ChE 548
Final Exam
Spring, 2003

Problem 1.

We know that one can write Fick's law in an arbitrary form given three pieces of information:
(i) the nature of the flux
(ii) the nature of the driving force (gradient)
(ii) the frame of reference.

The diffusivity is defined by these three pieces of information. We can convert the diffusivity to be used in one arbitrary form of Fick's law to another arbitrary form, if we know these three pieces of information for both forms of Fick's law.

Consider the following two forms of Fick's law for binary diffusion:

Form 1 of Fick's Law:

$$\underline{j}_A = -\rho D^{\circ} \nabla w_A \tag{1.1}$$

where $\underline{j}_A$ is a mass flux of component A relative to the mass-averaged velocity, ρ is the mass density, and w_A is the mass fraction of component A. The frame of reference is the mass-averaged velocity, $\underline{v}$, defined as

$$\underline{v} = w_A \underline{v}_A + w_B \underline{v}_B \tag{1.2}$$

where $\underline{v}_A$ is the average molecular velocity of component A.

Form 2 of Fick's Law:

$$\underline{J}_A^* = -c D^{\bullet} \nabla \mu_A \tag{1.3}$$

where $\underline{J}_A^*$ is a molar flux of component A relative to the molar-averaged velocity, c is the molar density (concentration), and μ_A is the chemical potential of component A. The frame of reference is the molar-averaged velocity, $\underline{v}^*$, defined as

$$\underline{v}^* = x_A \underline{v}_A + x_B \underline{v}_B \tag{1.4}$$

where $\underline{v}_A$ is the average molecular velocity of component A.

Derive the functional relationship between D° and $D^{\bullet}$.

Problem 2.

Consider a plug-flow reactor of length, L, and diameter, D, operated under isothermal conditions. A stream of pure A enters the reactor with a volumetric flowrate, F_{in} and molar concentration, c_{in}. The following heterogeneous reaction takes place:

$$A + S \rightarrow AS \tag{2.1}$$

$$AS \rightarrow BS \tag{2.2}$$

$$BS \rightarrow B + S \tag{2.3}$$

All steps are irreversible with rates given below

$$rate_1 = k_1 c_A \theta_S f \tag{2.4}$$

$$rate_2 = k_2 \theta_A f \tag{25}$$

$$rate_3 = k_3 \theta_B f \tag{2.6}$$

The rate constants, k_1, k_2 and k_3 have appropriate units, so that the rates have units of moles/m^3/sec. The factor f is a conversion factor with units of moles of adsorption sites/m^3, so that, for example, $\theta_A f$ gives the moles of adsorbed A per unit volume of the reactor. The catalyst is sprayed uniformly onto the interior surface of the reactor wall. (There are *no* catalyst pellets.)

a. Derive the transient material balances for the total concentration, c, the mole fraction of A, x_A, the mole fraction of B, x_B, and the fractional loadings θ_A, θ_B, and θ_S.
b. Provide a complete set of initial and boundary conditions.

Your balance should be in terms of the six unkowns listed above (c, x_A, x_B, θ_A, θ_B, θ_S) and the given parameters: t (time), z (axial position), L, D, F_{in}, c_{in}, k_1, k_2, k_3, D_{AB} (the diffusivity of the system), and ρ_S (the surface density of adsorption sites on the wall, units of moles of adsorption sites/area).

Problem 3.

Recently at the University of Tennessee, molecular dynamics simulations were performed calculating the self-diffusivity of methane in mixtures of methane and ethane. A total of 242 simulations were performed in systems where the pressure, mole fraction of methane, and temperature were varied. The pressure varied from 0.1 atm to 1000 atm. The mole fraction varied from 0 to 1. The temperature varied from 275 to 700 K. In all cases, the mixture was above the critical temperature and thus was a single phase.

We fit the simulated self-diffusivities to the expression:

$$D_{self} = D_o \exp\left(-\frac{Ea}{RT}\right) \tag{3.1}$$

where D_{self} is the self diffusivity, D_o is the prefactor, E_a is the activation energy, R is the gas constant, and T is the temperature. D_o and E_a are further broken down into

$$D_o = \frac{\left(D_{on} + D_{ox} x_{Me}\right)}{n} \tag{3.2}$$

and

$$E_a = E_{ao} + E_{an} n \tag{3.3}$$

where x_{Me} is the mol fraction of methane and n is the molar density (concentration). The parameters D_{on}, D_{ox}, E_{ao}, and E_{an} are simply fitting constants, optimized to give the best representation of the simulation results.

When the optimization was complete, we found that the average error was under 5%. We found that the model predicted equally well at all mole fractions and equally well at all temperatures. However, we found that the model predicted the self-diffusivity well only at high-pressure, above 10 atm. The data points at low pressure, 0.1 and 1 atm, were fit extremely poorly.

Answer the following questions:

a. Why was the low pressure data fit so poorly?

b. What alternative do we have to predict the self-diffusivity of low-pressure mixtures?

Solution to Problem 1.

Start with the two forms of the mass and molar flux:

$$\underline{j}_A = -\rho D^\circ \nabla w_A \tag{1}$$

$$\underline{J}_A^* = -c D^\bullet \nabla \mu_A \tag{2}$$

Using the definition of the total flux, write an alternate form for the diffusive flux:

$$\underline{j}_A = \rho_A \left(\underline{v}_A - \underline{v}\right) \tag{3}$$

$$\underline{J}_A^* = c_A \left(\underline{v}_A - \underline{v}^*\right) \tag{4}$$

Equate equations (1) and (2); equate equations (3) and (4). Solve resulting equations for D° and $D^\bullet$.

$$D^\circ = -\frac{1}{\nabla w_A} w_A \left(\underline{v}_A - \underline{v}\right) \tag{5}$$

$$D^\bullet = -\frac{1}{\nabla \mu_A} x_A \left(\underline{v}_A - \underline{v}^*\right) \tag{6}$$

Substitute in definitions of mass-average and molar average velocity:

$$D^\circ = -\frac{1}{\nabla w_A} w_A \left(\underline{v}_A - w_A \underline{v}_A - w_B \underline{v}_B\right) = -\frac{1}{\nabla w_A} w_A w_B \left(\underline{v}_A - \underline{v}_B\right) \tag{7}$$

$$D^\bullet = -\frac{1}{\nabla \mu_A} x_A \left(\underline{v}_A - x_A \underline{v}_A - x_B \underline{v}_B\right) = -\frac{1}{\nabla \mu_A} x_A x_B \left(\underline{v}_A - \underline{v}_B\right) \tag{8}$$

Solve equation (7) for $\left(\underline{v}_A - \underline{v}_B\right)$

$$\left(\underline{v}_A - \underline{v}_B\right) = -\frac{D^\circ}{w_A w_B} \nabla w_A \tag{9}$$

Substitute equation (9) into equation (8).

$$D^{\bullet} = \frac{x_A x_B}{w_A w_B}\frac{\nabla w_A}{\nabla \mu_A} D^{\circ} = \frac{x_A x_B}{w_A w_B}\frac{\partial w_A}{\partial \mu_A} D^{\circ} \tag{10}$$

Useful Relations:

$$c = \rho \sum_{i=1}^{n_c} \frac{w_i}{MW_i} \tag{A.1}$$

$$x_j = \frac{c_j}{c} = \frac{\frac{w_j}{MW_j}}{\sum_{i=1}^{n_c} \frac{w_i}{MW_i}} \tag{A.2}$$

The reciprocal relations are:

$$\rho = C \sum_{i=1}^{n_c} x_i MW_i \tag{A.3}$$

$$w_j = \frac{\rho_j}{\rho} = \frac{x_j MW_j}{\sum_{i=1}^{n_c} x_i MW_i} \tag{A.4}$$

Alternate definition of mass and molar diffusive fluxes

$$\underline{j}_A = \rho_A \left(\underline{v}_A - \underline{v} \right) \tag{A.5}$$

$$\underline{J}_A^* = c_A \left(\underline{v}_A - \underline{v}^* \right) \tag{A.6}$$

The total mass and molar fluxes of the component A:

$$\underline{n}_A = \rho w_A \underline{v}_A = \rho w_A \underline{v} + \underline{j}_A \tag{A.7}$$

$$\underline{N}_A = c x_A \underline{v}_A^* = c x_A \underline{v}^* + \underline{J}_A^* \tag{A.8}$$

definition of mass and molar average velocities:

$$\underline{v} = \sum_{i=1}^{N_c} w_i \underline{v}_i \qquad \underline{v}^* = \sum_{i=1}^{N_c} x_i \underline{v}_i \tag{A.9}$$

Solution to Problem 2.

The total mole balance contains accumulation and convection terms. There is no diffusion term in the total mole balance. In the transient state, there is a net generation of moles because reactions 1 and 3 change the moles of material in the bulk and the rates of 1 and 3 are not equal in the transient state.

$$\frac{\partial c}{\partial t} = -\frac{\partial cv}{\partial z} - rate_1 + rate_3 = -\frac{\partial cv}{\partial z} - k_1 c x_A \theta_S f + k_3 \theta_B f \tag{2.1}$$

where $v = \frac{F_{in}}{A_x} = \frac{F_{in}}{\frac{\pi}{4}D^2}$ and where $f = \rho_S \frac{A_s}{V} = \rho_S \frac{\pi DL}{\frac{\pi}{4}D^2 L} = \rho_S \frac{4}{D}$

The balance on the mole fraction of A contains a convection term, diffusion term, reaction term and an accumulation term due to the change in the total concentration:

$$\begin{aligned}\frac{\partial x_A}{\partial t} &= \frac{1}{c}\left[-x_A \frac{\partial c}{\partial t} - \frac{\partial c x_A v}{\partial z} + \frac{\partial}{\partial z}\left(cD_{AB}\frac{\partial x_A}{\partial z}\right) - rate_1\right] \\ &= \frac{1}{c}\left[-x_A \frac{\partial c}{\partial t} - \frac{\partial c x_A v}{\partial z} + \frac{\partial}{\partial z}\left(cD_{AB}\frac{\partial x_A}{\partial z}\right) - k_1 c x_A \theta_S f\right]\end{aligned} \tag{2.2}$$

The balance on the mole fraction of B contains a convection term, diffusion term, reaction term and an accumulation term due to the change in the total concentration:

$$\begin{aligned}\frac{\partial x_B}{\partial t} &= \frac{1}{c}\left[-x_B \frac{\partial c}{\partial t} - \frac{\partial c x_B v}{\partial z} + \frac{\partial}{\partial z}\left(cD_{AB}\frac{\partial x_B}{\partial z}\right) + rate_3\right] \\ &= \frac{1}{c}\left[-x_B \frac{\partial c}{\partial t} - \frac{\partial c x_B v}{\partial z} + \frac{\partial}{\partial z}\left(cD_{AB}\frac{\partial x_B}{\partial z}\right) - k_3 \theta_B f\right]\end{aligned} \tag{2.3}$$

The balance on the fractional loadings contain no convection or diffusion terms, only reaction terms.

$$\frac{\partial \theta_A}{\partial t} = \frac{1}{f}\left[rate_1 - rate_2\right] = k_1 c x_A \theta_S - k_2 \theta_A \tag{2.4}$$

$$\frac{\partial \theta_B}{\partial t} = \frac{1}{f}\left[rate_2 - rate_3\right] = k_2 \theta_A - k_3 \theta_B \tag{2.5}$$

$$\frac{\partial \theta_S}{\partial t} = \frac{1}{f}\left[-\text{rate}_1 + \text{rate}_3\right] = -k_1 c x_A \theta_S + k_3 \theta_B \tag{2.6}$$

A complete set of initial and boundary conditions could be:

Initial conditions:

$c(t=0,z) = c_{in}$
$x_A(t=0,z) = x_{A,in} = 1$
$x_B(t=0,z) = x_{B,in} = 0$
$\theta_A(t=0,z) = \theta_{A,in} = 0$
$\theta_B(t=0,z) = \theta_{B,in} = 0$
$\theta_S(t=0,z) = \theta_{S,in} = 1$

Boundary conditions at the inlet:

$c(t,z=0) = c_{in}$
$x_A(t,z=0) = x_{A,in} = 1$
$x_B(t,z=0) = x_{B,in} = 0$

You don't need boundary conditions on the fractional loadings, because there is no spatial derivative (no gradients and no laplacians) in the balances on the fractional loadings.

Boundary conditions at the outlet:

$$\left.\frac{\partial c}{\partial z}\right|_{z=L} = 0$$

$$\left.\frac{\partial x_A}{\partial z}\right|_{z=L} = 0$$

$$\left.\frac{\partial x_B}{\partial z}\right|_{z=L} = 0$$

You don't need boundary conditions on the fractional loadings, because there is no spatial derivative (no gradients and no laplacians) in the balances on the fractional loadings.

Solution to Problem 3.

a. Why was the low pressure data fit so poorly?

We know from kinetic theory, that the self-diffusivity of low pressure gases is not an activated process. Fitting this to a model which assumes an Arrhenius form is therefore not going to work over a broad parameter space.

b. What alternative do we have to predict the self-diffusivity of low-pressure mixtures?

We should kinetic theory, which delivers quite reasonable results for low-pressure gases.