ChE 548
Advanced Transport Phenomena II
Final Exam
Friday, May 1, 2009
8:00-10:00 AM

Problem 1. Mass Transfer
Consider diffusion of through a reactive membrane of component A, which can react to form B via the first order, irreversible reaction, A → B. The rate constant is given by

$$k = k_o \exp\left(-\frac{E_a}{RT}\right) \tag{1.a}$$

where the rate of reaction is given by

$$rate = k\rho_A \tag{1.b}$$

The heat of reaction for this reaction is small and the system can be assumed to be isothermal. The prefactor is $k_o = 1.0x10^{-2}\frac{1}{s}$, the activation energy is $E_a = 1.0x10^4\frac{J}{mol}$, R is the ideal gas constant, $R = 8.314\frac{J}{mol \cdot K}$, and the temperature is $T = 300\,K$. There is no convection in the membrane. The Fickian diffusivity is $D = 1.0x10^{-5}\frac{m^2}{s}$ and can be considered independent of composition. The membrane is of thickness $L = 0.05\,m$. One of boundaries of the membrane is fixed at $\rho_A = 0.7\frac{kg}{m^3}$ and $\rho_B = 0.0\frac{kg}{m^3}$.

(a) Write the transient total mass balance and mass of A balance.

The total mass balance in general is

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

Since the velocity is zero, we have

$$\frac{\partial \rho}{\partial t} = 0 \tag{2}$$

In other words, the density is constant.

The balance on A is in general

$$\rho\frac{\partial w_A}{\partial t} = -\rho\mathbf{v}\cdot\nabla w_A - \nabla\cdot\mathbf{j}_A + \sum_{i=1}^{N_R} r_{i,A} \tag{3}$$

which for this specific case becomes

$$\frac{\partial w_A}{\partial t} = D\frac{\partial^2 w_A}{\partial z^2} - kw_A \tag{4}$$

(b) Determine the mass fraction of component A at the far side of the membrane at steady state.

At steady state, the mass balance becomes

$$0 = D\frac{\partial^2 w_A}{\partial z^2} - kw_A \tag{5}$$

$$\frac{d^2 w_A}{dz^2} = \frac{k}{D}w_A \tag{6}$$

The solution is of the form

$$w_A(z) = w_A(z=0)\exp\left(-\sqrt{\frac{k}{D}}z\right) \tag{7}$$

Numerically, $w_A(z=0)=1$, $k = 1.8146x10^{-4}\frac{1}{s}$, and $D = 1.0x10^{-5}\frac{m^2}{s}$, so that

$w_A(z=L) = 0.8082$

(c) If you want the conversion to be 90%, how thick would the membrane have to be?

$$w_A(z=L) = 0.1 = \exp\left(-\sqrt{\frac{k}{D}}L\right) \tag{8}$$

$$L = -\sqrt{\frac{D}{k}}\ln(0.1) = 0.54\,m \tag{9}$$

Possibly Useful Information:

The solution to an ODE of the form, $\frac{\partial^2 y(x)}{\partial x^2} = ky(x)$, is $y(x) = c\exp\left(-\sqrt{k}x\right)$.

Problem 2. Reference States in Energy Balances

The enthalpy of component i can be written as

$$H_i(T,p)=\int_{T_{ref}}^{T} C_{p,i}(T,p)dT+\int_{p_{ref}}^{p}\left(\frac{\partial H_i}{\partial p}\right)_{T=T_{ref}}dp+H_{f,i}(T_{ref},p_{ref}) \qquad (1)$$

where $H_{f,i}$ is the enthalpy of formation at the reference state. Typically we ignore the pressure dependence of the enthalpy. It can be ignored in this problem as well.

Consider a system with accumulation, convection and diffusion of a binary mixture, in which the mixture enthalpy is ideal

$$H_{mix}(T,p)=w_A H_A(T,p)+w_B H_B(T,p) \qquad (2)$$

The total conduction in the system is due to thermal conduction and enthalpy carried by diffusion,

$$\mathbf{q}=-k_c\nabla\cdot\mathbf{T}+H_A\mathbf{j}_A+H_B\mathbf{j}_B \qquad (3)$$

(a) If the system is non-reactive, show that the enthalpy of formation drops out of the energy balance.

We have the general energy balance,

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

We can use the product rule on the accumulation and convection term.

$$\begin{aligned}&\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)\frac{\partial\rho}{\partial t}+\rho\frac{\partial\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)}{\partial t}-\frac{\partial p}{\partial t}=\\&-\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)\cdot\nabla\rho\mathbf{v}-\rho\mathbf{v}\nabla\cdot\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)-\nabla\cdot\mathbf{q}-\nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v})\end{aligned} \quad . \qquad (5)$$

Based on the continuity equation, two of the terms cancel, leaving

$$\rho\frac{\partial\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)}{\partial t}-\frac{\partial p}{\partial t}=-\rho\mathbf{v}\nabla\cdot\left(\frac{1}{2}v^2+\hat{H}+\hat{\Phi}\right)-\nabla\cdot\mathbf{q}-\nabla\cdot(\boldsymbol{\tau}\cdot\mathbf{v}) \quad . \qquad (6)$$

The enthalpy that appears in this balance is the mixture enthalpy.

$$H_{mix}(T,p) = w_A\left(\int_{T_{ref}}^{T} C_{p,A}dT + H_{f,A}\right) + w_B\left(\int_{T_{ref}}^{T} C_{p,B}dT + H_{f,B}\right) \tag{7}$$

$$\begin{aligned} H_{mix}(T,p) &= w_A\left(\int_{T_{ref}}^{T} C_{p,A}dT\right) + w_B\left(\int_{T_{ref}}^{T} C_{p,A}dT\right) + w_A H_{f,A} + w_B H_{f,B} \\ &= w_A\left(\int_{T_{ref}}^{T} C_{p,A}dT\right) + w_B\left(\int_{T_{ref}}^{T} C_{p,A}dT\right) + w_A\left(H_{f,A} - H_{f,B}\right) + H_{f,B} \end{aligned} \tag{8}$$

We now concern ourselves only with the enthalpy of formation terms in equation (8). We substitute these terms into the accumulation term of equation (6) to obtain

$$\rho\frac{\partial H_{mix}(T,p)}{\partial t} = \rho\left(H_{f,A} - H_{f,B}\right)\frac{\partial w_A}{\partial t} \quad . \tag{9}$$

Similarly, the convection term in equation (6) becomes for the enthalpy of formation terms,

$$-\rho\mathbf{v}\nabla\cdot H_{mix} = -\rho\mathbf{v}\left(H_{f,A} - H_{f,B}\right)\nabla\cdot w_A \quad . \tag{10}$$

The portion of the heat conduction term in equation (6) that contains the enthalpies of formation is

$$-\nabla\cdot\mathbf{q} = -\nabla\cdot\left(H_{f,A}\mathbf{j}_A + H_{f,B}\mathbf{j}_B\right) = -\left(H_{f,A} - H_{f,B}\right)\nabla\cdot\mathbf{j}_A \tag{11}$$

Substituting all of the enthalpy of formation terms into the energy balance in (6) yields

$$\rho\left(H_{f,A} - H_{f,B}\right)\frac{\partial w_A}{\partial t} = -\rho\mathbf{v}\left(H_{f,A} - H_{f,B}\right)\nabla\cdot w_A - \left(H_{f,A} - H_{f,B}\right)\nabla\cdot\mathbf{j}_A \tag{12}$$

This simplifies to

$$\rho\frac{\partial w_A}{\partial t} = -\rho\mathbf{v}\nabla\cdot w_A - \nabla\cdot\mathbf{j}_A \tag{13}$$

which is identically zero, since it is the mass balance for component A in the absence of chemical reaction.

(b) If there is a chemical reaction term, show that the enthalpy of formations terms in the energy balance become the heat of reaction term.

If there is a chemical reaction with reaction rate, r, then the mass balance on component A is

$$\rho \frac{\partial w_A}{\partial t} = -\rho \mathbf{v} \cdot \nabla w_A - \nabla \cdot \mathbf{j}_A + r \tag{14}$$

$$r = \left(\rho \frac{\partial w_A}{\partial t} + \rho \mathbf{v} \cdot \nabla w_A + \nabla \cdot \mathbf{j}_A \right) \tag{15}$$

Equation (12) can be rewritten as

$$\left(H_{f,A} - H_{f,B}\right)\left(\rho \frac{\partial w_A}{\partial t} + \rho \mathbf{v} \cdot \nabla w_A + \nabla \cdot \mathbf{j}_A \right) = \left(H_{f,A} - H_{f,B}\right) r \tag{16}$$

At this point, we see that the sum of all of the terms in equation (12) is in fact the negative of the heat generated by the reaction, as it should be, $-\Delta H_r r$.

Problem 3. Adsorption
Consider a fluid adsorbing on a surface via the Langmuir Adsorption isotherm,

Consider a system where an ideal gas adsorbs onto a surface via the Langmuir adsorption isotherm.

$$\theta_i = \frac{K_i c_i}{1 + \sum_{j=1}^{N_c} K_i c_i} \tag{1}$$

where c_i is the molar concentration of component i (mole/m^3), θ_i is the fractional occupancy of the surface, and K_i is the adsorption/desorption equilibrium coefficient with units of m^3/mole. The equilibrium coefficient is given in terms of the entropy and enthalpy of adsorption as

$$K_i = k_{o,i} \exp\left(\frac{\Delta S_i}{R}\right) \exp\left(-\frac{\Delta H_i}{RT}\right) \tag{2}$$

(a) As the temperature increases, what happens to the amount of material adsorbed? Why?

As the temperature increases, the amount of material adsorbed decreases, because adsorption is an exothermic process, $\Delta H_i < 0$. An increase in temperature weakens the energetic contribution to the free energy, resulting in a redistribution of material to the higher energy (bulk) state.

(b) As the pressure increases, what happens to the amount of material adsorbed? Why?

As the pressure increases, the bulk concentration will increase (significantly for a gas and just a little for a liquid) and the amount of material adsorbed increases, as can be seen through direct inspection of the Langmuir adsorption isotherm.

(c) For a binary system, will the selectivity, s, (defined below), will the selectivity increase or decrease with temperature? Why?

$$s = \frac{x_{ads,B} / x_{bulk,B}}{x_{ads,A} / x_{bulk,A}} \qquad (3)$$

If the selectivity is based on differences in the enthalpy of adsorption, then the selectivity will decrease as temperature increases because, as mentioned in part (a), an increase in temperature results in a weakened influence of energetic contributions, moving the system toward a more random (less segregated) state.