CBE 548: Advanced Transport Phenomena II
Spring, 2010
Final Exam

Problem 1. Arbitrary Formulation of the Description of Mass Transfer

The multicomponent Fick diffusivities, $D_{\alpha\beta}^{\otimes}$, are defined with the following equations and constraints (BSL2, p. 767)

$$D_{\alpha\beta}^{\otimes} = -\frac{cRTa_{\alpha\beta}}{\rho_\alpha \rho_\beta} \tag{1.1}$$

$$D_{\beta\alpha}^{\otimes} = D_{\alpha\beta}^{\otimes} \tag{1.2}$$

$$\sum_{\alpha=1}^{N_c} w_\alpha D_{\alpha\beta}^{\otimes} = 0 \tag{1.3}$$

to be used in the generalized Fick equations, constitutive equations for the mass diffusive flux of component α relative to the center of mass velocity, of the form (BSL2 eq (24.2-3), p. 767)

$$\mathbf{j}_\alpha = -D_\alpha^T \nabla \ln(T) + \rho_\alpha \sum_{\beta=1}^{N_c} D_{\alpha\beta}^{\otimes} \mathbf{d}_\beta \tag{1.4}$$

where the diffusional driving forces are given by (BSL2 eq (24.1-8), p. 766)

$$cRT\mathbf{d}_\alpha = c_\alpha RT \nabla \ln(a_\alpha) + (\phi_\alpha - w_\alpha)\nabla p - \rho_\alpha \mathbf{g}_\alpha + w_\alpha \sum_{\beta=1}^{N_c} \rho_\beta \mathbf{g}_\beta \tag{1.5}$$

For binary, isothermal diffusion, we frequently write Fick's law as

$$\mathbf{j}_\alpha = -\rho D \nabla w_\alpha \tag{1.6}$$

where $\mathbf{j}_\alpha = \rho w_\alpha (\mathbf{v}_\alpha - \mathbf{v})$ and $\mathbf{v} = w_\alpha \mathbf{v}_\alpha + w_\beta \mathbf{v}_\beta$.

Rigorously derive the relationship between D and $D_{\alpha\beta}^{\otimes}$. State all assumptions made. The relationship should be expressed <u>exclusively</u> in terms of mole fractions, mass fractions and $\dfrac{\partial \ln(a_\alpha)}{\partial \ln(x_\alpha)}$.

Some of the following relations may be useful to you.

$$x_1 \left(\frac{\partial \overline{G}_1}{\partial x_1}\right)_{T,p} + x_2 \left(\frac{\partial \overline{G}_2}{\partial x_2}\right)_{T,p} = 0$$ (Gibbs-Duhem equation, binary, isothermal, isobaric)

$$\ln(a_1) = \frac{\overline{G}_1 - \underline{G}_1}{RT}$$ (relation between partial molar Gibbs free energy and activity)

$$\frac{\partial x_\alpha}{\partial w_\alpha} = \frac{x_\alpha x_\beta}{w_\alpha w_\beta}$$ (for binary systems only)

Problem 2. Chemical Potential Gradient Driven Diffusion

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, $x_1 = 0.15$, mole fraction of 2, $x_2 = 0.84$, 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, $x_1 = 0.10$, mole fraction of 3, $w_3 = 0.89$, 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

$$\mu_i = -RT\ln\left(\frac{V_m - b_{mix}}{x_i\Lambda_i^3}\right) + \frac{RTb_i}{V_m - b_{mix}} - \frac{2}{V_m}\sum_{j=1}^{N_c} x_j a_{ij} \tag{2.1}$$

where R is the gas constant, V_m is the molar volume, Λ_i 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 $V_m = 2.35\times10^{-2}$ m^3/mole.

Tasks.

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

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

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

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

(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?

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

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

Problem 3. Differential balances with varying cross-sectional area

(a) Derive the continuity equation for a conical pipe, where the cross sectional area is a function of axial position and there is only spatial variation in properties in the axial dimension.

(b) Derive the mass balance for component A for a conical pipe, where the cross-sectional area is a function of axial position and there is only spatial variation in properties in the axial dimension.

(c) What is the equation for the mass fraction of A for an isothermal, binary system in the absence of convection and the presence of a first order reaction A → B, where the cross-sectional area varies linearly with position, $A_x(z) = bz + A_o$ and Ficks law is given as $j_A = -\rho D \frac{\partial w_A}{\partial z}$ and the reaction rate is given as $r_A = -kw_A$. Assume the density, diffusivity and reaction rate constant are all constant. Put this equation in the simplest form possible.

(d) What does the steady state profile of the mass fraction of A look like in a pipe of constant cross-sectional area and the absence of reaction?

(e) Comparing the results for the constant cross-sectional area pipe and the varying cross-sectional area pipe for the case without reaction, which will yield a higher composition of A at the outlet for the same inlet conditions?

The following equations are provided for the exam. The continuity equation is

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}) \quad , \tag{A.1}$$

where ρ is the mass density, **v** is the center-of-mass velocity, and *t* is time. In BSL2, this is equation (3.1-4) on page 77 [1].

The mass balance on component A is

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A + \sum_{i=1}^{N_R} r_{i,A} \quad , \tag{A.2}$$

where w_A is the mass fraction of component *A*, $\mathbf{j}_A$ is the diffusive mass flux of component *A* relative to the center-of-mass velocity, N_R is the number of independent chemical reactions in the system, and $r_{i,A}$ is the rate of production of component *A* in reaction *i*, in units of mass/volume/time. In BSL2, this is equation (19.1-14) on page 584.

The momentum balance is

$$\rho \frac{\partial \mathbf{v}}{\partial t} = -\rho \mathbf{v} \cdot \nabla (\mathbf{v}) - \nabla p - \nabla \cdot \boldsymbol{\tau} - \rho \nabla \hat{\Phi} \quad , \tag{A.3}$$

where *p* is the pressure, $\boldsymbol{\tau}$ is the extra stress tensor, and $\hat{\Phi}$ is the specific external field imposed by, for example, gravity. This equation is a the difference of equation (3.2-9) on page 80 of BSL2 and the continuity equation , equation(1).

The energy balance is

$$\frac{\partial \rho \left(\frac{1}{2} v^2 + \hat{U} + \hat{\Phi} \right)}{\partial t} = -\nabla \cdot \rho \left(\frac{1}{2} v^2 \mathbf{v} + \hat{U} \mathbf{v} + \hat{\Phi} \mathbf{v} \right) - \nabla \cdot \mathbf{q} - \nabla \cdot p \mathbf{v} - \nabla \cdot (\boldsymbol{\tau} \cdot \mathbf{v}) \quad , \tag{A.4}$$

where $\hat{U}$ is the specific (per mass) internal energy, $\hat{\Phi}$ is the specific potential energy due to an external field, and **q** is the heat flux due to conduction. This is equation (11.1-9) on page 336 in BSL2.