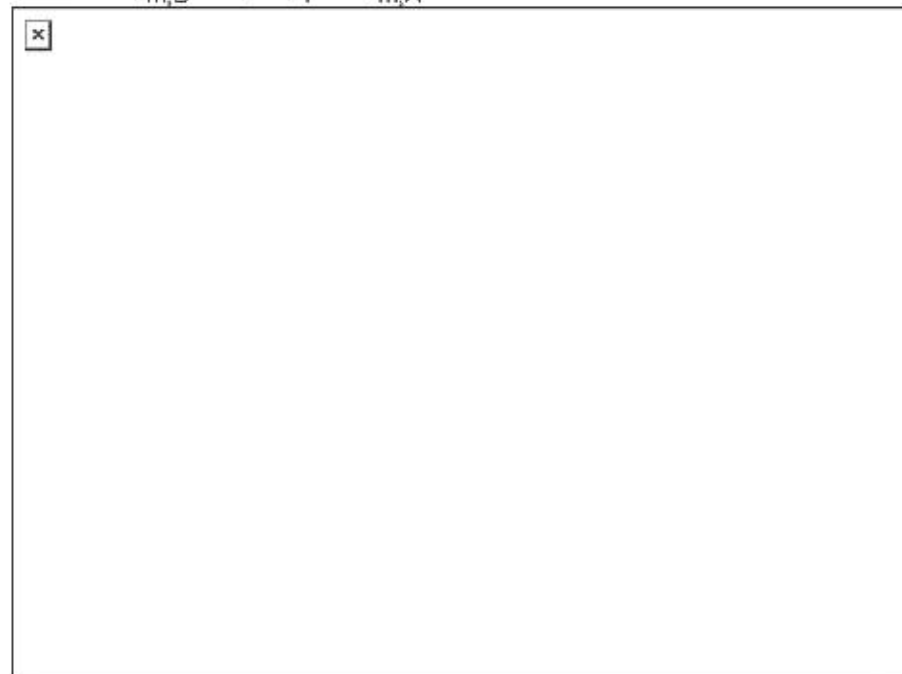
    o   What is happening in the second figure? We have reduced the temperature to the point where the stable state of pure B is a solid. Remember that the chemical potential is given by the end-points of the tangent to the free energy curve at a given composition. But we find that at T_1, a line can be 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.

References

1. Denbigh, K. 1997. *The Principles of Chemical Equilibrium*. Cambridge University Press, New York.
2. Bergeron, C. G., and S. H. Risbud. 1984. *Introduction to Phase Equilibria in Ceramics*. American Ceramic Society, Westerville, OH.
3. Sque, S.
4. Dill, K., and S. Bromberg. 2003. *Molecular Driving Forces*, New York.
5. Carter, W. C. 2002. 3.00 Thermodynamics of Materials Lecture Notes.