Homework Assignment Number Ten Assignment

Problem 1. (2 points)
Find the solution to the following system of nonlinear algebraic equations near (1,1,1).

$$f_1 = x_1 + 2x_2 + 3x_3 - 4$$
$$f_2 = {x_1}^3 - 4{x_2}^3$$
$$f_3 = 2x_3 - sin\, x_3 + 1$$

Problem 2. (4 points)
Perform 2 iterations of multivariate Newton-Raphson on the following system of nonlinear algebraic equations.

$$f_1 = {x_1}^2 + {x_2}^2 - 4$$
$$f_2 = {x_1}^2 - x_2 + 1$$

Show the value of the Jacobian, residual and $\underline{\delta x}^{(k)}$ at each iteration. Use and initial guess of (x_1, x_2) = (1,2). Report the values of (x_1, x_2) for the first two iterations.

Problem 3. (4 points)
Consider the solid-liquid equilibrium of a binary alloy described by regular solution theory. Consider two materials, A and B with the following pure component properties:

component	melting temperature (K)	enthalpy of melting (J/mol)	entropy of melting (J/mol/K)
symbol	T_A^{melt}, T_B^{melt}	$\Delta H_A^{melt}, \Delta H_B^{melt}$	$\Delta S_A^{melt}, \Delta S_B^{melt}$
A	800.0	8,000.0	10.0
B	1200.0	12,000.0	10.0

The regular solution parameters for the enthalpy of mixing are given as

	liquid	solid
enthalpy of mixing parameter (J/mol) (Ω)	-5,000.0	0.0

(a) Plot the free energy curve of each phase at a temperature of T = 1000 K as a function of composition.
(b) Determine the liquid and solid equilibrium compositions at T = 1000 K.

Regular solution theory in a nutshell.
The total free energy of either liquid (liq) or solid (sol) phase is made up of two terms, one representing a phase change if the phase is not the equilibrium state and one representing the contribution due to mixing.

$$\Delta G_{liq} = \Delta G_{liq}^{phase} + \Delta G_{liq}^{mix} \quad \text{(1.liq)}$$

$$\Delta G_{sol} = \Delta G_{sol}^{phase} + \Delta G_{sol}^{mix} \quad \text{(1.sol)}$$

The mixing term has the following form which is the sum of an enthalpy term and an entropy term.

$$\Delta G_{liq}^{mix} = \Omega_{liq} x_A x_B + RT[x_A ln(x_A) + x_B ln(x_B)] \quad \text{(2.liq)}$$

$$\Delta G_{sol}^{mix} = \Omega_{sol} x_A x_B + RT[x_A ln(x_A) + x_B ln(x_B)] \quad \text{(2.sol)}$$

where R is the gas constant (8.314 J/mol/K) and where x_A is the atomic fraction of A, and x_B is the atomic fraction of B. Remember, in a binary mixture, x_B is not an independent variable. Rather, $x_B = 1 - x_A$. Note: Because of the natural logarithm in equation (2), the free energy does not exist exactly at $x_A = 0$ or $x_A = 1$.

The phase change term has the following form.

$$\Delta G_{liq}^{phase} = x_A \Delta G_{liq,A}^{phase} + x_B \Delta G_{liq,B}^{phase} \tag{3.liq}$$

$$\Delta G_{sol}^{phase} = x_A \Delta G_{sol,A}^{phase} + x_B \Delta G_{sol,B}^{phase} \tag{3.sol}$$

where $dG_{liq,A}^{phase}$ and $dG_{sol,A}^{phase}$ are phase change free energies of pure component A in the liquid and solid phases respectively. They are defined as

$$\Delta G_{liq,A}^{phase} = \begin{cases} \Delta G_A^{melt} & if\ T < T_A^{melt} \\ 0 & if\ T \geq T_A^{melt} \end{cases} \tag{4.liq}$$

$$\Delta G_{sol,A}^{phase} = \begin{cases} 0 & if\ T \leq T_A^{melt} \\ -\Delta G_A^{melt} & if\ T > T_A^{melt} \end{cases} \tag{4.sol}$$

where

$$\Delta G_A^{melt} = \Delta H_A^{melt} - T\Delta S_A^{melt} \tag{5}$$

Equations (4) and (5) were written for component A. Analogous versions can be written for component B.

For part (b) of the problem, we will solve two equations for two unknowns. The two equations can be understood from the point of view of the common tangent construction. There is a tangent line to the liquid free energy curve and a second tangent line to solid free energy curve, given in equation (a). These tangent lines have the age-old form.

$$y = mx + b \tag{6}$$

where m is the slope of the line and b is the y-intercept. At the equilibrium liquid and solid composition we can write this equation as

$$y_{liq} = m_{liq} x_{liq,A} + b_{liq} \tag{7.liq}$$

$$y_{sol} = m_{sol} x_{sol,A} + b_{sol} \tag{7.sol}$$

To be clear, our goal is to find the unknown liquid and solid compositions, $x_{liq,A}$ and $x_{sol,A}$. Because there is a common tangent, we have two equations that define the unknown compositions, namely the slopes are the same and the y-intercepts are the same.

$$f_1(x_{liq,A}, x_{sol,A}) = m_{liq} - m_{sol} = 0 \tag{8.i}$$

$$f_2(x_{liq,A}, x_{sol,A}) = b_{liq} - b_{sol} = 0 \tag{8.ii}$$

To evaluate equation (8.i), we must recognize that the slope of the liquid or solid free energy curve is the partial derivative of that curve with respect to the atomic fraction of A.

$$m_{liq} = \left.\frac{\partial \Delta G_{liq}}{\partial x_A}\right|_{x_{liq,A}} \tag{9.liq}$$

$$m_{sol} = \left.\frac{\partial \Delta G_{sol}}{\partial x_A}\right|_{x_{sol,A}} \tag{9.sol}$$

We can rearrange equation (7) to solve for the intercepts

$$b_{liq} = y_{liq} - m_{liq} x_{liq,A} \tag{10.liq}$$

$$b_{sol} = y_{sol} - m_{sol} x_{sol,A} \tag{10.sol}$$

where y_{liq} and y_{sol} are points on the respective free energy curves (equation 1) evaluated at $x_{liq,A}$ and $x_{sol,A}$.

$$y_{liq} = \Delta G_{liq}(x_{liq,A}) \tag{11.liq}$$

$$y_{sol} = \Delta G_{sol}(x_{sol,A}) \tag{11.sol}$$

Substitution of equations (9), (10) and (11) into equation (8) yields

$$f_1(x_{liq,A}, x_{sol,A}) = \left.\frac{\partial \Delta G_{liq}}{\partial x_A}\right|_{x_{liq,A}} - \left.\frac{\partial \Delta G_{sol}}{\partial x_A}\right|_{x_{sol,A}} = 0 \tag{12.i}$$

$$f_2(x_{liq,A}, x_{sol,A}) = \Delta G_{liq}(x_{liq,A}) - \left.\frac{\partial \Delta G_{liq}}{\partial x_A}\right|_{x_{liq,A}} x_{liq,A} - \Delta G_{sol}(x_{sol,A}) + \left.\frac{\partial \Delta G_{sol}}{\partial x_A}\right|_{x_{sol,A}} x_{sol,A} = 0 \tag{12.ii}$$

Addendum: Help with obtaining the analytical derivative of free energy with respect to the atomic fraction of A.

Start by differentiating equation (1)

$$\frac{\partial \Delta G_{liq}}{\partial x_A} = \frac{\partial \Delta G_{liq}^{phase}}{\partial x_A} + \frac{\partial \Delta G_{liq}^{mix}}{\partial x_A} \tag{13.liq}$$

$$\frac{\partial \Delta G_{sol}}{\partial x_A} = \frac{\partial \Delta G_{sol}^{phase}}{\partial x_A} + \frac{\partial \Delta G_{sol}^{mix}}{\partial x_A} \tag{13.sol}$$

Next we differentiate the mixing term in equation (2). Remember, in a binary mixture, x_B is not an independent variable. Rather, $x_B = 1 - x_A$. So, first rewrite equation (2) substituting $1 - x_A$ for x_B.

$$\Delta G_{liq}^{mix} = \Omega_{liq} x_A (1 - x_A) + RT[x_A ln(x_A) + (1 - x_A) ln(1 - x_A)] \tag{14.liq}$$

$$\Delta G_{sol}^{mix} = \Omega_{sol} x_A (1 - x_A) + RT[x_A ln(x_A) + (1 - x_A) ln(1 - x_A)] \tag{14.sol}$$

Now differentiate with respect to x_A. We left out intermediate steps. Check for yourself.

$$\frac{\partial \Delta G_{liq}^{mix}}{\partial x_A} = \Omega_{liq}(1 - 2x_A) + RT ln\left(\frac{x_A}{1 - x_A}\right) \tag{15.liq}$$

$$\frac{\partial \Delta G_{sol}^{mix}}{\partial x_A} = \Omega_{sol}(1 - 2x_A) + RT ln\left(\frac{x_A}{1 - x_A}\right) \tag{15.sol}$$

Next we differentiate the phase change term in equation (3). Remember, in a binary mixture, x_B is not an independent variable. Rather, $x_B = 1 - x_A$. So, first rewrite equation (3) substituting $1 - x_A$ for x_B.

$$\Delta G_{liq}^{phase} = x_A \Delta G_{liq,A}^{phase} + (1 - x_A)\Delta G_{liq,B}^{phase} \tag{16.liq}$$

$$\Delta G_{sol}^{phase} = x_A \Delta G_{sol,A}^{phase} + (1 - x_A)\Delta G_{sol,B}^{phase} \tag{16.sol}$$

Now differentiate with respect to x_A.

$$\frac{\partial \Delta G_{liq}^{phase}}{\partial x_A} = \Delta G_{liq,A}^{phase} - \Delta G_{liq,B}^{phase} \tag{17.liq}$$

$$\frac{\partial \Delta G_{sol}^{phase}}{\partial x_A} = \Delta G_{sol,A}^{phase} - \Delta G_{sol,B}^{phase} \tag{17.sol}$$

We now have everything we need to solve this problem.