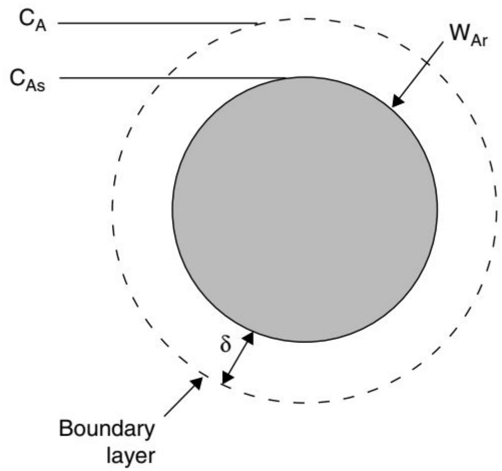
Catalysis

Relation between mass transfer coefficient and reaction rate (continue)

Example

Example 14–1 Rapid Reaction on the Surface of a Catalyst

Calculate the molar flux, W_{Ar}, of reactant A to a single catalyst pellet 1 cm in diameter suspended in a large body of liquid B. The reactant is present in dilute concentrations, and the reaction is considered to take place instantaneously at the external pellet surface (i.e., $C_{As} \simeq 0$). The bulk concentration of the reactant A is 1.0 M, and the free-stream liquid velocity past the sphere is 0.1 m/s. The kinematic viscosity (i.e., $\frac{\mu}{\rho}$) is 0.5 centistoke (cS; 1 centistoke = 10^{-6} m²/s), and the liquid diffusivity of A in B is $D_{AB} = 10^{-10}$ m²/s, at 300 K.



Solution

For dilute concentrations of the solute, the radial flux is

$$W_{Ar} = k_c(C_{Ab} - C_{As}) \tag{14-28}$$

Because reaction is assumed to occur instantaneously on the external surface of the pellet, $C_{As} = 0$. Also, C_{Ab} is given as 1 mol/dm³. The mass transfer coefficient for single spheres is calculated from the Frössling correlation

$$\text{Sh} = \frac{k_c d_p}{D_{\text{AB}}} = 2 + 0.6\text{Re}^{1/2}\text{Sc}^{1/3} \tag{14-41}$$

$$\text{Re} = \frac{\rho d_p U}{\mu} = \frac{d_p U}{\nu} = \frac{(0.01 \text{ m})(0.1 \text{ m/s})}{0.5 \times 10^{-6} \text{ m}^2/\text{s}} = 2000$$

$$\text{Sc} = \frac{\nu}{D_{\text{AB}}} = \frac{5 \times 10^{-7} \text{ m}^2/\text{s}}{10^{-10} \text{ m}^2/\text{s}} = 5000$$

Substituting these values into Equation (14-40) gives us

$$\text{Sh} = 2 + 0.6(2000)^{0.5}(5000)^{1/3} = 460.7 \tag{E14-1.1}$$

$$k_c = \frac{D_{\text{AB}}}{d_p}\text{Sh} = \frac{10^{-10} \text{ m}^2/\text{s}}{0.01 \text{ m}} \times 460.7 = 4.61 \times 10^{-6} \text{ m/s} \tag{E14-1.2}$$

$$C_{\text{A}b} = 1.0 \text{ mol/dm}^3 = 10^3 \text{ mol/m}^3$$

Substituting for k_c and $C_{\text{A}b}$ in Equation (14-26), the molar flux to the surface is

$$W_{\text{A}r} = (4.61 \times 10^{-6}) \text{ m/s } (10^3 - 0) \text{ mol/m}^3 = 4.61 \times 10^{-3} \text{ mol/m}^2 \cdot \text{s}$$

Because $W_{\text{A}r} = -r''_{\text{A}s}$, this rate is also the rate of reaction per unit surface area of catalyst.

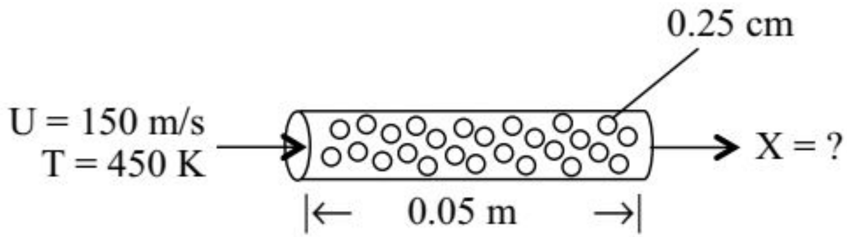
$$\boxed{-r''_{\text{A}s} = 0.0046 \text{ mol/m}^2 \cdot \text{s} = 0.46 \text{ mol/dm}^2 \cdot \text{s}}$$

Example 14–2 Mass Transfer Effects in Maneuvering a Space Satellite

Hydrazine has been studied extensively for use in monopropellant thrusters for space flights of long duration. Thrusters are used for altitude control of communication satellites. Here, the decomposition of hydrazine over a packed bed of alumina-supported iridium catalyst is of interest.[14] In a proposed study, a 2% hydrazine in 98% helium mixture is to be passed over a packed bed of cylindrical particles 0.25 cm in diameter and 0.5 cm in length at a gas-phase velocity of 150 m/s and a temperature of 450 K. The kinematic viscosity of helium at this temperature is 4.94×10^{-5} m²/s. The hydrazine decomposition reaction is believed to be externally mass transfer–limited under these conditions. If the packed bed is 0.05 m in length, what conversion can be expected? Assume isothermal operation.

Additional information:

$D_{AB} = 0.69 \times 10^{-4}$ m²/s at 298 K
Bed porosity: 40%
Bed fluidicity: 95.7%



Solution

The following solution is detailed and a bit tedious, but it is important to know the details of how a mass transfer coefficient is calculated.
Rearranging Equation (14-64) gives us

$$\boxed{X = 1 - e^{-(k_c a_c / U)L}} \qquad \text{(E14-2.1)}$$

(a) Using the Thoenes–Kramers correlation to calculate the mass transfer coefficient, k_c

1. First we find the volume-average particle diameter

$$d_p = \left(\frac{6V}{\pi}\right)^{1/3} = \left(6\,\frac{\pi D^2}{4}\,\frac{L}{\pi}\right)^{1/3} \qquad \text{(E14-2.2)}$$

$$= [1.5(0.0025\text{ m})^2(0.005\text{ m})]^{1/3} = 3.61 \times 10^{-3}\text{ m}$$

2. Surface area per volume of bed

$$a_c = 6\left(\frac{1-0.4}{d_p}\right) = 6\left(\frac{1-0.4}{3.61\times 10^{-3}\text{ m}}\right) = 998\text{ m}^2/\text{m}^3 \qquad \text{(E14-2.3)}$$

3. Mass transfer coefficient

$$\text{Re} = \frac{d_p U}{\nu} = \frac{(3.61 \times 10^{-3}\ \text{m})(150\ \text{m/s})}{4.94 \times 10^{-4}\ \text{m}^2/\text{s}} = 10942$$

For cylindrical pellets

$$\gamma = \frac{2\pi r L_p + 2\pi r^2}{\pi d_p^2} = \frac{(2)(0.0025/2)(0.005) + (2)(0.0025/2)^2}{(3.61 \times 10^{-3})^2} = 1.20 \quad \text{(E14-2.4)}$$

$$\text{Re}' = \frac{\text{Re}}{(1-\phi)\gamma} = \frac{10942}{(0.6)(1.2)} = 15173$$

Correcting the diffusivity to 450 K using Table 14-2 gives us

$$D_{\text{AB}}(450\ \text{K}) = D_{\text{AB}}(298\ \text{K}) \times \left(\frac{450}{298}\right)^{1.75} = (0.69 \times 10^{-4}\ \text{m}^2/\text{s})(2.06)$$

$$\text{D}_{\text{AB}}\ (450\ \text{K}) = 1.42 \times 10^{-4}\ \text{m}^2/\text{s} \quad \text{(E14-2.5)}$$

$$\text{Sc} = \frac{\nu}{D_{\text{AB}}} = \frac{4.94 \times 10^{-5}\ \text{m}^2/\text{s}}{1.42 \times 10^{-4}\ \text{m}^2/\text{s}} = 0.35$$

Substituting Re′ and Sc into Equation (14-65) yields

$$\mathrm{Sh}' = (15173.92)^{1/2}(0.35)^{1/3} = (123.18)(0.70) = 86.66 \qquad \text{(E14-2.6)}$$

$$k_c = \frac{D_{\mathrm{AB}}(1-\phi)}{d_p\phi}\,\gamma(\mathrm{Sh}') = \left(\frac{1.42\times10^{-4}\ \mathrm{m^2/s}}{3.61\times10^{-3}\ \mathrm{m}}\right)\left(\frac{1-0.4}{0.4}\right)\times(1.2)(86.66)$$

$$\boxed{k_c = 6.15\ \mathrm{m/s}} \qquad \text{(E14-2.7)}$$

The conversion is

$$X = 1-\exp\left[-(6.15\ \mathrm{m/s})\left(\frac{998\ \mathrm{m^2/m^3}}{150\ \mathrm{m/s}}\right)(0.05\ \mathrm{m})\right] \qquad \text{(E14-2.8)}$$

$$= 1-0.13 \simeq 0.87$$

We find 87% conversion.

(b) Colburn J_D factor to calculate k_c. To find k_c, we first calculate the surface-area-average particle diameter.

For cylindrical pellets, the external surface area is

$$A = \pi d L_p + 2\pi \left(\frac{d^2}{4}\right) \tag{E14-2.9}$$

$$d_p = \sqrt{\frac{A}{\pi}} = \sqrt{\frac{\pi d L_p + 2\pi (d^2/4)}{\pi}} \tag{E14-2.10}$$

$$= \sqrt{(0.0025)(0.005) + \frac{(0.0025)^2}{2}} = 3.95 \times 10^{-3} \text{ m}$$

$$a_c = \frac{6(1-\phi)}{d_p} = 910.74 \text{ m}^2/\text{m}^3$$

$$\text{Re} = \frac{d_p U}{\nu} = \frac{(3.95 \times 10^{-3} \text{ m})(150 \text{ m/s})}{4.94 \times 10^{-5} \text{m}^2/\text{s}}$$

$$= 11996.04$$

$$\phi J_D = \frac{0.765}{\mathrm{Re}^{0.82}} + \frac{0.365}{\mathrm{Re}^{0.386}} \tag{14-69}$$

$$= \frac{0.765}{(11996)^{0.82}} + \frac{0.365}{(11996)^{0.386}} = 3.5 \times 10^{-4} + 9.7 \times 10^{-3} \tag{E14-2.11}$$

$$= 0.010$$

$$J_D = \frac{0.010}{0.4} = 0.25 \tag{E14-2.12}$$

$$\mathrm{Sh} = \mathrm{Sc}^{1/3}\mathrm{Re}(J_D) \tag{E14-2.13}$$

$$= (0.35)^{1/3}(11996)(0.025) = 212$$

$$k_c = \frac{D_{\mathrm{AB}}}{d_p}\,\mathrm{Sh} = \frac{1.42 \times 10^{-4}}{3.95 \times 10^{-3}}\,(212) = 7.63\ \mathrm{m/s}$$

$$\text{Then } X = 1 - \exp\left[-(7.63\ \mathrm{m/s})\left(\frac{910\ \mathrm{m^2/m^3}}{150\ \mathrm{m/s}}\right)(0.05\ \mathrm{m})\right] \tag{E14-2.14}$$

$$\simeq 0.9$$

Effect of Parallel and Series arrangement on Mass Transfer–Limited Reactions in Packed Beds

Last section, we developed an expression that relates mass transfer resistance to conversion as sown bellow

$$X = 1 - e^{-\frac{k_c a_c}{u} z}$$

or

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L$$

What will happen to conversion of this column is connected with another similar column in series or a flow rate is splitty between two column in parallel?

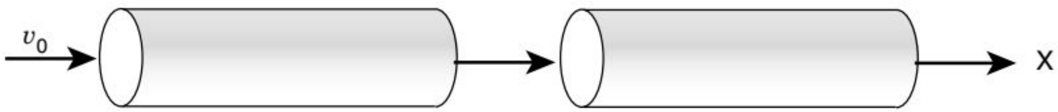


Figure E14-3.1 Series arrangement.

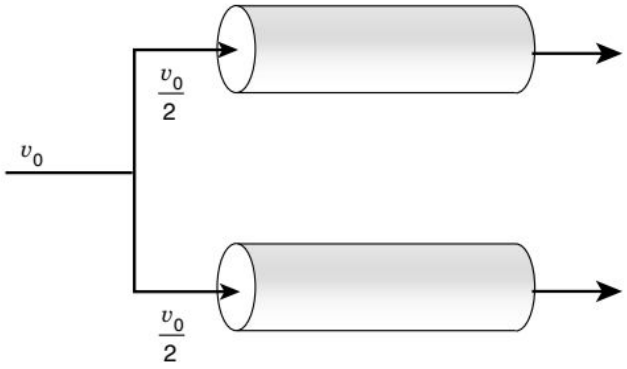


Figure E14-3.2 Parallel arrangement.

For series arrangement, the case is easy. We can treat both columns as on column with total length equal the length of both reactors and directly use the equations derived above.

$$X = 1 - e^{-\frac{k_c a_c}{u} z}$$

$$\ln \frac{1}{1-X} = \frac{k_c a_c}{U} L$$

However, for parallel configuration, the case is different. To estimate the overall conversion, let us assume the conversion from two reactors in series is 0.865. Will this value increase or decrease for parallel arrangements?

Take the ratio of divided system to undivided system as

$$\frac{\ln \frac{1}{1-X_2}}{\ln \frac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}} \left(\frac{L_2}{L_1}\right) \frac{U_1}{U_2}$$

The surface area per unit volume a_c is the same for both systems.

From the conditions of the problem statement we know that

$$L_2 = \tfrac{1}{2} L_1,\ U_2 = \tfrac{1}{2} U_1, \text{ and } X_1 = 0.865$$

$$X_2 = ?$$

Previously, we had the relation of Sherwood Number at high value of Reynold's Number.

$$k_c = 0.6 \left(\frac{D_{AB}}{d_p} \right) Re^{1/2} Sc^{1/3}$$

$$= 0.6 \left(\frac{D_{AB}}{d_p} \right) \left(\frac{U d_p}{\nu} \right)^{1/2} \left(\frac{\nu}{D_{AB}} \right)^{1/3}$$

$$k_c = 0.6 \times \frac{D_{AB}^{2/3}}{\nu^{1/6}} \times \frac{U^{1/2}}{d_p^{1/2}}$$

As shown here, the mass transfer coefficient is proportional with the square root of the velocity.
or

$$k_c \propto U^{1/2}$$

When the ratio of mass transfer for the divided columns to that in series is taken, then this relation becomes

$$\frac{k_{c2}}{k_{c1}} = \left(\frac{U_2}{U_1} \right)^{1/2}$$

Multiplying by the ratio of superficial velocities yields

$$\frac{U_1}{U_2}\left(\frac{k_{c2}}{k_{c1}}\right) = \left(\frac{U_1}{U_2}\right)^{1/2}$$

$$\frac{\ln \dfrac{1}{1-X_2}}{\ln \dfrac{1}{1-X_1}} = \frac{k_{c2}}{k_{c1}}\left(\frac{L_2}{L_1}\right)\frac{U_1}{U_2}$$

$$\ln \frac{1}{1-X_2} = \left(\ln \frac{1}{1-X_1}\right)\frac{L_2}{L_1}\left(\frac{U_1}{U_2}\right)^{1/2}$$

$$= \left(\ln \frac{1}{1-0.865}\right)\left[\frac{\frac{1}{2}L_1}{L_1}\left(\frac{U_1}{\frac{1}{2}U_1}\right)^{1/2}\right]$$

$$= 2.00\left(\frac{1}{2}\right)\sqrt{2} = 1.414$$

Solving for X_2 gives us

$$X_2 = 0.76$$

Analysis and conclusion:

We see that although the divided arrangement will have the advantage of a smaller pressure drop across the bed, it is a bad idea in terms of conversion. Recall that the series arrangement gave X = 0.865; the parallel arrangement gave X=0.76. Therefore (X2 < X1).