Chapter 7

Principles of Unsteady - State and Convective Mass Transfer

This chapter covers different situations where mass transfer is taking place, when the conditions are changing with time and where there is a fluid stream that contributes to these mass transfer processes. The following examples illustrate convective and transient mass transfer in fuel cell systems.

Example 7.5-2 Diffusion and Chemical Reaction in the Anode Chamber of a Direct Methanol Fuel Cell

An aqueous 40 mole % methanol solution is entering the anode of a direct – methanol fuel cell. The fuel is diffusing through the gas diffusion layer (GDL) with a thickness of 0.018 cm [1]. The diffusion coefficient of the fuel in the GDL is estimated by García et al. [1] to be $1\times10^{-9}\,\frac{m^2}{s}$. The governing equation for methanol in the GDL is given by:

$$\frac{d^2C_A}{dz^2}=0$$

with the following boundary conditions:

$$\text{At } z=0:\ C_A=C_b$$

$$\text{At } z=\delta:\ N_A=k_1C_A$$

The rate constant for the chemical reaction occurring at the catalyst layer located at z = δ is $k_1=2.8\times10^{-6}\,\frac{m}{s}$. Determine the molar fraction of methanol at z = δ and steady state, if the initial concentration C_b of methanol is $500\,\frac{mol}{m^3}$.

Strategy

The molar fraction at the catalyst layer can be obtained by solving the governing differential equation.

Solution

We can start by solving the given differential equation given in the problem statement, as shown in the following steps:

$$\int\frac{d^2C_A}{dz^2}=\int 0$$

$$\underline{\qquad\qquad}=c_1 \tag{1}$$

$$\int dC_A=c_1\int dz$$

$$C_A=\underline{\qquad\qquad\qquad\qquad}$$

1. García, B.L., Sethuraman, V.A., Weidner, J.W., White, R.E., Dougal, R., *Journal of Fuel Cell Science and Technology*, 1, 43 – 48 (2004).

Applying the first boundary condition at z = 0, we have:

$$C_b = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_$$

$$c_2 = \_\_\_\_\_\_$$

Substituting c_2 into Equation 2 yields:

$$C_A = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \tag{2}$$

At z = δ:

$$C_A = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \tag{3}$$

The equation for methanol flux through the GDL is described by Fick's Law, given by:

$$N_A = -D\frac{dC_A}{dz} \tag{4}$$

At z = δ, the molar flux of methanol is equal to the reaction rate. Therefore:

$$N_{A_{z=\delta}} = \_\_\_\_\_\_\_\_\_\_ \tag{5}$$

Since this process is at steady state, we can equal Equations 4 and 5 to get:

$$-D\frac{dC_A}{dz} = \_\_\_\_\_\_\_\_\_ \tag{6}$$

From Equation 1, we have that $c_1 = \_\_\_\_\_\_\_\_\_$. Substituting this into Equation 6 gives:

$$-D\,\_\_\_\_ = \_\_\_\_\_\_\_\_\_ \tag{7}$$

We can substitute Equation 3 into Equation 7 to solve for c_1, as shown in the following steps:

$$-Dc_1 = k_1(\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_)$$

$$-Dc_1 = k_1c_1\delta + k_1C_b$$

$$-c_1(\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_) = \_\_\_\_\_\_\_\_\_\_\_$$

$$c_1 = \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ \tag{8}$$

Now we can substitute this equation for c_1 into Equation 2 to yield:

$$C_A = \underline{\hspace{4cm}} + C_b \tag{9}$$

Equation 9 can be evaluated at the boundary condition for z = δ to obtain the molar fraction at this point. Hence,

$$C_A = \underline{\hspace{8cm}}$$

Reducing this equation and writing C_A in terms of the molar fraction of methanol, we have:

$$C\underline{\hspace{1cm}} = \frac{\underline{\hspace{1.5cm}}}{\left(D + \underline{\hspace{1.5cm}}\right)} \tag{10}$$

where C is the overall concentration of the fuel entering the fuel cell. The overall concentration can be obtained by dividing the feed concentration of methanol C_b by the feed molar fraction of 0.4.

Substituting numeric values into Equation 10 gives:

$$\frac{\left(\underline{\hspace{1.5cm}}\,\frac{\text{mol } CH_3OH}{m^3}\right)}{0.4\frac{\text{mol } CH_3OH}{\text{mol}}}\underline{\hspace{1.2cm}} = \frac{\underline{\hspace{1.5cm}}\,\frac{\text{mol } CH_3OH}{m^3}\left(\underline{\hspace{4cm}}\,\frac{m^2}{s}\right)}{\left[\left(\underline{\hspace{4cm}}\,\frac{m^2}{s}\right)+\left(\underline{\hspace{4cm}}\,\frac{m}{s}\right)\left(1.8\times10^{-4}\,m\right)\right]}$$

$$x_A = \frac{\underline{\hspace{1.5cm}}\,\frac{\text{mol}}{cm^3}\left(\underline{\hspace{4cm}}\,\frac{m^2}{s}\right)}{\left[\left(\underline{\hspace{4cm}}\,\frac{m^2}{s}\right)+\left(\underline{\hspace{4cm}}\,\frac{m}{s}\right)\left(1.8\times10^{-4}\,m\right)\right]}$$

$$\boxed{x_A = \underline{\hspace{1.5cm}}}$$

Example 7.5-4: Diffusion of CO_2 and O_2 through stagnant N_2 in a Solid – Oxide Fuel Cell

A solid - oxide fuel cell operating at a temperature of 923.15 K and a pressure of 1.9 atm, is producing CO_2 from an electrochemical reaction of CO with oxygen from air. The partial pressures of each gas at the gas diffusion layer the bipolar plate channels, located 0.729 mm away, are given in the following table.

Label	Gas	Partial Pressure (atm) at Gas – Diffusion Layer	Partial Pressure (atm) at Bipolar Plate
A	CO_2	0.47	0.01
B	O_2	0.31	0.47
C	N_2	1.12	1.42

Determine the molar flux of CO_2 and O_2 in non – diffusing N_2. The diffusion coefficients are given below:

$$D_{AB} = 5.84\times10^{-5}\ \frac{m^2}{s}$$

$$D_{AC} = 5.93\times10^{-5}\ \frac{m^2}{s}$$

$$D_{BC} = 7.49\times10^{-5}\ \frac{m^2}{s}$$

Where: A = CO_2, B = O_2 and C = N_2. These diffusion coefficients were estimated using Fuller et al. method described in Section 6.2E of Geankoplis.

The following equations describe multicomponent diffusion for two components diffusing in stagnant C [2]:

$$\frac{N_A}{D_{AC}} + \frac{N_B}{D_{BC}} = \frac{P}{RT\left(z_2 - z_1\right)} \ln\left(\frac{P_{C_2}}{P_{C_1}}\right)$$

2. Geankoplis, C.J., Mass Transport Phenomena, Holt, Rinehart and Winston Inc., New York, 1972.

$$N_A + N_B = \frac{D_{AB}P}{RT(z_2 - z_1)} \ln \left[\frac{\dfrac{\dfrac{1}{D_{AB}} - \dfrac{1}{D_{AC}}}{\dfrac{1}{D_{AB}} - \dfrac{1}{D_{BC}}} \dfrac{N_A + N_B}{N_B} P_{B_2} - \dfrac{N_A + N_B}{N_B} P_{A_2} + \dfrac{\dfrac{1}{D_{AC}} - \dfrac{1}{D_{BC}}}{\dfrac{1}{D_{AB}} - \dfrac{1}{D_{BC}}} P}{\dfrac{\dfrac{1}{D_{AB}} - \dfrac{1}{D_{AC}}}{\dfrac{1}{D_{AB}} - \dfrac{1}{D_{BC}}} \dfrac{N_A + N_B}{N_B} P_{B_1} - \dfrac{N_A + N_B}{N_B} P_{A_1} + \dfrac{\dfrac{1}{D_{AC}} - \dfrac{1}{D_{BC}}}{\dfrac{1}{D_{AB}} - \dfrac{1}{D_{BC}}} P} \right]$$

In this problem, the flux will be assumed positive from the bipolar plate to the gas – diffusion layer.

Strategy

We can determine the fluxes N_A and N_B by simultaneously solving the equations given in the problem statement.

Solution

First, we can substitute the pressures given and the diffusivity coefficients, as well as the operating conditions of the fuel cell. Thus,

$$\frac{N_A}{5.93\times10^{-5}\ \frac{m^2}{s}} + \frac{N_B}{7.49\times10^{-5}\ \frac{m^2}{s}} = \frac{1.9\ \text{atm}}{\left(\underline{\qquad\qquad}\ \frac{L\cdot atm}{mol\cdot K}\right)(923.15K)(\underline{\qquad\qquad}\ m)} \ln\left(\frac{\underline{\qquad}\ atm}{\underline{\qquad}\ atm}\right)$$

We can solve this equation for N_B by following the next steps:

$$N_A = \left[\frac{1.9\ \text{atm}}{\left(\underline{\qquad\qquad}\ \frac{m^3\cdot atm}{mol\cdot K}\right)(923.15K)(\underline{\qquad\qquad}\ m)} \ln\left(\frac{\underline{\qquad}\ atm}{1.12\ atm}\right) - \frac{N_B}{7.49\times10^{-5}\ \frac{m^2}{s}}\right] \underline{\qquad\qquad\qquad} \frac{m^2}{s}$$

$$N_B = 0.612 \frac{mol}{m^2 \cdot s} - \underline{\qquad\qquad} \tag{1}$$

So far we have obtained one of the simultaneous equations for the diffusion process occurring in this fuel cell. However, in order to solve this problem, we need a second equation, obtained from the equation for $N_A + N_B$, as shown below:

$$N_A + N_B = \frac{\underline{\qquad\qquad} \frac{m^2}{s}(1.9\text{atm})}{\left(\underline{\qquad\qquad} \frac{m^3\cdot\text{atm}}{\text{mol}\cdot\text{K}}\right)(923.15\,\text{K})\left(7.29\times10^{-4}\,\text{m}\right)}$$

$$\times\ln\left[\frac{\dfrac{\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}-\frac{1}{5.93\times10^{-5}\frac{m^2}{s}}}{\frac{1}{5.84\times10^{-5}\frac{m^2}{s}}-\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}}\dfrac{N_A+N_B}{N_B}(\underline{\qquad}\ \text{atm})-\dfrac{N_A+N_B}{N_B}(0.01\ \text{atm})+\dfrac{\frac{1}{5.93\times10^{-5}\frac{m^2}{s}}-\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}}{\frac{1}{5.84\times10^{-5}\frac{m^2}{s}}-\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}}(1.9\ \text{atm})}{\dfrac{\frac{1}{5.84\times10^{-5}\frac{m^2}{s}}-\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}}{\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}-\frac{1}{7.49\times10^{-5}\frac{m^2}{s}}}\dfrac{N_A+N_B}{N_B}(0.31\ \text{atm})-\dfrac{N_A+N_B}{N_B}(\underline{\qquad}\ \text{atm})+\dfrac{\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}-\frac{1}{7.49\times10^{-5}\frac{m^2}{s}}}{\frac{1}{\underline{\qquad\qquad}\frac{m^2}{s}}-\frac{1}{7.49\times10^{-5}\frac{m^2}{s}}}(1.9\ \text{atm})}\right]$$

In this equation, it can be seen that some terms have the factor $\frac{N_A + N_B}{N_B}$ in common. Thus, this expression can be simplified as follows:

$$N_A + N_B = \underline{\qquad\quad}\frac{\text{mol}}{m^2\cdot s}\times\ln\left\{\frac{\left[(\underline{\qquad\qquad})(0.47\ \text{atm})-(\underline{\qquad}\ \text{atm})\right]\frac{N_A+N_B}{N_B}+(\underline{\qquad\quad})(1.9\ \text{atm})}{\left[(\underline{\qquad\qquad})(\underline{\qquad}\ \text{atm})-(0.47\ \text{atm})\right]\frac{N_A+N_B}{N_B}+(\underline{\qquad\quad})(1.9\ \text{atm})}\right\}$$

We can further simplify this equation by removing the molar flow of oxygen in the denominator as shown in the following step:

$$N_A + N_B = \underline{\qquad\quad}\frac{\text{mol}}{m^2\cdot s}\times\ln\left[\frac{\underline{\qquad\quad}(N_A+N_B)+\underline{\qquad\qquad}N_B}{-0.449(N_A+N_B)+\underline{\qquad\qquad}N_B}\right] \tag{2}$$

Now we can substitute Equation 1 into Equation 2 to get:

$$N_A + (0.612-1.263N_A) = \underline{\qquad\quad}\frac{\text{mol}}{m^2\cdot s}\times\ln\left[\frac{\underline{\qquad\quad}(N_A+0.612-1.263N_A)+\underline{\qquad\quad}(0.612-1.263N_A)}{-0.449(N_A+0.612-1.263N_A)+\underline{\qquad\quad}(0.612-1.263N_A)}\right]$$

Simplifying similar terms and moving all terms to the left side, we have:

$$\underline{\qquad\quad}N_A + \ln\left(\frac{\underline{\qquad\quad}N_A + 1.096}{\underline{\qquad\quad}N_A + \underline{\qquad\quad}}\right) - \underline{\qquad\quad} = 0$$

This equation can be solved by trial and error or using computer software to obtain the molar flow rate of carbon dioxide to be:

$$\boxed{N_A = \underline{\hspace{4cm}}\ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}}$$

We can enter this value into Equation 1 to determine the flux of oxygen as shown below:

$$N_B = 0.612 \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} - 1.263 \left(\underline{\hspace{4cm}}\ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}} \right)$$

$$\boxed{N_B = \underline{\hspace{2cm}}\ \frac{\text{mol}}{\text{m}^2 \cdot \text{s}}}$$

The following figure illustrates the diffusion process occurring in the fuel cell cathode.