we have discussed diffusion in gases and liquids in systems of simple geometry. We now wish to 
apply the shell mass balance method and Fick's first law to describe diffusion within a porous 
catalyst pellet.

A spherical catalyst that is porous. For a magnified version of the inset,

![Diagram of a spherical catalyst particle with concentration and mass balance equations]

diffusion inside the tortuous void passages in the pellet. Instead, we describe the "averaged" 
diffusion of the reactant in terms of an "effective diffusivity."

mass balance for species A on a spherical shell of thickness $\Delta r$ within a single catalyst 
particle:

\[ N_{A,r} \cdot 4\pi r^2 - \frac{d}{dt} \cdot 4\pi(r + \Delta r)^2 + R_A \cdot 4\pi r^2 \Delta r = 0 \]

Here $N_{A,r}$ is the number of moles of A passing in the $r$ direction through an imaginary 
spherical surface at a distance $r$ from the center of the sphere. The source term $R_A \cdot 
4\pi r^2 \Delta r$ is the molar rate of production of A by chemical reaction in the shell of thickness 
$\Delta r$. Dividing by $4\pi r$ $\Delta r$ and letting $\Delta r \to 0$ gives

\[ \lim_{\Delta r \to 0} \frac{(r^2 N_{A,r})\big|_{r+\Delta r} - (r^2 N_{A,r})\big|_r}{\Delta r} = r^2 R_A \]

or, using the definition of the first derivative,

\[ \frac{d}{dr} (r^2 N_{A,r}) = r^2 R_A \]

We now define an "effective diffusivity" for species A in the porous medium by
in which $c_A$ is the concentration of the gas A contained within the pores. The effective diffusivity $D_A$ must be measured experimentally. It depends generally on pressure and temperature and also on the catalyst pore structure. The actual mechanism for diffusion in pores is complex, since the pore dimensions may be smaller than the mean free path of the diffusing molecules.

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d c_A}{dr} \right) = -R_A$$

We now consider the situation where species A disappears according to a first-order chemical reaction on the catalytic surfaces that form all or part of the "walls" of the winding passages. Let $a$ be the available catalytic surface per unit volume (of solids + voids). Then $R_A = -k_a c_A$.

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d c_A}{dr} \right) = k_a c_A$$

This equation is to be solved with the boundary conditions that $c_A = C_{AR}$ at $r = R$, and that $C_A$ is finite at $r = 0$.

Equations containing the operator $(1/r^2)(d/dr)[r^2(d/dr)]$ can frequently be solved by using a "standard trick"—namely, a change of variable $c_A/c_{AR} = (1/r)(r)$. The equation for $f(r)$ is then

$$\frac{d^2 f}{dr^2} = \left( \frac{k_a}{D_A} \right) f$$

in terms of hyperbolic functions

$$\frac{c_A}{c_{AR}} = \frac{C_1}{r} \cosh \sqrt{\frac{k_p}{D_A}} r + \frac{C_2}{r} \sinh \sqrt{\frac{k_p}{D_A}} r$$

Application of the boundary conditions gives finally

$$\frac{c_A}{c_{AR}} = \left( \frac{R}{r} \right) \frac{\sinh \sqrt{k'_a / D_A} R}{\sinh \sqrt{k'_a / D_A} R}$$

chemical kinetics and catalysis one is frequently interested in the molar flux $N_{AR}$ or the molar flow $W_{AR}$ at the surface $r = R$:

$$W_{AR} = 4\pi R^2 N_{AR} = -4\pi R^2 D_A \left. \frac{dc_A}{dr} \right|_{r=R}$$

in this expression, we get

$$W_{AR} = 4\pi R D_A c_A \left( 1 - \sqrt{\frac{k''_a}{D_A}} R \coth \sqrt{\frac{k''_a}{D_A}} R \right)$$

The molar rate of conversion would then be given by the product of the available surface and the surface reaction rate:

$$W_{A,R} = (1/3) \pi R^3 \lambda(-k''_a c_{AR})$$

Taking the ratio of the last two equations, we get

$$\eta_R = \frac{W_{AR}}{W_{A,R}} = \frac{3}{d^2} (\phi \coth \phi - 1)$$

in which $\phi = \sqrt{k''_a / D_A} R$ is the Thiele modulus encountered. The quantity $\eta_R$ is
called the effectiveness factor. It is the quantity by which \( W_{AR0} \) has to be multiplied to account for the intraparticle diffusional resistance to the overall conversion process.

For non spherical catalyst particles, the foregoing results may be applied approximately by reinterpreting \( R \). We note that for a sphere of radius \( R \) the ratio of volume to external surface is \( R/3 \). For nonspherical particles, we redefine \( R \) in Eq as

\[
R_{\text{nonsph}} = 3 \left( \frac{V_p}{S_p} \right)
\]

where \( V_p \) and \( S_p \) are the volume and external surface of a single catalyst particle. The absolute value of the conversion rate is then given approximately by

\[
|W_{AR}| \approx V_p k_{p}^0 C_AR \eta \quad \eta = \frac{1}{3\Lambda^2} (3\Lambda \coth 3\Lambda - 1)
\]

in which the quantity \( \Lambda = \sqrt{k_p^0 D} (V_p / S_p) \) is a generalized modulus.

when the exact theoretical expressions for \( \eta \) are plotted as functions of \( \Lambda \), the curves Effectiveness factors for porous solid catalysts of various shapes

![Diagram showing effectiveness factors for different particle shapes](image)

Solution of some unsolved problems:

18A.3. Estimating the error in calculating the absorption rate.
18B.2. Error in neglecting the convection term in evaporation
18B.3. Effect of mass transfer rate on the concentration profiles.
18B.6 Two-bulb experiment for measuring gas diffusivity—quasi-steady-state analysis
18A.3. **Estimating the error in calculating the absorption rate.** What is the maximum possible error in computing the absorption rate from Eq. 18.5-18, if the solubility of A in B is known within ±5% and the diffusivity of A in B is known within ±15%? Assume that the geometric quantities and the velocity are known very accurately.

18A.3 Estimating the error in calculating the absorption rate.

Equation 18.5-18 gives

\[ W_A = K c_{A0} \sqrt{D_{AB}} \]

in which \( K \) is a product of known quantities. Then the error in \( W_A \) resulting from small errors \( \Delta c_{A0} \) and \( \Delta D_{AB} \) is

\[
\Delta W_A = \left( \frac{\partial W_A}{\partial c_{A0}} \right) \Delta c_{A0} + \left( \frac{\partial W_A}{\partial D_{AB}} \right) \Delta D_{AB}
\]

\[
= K \sqrt{D_{AB}} \Delta c_{A0} + \frac{K c_{A0}}{2 \sqrt{D_{AB}}} \Delta D_{AB}
\]

Division by \( W_A \) then gives the fractional error expression

\[
\frac{\Delta W_A}{W_A} \approx \frac{\Delta c_{A0}}{c_{A0}} + \frac{1}{2} \frac{\Delta D_{AB}}{D_{AB}}
\]

Hence, the maximum absolute percentage error in the calculation of \( W_A \) under the given conditions is

\[
100 \frac{\Delta W_A}{W_A} \bigg|_{\text{max}} = 5\% + \frac{1}{2}(10\%) = 10\%
\]
18B.2 Error in neglecting the convection term in evaporation

a. Without the convection term, Eq. 18.2-1 and 4 become

\[ N_{A2} = -c \mathcal{D}_{AB} \frac{dx_A}{dz} \quad \text{and} \quad \frac{d^2 x_A}{dz^2} = 0 \]

Integration of the latter equation twice then gives

\[ x_A = C_1 z + C_2 \]

Then application of the boundary conditions gives two equations:

\[ x_{A1} = C_1 z_1 + C_2 \quad \text{and} \quad x_{A2} = C_1 z_2 + C_2 \]

These equation may be solved simultaneously to give

\[ C_1 = -\frac{x_{A1} - x_{A2}}{z_2 - z_1} \quad \text{and} \quad C_2 = x_{A1} + \frac{x_{A1} - x_{A2}}{z_2 - z_1} z_1 \]

Therefore, in the approximation being considered here, the mole-fraction profile in the system is given by

\[ \frac{x_{A1} - x_A}{x_{A1} - x_{A2}} = \frac{z - z_1}{z_2 - z_1} \]

b. To get the result in (a) from Eq. 18.2-14, we can expand the latter in a Taylor series, as was done in getting Eq. 18.2-16.

c. To get the solution of Example 18.2-2 by using the result in (a), we make the following calculation

\[ \mathcal{D}_{AB} = \frac{N_{A2}RT}{p(-dx_A/dz)} = \frac{N_{A2}RT(z_2 - z_1)}{p(x_{A1} - x_{A2})} = \frac{(7.26 \times 10^{-9})(82.06)(273)(17.1)}{(755/760)[(33/755) - 0]} \]

\[ = 0.0641 \ \text{cm}^2/\text{s} \]

Hence the error is \( \frac{0.0641 - 0.0636}{0.0636} \times 100 = 0.79\% \)
18B.3 Effect of mass transfer rate on the concentration profiles

a. Rewrite Eq. 18.2-14 as

\[ N_{Ae} = \frac{cD_{AB}}{z_2 - z_1} \ln \frac{1 - x_{A2}}{1 - x_{A1}} \quad \text{or} \quad \frac{1 - x_{A2}}{1 - x_{A1}} = \exp \frac{N_{Ae}(z_2 - z_1)}{cD_{AB}} \]

When this is substituted into the right side of Eq. 18.2-11, we get

\[ \frac{1 - x_A}{1 - x_{A1}} = \left( \exp \frac{N_{Ae}(z_2 - z_1)}{cD_{AB}} \right) \frac{(z - z_1)/(z_2 - z_1)}{(z - z_1)/(z_1 - z_1)} = \left( \exp \frac{N_{Ae}(z - z_1)}{cD_{AB}} \right) \]

b. Starting with Eq. 18.2-1 and integrating directly we get

\[ \frac{1}{1 - x_A} \frac{d}{dz} = -\frac{N_{Ae}}{cD_{AB}} \quad \text{and} \quad \int_{x_{A1}}^{x_A} \frac{1}{1 - x_A} \, dx_A = -\frac{N_{Ae}}{cD_{AB}} \int_{z_1}^{z} \, dz \]

When the integrals are evaluated we get

\[ -\ln \frac{1 - x_A}{1 - x_{A1}} = -\frac{N_{Ae}}{cD_{AB}} (z - z_1) \]

Changing signs and taking the antilogarithm of both sides then gives the result in (a).

c. Expanding the right side of Eq. 18B.3-1 in a Taylor series in the argument of the exponent, we get

\[ \frac{1 - x_A}{1 - x_{A1}} = 1 + \frac{N_{Ae}}{cD_{AB}} (z - z_1) + \cdots \]

If we retain just two terms in the Taylor series, and bring the "1" on the right side over to the left side, we get

\[ x_A = x_{A1} - \frac{N_{Ae} (1 - x_{A1})}{cD_{AB}} (z - z_1) \]

which is of the form \( x_A = mz + b \), that is, a straight line function.
18B.6 Two-bulb experiment for measuring gas diffusivity—quasi-steady-state analysis

a. The molar shell balance on $\Delta z$ gives for species $A$

$$SN_{Az}|_z - SN_{Az}|_{z+\Delta z} = 0$$

Division by $\Delta z$ and taking the limit as $\Delta z$ goes to zero gives $dN_{Az}/dz = 0$ or $N_{Az} = $ constant.

b. Equation 18.0-1, for this problem, may be simplified thus:

$$N_{Az} = -c\mathcal{D}_{AB}(dx_A/dz) + x_A(N_{Az} + N_{Bz}) = -c\mathcal{D}_{AB}(dx_A/dz)$$

since $N_{Az} = -N_{Bz}$; this is true, because in a system at constant $c$ for every molecule of $A$ that moves to the right, a molecule of $B$ must move to the left.

c. The equation in (b), with $N_{Az} = $ constant, then becomes $dx_A/dz = -(N_{Az}/c\mathcal{D}_{AB})$, which when integrated becomes

$$x_A = -\frac{N_{Az}}{c\mathcal{D}_{AB}}z + C_1$$

$$dx_A/dz = -(N_{Az}/c\mathcal{D}_{AB})$$

$$x_A = -\frac{N_{Az}}{c\mathcal{D}_{AB}}L + C_1$$

Subtracting the last two equations gives then

$$x_A - x_A^* = \frac{N_{Az}}{c\mathcal{D}_{AB}}(L - z)$$

$$1 - x_A^* - x_A = \frac{N_{Az}}{c\mathcal{D}_{AB}}(L - (-L))$$

From which Eq. 18B.6-2 follows directly.
f. A mass balance over the right bulb states that the time rate of change of moles within $V$ must exactly equal the rate at which moles enter $V$ by diffusion at the end of the tube. That is

$$\frac{d}{dt}(VcX_A^t) = SN_{Ac} \quad \text{or} \quad \frac{dx_A^t}{dt} = S\left(\frac{1}{2} - x_A^t\right) \frac{C_0}{L}$$

in which $S$ is the cross-section of the connecting tube.

g. The equation in (f) may be integrated

$$\int \frac{dx_A^t}{\frac{1}{2} - x_A^t} = \int \frac{S\mathcal{D}_{AB}}{LV} dt + C_2 \quad \text{or} \quad -\ln\left(\frac{1}{2} - x_A^t\right) = \frac{S\mathcal{D}_{AB}}{LV} t + C_2$$

The integration constant may be obtained by using the fact that at $t = 0$, we know that the mole fraction of $A$ in the right bulb will be zero, or $C_2 = -\ln\left(\frac{1}{2} - 0\right)$. Therefore

$$\ln\left(\frac{1}{2} - x_A^t\right) - \ln\frac{1}{2} = -\frac{S\mathcal{D}_{AB}}{LV} t \quad \text{or} \quad \frac{1}{2} - x_A^t = \exp\left(-\frac{S\mathcal{D}_{AB}}{LV} t\right)$$

h. If we plot

$$-\frac{LV}{S} \ln\left(\frac{\frac{1}{2} - x_A^t}{\frac{1}{2}}\right) \text{ vs. } t$$

the slope will be the diffusivity, $\mathcal{D}_{AB}$. 