ChE 548
Final Exam
May 2, 2008

Problem 1.

Consider the steady state behavior of a three component fluid located in an isothermal and isobaric system between two boundaries. The thermodynamic state of the boundary at z = 0 is defined by the mole fraction of 1, $x_1 = 0.25$, mole fraction of 2, $x_2 = 0.74$, temperature T = 300 K, and pressure p = 1 bar. The thermodynamic state of the boundary at z = 1 m is defined by the mole fraction of 1, $x_1 = 0.2$, mole fraction of 3, $w_3 = 0.79$, temperature T = 300 K, and pressure p = 1 bar.

The chemical potential of component i in a multicomponent van der Waals gas is given by

$$\mu_i = -k_B T \ln\left(\frac{V_m - b_{mix}}{x_i \Lambda_i^3}\right) + \frac{k_B T b_i}{V_m - b_{mix}} - \frac{2}{V_m}\sum_{j=1}^{N_c} x_j a_{ij} \qquad (1)$$

where kB is Boltzmann's constant, V_m is the molar volume, Li is the thermal de Broglie wavelength. For this example, we will set all of the van der Waal b parameters (all b_i and b_{mix}) to zero. The values of a are as follows: $a_{11} = a_{22} = a_{33} = a_{13} = a_{23} = a_{31} = a_{32} = 0$, $a_{12} = a_{21} = 20$ Joules-m^3/mole. Consider the molar volume to be constant at $V_m = 2.5\text{x}10^{-2}$ m^3/mole.

Tasks.

(a) Using a finite difference formula, determine the average mole fraction gradients for each component, based on the boundary values.

$$\overline{\left(\frac{\partial x_1}{\partial z}\right)} = \frac{x_1(z=1) - x_1(z=0)}{1} = 0.2 - 0.25 = -0.05\,m^{-1} \qquad (2.1)$$

$$\overline{\left(\frac{\partial x_2}{\partial z}\right)} = \frac{x_2(z=1) - x_2(z=0)}{1} = 0.01 - 0.74 = -0.73\,m^{-1} \qquad (2.2)$$

$$\overline{\left(\frac{\partial x_3}{\partial z}\right)} = \frac{x_3(z=1) - x_3(z=0)}{1} = 0.79 - 0.01 = 0.78\,m^{-1} \qquad (2.3)$$

(b) Based on the sign of the mole fraction gradients, in which direction would you expect the diffusive flux of each species to be?

One would expect that species diffuse from high mole fraction to low mole fraction.
Component 1 would move to the boundary at z = 1.
Component 2 would move to the boundary at z = 1.
Component 3 would move to the boundary at z = 0.

(c) Using a finite difference formula, determine the average chemical potential gradients for each component, based on the boundary values.

The chemical potential expressions are

$$\mu_1 = -k_B T \ln\left(\frac{V_m}{x_1 {\Lambda_1}^3} \right) - \frac{2}{V_m} x_2 a_{12} \tag{3.1}$$

$$\mu_2 = -k_B T \ln\left(\frac{V_m}{x_2 {\Lambda_2}^3} \right) - \frac{2}{V_m} x_1 a_{21} \tag{3.2}$$

$$\mu_3 = -k_B T \ln\left(\frac{V_m}{x_3 {\Lambda_3}^3} \right) \tag{3.3}$$

The average chemical potential gradients are

$$\begin{aligned}
\overline{\left(\frac{\partial \mu_1}{\partial z} \right)} &= \frac{\mu_1(z=1) - \mu_1(z=0)}{1} = \\
&= -k_B T \ln\left(\frac{V_m}{x_1(z=1){\Lambda_1}^3} \right) - \frac{2}{V_m} x_2(z=1) a_{12} + k_B T \ln\left(\frac{V_m}{x_1(z=0){\Lambda_1}^3} \right) + \frac{2}{V_m} x_2(z=0) a_{12} \quad (4.1) \\
&= k_B T \ln\left(\frac{x_1(z=1)}{x_1(z=0)} \right) + \frac{2}{V_m} a_{12} \left[\left(x_2(z=0) - x_2(z=1) \right) \right]
\end{aligned}$$

$$\overline{\left(\frac{\partial \mu_2}{\partial z} \right)} = k_B T \ln\left(\frac{x_2(z=1)}{x_2(z=0)} \right) + \frac{2}{V_m} a_{21} \left[\left(x_1(z=0) - x_1(z=1) \right) \right] \tag{4.2}$$

$$\overline{\left(\frac{\partial \mu_3}{\partial z} \right)} = k_B T \ln\left(\frac{x_3(z=1)}{x_3(z=0)} \right) \tag{4.3}$$

Numerical evaluation yields

$$\overline{\left(\frac{\partial \mu_1}{\partial z} \right)} = 611.4 \tag{5.1}$$

$$\overline{\left(\frac{\partial \mu_2}{\partial z} \right)} = \text{-}10655 \tag{5.2}$$

$$\overline{\left(\frac{\partial \mu_3}{\partial z} \right)} = 10898 \tag{5.3}$$

(d) Based on the sign of the chemical potential gradients, in which direction would you expect the diffusive flux of each species to be?

One would expect that species diffuse from high chemical potential to low chemical potential.

Component 1 would move to the boundary at z = 0.
Component 2 would move to the boundary at z = 1.
Component 3 would move to the boundary at z = 0.

(e) Based on your conclusions in parts (b) and (d), which fluxes will one actually observe, those given in part (b) or part (d)? Why?

One will observe the fluxes predicted in part (d), because part (d) is based on the thermodynamic driving force for diffusion. Following the chemical potential gradient will lead the system to a lower free energy. Here, because component 1 interacts more favorably with component 2 than it does with component 3, the advantage of the energetic driving force outweighs the disadvantage of the entropic driving force associated with going up a concentration gradient.

(f) What is the common term given to the transport phenomena exhibited by one of the components?

Component one will display “uphill diffusion”, where it diffuses up the concentration gradient.

(g) Name a chemical engineering unit operation in which this transport phenomena is frequently exploited.

In liquid-liquid extraction, a good solvent is used to extract a solute from a less good solvent. The goodness of a solvent is really an indicator of the chemical potential of the solute in that solvent. Thus, one can extract a solute to a higher concentration in the good solvent than was originally present in the less good solvent, due to the overall reduction in free energy.

Problem 2.

Consider the driving force for mass flux given in equation (24.1-8) of BSL2 on page 766 and the flux law given in equation (24.2-3) on page 767. Further consider an isothermal, isobaric system in the absence of external forces. Note that the diffusivities that appear in (24.2-3) are symmetric $D_{\alpha\beta} = D_{\beta\alpha}$ and satisfy the constraints $\sum_{\alpha} w_{\alpha} D_{\alpha\beta} = 0$.

(a) How many independent diffusivities are there for a ternary system?
(b) For a ternary system, express the off-diagonal elements of the diffusivity as a function of the diagonal components.

First, we write out the constraints that the weighted diffusivities sum to zero.

$$w_A D_{AA} + w_B D_{AB} + w_C D_{AC} = 0 \tag{6.1}$$

$$w_A D_{BA} + w_B D_{BB} + w_C D_{BC} = 0 \tag{6.2}$$

$$w_A D_{CA} + w_B D_{CB} + w_C D_{CC} = 0 \tag{6.3}$$

Using the symmetry relations, we have

$$w_A D_{AA} + w_B D_{AB} + w_C D_{AC} = 0 \tag{7.1}$$

$$w_A D_{AB} + w_B D_{BB} + w_C D_{BC} = 0 \tag{7.2}$$

$$w_A D_{AC} + w_B D_{BC} + w_C D_{CC} = 0 \tag{7.3}$$

Solving for off-diagonal components in terms of the diagonal components, we have

$$D_{AC} = -\frac{w_A D_{AA} + w_B D_{AB}}{w_C} \tag{8.1}$$

$$D_{BC} = -\frac{w_A D_{AB} + w_B D_{BB}}{w_C} \tag{8.2}$$

$$-w_A \frac{w_A D_{AA} + w_B D_{AB}}{w_C} - w_B \frac{w_A D_{AB} + w_B D_{BB}}{w_C} + w_C D_{CC} = 0 \tag{8.3}$$

Solving equation (5) for the remaining off-diagonal elements, we have

$$D_{AB} = \frac{-w_A^2 D_{AA} - w_B^2 D_{BB} + w_C^2 D_{CC}}{2 w_B w_A} \tag{9.1}$$

$$D_{BC} = \frac{w_A^2 D_{AA} - w_B^2 D_{BB} - w_C^2 D_{CC}}{2 w_B w_C} \tag{9.2}$$

$$D_{AC} = \frac{-w_A^2 D_{AA} + w_B^2 D_{BB} - w_C^2 D_{CC}}{2 w_A w_C} \tag{9.3}$$

(c) In this formulation, if the diagonal components are constants with respect to composition, are the off-diagonal components also constant with respect to composition.

No, clearly the off-diagonal components are functions of composition.

(d) Consider a ternary system, free of convection at steady state, where the diffusive fluxes are constant. Express each flux in terms of the minimum number of independent driving forces. For simplicity, you may assume that the fluid is an ideal mixture where the activity of component i is equal to the mole fraction of component i.

The constitutive equations come from equation (24.2-3) and equation (24.1-8)

$$j_A = \rho w_A \left[x_A D_{AA} \frac{\partial \ln a_A}{\partial z} + x_B D_{AB} \frac{\partial \ln a_B}{\partial z} + x_C D_{AC} \frac{\partial \ln a_C}{\partial z} \right] \tag{10.1}$$

$$j_B = \rho w_B \left[x_A D_{BA} \frac{\partial \ln a_A}{\partial z} + x_B D_{BB} \frac{\partial \ln a_B}{\partial z} + x_C D_{BC} \frac{\partial \ln a_C}{\partial z} \right] \tag{10.2}$$

$$j_C = \rho w_C \left[x_A D_{CA} \frac{\partial \ln a_A}{\partial z} + x_B D_{CB} \frac{\partial \ln a_B}{\partial z} + x_C D_{CC} \frac{\partial \ln a_C}{\partial z} \right] \tag{10.3}$$

If the system is ideal,

$$x_C \frac{\partial \ln a_C}{\partial z} = x_C \frac{\partial \ln a_C}{\partial x_C} \frac{\partial x_C}{\partial z} = \left(\frac{\partial \ln a_C}{\partial \ln x_C} \right) \frac{\partial x_C}{\partial z} = \frac{\partial x_C}{\partial z} \tag{11}$$

Because the sum of the mole fractions is unity, we have

$$\frac{\partial x_C}{\partial z} = -\frac{\partial x_A}{\partial z} - \frac{\partial x_B}{\partial z} \tag{12}$$

Grouping the two driving forces yields,

$$j_A = \rho w_A \left[\left(D_{AA} - D_{AC} \right) \frac{\partial x_A}{\partial z} + \left(D_{AB} - D_{AC} \right) \frac{\partial x_B}{\partial z} \right] \tag{13.1}$$

$$j_B = \rho w_B \left[\left(D_{BA} - D_{BC} \right) \frac{\partial x_A}{\partial z} + \left(D_{BB} - D_{BC} \right) \frac{\partial x_B}{\partial z} \right] \tag{13.2}$$

$$j_C = \rho w_C \left[\left(D_{CA} - D_{CC} \right) \frac{\partial x_A}{\partial z} + \left(D_{CB} - D_{CC} \right) \frac{\partial x_B}{\partial z} \right] \tag{13.3}$$

where the off-diagonal elements have been previously defined.

Problem 3.

Consider the following composition balance

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A + \sum_{i=1}^{N_R} r_{i,A} \quad , \tag{14}$$

where the diffusive mass flux of component A relative to the center of mass velocity is defined as

$$\mathbf{j}_A = -\rho D \nabla w_A \cdot \quad , \tag{15}$$

and there is one chemical reaction in the system ($N_R = 1$) with a rate given by

$$r_A = -k\rho_A \quad , \tag{16}$$

Put this equation in dimensionless form. Identify all dimensionless numbers.

First, substitute equations (15) and (16) into equation (14).

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A + \nabla \cdot \left(\rho D \nabla w_A \cdot \right) - k\rho_A \quad , \tag{17}$$

define a dimensionless time, mass and length unit.

$$\zeta = \frac{z}{L} \quad , \tag{18.a}$$

$$\rho^* = \frac{\rho}{\rho_o} \quad , \tag{18.b}$$

$$\tau = tk \quad , \tag{18.c}$$

Substitute equation (18) into equation (17)

$$\rho^* \rho_o k \frac{\partial w_A}{\partial \tau} = -\rho^* \rho_o \frac{1}{L} \mathbf{v} \cdot \nabla_\zeta w_A + \nabla_\zeta \cdot \left(\rho^* \rho_o \frac{1}{L^2} D \nabla_\zeta w_A \cdot \right) - k\rho^* \rho_o w_A \quad , \tag{19}$$

Simplify.

$$\frac{\partial w_A}{\partial \tau} = -\frac{1}{kL} \mathbf{v} \cdot \nabla_\zeta w_A + \frac{1}{k\rho^*} \nabla_\zeta \cdot \left(\rho^* \frac{1}{L^2} D \nabla_\zeta w_A \cdot \right) - w_A \quad , \tag{20}$$

Expand derivative. Make no assumptions about density or diffusivity being constant,

$$\frac{\partial w_A}{\partial \tau} = -\frac{1}{kL} \mathbf{v} \cdot \nabla_\zeta w_A + \left(\frac{D}{kL^2} \nabla_\zeta \cdot \nabla_\zeta w_A + \frac{D}{kL^2 \rho^*} \nabla_\zeta w_A \cdot \nabla_\zeta \rho^* + \frac{1}{kL^2} \nabla_\zeta w_A \cdot \nabla_\zeta D \right) - w_A \tag{21}$$

Introduce dimensionless numbers:

$$\mathbf{A} = \frac{1}{kL}\mathbf{v} \quad , \qquad \text{the ratio of convection to reaction} \tag{22.1}$$

$$B = \frac{D}{kL^2} \quad , \qquad \text{the ratio of diffusion to reaction} \tag{22.2}$$

Note that B may not be constant if D varies.

The equation becomes

$$\frac{\partial w_A}{\partial \tau} = -\mathbf{A} \cdot \nabla_\zeta w_A + \left(B\nabla_\zeta \cdot \nabla_\zeta w_A + \frac{B}{\rho^*}\nabla_\zeta w_A \cdot \nabla_\zeta \rho^* + \nabla_\zeta w_A \cdot \nabla_\zeta B \right) - w_A \tag{23}$$