EXAMPLE 18.3-1

Diffusion with a Slow Heterogeneous Reaction

Rework the problem just considered when the reaction $2A \rightarrow B$ is not instantaneous at the catalytic surface at $z = \delta$. Instead, assume that the rate at which A disappears at the catalyst-coated surface is proportional to the concentration of A in the fluid at the interface,

$$N_{Az} = k_1''c_A = k_1''cx_A \tag{18.3-10}$$

in which k_1'' is a rate constant for the pseudo-first-order surface reaction.

SOLUTION

We proceed exactly as before, except that B.C. 2 in Eq. 18.3-7 must be replaced by

$$\text{B.C. 2}': \qquad \text{at } z = \delta, \qquad x_A = \frac{N_{Az}}{k_1''c} \tag{18.3-11}$$

N_{Az} being, of course, a constant at steady state. The determination of the integration constants from B.C. 1 and B.C. 2′ leads to

$$(1 - \tfrac{1}{2}x_A) = \left(1 - \frac{1}{2}\frac{N_{Az}}{k_1''c}\right)^{z/\delta}(1 - \tfrac{1}{2}x_{A0})^{1-(z/\delta)} \tag{18.3-12}$$

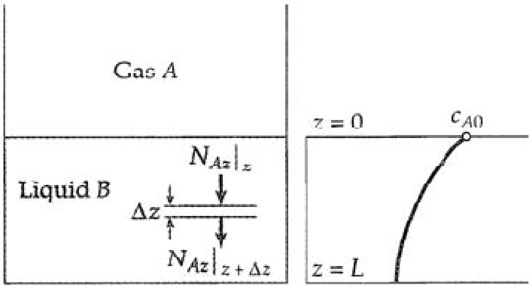
From this we evaluate $(dx_A/dz)|_{z=0}$ and substitute it into Eq. 18.3-2, to get

$$N_{Az} = \frac{2c\mathscr{D}_{AB}}{\delta}\ln\left(\frac{1 - \frac{1}{2}(N_{Az}/k_1''c)}{1 - \frac{1}{2}x_{A0}}\right) \tag{18.3-13}$$

This is a transcendental equation for N_{Az} as a function of x_{A0}, k_1'', $c\mathscr{D}_{AB}$, and δ. When k_1'' is large, the logarithm of $1 - \frac{1}{2}(N_{Az}/k_1''c)$ may be expanded in a Taylor series and all terms discarded but the first. We then get

$$N_{Az} = \frac{2c\mathscr{D}_{AB}/\delta}{1 + \mathscr{D}_{AB}/k_1''\delta}\ln\left(\frac{1}{1 - \frac{1}{2}x_{A0}}\right) \quad (k_1 \text{ large}) \tag{18.3-14}$$

Note once again that we have obtained the rate of the *combined* reaction and diffusion process. Note also that the dimensionless group $\mathscr{D}_{AB}/k_1''\delta$ describes the effect of the surface reaction kinetics on the overall diffusion-reaction process. The reciprocal of this group is known as the *second Damköhler number*[1] $\text{Da}^{\text{II}} = k_1''\delta/\mathscr{D}_{AB}$. Evidently we get the result in Eq. 18.3-9 in the limit as $\text{Da}^{\text{II}} \rightarrow 0$.



18B.5. **Absorption of chlorine by cyclohexene.** Chlorine can be absorbed from Cl_2–air mixtures by olefins dissolved in CCl_4. It was found[5] that the reaction of Cl_2 with cyclohexene (C_6H_{10}) is second order with respect to Cl_2 and zero order with respect to C_6H_{10}. Hence the rate of disappearance of Cl_2 per unit volume is $k_2'''c_A^2$ (where A designates Cl_2).

Rework the problem of §18.4 where B is a C_6H_{10}–CCl_4 mixture, assuming that the diffusion can be treated as pseudobinary. Assume that the air is essentially insoluble in the C_6H_{10}–CCl_4 mixture. Let the liquid phase be sufficiently deep that L can be taken to be infinite.

(a) Show that the concentration profile is given by

$$\frac{c_{A0}}{c_A} = \left[1 + \sqrt{\frac{k_2'''c_{A0}}{6\mathscr{D}_{AB}}}\,z\right]^2 \tag{18B.5-1}$$

(b) Obtain an expression for the rate of absorption of Cl_2 by the liquid.

(c) Suppose that a substance A dissolves in and reacts with substance B so that the rate of disappearance of A per unit volume is some arbitrary function of the concentration, $f(c_A)$. Show that the rate of absorption of A is given by

$$N_{Az}|_{z=0} = \sqrt{2\mathscr{D}_{AB}\int_0^{c_{A0}} f(c_A)dc_A} \tag{18B.5-2}$$

Use this result to check the result of (b).

EXAMPLE 19.1-1

Diffusion, Convection, and Chemical Reaction[3]

In Fig. 19.1-1 we show a system in which a liquid, B, moves slowly upward through a slightly soluble porous plug of A. Then A slowly disappears by a first-order reaction after it has dissolved. Find the steady-state concentration profile $c_A(z)$, where z is the coordinate upward from the plug. Assume that the velocity profile is approximately flat across the tube. Assume further that c_{A0} is the solubility of unreacted A in B. Neglect temperature effects associated with the heat of reaction.

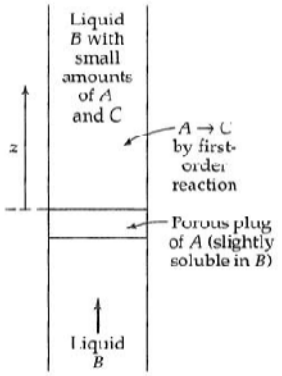


Fig. 19.1-1. Simultaneous diffusion, convection, and chemical reaction.

EXAMPLE 19.4-2

Concentration Profile in a Tubular Reactor

A catalytic tubular reactor is shown in Fig. 19.4-2. A dilute solution of solute A in a solvent S is in fully developed, laminar flow in the region $z < 0$. When it encounters the catalytic wall in the region $0 \leq z \leq L$, solute A is instantaneously and irreversibly rearranged to an isomer B. Write the diffusion equation appropriate for this problem, and find the solution for short distances into the reactor. Assume that the flow is isothermal and neglect the presence of B.

SOLUTION

For the conditions stated above, the flowing liquid will always be very nearly pure solvent S. The product $\rho\mathscr{D}_{AS}$ can be considered constant, and the diffusion of A in S can be described by the steady-state version of Eq. 19.1-14 (ignoring the presence of a small amount of the reaction product B). The relevant equations of change for the system are then

Continuity of A:

$$v_z \frac{\partial c_A}{\partial z} = \mathscr{D}_{AS}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_A}{\partial r}\right) + \underline{\frac{\partial^2 c_A}{\partial z^2}}\right] \tag{19.4-18}$$

Motion:

$$0 = -\frac{d\mathscr{P}}{dz} + \mu\frac{1}{r}\frac{d}{dr}\left(r\frac{dv_z}{dr}\right) \tag{19.4-19}$$

We make the usual assumption that axial diffusion can be neglected with respect to axial convection, and therefore delete the dashed-underlined term (compare with Eqs. 10.8-11 and 12). Equation 19.4-19 can be solved to give the parabolic velocity profile $v_z(r) = v_{z,\max}[1 - (r/R)^2]$. When this result is substituted into Eq. 19.4-18, we get

$$v_{z,\max}\left[1 - \left(\frac{r}{R}\right)^2\right]\frac{\partial c_A}{\partial z} = \mathscr{D}_{AS}\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c_A}{\partial r}\right) \tag{19.4-20}$$

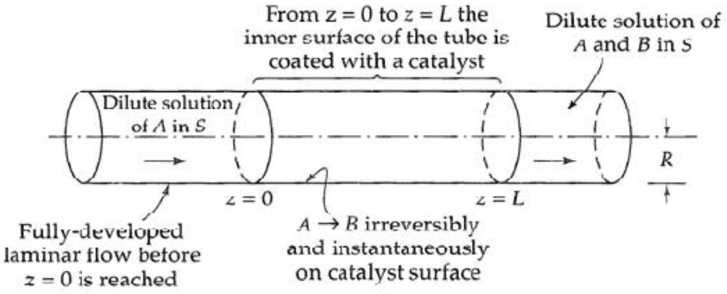


Fig. 19.4-2. Boundary conditions for a tubular reactor.

This is to be solved with the boundary conditions

B.C. 1: at $z = 0$, $c_A = c_{A0}$ (19.4-21)

B.C. 2: at $r = R$, $c_A = 0$ (19.4-22)

B.C. 3: at $r = 0$, $c_A = \text{finite}$ (19.4-23)

For short distances z into the reactor, the concentration c_A differs from c_{A0} only near the wall, where the velocity profile is practically linear. Hence we can introduce the variable $y = R - r$, neglect curvature terms, and replace B.C. 3 by a fictitious boundary condition at $y = \infty$ (see Example 12.2-2 for a detailed discussion of this method of treating the entrance region of the tube).

The reformulated problem statement is then

$$2v_{z,\max}\frac{y}{R}\frac{\partial c_A}{\partial z} = \mathscr{D}_{AS}\frac{\partial^2 c_A}{\partial y^2} \tag{19.4-24}$$

with the boundary conditions

B.C. 1: at $z = 0$, $c_A = c_{A0}$ (19.4-25)

B.C. 2: at $y = 0$, $c_A = 0$ (19.4-26)

B.C. 3: at $y = \infty$, $c_A = c_{A0}$ (19.4-27)

This problem can be solved by the method of combination of independent variables by seeking a solution of the form $c_A/c_{A0} = f(\eta)$, where $\eta = (y/R)(2v_{z,\max}R^2/9\mathscr{D}_{AS}z)^{1/3}$. One thus obtains the ordinary differential equation $f'' + 3\eta^2 f' = 0$, which can be integrated to give (see Eq. C.1-9)

$$\frac{c_A}{c_{A0}} = \frac{\int_0^{\eta} \exp(-\overline{\eta}^3)\, d\overline{\eta}}{\int_0^{\infty} \exp(-\overline{\eta}^3)\, d\overline{\eta}} = \frac{\int_0^{\eta} \exp(-\overline{\eta}^3)\, d\overline{\eta}}{\Gamma(\frac{4}{3})} \qquad (19.4\text{-}28)$$