_____Dec. 2 2002: Lecture 28: _____

Uniformity of Chemical Potential at Equilibrium

<u>Last Time</u>

Single Component Phase Diagrams: Gibbs Phase Rule

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Single Component Phase Diagrams: Behavior of $\overline{G}$

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Freezing Point Depression

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_____ **Conditions for the Appearance of a New Phase** _____

Last time, it was observed that a a soluble species (i.e, salt) cannot continue to be added to a phase (i.e. salty water) and continue to lower the freezing point.

What happens when too much salt is added to a solution?

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Clearly, a solubility limit must exist and a new phase will appear.

This can be qualitatively understood by considering the behavior of the molar Gibbs free energy of forming a solution as a function of the amount of solute X_B:

To quantify the conditions for the appearance of new phases, consider the thermodynamics of binary (i.e. two component) alloys[28]

The Gibbs-Duhem equation of a system consisting of two components A and B is:

$$0 = SdT - VdP + \sum N_i d\mu_i = SdT - VdP + N_A d\mu_A + N_B d\mu_B$$

Consider a closed system consisting of one mole of molecules: $N_A + N_B = 1$ mole:

$$X_A = \frac{N_A}{N_A + N_B} \implies X_B = 1 - X_A = \frac{N_B}{N_A + N_B} \tag{28-1}$$

The state of the system (per mole) should be representable by three independent parameters, (T, P, X_B) or (T, P, X_A). Therefore, using $\mu_A = \mu_A(P, T, X_B)$ and $\mu_B = \mu_B(P, T, X_B)$ in the Gibbs-Duhem equation:

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\begin{aligned}
0 =& \overline{S}^{\text{total}} dT - \overline{V}^{\text{total}} dP \\
& + X_A(\frac{\partial \mu_A}{\partial T} dT + \frac{\partial \mu_A}{\partial P} dP + \frac{\partial \mu_A}{\partial X_B} dX_B) \\
& + X_B(\frac{\partial \mu_B}{\partial T} dT + \frac{\partial \mu_B}{\partial P} dP + \frac{\partial \mu_B}{\partial X_B} dX_B)
\end{aligned}
\tag{28-2}
$$

where

$$d\mu_A = \frac{\partial \mu_A}{\partial T} dT + \frac{\partial \mu_P}{\partial T} dP + \frac{\partial \mu_A}{\partial X_B} dX_B$$

Note that $\frac{\partial \mu_A}{\partial T} = -\overline{S_A}$ and $\frac{\partial \mu_B}{\partial T} = \overline{V_B}$, thus,

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[28] The notation for binary alloys uses X_A and $X_B = 1 - X_A$ for the composition. Because, there is only one free composition variable, sometimes people will simply use "X" to represent the amount of the second component—in our case $X = X_B$.

$$0 = \overline{S}^{total} dT - \overline{V}^{total} dP$$
$$- (X_A \overline{S_A} + X_B \overline{S_B})dT + (X_A \overline{V_A} + X_B \overline{V_B})dP \tag{28-3}$$
$$+ (X_A \frac{\partial \mu_A}{\partial X_B} + (1 - X_A)\frac{\partial \mu_B}{\partial X_B})dX_B$$

The first and third terms cancel and the second and fourth terms cancel. Therefore,

$$(1 - X_B)\frac{\partial \mu_A}{\partial X_B} + X_B \frac{\partial \mu_B}{\partial X_B} = 0 \tag{28-4}$$

This is a general result for binary solution. It is the form of the Gibbs-Duhem equation for solutions. Equation 28-4 gives a relation between the derivatives of the chemical potentials but not a relation between the chemical potentials themselves.

Graphical Constructions for the Free Energy of Solutions

A useful graphical construction can be utilized for extracting values of chemical potentials: Consider that the molar free energy of a solution is plotted as follows:

Figure 28-1: Example of the Molar Gibbs Free Energy of a Solution and related graphical constructions.
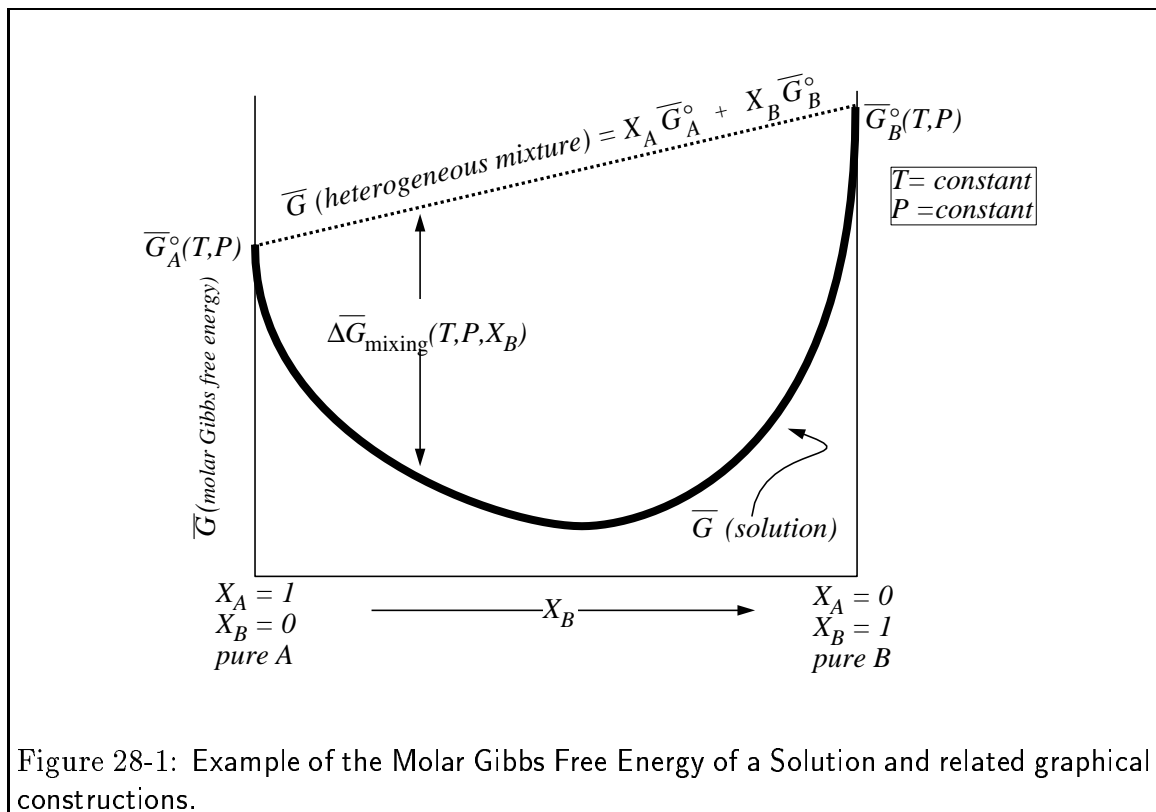
It would be particularly useful to obtain the chemical potentials of each species in solution as a function of composition. This relationship can be determined as follows:

Starting with an expression for the molar free energy of the solution being a weighted sum of the chemical potentials:

$$\overline{G_{sol}} = X_A \mu_A + X_B \mu_B \tag{28-5}$$

$d\overline{G_{sol}}$ becomes when using $dX_B = -dX_A$.

or

$$\frac{\partial \overline{G_{sol}}}{\partial X_A} = \mu_A - \mu_B \tag{28-6}$$

at constant P and T; similarly,

$$\frac{\partial \overline{G_{sol}}}{\partial X_B} = \mu_B - \mu_A \tag{28-7}$$
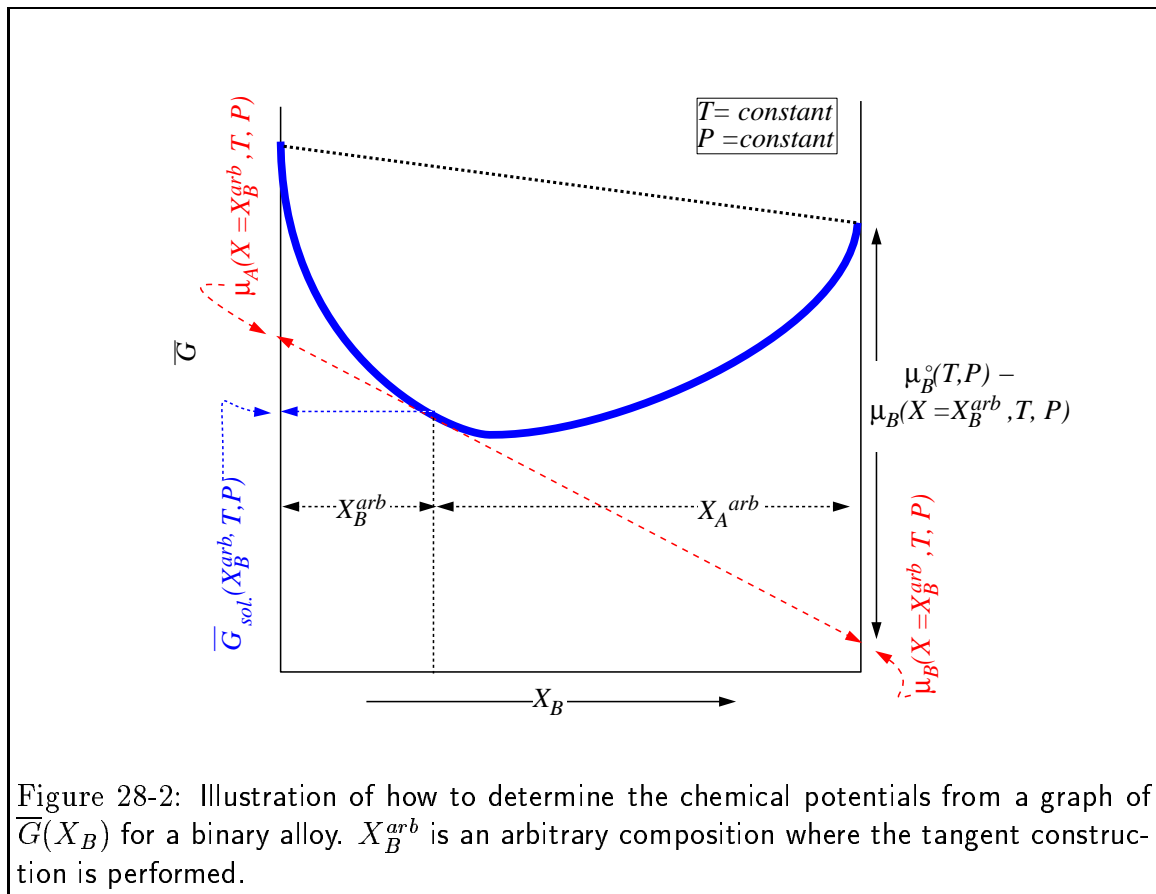
Multiplying $\partial \overline{G_{sol}}/\partial X_B$ by X_B and subtracting it from $\overline{G_{sol}}$:

$$\overline{G_{sol}} - X_B \frac{\partial \overline{G_{sol}}}{\partial X_B} = X_A \mu_A + X_B \mu_B - (X_B \mu_B - X_B \mu_A) = \mu_A \tag{28-8}$$

or

$$\mu_A = \overline{G_{sol}} + X_B \frac{\partial \overline{G_{sol}}}{\partial X_A} = \boxed{\overline{G_{sol}} - X_B \frac{\partial \overline{G_{sol}}}{\partial X_B}}$$

$$\mu_B = \boxed{\overline{G_{sol}} + X_A \frac{\partial \overline{G_{sol}}}{\partial X_B}} = \overline{G_{sol}} - X_A \frac{\partial \overline{G_{sol}}}{\partial X_A} \tag{28-9}$$

These equations can be interpreted with the following figure.

Figure 28-2: Illustration of how to determine the chemical potentials from a graph of $\overline{G}(X_B)$ for a binary alloy. X_B^{arb} is an arbitrary composition where the tangent construction is performed.

Equilibria between Phases

To calculate the equilibrium condition between several phases, the condition that the chemical potential of each component μ_i is the same in each phase. The graphical construction for chemical potential can be used to obtain this condition—this condition will be called the "common tangent" condition.

Suppose another curve corresponding to another phase that can also form a solution of A-B is considered. Below, another graphical construction will be demonstrated that will determine the properties of stable phases.

Consider two phases; to fix our ideas let one curve be the molar Gibbs free energy as a function of composition at constant pressure and temperature be for a *solid* solution. Another curve for the liquid solution will be added:

Figure 28-3: Molar Gibbs Free Energies for a liquid and solid solution at a particular pressure and temperature.
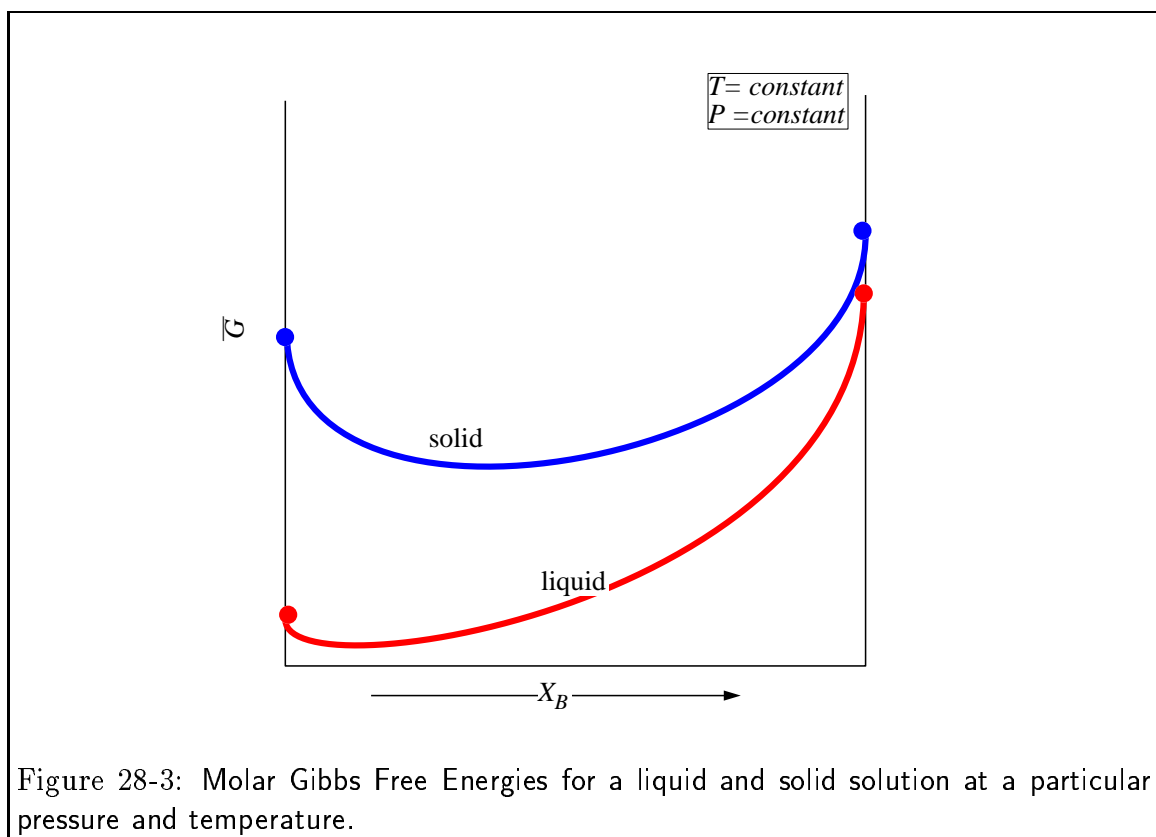
Questions:

1. What is the molar free energy charge for melting pure A? For melting pure B?

2. What is the molar free energy charge for melting a solid solution at $X_\circ$?

3. What is the free energy charge for forming a liquid solution from $X_\circ$ moles of pure B and $1 - X_\circ$ moles of pure A?

4. In the picture as it's drawn, rank the following with respect to stability from most stable to least stable at some fixed composition.

A^{solid}—B^{solid} A heterogeneous mixture of pure solid A and pure solid B.

A^{solid}—B^{liquid} Heterogeneous mixture of pure solid A and pure liquid B.

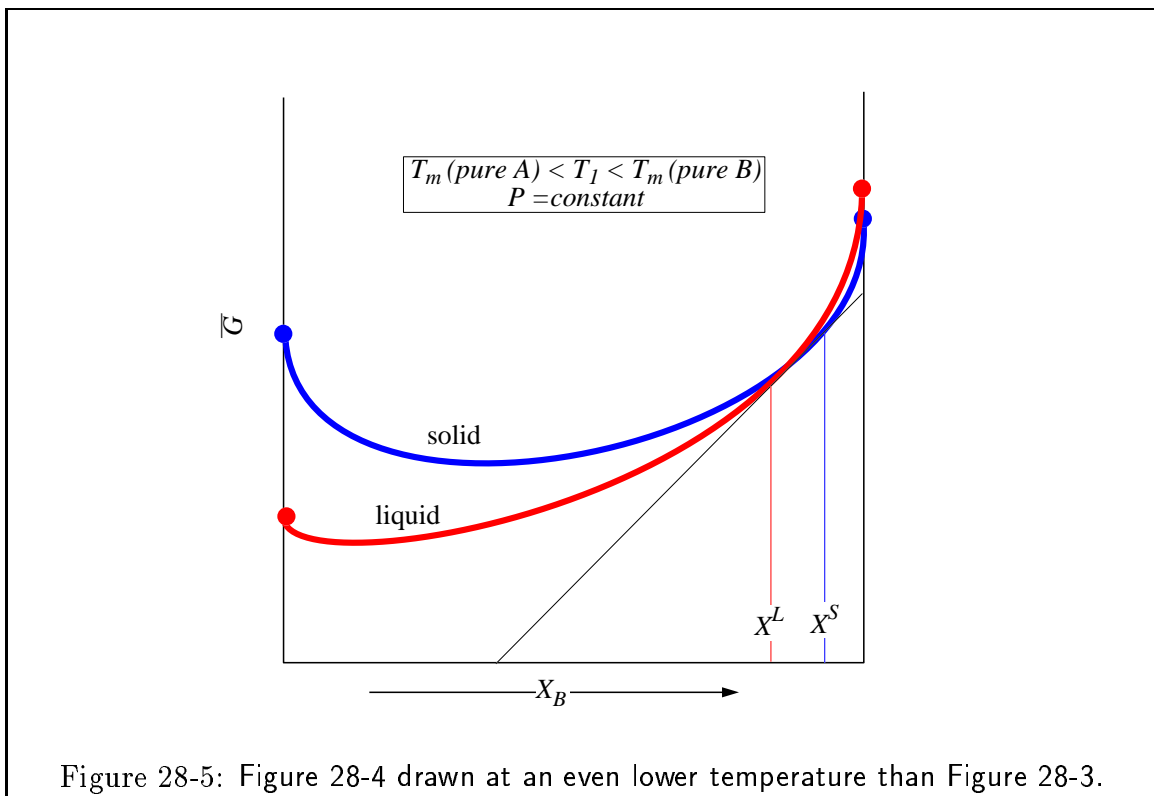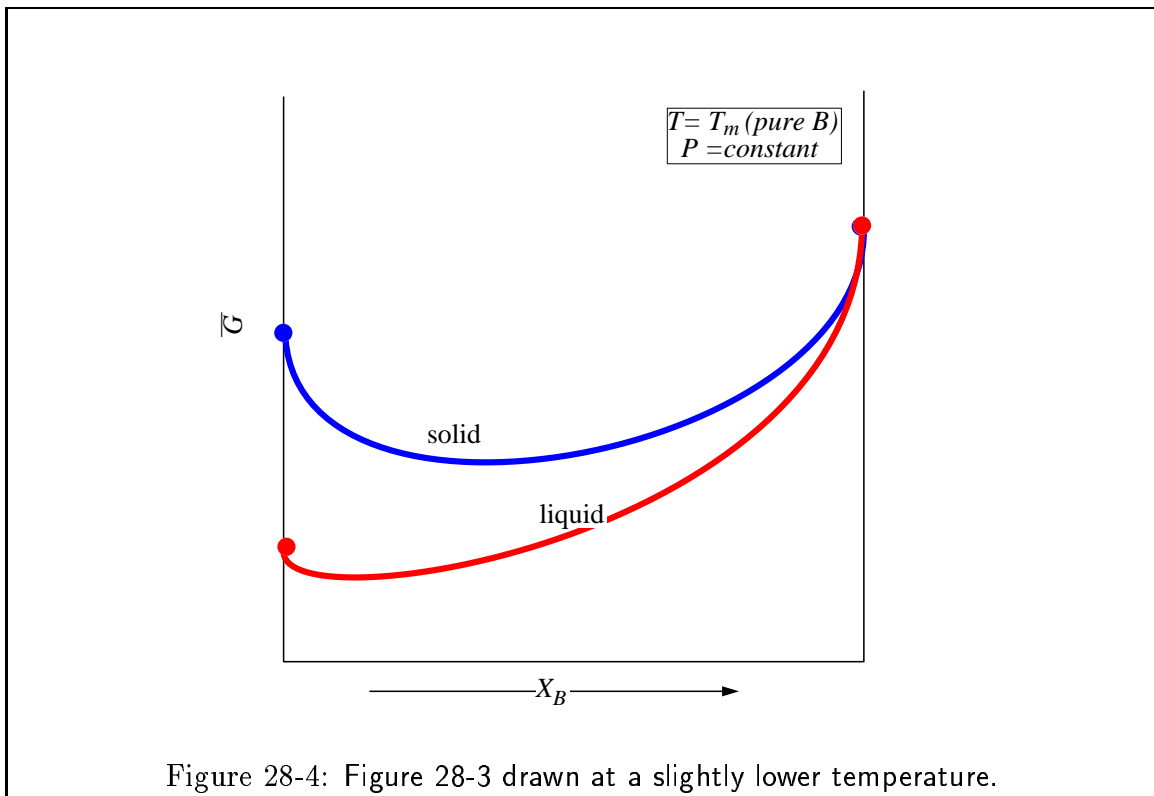A^{liquid}—B^{solid} A heterogeneous mixture of pure liquid A and pure solid B.

A^{liquid}—B^{liquid} A heterogeneous mixture of pure liquid A and pure liquid B.

$(AB)^{\text{solid}}$ Homogeneous solid solution of A and B.

$(AB)^{\text{liquid}}$ Homogeneous liquid solution of A and B.

5. Considering that $\overline{G} = \overline{H} - T\overline{S}$, which curve will "move" the most as T changes?

Consider the effect of lowering the temperature slightly.

Figure 28-4: Figure 28-3 drawn at a slightly lower temperature.

Figure 28-5: Figure 28-4 drawn at an even lower temperature than Figure 28-3.

Question: Which combination is the most stable in Figure 28-5?

Hint: Consider that at equilibrium $\mu_A{}^{\text{liquid}} = \mu_A{}^{\text{solid}}$ and $\mu_B{}^{\text{liquid}} = \mu_B{}^{\text{liquid}}$