10.15 Diffusion and Reaction in Falling Laminar Liquid Film of Finite Thickness

10.15.1 Concepts Demonstrated

Unsteady-state mass transfer with gas absorption, liquid-phase diffusion, and first-order reaction in a falling Newtonian fluid of finite thickness.

10.15.2 Numerical Methods Utilized

Application of the numerical method of lines to solve a partial differential equation which can be expressed as a system of simultaneous ordinary differential equations.

10.15.3 Problem Statement

Consider the absorption of CO_2 gas into a falling liquid film of alkaline solution in which there is a first-order irreversible reaction. A similar process without flow is discussed in Problem 10.14. The resulting concentration of the dissolved CO_2 in the film is quite small so that the viscosity of the liquid is not affected, and the mass transport in the liquid by bulk flow is negligible. The steady-state laminar flow of a Newtonian fluid down a vertical wall results in a velocity distribution, which is given by

$$v_z = \frac{\rho g \delta^2}{2\mu}\left[1-\left(\frac{x}{\delta}\right)^2\right] = v_{z_{max}}\left[1-\left(\frac{x}{\delta}\right)^2\right] \tag{10-131}$$

as has been discussed in Problem 8.3.

A steady-state material balance on a differential volume within the liquid film yields the partial differential equation given by

$$v_z \frac{\partial C_A}{\partial z} = D_{AB}\frac{\partial^2 C_A}{\partial x^2} - k' C_A \tag{10-132}$$

where v_z is the velocity in m/s, C_A is the concentration of dissolved CO_2 in kg-mol/m^3, D_{AB} is the diffusivity of dissolved CO_2 in the alkaline solution with units of m^2/s, and k' is a first-order reaction rate constant for the neutralization reaction in s^{-1}. The numerical values of all variables are the same as in Problem 10.14 except for k'. The film thickness is $\delta = 3 \times 10^{-4}$ m, $v_{z_{max}} = 0.6$ m/s, and $v_{z_{avg}} = (2/3)v_{z_{max}} = 0.4$ m/s.

The boundary condition for Equation (10-132) in the z direction is that C_A is zero at the point where the film begins to flow down the wall. Thus

$$C_A\big|_{z=0} = 0 \tag{10-133}$$

The first boundary condition in the x direction is that C_A is known at the surface of the film, and this can be expressed as

$$C_A\Big|_{x=0,\, z>0} = C_{As} = 0.03 \qquad \textbf{(10-134)}$$

which implies that the external mass transfer coefficient is very large. The second boundary condition in the x direction is that there is no mass transfer at the wall. Thus

$$\frac{\partial C_A}{\partial x}\Big|_{x=\delta,\, z\geq 0} = 0 \qquad \textbf{(10-135)}$$

(a) Calculate the concentration of dissolved A at each node point within the liquid when there is no reaction and at $z = 1$ m. Utilize the numerical method of lines with 11 nodes (10 intervals), as shown in Figure 10–13.
(b) Extend part (a) by calculating the average flux of A absorbed by the film in kg-mol/s to $z = 1$ m.
(c) Plot the concentration of A versus z at nodes 3, 5, 7, and 9 for part (a).
(d) Verify the results of part (a) by calculating the molar rate of A absorbed at the film surface and comparing this with the calculated molar rate of A exiting in the liquid film at $z = 1$ m. Consider the film to be 1 m wide.
(e) Repeat parts (a) and (c) for the case where a weak alkaline solution causes an irreversible first-order reaction of A with a rate constant of $k' = 1\ \mathrm{s}^{-1}$.
(f) What is the percentage increase in absorption of A from the gas phase because of the reaction in part (e) relative to that of part (a) that had no reaction?

10.15.4 Solution (Partial)

(a) The numerical method of lines is introduced in Problem 6.8, and it is applied in Problem 10.13 to unsteady-state diffusion in a finite slab with no reaction. However, this current problem is at steady state, with C_A being a function of depth within the film, designated as x, and the distance from the top of the falling film, designated as z. The finite difference elements for this problem are shown in Figure 10–13, where the interior of the slab has been divided into $N = 10$ intervals involving $N + 1 = 11$ nodes.

The method of lines allows ordinary differential equations to describe the variation of C_A with the z direction and can utilize finite elements to describe the variation in the x direction. This treatment gives a working equation set from

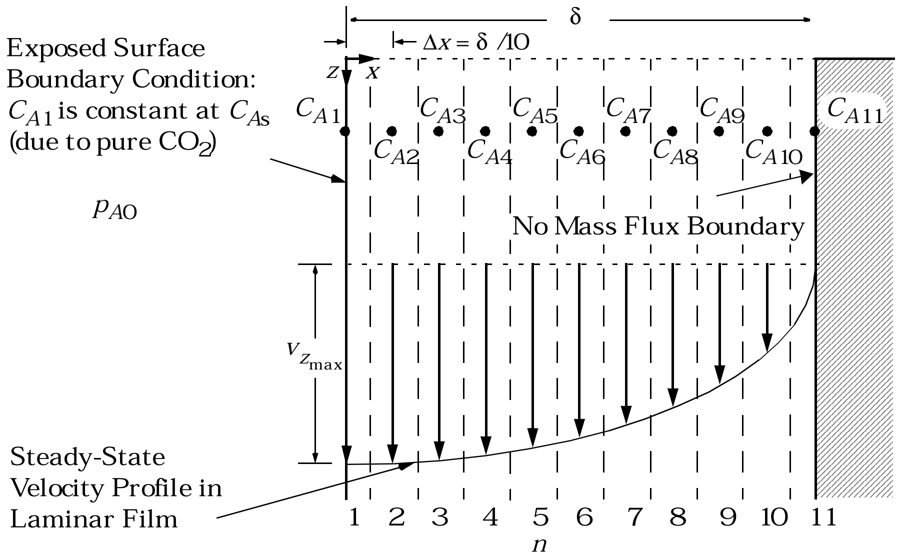

Figure 10–13 Mass Transfer with Reaction within a Falling Laminar Film

Equation (10-132) as

$$\frac{dC_{A_n}}{dz} = \left(\frac{D_{AB}}{(\Delta x)^2}(C_{A_{n+1}} - 2C_{A_n} + C_{A_{n-1}}) - k'C_{A_n}\right) / v_{z_n} \quad \text{for } (2 \le n \le 10) \qquad \textbf{(10-136)}$$

where the second-order central difference approximation of Equation (A-9) is used for the second derivative.

The velocity v_{z_n} in Equation (10-136) varies only with x, and this can be expressed by writing Equation (10-131) as

$$v_{z_n} = v_{z_{max}}\left[1 - \left(\frac{(n-1)\Delta x}{\delta}\right)^2\right] \quad \text{for } (2 \le n \le 10) \qquad \textbf{(10-137)}$$

Boundary Conditions

The initial condition of Equation (10-133) applies to the C_A in each of the internal finite elements. Thus

$$C_{A_n} = 0 \text{ at } z = 0 \text{ for } (2 \le n \le 10) \qquad \textbf{(10-138)}$$

The boundary condition given by Equation (10-134) applies to the first finite element, giving

$$C_{A_1} = 0.03 \text{ for } z \ge 0 \qquad \textbf{(10-139)}$$

Equation (10-135) involves the derivative of C_A at the wall, which can be obtained using the second-order backward finite difference approximation of Equation (A-7) for the derivative as

$$\frac{\partial C_{A11}}{\partial x} = \frac{3C_{A11} - 4C_{A10} + C_{A9}}{2\Delta x} = 0 \tag{10-140}$$

The preceding equation can be solved for C_{A11} to yield

$$C_{A11} = \frac{4C_{A10} - C_{A9}}{3} \tag{10-141}$$

Sometimes numerical noise may enter into the preceding equation to yield negative values. This can be handled by logic to keep C_{A11} at zero whenever a negative value is calculated.

Numerical Solution

The general finite difference expression for Equation (10-132) with the velocity expression from Equation (10-137) can be combined and written as

$$\frac{dC_{An}}{dz} = \left[\frac{D_{AB}}{(\Delta x)^2}(C_{An+1} - 2C_{An} + C_{An-1}) - k'C_{An}\right] \Big/ \left\{ v_{z_{\max}}\left[1 - \left(\frac{(n-1)\Delta x}{\delta}\right)^2\right]\right\}$$

$$\text{for } (2 \le n \le 10) \tag{10-142}$$

The initial conditions are all zero from the boundary condition of Equation (10-138). These nine ordinary differential equations plus Equations (10-139) and (10-141) from the remaining boundary conditions allow the C_A's at the 11 nodes to be calculated as a function of z. Note that more accurate results could be obtained by utilizing more node points.

The POLYMATH *Simultaneous Differential Equation Solver* or any other ODE package can be used to solve this set of equations. The equation set for POLYMATH is given in Table 10–17 where the capability of the full-screen editor to duplicate an equation was used during problem entry of the repetitive differential equations so that only the node values needed to be changed:

Table 10–17 POLYMATH Program - File **P10-15A.POL**

Line	Equation
1	d(CA2)/d(z)=(DAB*(CA3-2*CA2+CA1)/deltax^2-kprime*CA2)/(vmax*(1-((2-1)*deltax/delta)^2))
2	d(CA4)/d(z)=(DAB*(CA5-2*CA4+CA3)/deltax^2-kprime*CA4)/(vmax*(1-((4-1)*deltax/delta)^2))
3	d(CA5)/d(z)=(DAB*(CA6-2*CA5+CA4)/deltax^2-kprime*CA5)/(vmax*(1-((5-1)*deltax/delta)^2))
4	d(CA3)/d(z)=(DAB*(CA4-2*CA3+CA2)/deltax^2-kprime*CA3)/(vmax*(1-((3-1)*deltax/delta)^2))
5	d(CA6)/d(z)=(DAB*(CA7-2*CA6+CA5)/deltax^2-kprime*CA6)/(vmax*(1-((6-1)*deltax/delta)^2))
6	d(CA7)/d(z)=(DAB*(CA8-2*CA7+CA6)/deltax^2-kprime*CA7)/(vmax*(1-((7-1)*deltax/delta)^2))
7	d(CA8)/d(z)=(DAB*(CA9-2*CA8+CA7)/deltax^2-kprime*CA8)/(vmax*(1-((8-1)*deltax/delta)^2))
8	d(CA9)/d(z)=(DAB*(CA10-2*CA9+CA8)/deltax^2-kprime*CA9)/(vmax*(1-((9-1)*deltax/delta)^2))
9	d(CA10)/d(z)=(DAB*(CA11-2*CA10+CA9)/deltax^2-kprime*CA10)/(vmax*(1-((10-1)*deltax/delta)^2))

Table 10–17 POLYMATH Program - File **P10-15A.POL**

Line	Equation
10	DAB=1.5E-9
11	kprime=0
12	vmax=0.6
13	delta=3.E-4
14	CA1=0.03
15	CA11=if(4*CA10<CA9)then(0)else((4*CA10-CA9)/3)
16	deltax=0.1*delta
17	vavg=(2/3)*vmax
18	z(0)=0
19	CA2(0)=0
20	CA4(0)=0
21	CA5(0)=0
22	CA3(0)=0
23	CA6(0)=0
24	CA7(0)=0
25	CA8(0)=0
26	CA9(0)=0
27	CA10(0)=0
28	z(f)=1

The POLYMATH problem solution file for part (a) is found in directory CHAPTER 10 with file named **P10-15A.POL**.

(b) The average flux of A to a liquid film of height H is given by

$$N_{A_{avg}} = \frac{\int_0^H \left(-D_{AB} \frac{dC_A}{dx}\bigg|_{x=0,\,z} \right) dz}{H} \qquad \textbf{(10-143)}$$

where $N_{A_{avg}}$ is the average flux of A transferred to the liquid film in kg-mol/m^2·s and H is the film height in m. Equation (10-143) can be differentiated to yield

$$\frac{dN_{A_{avg}}}{dz} = \frac{\left(-D_{AB} \frac{dC_A}{dx}\bigg|_{x=0,\,z} \right)}{H} \qquad \textbf{(10-144)}$$

with an initial condition that $N_{A_{avg}} = 0$ at $z = 0$. Integration of this equation to any distance z yields the value of $N_{A_{avg}}$ over the film height.

Equation (10-144) can be written using a second-order forward finite difference approximation as

$$\frac{dN_{A_{\text{avg}}}}{dz} = -\frac{D_{AB}}{H}\frac{(-3C_{A1} + 4C_{A2} - C_{A3})}{2\Delta x} \tag{10-145}$$

The integration of the preceding equation for $H = 1$ m simultaneously with the equation set from part (a) to a final value of $z = 1$ m allows the determination of the requested $N_{A_{\text{avg}}}$.

(d) An overall steady-state material balance on A within the film when there is no reaction requires that the A that is transferred at the film surface must equal the A that flows out with the film. For a film of height H in m and width W in m, the input is given by

$$M_A = N_{A_{\text{avg}}} HW \tag{10-146}$$

where M_A is in kg-mol/s.

The output of A that exits the film at height H can be calculated from

$$M_A = W\int_0^{\delta} v_z C_A \, dx \tag{10-147}$$

in which v_z varies with z according to Equation (10-131) and C_A is the concentration profile determined from the numerical solution in part (a) at height H.

In order to evaluate Equation (10-147), the numerical values of C_A at the 11 node locations from the solution of part (a) can be used. The integral can be evaluated by fitting the product of $v_z C_A$ versus x with a cubic spline or polynomial and evaluating the integral with the POLYMATH *Curve Fitting and Regression Program*. The comparison of the calculations from Equations (10-146) and (10-147) should be made with $H = W = 1$ m.