Generating Complex Phase Diagrams Using Regular Solution Theory

**A Computer Project Applying
the Ability to Numerically Solve Systems
of Nonlinear Algebraic Equations
and Ordinary Differential Equations
to Engineering Problems**

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ChE 505
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I. Objective:

Engineering Objectives:

Using regular solution theory, create a temperature vs. composition phase diagram of solid-liquid equilibria of a binary mixture. Use this phase diagram, to design a continuous process that precipitates out solid of a specified composition.

Computational Objectives:

Apply the ability to numerically solve systems of nonlinear algebraic equations and nonlinear ordinary differential equations to engineering problems. Specifically, use the ability to solve a system of two nonlinear algebraic equations to determine the composition of co-existing phases over a range of temperatures, in order to generate the phase diagram. Use the ability to solve a system of two nonlinear ordinary differential equations to determine the transient and steady state behavior of a continuous process intended to precipitate solid material from a liquid mixture at a particular composition.

II. Background: Gibbs Free Energy Curves

In determining the phase equilibria of binary mixtures we are generally asked to perform two tasks: For a given pressure, P, and temperature, T, find (i) the phases present and (ii) the composition of the phases.

The first task can be accomplished by examining the Gibbs Free Energy of the two phases. Consider a case where we could reasonably expect to find a solid and liquid. In general, we plot the molar Gibbs free energy of the mixture in both phases. The phase with the lower Gibbs free energy is the one we expect to see.

For example, in Figure 1., we plot the molar Gibbs free energy of a hypothetical mixture in the solid and liquid phases. We specify a temperature. Because we are dealing with condensed phases, we may often assume that the pressure dependence of the Gibbs free energy is minimal and neglect considering the pressure, i.e. we assume that our results hold for all pressures. In Figure 1., we see that the Gibbs free energy of the solid is less than that of the solid for all compositions. Therefore, we expect to observe only the solid phase, regardless of the composition of the bulk material.

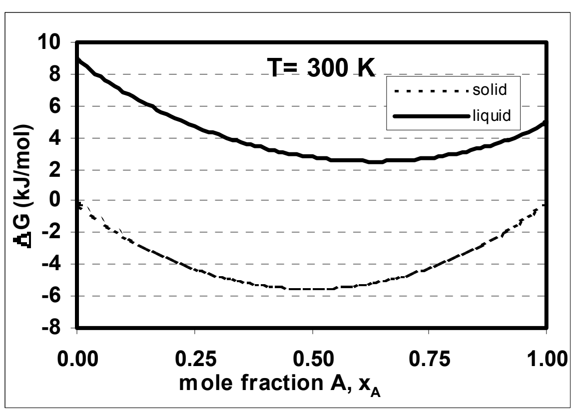

Figure 1. (Ω^{sol} = -15 kJ/mol, Ω^{liq} = -10 kJ/mol, T=300 K)

In Figure 2., at a higher temperature, we see that the Gibbs free energy of the liquid is lower at all compositions, so we expect only to see the liquid phase.

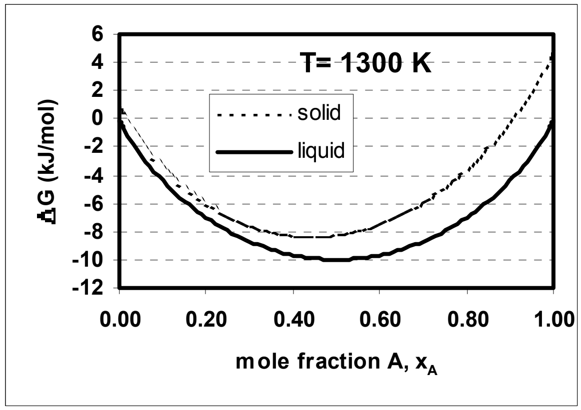

Figure 2. (Ω^{sol} = -15 kJ/mol, Ω^{liq} = -10 kJ/mol, T=1300 K)

In Figure 3., at an intermediate temperature, we see that the Gibbs free energy of the solid is lower at low mole fractions of component A but the Gibbs free energy of the liquid is lower at high mole fractions of component A. In this case, the phases present are more complicated. At low mole fractions of A, we expect only solid. At very high mole fractions of A, we expect only liquid. However, at intermediate values, for bulk mole fractions of A between 0.694 and 0.787, we expect to see two phases, one liquid and one solid, with the liquid phase being A-rich, that is having a mole fraction of A (namely 0.787) higher than the bulk value and a solid being A-poor, that is having a mole fraction of A (namely 0.694) lower than the bulk value. We will see how we determine this two phase region and how we determine the compositions of each phase.

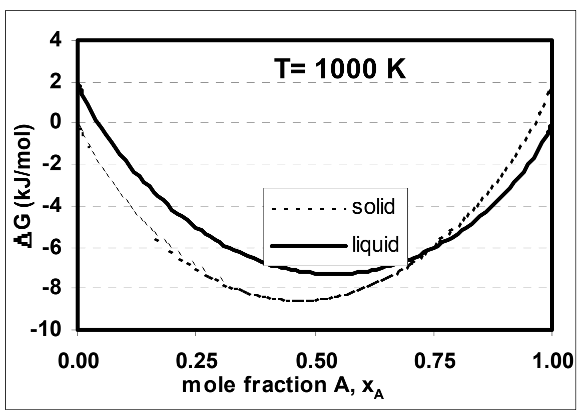

Figure 3. (Ω^{sol} = -15 kJ/mol, Ω^{liq} = -10 kJ/mol, T=1000 K)

III. Background: Phase equilibria

As shown in Figures 1. and 2., when one phase has a lower Gibbs free energy at all components, then that phase will be present. As shown in Figure 3., when the phase with the lower Gibbs free energy changes with composition, we will observe two phases for some values of bulk composition.

Determining the composition of the two phases (and thus the range of the two-phase region) requires we satisfy the constraint of chemical equilibria. The constraint of chemical equilibria says that the partial molar Gibbs free energy of component A in the solid phase is equal to the partial molar Gibbs free energy of component A in the liquid phase. Mathematically,

$$\overline{G}_A^{liq} = \overline{G}_A^{sol} \tag{1}$$

The partial molar Gibbs free energies of component A in each phase is expressed as

$$\overline{G}_A^{liq} \equiv \left(\frac{\partial G^{liq}}{\partial x_A}\right)_{T,P} \quad \text{and} \quad \overline{G}_A^{sol} \equiv \left(\frac{\partial G^{sol}}{\partial x_A}\right)_{T,P} \tag{2}$$

We don't need to worry about component B, due to the constraint that the mole fractions must sum to unity,

$$x_A^{liq} + x_B^{liq} = 1 \quad \text{so} \quad x_B^{liq} = 1 - x_A^{liq} \tag{3}$$

so the mole fraction of component B is not an independent variable. Analogous equations can be written for the solid phase.

Substituting equation (2) into equation (1) and rearranging yields:

$$f_1(x_A^{liq}, x_A^{sol}) = \overline{G}_A^{liq} - \overline{G}_A^{sol} = \left(\frac{\partial G^{liq}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{liq}} - \left(\frac{\partial G^{sol}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{sol}} = 0 \tag{4}$$

This equation has two unknowns, x_A^{liq}, x_A^{sol}. So long as we can obtain the partial derivatives of the Gibbs free energy we have a nonlinear algebraic equation. But we have two unknowns, so we need another equation. Equation (1) and (2) are the mathematical statement that the slopes of the curves in Figure 3. must be equal at the equilibrium compositions. The second equation we need is that the lines defined by the equilibrium compositions and their respective slopes be equal. This boils down to the intercepts being equal. Consider the basic equation of a line:

$$y = m \cdot x + b \tag{5}$$

If we write this for both liquid and solid phases we have,

$$G^{liq} = \left(\frac{\partial G^{liq}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{liq}} \cdot x_A^{liq} + b \quad \text{and} \quad G^{sol} = \left(\frac{\partial G^{sol}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{sol}} \cdot x_A^{sol} + b \tag{6}$$

The intercepts, b, are the same. If we equate intercepts, we can rewrite

$$b = G^{liq} - \left(\frac{\partial G^{liq}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{liq}} \cdot x_A^{liq} = G^{sol} - \left(\frac{\partial G^{sol}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{sol}} \cdot x_A^{sol} \tag{7}$$

This yields the equation:

$$f_2(x_A^{liq}, x_A^{sol}) = G^{liq} - \left(\frac{\partial G^{liq}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{liq}} \cdot x_A^{liq} - G^{sol} + \left(\frac{\partial G^{sol}}{\partial x_A}\right)_{T,P}\Bigg|_{x_A^{sol}} \cdot x_A^{sol} = 0 \quad (8)$$

Equations (4) and (8) provide two equations necessary to solve for the two unknown compositions. Graphically, equations (4) and (8) can be shown on the free energy curve in Figure 4. This graphical method of finding the compositions is called the "common tangent" method. In Figure 4., the common tangent is drawn. As you can see, it is practically impossible to distinguish the tangent points by eye.

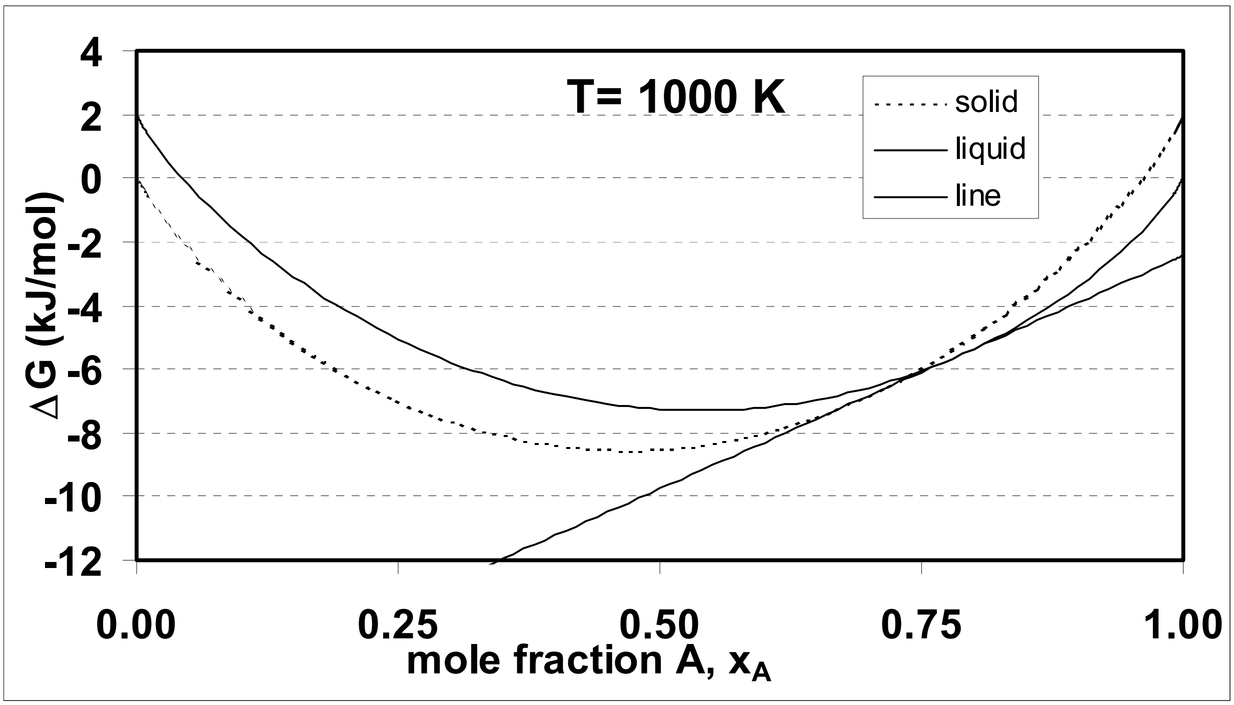

Figure 4. (Ω^{sol} = -15 kJ/mol, Ω^{liq} = -10 kJ/mol, T=1000 K)

Even if we focus on the area of interest in Figure 4., as is done in Figure 5., still it is difficult to determine the tangent points. We see that the graphical method has practical impediments toward implementation.

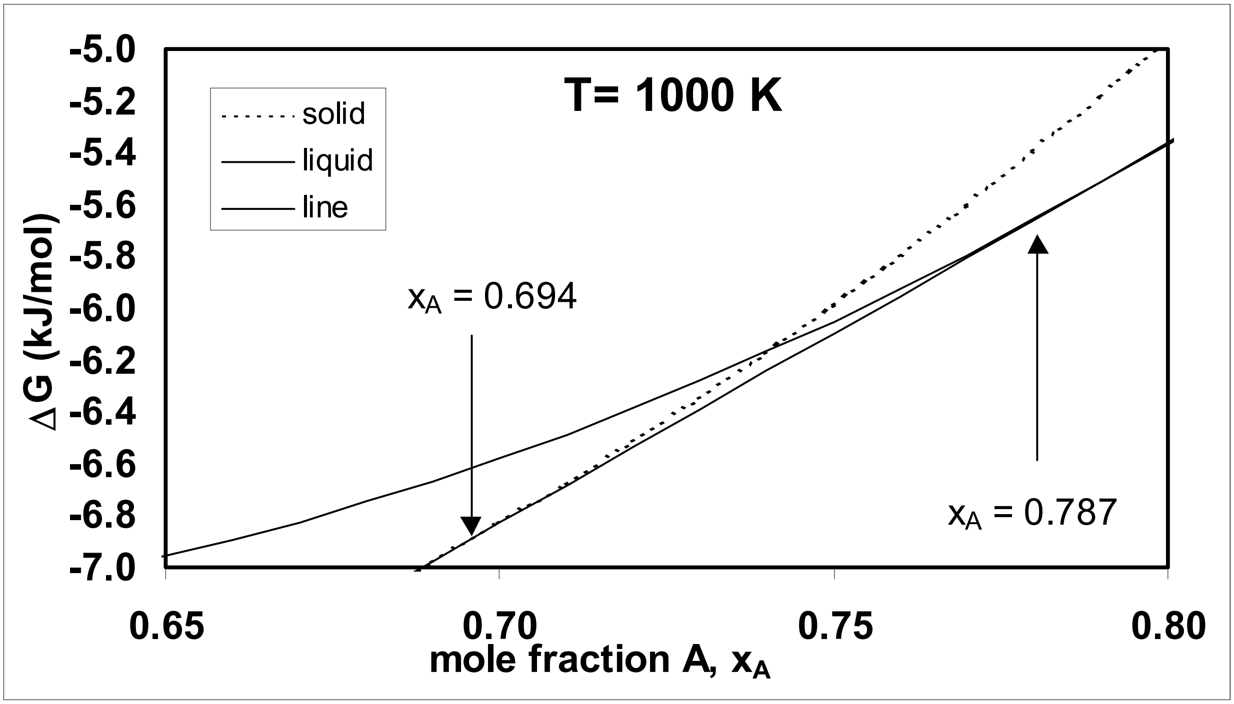

Figure 5. Magnification of Figure 4.

However we can solve equations (4) and (8) simultaneously, as a set of coupled nonlinear algebraic equations, using any of a number of standard routines covered in this course and implemented in *syseqn.m*. We can use the plots of the free energy curves to get some good initial guesses for the equilibrium compositions.

IV. Background: Creating the phase diagram

From the Gibbs free energy curves at a specified temperature, we determine (i) which phases are present and (ii) the compositions of the phases. If we repeat this procedure over a series of temperatures, we can generate a phase diagram.

Consider the free energy curves in Figure 6. At T = 700 K, we see there is only a solid phase. At T = 800 K, we see that the curves coincide only at x_A = 1.0, or pure A. At T = 900 K, we see that there are two phases with x_A^{liq} = 0.919 and x_A^{sol} = 0.839. At T = 1000 K, we see that there are two phases with x_A^{liq} = 0.787and x_A^{sol} =0.694. At T = 1000 K, we see that there are two phases with x_A^{liq} = 0.597and x_A^{sol} =0.523. At T=1200K, we see that the curves coincide only at x_A = 0.0, or pure B. At T= 1300 K, we see there is only a liquid phase.

These compositions could have been estimated graphically by the method of common tangents. In fact, they were obtained numerically, as we will discuss below. Regardless of how the compositions were obtained, we can create the phase diagram by combining the data from Figure 6 into a single plot with temperature as a function of mole fraction. This phase diagram (using more points that the seven points given below) is plotted in Figure 7.

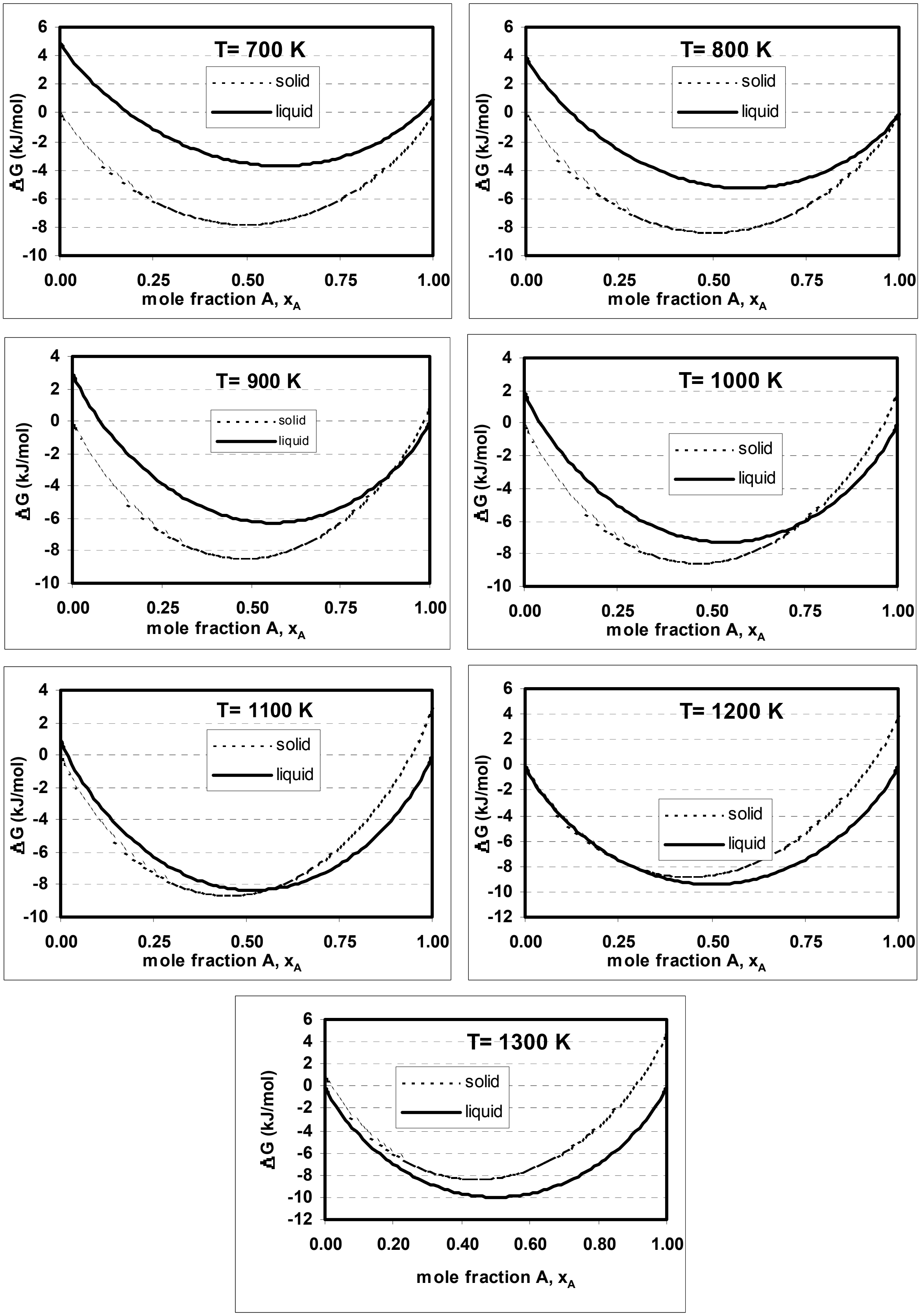

Figure 6. Free energy curves for example 1.

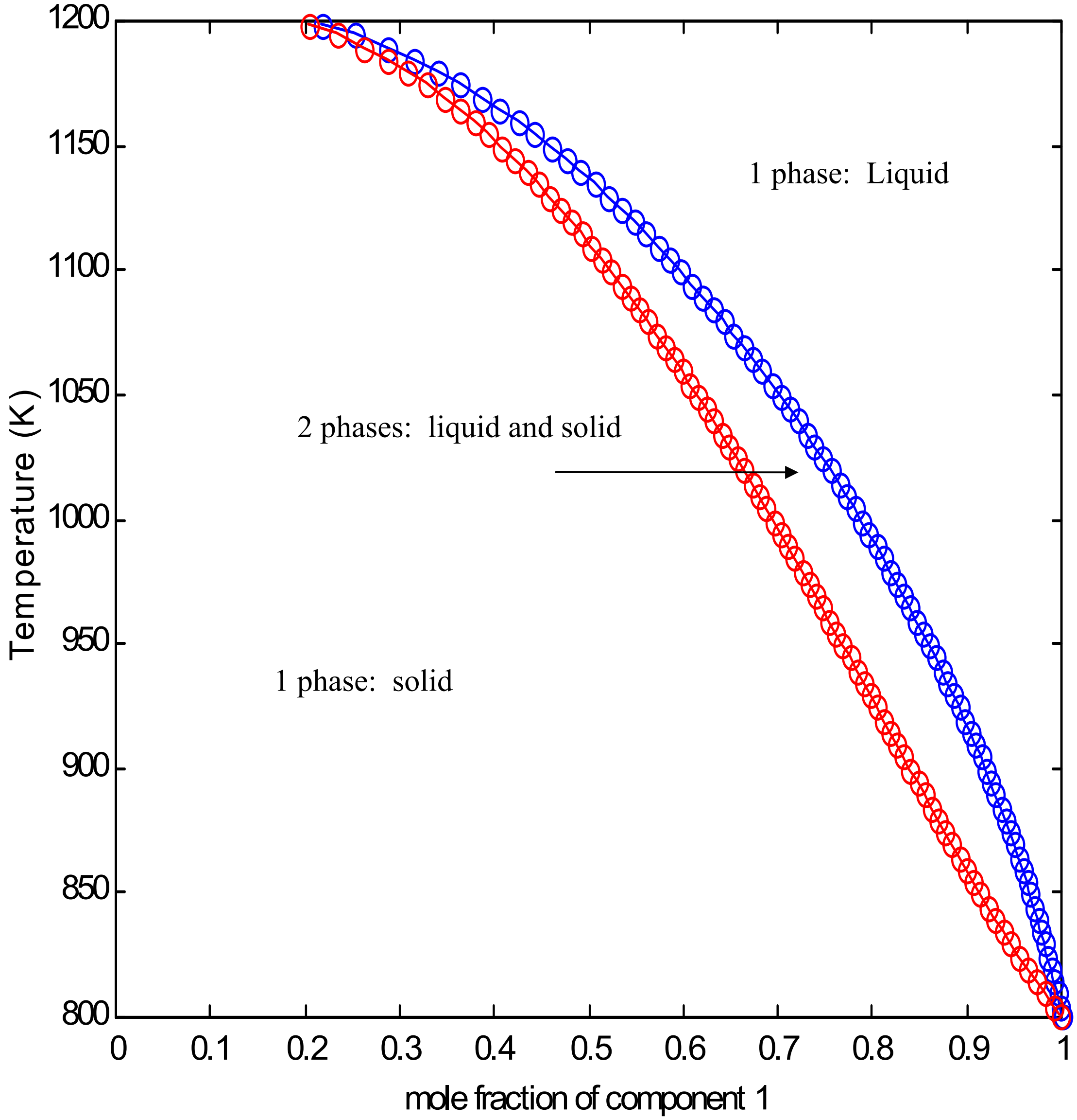

Figure 7. Phase diagram for example 1. (Ω^{sol} = -15 kJ/mol, Ω^{liq} = -10 kJ/mol) red circles=solid equilibrium mole

The phase diagram in Figure 7. shows a single liquid present above 1200 K, a single solid phase present below 800 K, and both liquid and solid phases possible at intermediate temperatures. Whether you observe two phases depends upon the composition. If you have a chunk of solid that is 80% A, it will remain a single solid phase as long as the temperature is below about 925 K. If you have a liquid of 80% A, it will remain a single liquid phase until you cool it down to about 1000 K. If you have a liquid of 80% A, which you rapidly cool to 950 K, then you will observe a solid forming, with composition 76.8% A, leaving a liquid that is 85.9% A.

You can use a mass balance to determine the respective amounts of liquid and solid.

$$\mathrm{acc} = \mathrm{in} - \mathrm{out} + \mathrm{gen} \tag{9}$$

At equilibrium there is no accumulation and our system is without reaction, so there is also no generation term. The in term is the amount of bulk material (80% A) and the out term is the respective amounts of liquid and solid at equilibrium. The mass balance on A becomes:

$$0 = m_{bulk} x_A^{bulk} - m_{liq} x_A^{liq} - m_{sol} x_A^{sol} \tag{10}$$

and the total mass balance is

$$0 = m_{bulk} - m_{liq} - m_{sol} \tag{11}$$

Solving for m_{liq} we have

$$\begin{aligned}
&0 = m_{bulk} x_A^{bulk} - m_{liq} x_A^{liq} - (m_{in} - m_{liq}) x_A^{sol} \\
&0 = m_{bulk}(x_A^{bulk} - x_A^{sol}) + m_{liq}(x_A^{sol} - x_A^{liq}) \\
&f_{liq} = \frac{m_{liq}}{m_{bulk}} = \frac{(x_A^{bulk} - x_A^{sol})}{(x_A^{liq} - x_A^{sol})} \quad \text{and} \quad f_{sol} = 1 - f_{liq}
\end{aligned} \tag{12}$$

Sometimes equation (12) is called “the lever rule”. It’s just a result of the two mass balances in equation (10) and (11). If m_{bulk} is not given, we can select an arbitrary basis of 1 mole of starting material.

In the example above, if we quickly cooled 1 mole of a liquid that was originally 80% A down to 950 K, we would have 0.352 moles of liquid with composition 85.9% A and 0.648 moles of solid with composition 76.8% A.

V. Theory: Free energies of phase changes

At this point we see conceptually how to create a phase diagram given the free energy curves. Now, we will discuss a simple theory that allows us to generate the free energy curves themselves.

The Gibbs free energy of the binary mixture in a phase ϕ is given by the sum of the Gibbs free energies of the pure components in their reference states plus a free energy change due to mixing.

$$G^{\phi}(T,x) = G_A^o(T) + G_B^o(T) + \Delta G_{mix}^{\phi}(T,x_A) \tag{13}$$

Because we will ultimately be interested only in the relative values of $G_{mix}^{\phi}(T,x)$ for each of the phases, and because the reference terms are the same for each phase ϕ, we can ignore the reference terms. The reference state has associated with it a phase. If we choose the reference state to be the pure component phase present at the given temperature, then we have to account for the free energy due to a phase change.

$$G^{\phi}(T,x) = \sum_{A}^{N} x_A \Delta G_A^{phase}(T) + \Delta G_{mix}^{\phi}(T,x_A) \tag{14}$$

We can encounter three cases where the free energy due to phase change is different.

Case 1. Temperature lower than both pure component melting temperatures ($T < T_A$ and $T < T_B$)

In this case, the reference states of the pure components are both solids.

If the mixture is a solid,

$$A_s + B_s \rightarrow AB_s$$

And the associated free energy due to phase change is zero.

$$\Delta G_A^{phase} = 0 \text{ and } \Delta G_B^{phase} = 0$$

If the mixture is a liquid, then the process we are observing is

$$A_s + B_s \rightarrow A_L + B_L \rightarrow AB_L$$

And the associated free energy due to phase change is the free energy of melting, which is a positive number, since the free energy of a liquid is greater than that of a solid.

$$\Delta G_A^{phase} = \Delta G_A^{melt} \text{ and } \Delta G_B^{phase} = \Delta G_B^{melt}$$

Case 2. Temperature between pure component melting temperatures ($T < T_A$ and $T > T_B$)

In this case, the reference state of pure A is a solid and B is a liquid.

If the mixture is a solid,

$$A_s + B_L \rightarrow A_s + B_S \rightarrow AB_s$$

And the associated free energy due to phase change is that due to B freezing, which is the negative of the free energy of melting.

$$\Delta G_A^{phase} = 0 \text{ and } \Delta G_B^{phase} = -\Delta G_B^{melt}$$

If the mixture is a liquid, then the process we are observing is

$$A_s + B_L \rightarrow A_L + B_L \rightarrow AB_L$$

And the associated free energy due to phase change is the free energy of melting A, which is a positive number, since the free energy of a liquid is greater than that of a solid.

$$\Delta G_A^{phase} = \Delta G_A^{melt} \text{ and } \Delta G_B^{phase} = 0$$

Case 3. Temperature greater than both pure component melting temps ($T > T_A$ and $T > T_B$)

In this case, the reference state of both pure A and B is liquid.
If the mixture is a solid,

$$A_L + B_L \rightarrow A_s + B_S \rightarrow AB_s$$

And the associated free energy due to phase change is that due to A and B freezing, which is the negative of the free energy of melting.

$$\Delta G_A^{phase} = -\Delta G_A^{melt} \text{ and } \Delta G_B^{phase} = -\Delta G_B^{melt}$$

If the mixture is a liquid, then the process we are observing is

$$A_L + B_L \rightarrow A_L + B_L \rightarrow AB_L$$

And the associated free energy due to phase change is zero.

$$\Delta G_A^{phase} = 0 \text{ and } \Delta G_B^{phase} = 0$$

A simple expression for the free energy of melting is given by the difference of the energetic and entropic contributions to the free energy of melting:

$$\Delta G_A^{melt} = \Delta H_A^{melt} - T\Delta S_A^{melt} \tag{15}$$

VI. Theory: Free energies of mixing

As soon as we consider a mixture, we need to include a Gibbs free energy due to mixing. Regular solution theory provides us with an expression for the Gibbs free energy due to mixing in phase j

$$\Delta G_{mix}^{\phi} = \Omega^{\phi} x_A (1 - x_A) + kT \sum_i x_i \ln(x_i) \tag{16}$$

In binary mixtures, this becomes:

$$\Delta G_{mix}^{\phi} = \Omega^{\phi} x_A (1 - x_A) + kT\left[x_A \ln(x_A) + (1 - x_A)\ln(1 - x_A)\right] \tag{17}$$

We express the functions explicitly in x_A because x_B is not independent. ($x_B = 1 - x_A$)

Regular solution theory for a binary mixture then requires two parameters, the interaction parameter in the liquid phase, Ω^L, and the interaction parameter in the solid phase, Ω^S. A positive interaction parameter physically equates to a repulsive interaction between components A and B, in which case, A and B would rather separate than mix. A negative interaction parameter physically equates to an attractive interaction between components A and B, in which case, A and B would rather mix than separate.

The total molar Gibbs free energy of the mixture is then the sum of the free energy due to phase change and free energy due to mixing. Substituting equation (17) into equation (14) we have

$$G^{\phi}(T,x) = \sum_{A}^{N}\left[x_A \Delta G_A^{phase}(T)\right] + \Omega^{\phi} x_A (1-x_A) + kT\left[x_A \ln(x_A) + (1-x_A)\ln(1-x_A)\right] \quad (18)$$

Equation (18) can be written for all phases. The phase change term is non zero for each component with a pure component phase different than the mixture phase at the given temperature.

Equation (18) is what is plotted in Figures 1. through 6., for ϕ = solid and ϕ = liquid. (For your information, in Figures 1. through 6., we used the following parameters:

$$T_A = 800K\text{ , } T_B = 1200K\text{ , } \Omega^{sol} = -15\text{ kJ/mol , } \Omega^{liq} = -10\text{ kJ/mol}$$
$$\Delta H_A^{melt} = 8\ \mathit{kJ/mol}\text{ , } \Delta H_B^{melt} = 12\ \mathit{kJ/mol}\text{ , } \Delta S_A^{melt} = 10\ \mathit{J/mol/K}\text{ , } \Delta S_B^{melt} = 10\ \mathit{J/mol/K}$$

Since both interaction parameters were negative, both pure components preferred to mix in both the liquid and solid phases.

VII. Assignment

Consider the binary system described by the following data:

$$T_A = 800K\ ,\ T_B = 1200K\ ,\ \Omega^{sol} = 15\ kJ/mol\ ,\ \Omega^{liq} = -10\ kJ/mol$$
$$\Delta H_A^{melt} = 8\ kJ/mol\ ,\ \Delta H_B^{melt} = 12\ kJ/mol\ ,\ \Delta S_A^{melt} = 10\ J/mol/K\ ,\ \Delta S_B^{melt} = 10\ J/mol/K$$

Task One. Generate Free Energies for the solid and liquid phases for temperature from 300, 400, …1300 K. These plots should have the form of Figure 6.

Task Two. Using the free energy plots, determine the number and type of phases present at each temperature. Then, using the free energy plots for initial guesses of the phase compositions, determine the compositions of each phase, using your choice of technique to solve a system of two equations (equations (4) and (8)) for two unknowns. (Note, this problem will yield a more complicated phase diagram than the example worked out above. At some temperatures, you will have two solid phases in equilibrium. At other temperatures, you will have 2 different solid-liquid equilibria, depending upon the bulk composition.)

Task Three. Create the phase diagram using the information from Task Two. This should be in the general form of Figure 7.

Task Four. Use the phase diagram to find the transient behavior of a process.

The purpose of the process is to produce a solid metal material with a composition $x_A^{prod} = 0.02537$. Available as feedstock is an ore with composition $x_A^{prod} = 0.25$ and a pure B solid. A schematic of the diagram is given as Figure 8.

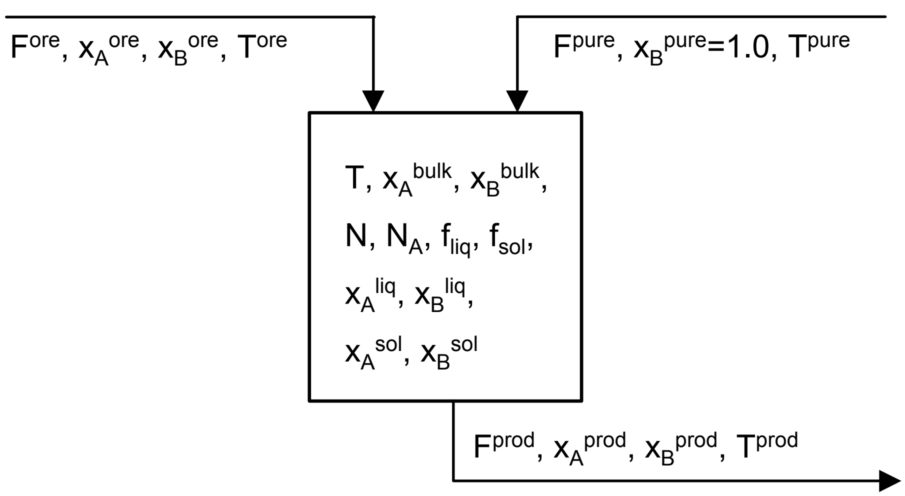

Figure 8. Schematic of Solid Mixture Process

For the purposes of this project, we assume that the contents of the reactor are at thermodynamic equilibrium. Therefore, for a given T, the compositions of the liquid and solid phases in equilibrium, $x_A^{liq}, x_B^{liq}, x_A^{sol}, x_B^{sol}$ can be obtained from the phase diagram obtained in Task 3. The bulk composition inside the reactor, x_A^{bulk}, x_B^{bulk}, can be determined from the total moles, N, and the moles of species A, N_A, inside the reactor. The fractions of liquid and solid inside the reactor, f^{liq}, f^{sol}, can be determined using the lever rule and the above liquid, solid, and bulk mole fractions. The reactor is well mixed so the reactor effluent is the same as the reactor contents (i.e. $x_A^{prod} = x_A^{sol}, x_B^{prod} = x_B^{sol}, T^{prod} = T$). (We equate the product compositions to the solid compositions inside the reactor, because we are removing solid product from the reactor.) The inlet feedrate of the ore, F^{ore}, is 1.0 kmol/min. The inlet feedrate of pure B, F^{pure}, is 8.0 kmol/min. The product feedrate F^{prod}, is desired to be 9.0 kmol/min. Since the reactor is running in isothermal conditions, we don't necessarily need to worry about the temperatures of the inlet streams unless we desire to calculate the amount of heat, Q, required to maintain a constant temperature.

(a) Find the temperature that will yield the desired solid product composition.

(b) Running the reactor at the temperature from part (a) leaves two unknown functions: the total number of moles in the reactor, N, and the moles of species A in the reactor, N_A. Write non-steady-state mass balances for the total number of moles and the moles of A.

(c) Solve the two mass balances (analytically or numerically) for N and N_A as a function of time from 0 to 1500 minutes. From this data plot $x_A^{bulk}, f^{liq}, f^{sol}$ as functions of time.

(d) Does this process have a steady state?

(e) At what time must the process be stopped? Why?

Nomenclature

f^{ϕ}	mole fraction of bulk in phase ϕ
F^{j}	molar flowrate of stream j
G_i^o	molar Gibbs free energy of pure component i in reference state
G^{ϕ}	molar Gibbs free energy of a mixture
$\overline{G}_i^{\phi}$	partial molar Gibbs free energy of component i in phase ϕ
ΔG_i^{melt}	molar Gibbs free energy of melting of pure component i
ΔG_{mix}^{ϕ}	molar Gibbs free energy of mixing in phase ϕ
ΔG_i^{phase}	change in molar Gibbs free energy due to phase change of pure component i
ΔH_i^{melt}	molar enthalpy of melting of pure component i
k	Boltzmann constant
N	total number of moles
N_i	moles of species i in bulk
P	pressure
ΔS_i^{melt}	molar entropy of melting of pure component i
T	temperature
x_i^{ϕ}	mole fraction of component i in phase ϕ
Ω^{ϕ}	regular solution theory interaction parameter for phase ϕ

Acknowledgements

My first exposure to the rich phase behavior provided by regular solution theory came while I was a graduate student at the University of Minnesota, Minneapolis, while a teaching assistant to Prof. Alon McCormick for an introduction to materials science course (MatS 3600) in the winter quarter of 1996. This project is an extension of what I learned there.