10.6. MASS TRANSFER AND CHEMICAL REACTION

In many applications of mass transfer the solute reacts with the medium as in the case, for example, of the absorption of carbon dioxide in an alkaline solution. The mass transfer rate then decreases in the direction of diffusion as a result of the reaction. Considering the unidirectional molecular diffusion of a component A through a distance $\delta y$ over area A, then, neglecting the effects of bulk flow, a material balance for an irreversible reaction of order $n$ gives:

$$\text{moles IN/unit time} - \text{moles OUT/unit time} = \text{rate of change of + reacted moles/unit volume} \times \text{element}$$

or:

$$\frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2} - k C_A^n$$

where $k$ is the reaction rate constant. This equation has no analytical solution for the general case.

10.6.1. Steady-state process

For a steady-state process:

$$D \frac{d^2 C_A}{dy^2} - k C_A^n = 0$$

Equation 10.171 may be integrated using the appropriate boundary conditions.

**First-order reaction**

For a first-order reaction, putting $n = 1$ in equation 10.171, then:

$$D \frac{d^2 C_A}{dy^2} - k C_A = 0$$

The solution of equation 10.172 is:

$$C_A = B_1' e^{\sqrt{(k/D)y}} + B_2' e^{-\sqrt{(k/D)y}}$$

$B_1'$ and $B_2'$ must then be evaluated using the appropriate boundary conditions.

As an example, consideration is given to the case where the fluid into which mass transfer is taking place is initially free of solute and is semi-infinite in extent. The surface concentration $C_{Ai}$ is taken as constant and the concentration at infinity as zero. The boundary conditions are therefore:

$$\begin{align*}
y = 0 & \quad C_A = C_{Ai} \\
y = \infty & \quad C_A = 0
\end{align*}$$

Substituting these boundary conditions in equation 10.173 gives:

$$\begin{align*}
B_1' &= 0 \\
B_2' &= C_{Ai} \\
C_A &= C_{Ai} e^{-\sqrt{(k/D)y}}
\end{align*}$$
\[ \frac{dC_A}{dy} = -\sqrt{\frac{k}{D}C_{Ai}e^{-\sqrt{(k/D)y}}} \]

and:

\[ N_A = -D \frac{dC_A}{dy} = \sqrt{kDC_{Ai}e^{-\sqrt{(k/D)y}}} \]  

(10.175)

At the interface \( y = 0 \) and:

\[ N_A = \sqrt{kDC_{Ai}} \]  

(10.176)

### nth-order reaction

The same boundary conditions will be used as for the first-order reaction. Equation 10.171 may be re-arranged to give:

\[ \frac{d^2C_A}{dy^2} - \frac{k}{D}C^n_A = 0 \]  

(10.177)

Putting:

\[ \frac{dC_A}{dy} = q \]

\[ \frac{d^2C_A}{dy^2} = \frac{dq}{dy} = \frac{dq}{dC_A} \frac{dC_A}{dy} = q \frac{dq}{dC_A} \]

and:

\[ q \frac{dq}{dC_A} - \frac{k}{D}C^n_A = 0 \]

Multiplying through by \( dC_A \) and integrating:

\[ \frac{q^2}{2} - \frac{1}{n + 1} \frac{k}{D}C^{n+1}_A = B'_3 \]

When \( y = \infty \), \( C_A = 0 \) and \( \frac{dC_A}{dy} = q = 0 \) \( \therefore B'_3 = 0 \)

and:

\[ \left( \frac{dC_A}{dy} \right)^2 = \frac{2k}{n + 1} C^{n+1}_A \]

Since \( \frac{dC_A}{dy} \) is negative, the negative value of the square root will be taken to give:

\[ \frac{dC_A}{dy} = -\sqrt{\frac{2}{n + 1} \sqrt{\frac{k}{D}C^{n+1}_A}} \]  

(10.178)

\[ N_A = -D \frac{dC_A}{dy} = \sqrt{\frac{2}{n + 1} \sqrt{kDC^{n+1}_A}} \]  

(10.179)

At the free surface, \( C_A = C_{Ai} \) and

\[ N_A = \sqrt{\frac{2}{n + 1} \sqrt{kDC^{n+1}_{Ai}}} \]  

(10.180)

which is identical to equation 10.176 for a first-order reaction when \( n = 1 \).
Integrating equation 10.178 gives:

\[ C_A^{\frac{n+1}{2}} \, dC_A = -\sqrt{\frac{2}{n+1}} \sqrt{\frac{k}{D}} \, dy \]

or:

\[ \frac{2}{1-n} C_A^{-\frac{1-n}{2}} = -\sqrt{\frac{2}{n+1}} \sqrt{\frac{k}{D}} \, y + B'_4 \]

When \( y = 0, \) \( C_A = C_{A_{i}} \) and \( B'_4 = 2 \frac{1-n}{1-n} C_{A_{i}}^{\frac{1-n}{2}} \)

and:

\[ C_A^{-\frac{1}{2}} - C_{A_{i}}^{-\frac{1}{2}} = (n - 1) \sqrt{\frac{1}{2(n + 1)}} \sqrt{\frac{k}{D}} \, y \]  
(10.181)

This solution cannot be used for a first-order reaction where \( n = 1 \) because it is then indeterminate.

**Second-order reaction \((n = 2)\)**

In this case, equation 10.181 becomes:

\[ C_A^{-\frac{1}{2}} - C_{A_{i}}^{-\frac{1}{2}} = \sqrt{\frac{k}{6D}} \, y \]  
(10.182)

and equation 10.180 becomes:

\[ N_A = \sqrt{\frac{2}{3 \sqrt{k DC_A^{\frac{3}{2}}}}} \]  
(10.183)

**Example 10.9**

In a gas absorption process, the solute gas \( A \) diffuses into a solvent liquid with which it reacts. The mass transfer is one of steady state unidirectional molecular diffusion and the concentration of \( A \) is always sufficiently small for bulk flow to be negligible. Under these conditions the reaction is first order with respect to the solute \( A \).

At a depth \( l \) below the liquid surface, the concentration of \( A \) has fallen to one-half of the value at the surface. What is the ratio of the mass transfer rate at this depth \( l \) to the rate at the surface? Calculate the numerical value of the ratio when \( l \sqrt{k/D} = 0.693 \), where \( D \) is the molecular diffusivity and \( k \) the first-order rate constant.

**Solution**

This process is described by:

\[ C_A = B'_1 e^{\sqrt{(k/D)y}} + B'_2 e^{-\sqrt{(k/D)y}} \]  
(equation 10.173)

If \( C_{A_{i}} \) is the surface concentration \((y = 0)\):

\[ C_{A_{i}} = B'_1 + B'_2 \]

At \( y = l \), \( C_A = C_{A_{i}}/2 \), and:

\[ \frac{C_{A_{i}}}{2} = B'_1 e^{\sqrt{(k/D)l}} + B'_2 e^{-\sqrt{(k/D)l}} \]
Solving for $B'_1$ and $B'_2$:

$$B'_1 = \frac{C_{AI}}{2} \left[ 1 - 2e^{-(k/D)y} \right] (e^{(k/D)y} - e^{-\sqrt{(k/D)y}})^{-1}$$

$$B'_2 = -\frac{C_{AI}}{2} \left[ 1 - 2e^{\sqrt{(k/D)y}} \right] (e^{\sqrt{(k/D)y}} - e^{-\sqrt{(k/D)y}})^{-1}$$

$$\frac{(N_A)_{y=1}}{(N_A)_{y=0}} = \frac{-D(dC_A/dy)_{y=1}}{-D(dC_A/dy)_{y=0}} = \frac{(dC_A/dy)_{y=1}}{(dC_A/dy)_{y=0}}$$

$$\frac{dC_A}{dy} = \sqrt{\frac{k}{D}} \left[ (B'_1 e^{\sqrt{(k/D)y}} - B'_2 e^{-\sqrt{(k/D)y}}) \right]$$

$$\frac{(N_A)_{y=1}}{(N_A)_{y=0}} = \frac{B'_1 e^{\sqrt{(k/D)y}} - B'_2 e^{-\sqrt{(k/D)y}}}{B'_1 - B'_2}$$

$$= \frac{(1 - 2e^{-(k/D)y})e^{\sqrt{(k/D)y}} + (1 - 2e^{\sqrt{(k/D)y})}e^{-\sqrt{(k/D)y}}}{(1 - 2e^{-(k/D)y}) + (1 - 2e^{\sqrt{(k/D)y}})}$$

$$= \frac{e^{\sqrt{(k/D)y}} + e^{-\sqrt{(k/D)y}} - 4}{2(1 - e^{\sqrt{(k/D)y}} - e^{-\sqrt{(k/D)y}})}$$

When:

$$l \sqrt{\frac{k}{D}} = 0.693, \quad e^{\sqrt{(k/D)y}} = 2, \quad e^{-\sqrt{(k/D)y}} = 0.5$$

and:

$$\frac{(N_A)_{y=1}}{(N_A)_{y=0}} = \frac{2^{1/2} - 4}{2(1 - 2^{1/2})} = 0.5$$

**Example 10.10**

In a steady-state process, a gas is absorbed in a liquid with which it undergoes an irreversible reaction. The mass transfer process is governed by Fick's law, and the liquid is sufficiently deep for it to be regarded as effectively infinite in depth. On increasing the temperature, the concentration of reactant at the liquid surface decreases to 0.8 times its original value. The diffusivity is unchanged, but the reaction constant increases by a factor of 1.35. It is found that the mass transfer rate at the liquid surface falls to 0.83 times its original value. What is the order of the chemical reaction?

**Solution**

The mass transfer rate (moles/unit area and unit time) is given by equation 10.180, where denoting the original conditions by subscript 1 and the conditions at the higher temperature by subscript 2 gives:

$$N_{A1} = \sqrt{\frac{2}{n+1} \sqrt{k_1 DC_{AI}}} \left[ \frac{n+1}{2} \right]$$

(equation 10.180)

and:

$$N_{A2} = 0.83N_{A1} = \sqrt{\frac{2}{n+1} \sqrt{1.35k_1 D(0.8C_{AI}) \left[ \frac{n+1}{2} \right]}}$$

Substituting the numerical values gives:

$$0.83 = \sqrt{1.35(0.8)} \left[ \frac{n+1}{2} \right]$$

or:

$$\left[ \frac{n+1}{2} \right] = 0.714$$
Thus:

\[ \frac{n + 1}{2} = 1.506 \]

and:

\[ n = 2.01 \]

Thus, the reaction is of **second-order**.

**Example 10.11**

A pure gas is absorbed into a liquid with which it reacts. The concentration in the liquid is sufficiently low for the mass transfer to be covered by Fick's Law and the reaction is first-order with respect to the solute gas. It may be assumed that the film theory may be applied to the liquid and that the concentration of solute gas falls from the saturation value to zero across the film. The reaction is initially carried out at 293 K. By what factor will the mass transfer rate across the interface change, if the temperature is raised to 313 K?

The reaction rate constant at 293 K

\[ = 2.5 \times 10^{-6} \text{ s}^{-1} \]

The energy of activation for reaction in the Arrhenius equation

\[ = 26430 \text{ kJ/kmol} = 2.643 \times 10^7 \text{ J/kmol} \]

Universal gas constant,

\[ R = 8314 \text{ J/kmol K} \]

Molecular diffusivity,

\[ D = 10^{-9} \text{ m}^2/\text{s} \]

Film thickness,

\[ L = 10 \text{ mm} \]

Solubility of gas at 313 K is 80 per cent of the solubility at 293 K.

**Solution**

For a first-order reaction:

\[ D \frac{d^2C_A}{dy^2} - kC_A = 0 \]

(equation 10.170)

Solving:

\[ C_A = B'_1 e^{\sqrt{(k/D)y}} + B'_2 e^{-\sqrt{(k/D)y}} \]

(equation 10.171)

When

\[ y = 0, \ C_A = C_{AS} \]

and when \[ y = L, \ C_A = 0. \]

Substituting:

\[ B'_1 = -C_{AS} e^{-2L\sqrt{(k/D)}}(1 - e^{-2L\sqrt{(k/D)}})^{-1} \]

and:

\[ B'_2 = C_{AS}(1 - e^{-2L\sqrt{(k/D)}})^{-1} \]

and thus:

\[ \frac{C_A}{C_{AS}} = (e^{-\sqrt{(k/D)y}} - e^{-2L\sqrt{(k/D)}}) \frac{(1 - e^{-2L\sqrt{(k/D)}})^{-1}}{(1 - e^{-2L\sqrt{(k/D)}})^{-1}} \]

Differentiating and putting \[ y = 0: \]

\[ \frac{1}{C_{AS}}\left( \frac{dC_A}{dy} \right)_{y=0} = \frac{(-\sqrt{(k/D)} - \sqrt{(k/D)}e^{-2L\sqrt{(k/D)}})}{(1 - e^{-2L\sqrt{(k/D)}})} \]

The mass transfer rate at the interface is then:

\[ -D \left( \frac{dC_A}{dy} \right)_{y=0} = \frac{C_{AS}\sqrt{(k/D)}(1 + e^{-2L\sqrt{(k/D)}})(1 - e^{-2L\sqrt{(k/D)}})^{-1}}{C_{AS}\sqrt{(k/D)}(1 + e^{-2L\sqrt{(k/D)}})(1 - e^{-2L\sqrt{(k/D)}})^{-1}} \]

When \[ D = 1 \times 10^{-9} \text{ m}^2/\text{s}, \] then at 293 K:

\[ k = A e^{-2.643 \times 10^7/(8314 \times 293)} \]
\[ A = 0.129 \, \text{s}^{-1} \]

Since \( L = 0.01 \, \text{m} \), then:

\[ 2L \sqrt{\frac{k}{D}} = 2 \times 0.01 \frac{2.5 \times 10^{-6}}{(1 \times 10^{-3})^{0.5}} = 1.0 \]

\[ e^{-2L \sqrt{\frac{k}{D}}} = e^{-1} = 0.368 \]

and:

\[ C_{AS} = C_{AS1} \]

The mass transfer rate is then:

\[ N_{A293} = C_{AS1} \left( \frac{2.5 \times 10^{-6}}{1 \times 10^{-9}} \right)^{0.5} \frac{(1 + 0.368)}{(1 - 0.368)} \]

\[ = 108.2C_{AS1} \]

At 313 K:

\[ k = A e^{-2.643 \times 10^7/(8314 \times 313)} = (0.129 \times 3.37 \times 10^{-3}) = 5.0 \times 10^{-6} \, \text{s}^{-1} \]

\[ C_{AS} = 0.8C_{AS1} \]

\[ 2L \sqrt{\frac{k}{D}} = (2 \times 0.01 \frac{5 \times 10^{-6}}{(1 \times 10^{-9})^{0.5}} = 1.414 \]

and:

\[ e^{-1.414} = 0.243 \]

The mass transfer rate at 313 K is then:

\[ N_{A313} = 0.8C_{AS1} (5 \times 10^6 \times 1 \times 10^{-9})^{0.5} (1 + 0.243)/(1 - 0.243) \]

\[ = 92.9C_{AS1} \]

Hence the change in the mass transfer rate is given by the factor:

\[ \frac{N_{A313}}{N_{A293}} = \frac{92.9C_{AS1}}{108.2C_{AS1}} \]

\[ = 0.86 \]

### 10.6.2. Unsteady-state process

For an unsteady-state process, equation 10.170 may be solved analytically only in the case of a first-order reaction \( n = 1 \). In this case:

\[ \frac{\partial C_A}{\partial t} = D \frac{\partial^2 C_A}{\partial y^2} - k C_A \quad (10.174) \]

The solution of this equation has been discussed by DANCKWERTS\(^{(28)}\), and here a solution will be obtained using the Laplace transform method for a semi-infinite liquid initially free of solute. On the assumption that the liquid is in contact with pure solute gas, the concentration \( C_{Ai} \) at the liquid interface will be constant and equal to the saturation value. The boundary conditions will be those applicable to the penetration theory, that is:

\[ t = 0 \quad 0 < y < \infty \quad C_A = 0 \]

\[ t > 0 \quad y = 0 \quad C_A = C_{Ai} \]

\[ t > 0 \quad y = \infty \quad C_A = 0 \]
From equations 10.103 and 10.104, taking Laplace transforms of both sides of equation 10.184 gives:

\[ p\bar{C}_A = D \frac{d^2 \bar{C}_A}{dy^2} - k \bar{C}_A \]

or:

\[ \frac{d^2 \bar{C}_A}{dy^2} - \frac{p + k}{D} \bar{C}_A = 0 \]

Thus:

\[ \bar{C}_A = B_1 e^{\sqrt{(p+k)/D}y} + B_2 e^{-\sqrt{(p+k)/D}y} \]  

(10.185)

When \( y = \infty \), \( C_A = 0 \) and therefore \( \bar{C}_A = 0 \), from which \( B_1 = 0 \).

Equation 10.185 therefore becomes:

\[ \bar{C}_A = C_{Ai} \frac{e^{-\sqrt{(p+k)/D}y}}{p} \]  

(10.186)

The mass transfer rate \( N_A \) at the interface must be evaluated in order to obtain the rate at which gas is transferred to the liquid from the gas.

Differentiating equation 10.186 with respect to \( y \) gives:

\[ \frac{d\bar{C}_A}{dy} = \frac{d\bar{C}_A}{dy} = -\sqrt{\frac{p + k}{D}} \frac{C_{Ai}}{p} e^{-\sqrt{(p+k)/D}y} \]  

(10.187)

At the interface (\( y = 0 \)):

\[ \left( \frac{d\bar{C}_A}{dy} \right)_{y=0} = -\frac{C_{Ai} \sqrt{p + k}}{\sqrt{D} p} \]  

(10.188)

It is not possible to invert equation 10.188 directly using the transforms listed in Table 12 in Appendix A4. On putting \( a = \sqrt{k} \), however, entry number 38 gives:

\[ \text{Inverse of } \frac{\sqrt{p}}{p - k} = \frac{1}{\sqrt{\pi t}} + \sqrt{k} e^{kt} \text{ erf}(\sqrt{k}t) \]

From the shift theorem, if \( \tilde{f}(t) = \tilde{f}(p) \), and then:

\[ \tilde{f}(t)e^{-kt} = \int_0^\infty f(t)e^{-kt} e^{-pt}dt = \int_0^\infty f(t)e^{-(p+k)t}dt = \tilde{f}(p + k) \]

Thus, inverse of \( \frac{\sqrt{p + k}}{p} \) is \( \frac{1}{\sqrt{\pi t}} e^{-kt} + \sqrt{k} \text{ erf}(\sqrt{k}t) \)

Hence, inverting equation 10.188 gives:

\[ \left( \frac{d\bar{C}_A}{dy} \right)_{y=0} = -\frac{C_{Ai}}{\sqrt{D}} \left\{ \frac{1}{\sqrt{\pi t}} e^{-kt} + \sqrt{k} \text{ erf}(\sqrt{k}t) \right\} \]

and:

\[ (N_A)_r = -D \left( \frac{d\bar{C}_A}{dy} \right)_{y=0} = C_{Ai} \sqrt{\frac{D}{k}} \left\{ \sqrt{\frac{k}{\pi t}} e^{-kt} + k \text{ erf}(\sqrt{k}t) \right\} \]  

(10.189)

Equation 10.189 gives the instantaneous value of \( (N_A)_r \) at time \( t \).
The average value \( N_A \) for mass transfer over an exposure time \( t_e \) is given by:

\[
N_A = \frac{1}{t_e} \int_0^{t_e} N_A \, dt = \frac{1}{t_e} \, C_{Ai} \sqrt{\frac{D}{k}} \int_0^{t_e} \left\{ \left( k \, \text{erf} \sqrt{k t} + k t \sqrt{\frac{k}{\pi t}} \right) + \left( -k t \sqrt{\frac{k}{\pi t}} e^{-k t} + \frac{1}{2} \sqrt{\frac{k}{\pi t}} e^{-k t} \right) + \frac{1}{2} \sqrt{\frac{k}{\pi t}} e^{-k t} \right\} \, dt
\]  
(10.190)

The terms in the integral of equation 10.190 cannot be evaluated directly. Although, the integral can be re-arranged to give three terms [(i), (ii) and (iii)], each of which can be integrated, by both adding and subtracting \( k t \sqrt{(k/\pi t)} e^{-k t} \), and splitting the first term into two parts. This gives:

\[
N_A = \frac{1}{t_e} \, C_{Ai} \sqrt{\frac{D}{k}} \int_0^{t_e} \left\{ \left( k \, \text{erf} \sqrt{k t} + k t \sqrt{\frac{k}{\pi t}} \right) + \left( -k t \sqrt{\frac{k}{\pi t}} e^{-k t} + \frac{1}{2} \sqrt{\frac{k}{\pi t}} e^{-k t} \right) + \frac{1}{2} \sqrt{\frac{k}{\pi t}} e^{-k t} \right\} \, dt
\]

Considering each of the above terms (i), (ii), (iii) in turn:

(i) Noting that:

\[
\frac{d}{dr} (k \, \text{erf} \sqrt{k t}) = k \frac{d}{dr} \left\{ \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{k t}} e^{-k t} \, d(\sqrt{k t}) \right\}
\]

\[
= k \frac{d}{dr} \left\{ \frac{2}{\sqrt{\pi}} \int_0^{\sqrt{k t}} e^{-k t} \left( \frac{1}{2} \sqrt{\frac{k}{t}} \right) \, d\sqrt{k t} \right\} = k \sqrt{\frac{k}{\pi t}} e^{-k t}
\]

\[
\int_0^{t_e} \left( k \, \text{erf} \sqrt{k t} + k t \sqrt{\frac{k}{\pi t}} e^{-k t} \right) \, dt = k \int_0^{t_e} \left( \frac{d}{dr} (t \, \text{erf} \sqrt{k t}) \right) \, dt = k t_e \, \text{erf} \sqrt{k t_e}
\]

(ii)\[
\int_0^{t_e} \left( \sqrt{\frac{k t}{\pi}} (-k e^{-k t}) + \frac{1}{2} \sqrt{\frac{k}{\pi t}} \frac{d}{dr} \left( \sqrt{\frac{k}{\pi t}} e^{-k t} \right) \right) \, dt = \int_0^{t_e} \left( \frac{d}{dr} \left( \sqrt{\frac{k}{\pi t}} e^{-k t} \right) \right) \, dt = \sqrt{\frac{k t_e}{\pi}} e^{-k t_e}
\]

(iii)\[
\int_0^{t_e} \left( \frac{1}{2} \sqrt{\frac{k}{\pi t}} e^{-k t} \right) \, dt = \int_0^{t_e} \left( \frac{1}{2} \sqrt{\frac{k}{\pi t}} e^{-k t} \right) \left( 2 \sqrt{k t} \right) \, dt
\]

\[
= \frac{1}{2} \cdot 2 \frac{2}{\sqrt{\pi}} \int_0^{t_e} e^{-k t} \, d\sqrt{k t} = \frac{1}{2} \, \text{erf} \sqrt{k t_e}
\]

Thus:

\[
N_A = \frac{1}{t_e} \, C_{Ai} \sqrt{\frac{D}{k}} \left\{ k t_e \, \text{erf} \sqrt{k t_e} + \sqrt{\frac{k t_e}{\pi}} e^{-k t_e} + \frac{1}{2} \, \text{erf} \sqrt{k t_e} \right\}
\]

\[
= C_{Ai} \sqrt{\frac{D}{k}} \left\{ \left( k + \frac{1}{2t_e} \right) \, \text{erf} \sqrt{k t_e} + \sqrt{\frac{k}{\pi t_e}} e^{-k t_e} \right\}
\]

(10.191)
Thus the mass transfer coefficient, enhanced by chemical reaction, $h_D'$ is given by:

$$
\frac{N_A}{C_{Ai}} = \sqrt{\frac{D}{k}} \left\{ \left(k + \frac{1}{2t_e} \right) \text{erf}\sqrt{k t_e} + \sqrt{\frac{k}{\pi t_e}} e^{-k t_e} \right\}
$$

(10.192)

Two special cases are now considered:

(1) When the reaction rate is very low and $k \to 0$.

Using the Taylor series, for small values of $\sqrt{k t_e}$, and therefore neglecting higher powers of $\sqrt{k t_e}$:

$$
\text{erf}\sqrt{k t_e} = (\text{erf}\sqrt{k t_e})_{\sqrt{k t_e} \to 0} + \left[ \sqrt{k t_e} \left\{ \frac{d}{d\sqrt{k t}} (\text{erf}\sqrt{k t}) \right\} \right]_{\sqrt{k t_e} \to 0}
$$

Then:

$$
\lim \left[ \left(k + \frac{1}{2t_e} \right) \text{erf}\sqrt{k t_e} \right]_{k \to 0} = \frac{1}{2t_e} \left[ \sqrt{k t_e} \left\{ \frac{d}{d\sqrt{k t}} \left\{ \frac{2}{\sqrt{\pi}} \int_0^{t_e} e^{-k t} d\sqrt{k t} \right\} \right\} \right]_{k \to 0}
$$

$$
= \frac{1}{2t_e} \left[ \frac{2}{\sqrt{\pi}} e^{-k t_e} \right]_{k \to 0}
$$

$$
= \sqrt{\frac{k}{\pi t_e}}
$$

Also:

$$
\lim \left[ \sqrt{\frac{k}{\pi t_e}} e^{-k t_e} \right]_{k \to 0} = \sqrt{\frac{k}{\pi t_e}}
$$

Substituting in equation 10.192 gives:

$$
\frac{D}{k} \left\{ \sqrt{\frac{k}{\pi t_e}} \right\} = 2 \sqrt{\frac{D}{\pi t_e}}
$$

(10.193)

as for mass transfer without chemical reaction (equation 10.115)

(2) When the reaction rate is very high, $\text{erf}\sqrt{k t_e} \to 1$, $k \gg (1/t_e)$, and from equation 10.192:

$$
\frac{D}{k} \left[ [k \times 1] + 0 \right] = \sqrt{Dk}
$$

(10.194)

and is independent of exposure time.

### 10.7. Mass Transfer and Chemical Reaction in a Catalyst Pellet

When an irreversible chemical reaction is carried out in a packed or fluidised bed composed of catalyst particles, the overall reaction rate is influenced by:

(i) the chemical kinetics

(ii) mass transfer resistance within the pores of the catalyst particles

and (iii) resistance to mass transfer of the reactant to the outer surface of the particles.
In general, the concentration of the reactant will decrease from $C_{Ao}$ in the bulk of the fluid to $C_{Ai}$ at the surface of the particle, to give a concentration driving force of $(C_{Ao} - C_{Ai})$. Thus, within the pellet, the concentration will fall progressively from $C_{Ai}$ with distance from the surface. This presupposes that no distinct adsorbed phase is formed in the pores. In this section the combined effects of mass transfer and chemical reaction within the particle are considered, and the effects of external mass transfer are discussed in Section 10.8.4.

In the absence of a resistance to mass transfer, the concentration of reactant will be uniform throughout the whole volume of the particle, and equal to that at its surface ($C_{Ai}$).

The reaction rate per unit volume of particle $\mathcal{M}_{rn}$ for an $n$th-order reaction is then given by:

$$\mathcal{M}_{rn} = k C_{Ai}^n$$

(10.195)

When the mass transfer resistance within the particle is significant, a concentration gradient of reactant is established within the particle, with the concentration, and hence the reaction rate, decreasing progressively with distance from the particle surface. The overall reaction rate is therefore less than that given by equation 10.195.

The internal structure of the catalyst particle is often of a complex labyrinth-like nature, with interconnected pores of a multiplicity of shapes and sizes. In some cases, the pore size may be less than the mean free path of the molecules, and both molecular and Knudsen diffusion may occur simultaneously. Furthermore, the average length of the diffusion path will be extended as a result of the tortuosity of the channels. In view of the difficulty of precisely defining the pore structure, the particle is assumed to be pseudo-homogeneous in composition, and the diffusion process is characterised by an effective diffusivity $D_e$ (equation 10.8).

The ratio of the overall rate of reaction to that which would be achieved in the absence of a mass transfer resistance is referred to as the effectiveness factor $\eta$. SCOTT and DULLION(29) describe an apparatus incorporating a diffusion cell in which the effective diffusivity $D_e$ of a gas in a porous medium may be measured. This approach allows for the combined effects of molecular and Knudsen diffusion, and takes into account the effect of the complex structure of the porous solid, and the influence of tortuosity which affects the path length to be traversed by the molecules.

The effectiveness factor depends, not only on the reaction rate constant and the effective diffusivity, but also on the size and shape of the catalyst pellets. In the following analysis detailed consideration is given to particles of two regular shapes:

(i) Flat platelets in which the mass transfer process can be regarded as one-dimensional, with mass transfer taking place perpendicular to the faces of the platelets. Furthermore, the platelets will be assumed to be sufficiently thin for deviations from unidirectional transfer due to end-effects to be negligible.

(ii) Spherical particles in which mass transfer takes place only in the radial direction and in which the area available for mass transfer decreases towards the centre of the particle.

Some consideration is also given to particles of other shapes (for example, long, thin cylinders), but the mathematics becomes complex and no detailed analysis will be given.
It will be shown, however, that the effectiveness factor does not critically depend on the shape of the particles, provided that their characteristic length is defined in an appropriate way. Some comparison is made between calculated results and experimental measurements with particles of frequently ill-defined shapes.

The treatment here is restricted to first-order irreversible reactions under steady-state conditions. Higher order reactions are considered by ARIS\(^{(30)}\).

### 10.7.1. Flat platelets

In a thin flat platelet, the mass transfer process is symmetrical about the centre-plane, and it is necessary to consider only one half of the particle. Furthermore, again from considerations of symmetry, the concentration gradient, and mass transfer rate, at the centre-plane will be zero. The governing equation for the steady-state process involving a first-order reaction is obtained by substituting \( D_e \) for \( D \) in equation 10.172:

\[
\frac{d^2 C_A}{dy^2} - \frac{k}{D_e} C_A = 0
\]

\( (10.196) \)

![Figure 10.10. Mass transfer and reaction in a platelet](image)

The process taking place only in the right-hand half of the pellet illustrated in Figure 10.10 is considered. If the plate has a total thickness \( 2L \), and the centre-plane is taken as the...
origin \((y = 0)\), then the following boundary conditions will apply:

\[
y = 0, \quad \frac{dC_A}{dy} = 0 \quad \text{(from symmetry)}
\]

\[
y = L, \quad C_A = C_{Ai} \quad \text{(the concentration at the surface of the particle)}
\]

The general solution of equation 10.196 is:

\[
C_A = B_1'e^{\sqrt{k/D_c}y} + B_2'e^{-\sqrt{k/D_c}y}
\]

Putting \(\frac{k}{D_c} = \lambda^2\):

\[
C_A = B_1'e^{\lambda y} + B_2'e^{-\lambda y}
\]

and:

\[
\frac{dC_A}{dy} = \lambda(B_1'e^{\lambda y} - B_2'e^{-\lambda y})
\]

When \(y = 0\), \(\frac{dC_A}{dy} = 0\), and:

\[
B_1' = B_2'
\]

and:

\[
C_A = B_1'(e^{\lambda y} + e^{-\lambda y})
\]

When \(y = L\),

\[
C_A = C_{Ai}, \quad \text{and} \quad B_2' = C_{Ai}(e^{\lambda L} + e^{-\lambda L})^{-1}
\]

and:

\[
\frac{C_A}{C_{Ai}} = \frac{e^{\lambda y} + e^{-\lambda y}}{e^{\lambda L} + e^{-\lambda L}}
\]

The concentration gradient at a distance \(y\) from the surface is therefore given by:

\[
\frac{1}{C_{Ai}} \frac{dC_A}{dy} = \frac{\lambda(e^{\lambda y} + e^{-\lambda y})}{e^{\lambda L} + e^{-\lambda L}}
\]

The mass transfer rate per unit area at the surface of the particle is then:

\[
(N_A)_{y=L} = -D_c \left( \frac{dC_A}{dy} \right)_{y=L} = -C_{Ai}D_c \lambda \frac{e^{\lambda L} - e^{-\lambda L}}{e^{\lambda L} + e^{-\lambda L}}
\]

or:

\[
(N_A)_{y=L} = -C_{Ai} \sqrt{k/D_c} \tanh \lambda L
\]

The quantity \(\sqrt{k/D_c} = \lambda L\) is known as the Thiele modulus, \(\phi^{(31)}\). The negative sign indicates that the transfer is in the direction of \(y\) negative, that is, away from the centre of the pellet. The rate of transfer of \(A\) (moles/unit area and unit time) from the external fluid to the surface of the half-pellet (and therefore, in a steady-state process, the rate at which it is reacting) is therefore:

\[
(N_A)_{y=L} = C_{Ai} \sqrt{k/D_c} \tanh \lambda L
\]

If there were no resistance to mass transfer, the concentration of \(A\) would be equal to \(C_{Ai}\) everywhere in the pellet and the reaction rate per unit area in the half-pellet (of volume
per unit area equal to $L$) would be given by:

$$\eta = \frac{kCAi}{L} \quad (10.201)$$

The effectiveness factor $\eta$ is equal to the ratio of the rates given by equations 10.200 and 10.201, or:

$$\eta = \frac{1}{\phi} \tanh \phi \quad (10.202)$$

A logarithmic plot of the dimensionless quantities $\phi$ and $\eta$ is shown in Figure 10.11. It may be seen that $\eta$ approaches unity at low values of $\phi$, and becomes proportional to $\phi^{-1}$ at high values of $\phi$.

![Figure 10.11. Effectiveness factor $\eta$ as a function of Thiele modulus $\phi$ (for platelet, $\phi = \lambda L$; for cylinder, $\phi = \lambda r_c$; for sphere, $\phi = \lambda r_0$).](image)

Three regions can be distinguished:

(i) $\phi < \text{approximately } 0.3$ \hspace{1em} $\tanh \phi \rightarrow \phi$, \hspace{1em} $\eta \rightarrow 1$

In this region, the mass transfer effects are small and the rate is determined almost entirely by the reaction kinetics.

(ii) $\phi > \text{approximately } 3$ \hspace{1em} $\tanh \phi \rightarrow 1$ \hspace{1em} $\eta \rightarrow \phi^{-1}$

Since $\phi = \sqrt{\frac{k}{D_e} L}$, this corresponds to a region with high values of $k$ (implying high reaction rates), coupled with low values of $D_e$ and high values of $L$ (implying a high mass transfer resistance). In this region mass transfer considerations are therefore of dominant importance.

(iii) $0.3 < \phi < 3$

This is a transitional region in which reaction kinetics and mass transfer resistance both affect the overall reaction rate.

### 10.7.2. Spherical pellets

The basic differential equation for mass transfer accompanied by an $n$th order chemical reaction in a spherical particle is obtained by taking a material balance over a spherical shell of inner radius $r$ and outer radius $r + \delta r$, as shown in Figure 10.12.
At radius \( r \), the mass transfer rate (moles per unit time) is given by:

\[
-D_e \frac{\partial C_A}{\partial r} 4\pi r^2
\]

The corresponding mass transfer rate at radius \( r + \delta r \) is:

\[
-D_e \frac{\partial C_A}{\partial r} 4\pi r^2 + \frac{\partial}{\partial r} \left(-D_e \frac{\partial C_A}{\partial r} 4\pi r^2\right) \delta r
\]

The increase in mass transfer rate over the distance \( \delta r \) is therefore:

\[
4\pi D_e \frac{\partial}{\partial r} \left\{ r^2 \frac{\partial C_A}{\partial r} \right\} \delta r
\]

The rate of removal of \( A \) (moles/unit time) by chemical reaction is:

\[
k C_A^n (4\pi r^2 \delta r)
\]

The rate of accumulation of \( A \) (moles/unit time) is given by:

\[
\frac{\partial C_A}{\partial t} (4\pi r^2 \delta r)
\]

A material balance gives:

\[
4\pi D_e \frac{\partial}{\partial r} \left\{ r^2 \frac{\partial C_A}{\partial r} \right\} \delta r = k C_A^n (4\pi r^2 \delta r) + \frac{\partial C_A}{\partial t} (4\pi r^2 \delta r)
\]

i.e.:

\[
\frac{\partial C_A}{\partial t} = D_e \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial C_A}{\partial r} \right) - k C_A^n
\]

(10.203)

It may be noted that, in the absence of a chemical reaction, equation 10.203 reduces to equation 10.146. For a steady-state process \( \partial C_A/\partial t = 0 \), and for a first-order reaction \( n = 1 \). Thus:

\[
\frac{d}{dr} \left( r^2 \frac{dC_A}{dr} \right) = \frac{k}{D_e} r^2 C_A = \lambda^2 r^2 C_A
\]

where \( \lambda^2 = k / D_e \).
Thus:

\[ r^2 \frac{d^2 C_A}{dr^2} + 2r \frac{dC_A}{dr} = \frac{k}{D_e} r^2 C_A = \lambda^2 r^2 C_A \]  

(10.204)

or:

\[ \frac{d^2 C_A}{dr^2} + \frac{2}{r} \frac{dC_A}{dr} - \lambda^2 C_A = 0 \]  

(10.205)

Equation 10.205, may be solved by putting \( C_A = \frac{\psi}{r} \) to give:

\[ \frac{d^2 \left( \frac{\psi}{r} \right)}{dr^2} + 2r \frac{d}{dr} \left( \frac{\psi}{r} \right) = \lambda^2 r \psi \]  

(10.206)

Since:

\[ \frac{d}{dr} \left( \frac{\psi}{r} \right) = \frac{1}{r} \frac{d\psi}{dr} - \frac{1}{r^2} \psi \]

and:

\[ \frac{d^2 \left( \frac{\psi}{r} \right)}{dr^2} = \frac{1}{r} \frac{d^2 \psi}{dr^2} - \frac{1}{r^2} \frac{d\psi}{dr} - \frac{1}{r^2} \frac{d\psi}{dr} + \frac{2}{r^3} \psi \]

Substituting in equation 10.206 gives:

\[ \frac{r}{r^2} \frac{d^2 \psi}{dr^2} - 2 \frac{d\psi}{dr} + \frac{2}{r} \psi + 2 \frac{d\psi}{dr} - \frac{2}{r} \psi = \lambda^2 r \psi \]

or:

\[ \frac{d^2 \psi}{dr^2} - \lambda^2 \psi = 0 \]

Solving:

\[ \psi = B'_1 e^{\lambda r} + B''_2 e^{-\lambda r} \]

or:

\[ C_A = B'_1 \frac{1}{r} e^{\lambda r} + B''_2 \frac{1}{r} e^{-\lambda r} \]

and:

\[ \frac{dC_A}{dr} = B'_1 \left( \frac{1}{r} \lambda e^{\lambda r} - \frac{1}{r^2} e^{\lambda r} \right) + B''_2 \left( \frac{1}{r} (-\lambda) e^{-\lambda r} - \frac{1}{r^2} e^{-\lambda r} \right) \]

The boundary conditions are now considered. When \( r = 0 \), then from symmetry:

\[ \frac{dC_A}{dr} = 0 \]

giving:

\[ 0 = B'_1 \left( -\frac{1}{r^2} e^0 \right) + B''_2 \left( -\frac{1}{r^2} e^0 \right) \]  

since \( \left( \frac{1}{r^2} \gg \frac{1}{r} \right) \) \( r \to 0 \)

Thus:

\[ B'_2 = -B''_1 \]

When \( r = r_0 \):

\[ C_A = C_{Ai} \]

and:

\[ C_{Ai} = B'_1 \frac{1}{r_0} e^{\lambda r_0} - B''_1 \frac{1}{r_0} e^{-\lambda r_0} \]

and:

\[ B'_1 = C_{Ai} r_0 \left( e^{\lambda r_0} - e^{-\lambda r_0} \right)^{-1} \]
Thus:

\[
\frac{C_A}{C_{Ai}} = \frac{r_0}{r} \frac{e^{\lambda r} - e^{-\lambda r}}{e^{\lambda r_0} - e^{-\lambda r_0}}
\]

and:

\[
\frac{C_A}{C_{Ai}} = \frac{r_0}{r} \frac{\sinh \lambda r}{\sinh \lambda r_0}
\]

(10.207)

Differentiating with respect to \( r \) to obtain the concentration gradient:

\[
\frac{1}{C_{Ai}} \frac{dC_A}{dr} = \frac{r_0}{\sinh r_0} \left\{ \frac{\lambda}{r} \cosh \lambda r - \frac{1}{r^2} \sinh \lambda r \right\}
\]

At the surface:

\[
\left( \frac{dC_A}{dr} \right)_{r=r_0} = \frac{C_{Ai} r_0}{\sinh r_0} \left\{ \frac{1}{r_0} \cosh \lambda r_0 - \frac{1}{r_0^2} \sinh \lambda r_0 \right\}
\]

\[
= \frac{C_{Ai}}{r_0} \{ \lambda r_0 \coth \lambda r_0 - 1 \}
\]

Thus the mass transfer at the outer surface of the pellet (moles/unit time) is:

\[
-D_e \left( \frac{dC_A}{dr} \right)_{r=r_0} (4\pi r_0^2) = -C_{Ai} D_e 4\pi r_0 \{ \lambda r_0 \coth \lambda r_0 - 1 \}
\]

(10.208)

in the direction of \( r \) positive (away from the centre of the particle), and

\[
C_{Ai} D_e 4\pi r_0 \{ \lambda r_0 \coth \lambda r_0 - 1 \}
\]

(10.209)
towards the centre of the pellet.

With no resistance to mass transfer, the concentration is \( C_{Ai} \) throughout the whole spherical pellet, and the reaction rate, which must be equal to the mass transfer rate in a steady-state process, is:

\[
= \frac{4}{3} \pi r_0^3 k C_{Ai}
\]

(10.210)

The effectiveness factor \( \eta \) is obtained by dividing equation 10.209 by equation 10.210 to give:

\[
\eta = \frac{-C_{Ai} D_e 4\pi r_0 \{ \lambda r_0 \coth \lambda r_0 - 1 \}}{\frac{4}{3} \pi r_0^3 k C_{Ai}}
\]

\[
= 3 \frac{D_e}{k} \frac{1}{r_0^2} \{ \lambda r_0 \coth \lambda r_0 - 1 \}
\]

\[
= \frac{3}{r_0^2 \lambda^2} \{ \lambda r_0 \coth \lambda r_0 - 1 \}
\]

(10.211)

Thus:

\[
\eta = \frac{3}{\phi_0} \coth \phi_0 - \frac{3}{\phi_0^2} = \frac{3}{\phi_0} \left( \coth \phi_0 - \frac{1}{\phi_0} \right)
\]

(10.212)

where \( \phi_0 = \lambda r_0 \) is the \textit{Thiele modulus} for the spherical particle.
It is useful to redefine the characteristic linear dimension $L$ of the spherical particle as its volume per unit surface area. This is, in effect, consistent with the definition of $L$ adopted for the platelet where $L$ is half its thickness. Then, for the sphere:

$$L = \frac{(4/3)\pi r_0^3}{4\pi r_0^2} = \frac{r_0}{3}$$

(10.213)

The Thiele modulus $\phi_L$ then becomes:

$$\phi_L = \lambda L = \sqrt{\frac{k}{D_e}} L$$

(10.214)

Substituting for $r_0$ in equation 10.215, the effectiveness factor $\eta$ may be written as:

$$\eta = \frac{3}{9\lambda^2 L^2} \left\{ 3\lambda L \coth 3\lambda L - 1 \right\}$$

$$= \frac{1}{\phi_L} \left( \coth 3\phi_L - \frac{1}{3\phi_L} \right)$$

(10.215)

A logarithmic plot of $\eta$ versus $\phi_L$ in Figure 10.13 shows that, using this definition of $L$, the curves for the slab or platelet and the spherical particle come very close together.

![Figure 10.13. Effectiveness factors $\eta$ as a function of normalised Thiele modulus $\phi_L = \lambda \frac{V_p}{A_p} = \lambda L$ for a first-order reaction](image)

**10.7.3. Other particle shapes**

The relationship between effectiveness factor $\eta$ and Thiele modulus $\phi_L$ may be calculated for several other regular shapes of particles, where again the characteristic dimension of the particle is defined as the ratio of its volume to its surface area. It is found that
the results all fall quite closely together, irrespective of the particle shape. For a long cylindrical particle with a high length to diameter ratio, the effects of diffusion at the end faces may be neglected, and the mass transfer process may be regarded as taking place solely in the radial direction. The equation for mass transfer and chemical reaction in the cylinder may be derived in a manner analogous to that used for equation 10.205 for the sphere:

\[
\frac{d^2 C_A}{dr^2} + \frac{1}{r} \frac{dC_A}{dr} - \lambda^2 C_A = 0 \quad (10.216)
\]

The solution of this equation is in the form of a Bessel function\(^{(32)}\). Again, the characteristic length of the cylinder may be defined as the ratio of its volume to its surface area; in this case, \(L = r_c/2\). It may be seen in Figure 10.13 that, when the effectiveness factor \(\eta\) is plotted against the normalised Thiele modulus, the curve for the cylinder lies between the curves for the slab and the sphere. Furthermore, for these three particles, the effectiveness factor is not critically dependent on shape.

The results of investigations with particles of a variety of shapes, mainly irregular ones, have been reported by RESTER and ARIS\(^{(33)}\), and the results are shown as data points in Figure 10.13. This provides additional evidence that the \(\eta - \Phi_L\) plot is not particularly sensitive to the shape of the particles, and a single curve can be used for most practical applications.

**Example 10.12**

Estimate the Thiele modulus and the effectiveness factor for a reactor in which the catalyst particles are:

(i) Thin rectangular platelets, the ends of which are sealed so that mass transfer is unidirectional and perpendicular to the surface of the particle. The total thickness of the particles is 8 mm.

(ii) Spherical particles, 10 mm in diameter.

The first-order rate constant is \(5 \times 10^{-4} \text{ s}^{-1}\) and the effective diffusivity of the reactants in the pores of the particles is \(2 \times 10^{-9} \text{ m}^2/\text{s}\).

**Solution**

For the reacting system: \(\lambda = \sqrt{\frac{k}{D_e}} = \sqrt{\frac{5 \times 10^{-4}}{2 \times 10^{-9}}} = 500 \text{ m}^{-1}\)

(i) For the platelet of thickness 8 mm, \(L = \left(\frac{1}{2} \times 8 \times 10^{-3}\right) = 0.004 \text{ m}^{-1}\)

and the Thiele modulus \(\Phi = \lambda L = (500 \times 0.004) = 2.0\)

From equation 10.202, the effectiveness factor \(\eta\) is given by:

\[
\eta = \frac{1}{\Phi} \tanh \Phi = \frac{1}{2} \tanh 2 = 0.482
\]

(ii) For the sphere of diameter 10 mm, \(r_0 = 0.005 \text{ m}^{-1}\).

and the Thiele modulus \(\Phi_0 = \lambda r_0 = (500 \times 0.005) = 2.5\)

From equation 10.212, the effectiveness factor \(\eta\) is given by:

\[
\eta = \frac{3}{\Phi_0} \left( \coth \Phi_0 - \frac{1}{\Phi_0} \right) = \frac{3}{2.5} \left( \coth 2.5 - \frac{1}{2.5} \right) = 0.736
\]
Alternatively:
\[ \phi_L = \frac{\phi_0}{3} = \frac{(500 \times 0.005)}{3} = 0.833 \]
and from equation 10.215:
\[ \eta = \frac{1}{\phi_L} \left( \coth 3\phi_L - \frac{1}{3\phi_L} \right) = \frac{1}{0.833} \left( \coth(3 	imes 0.833) - \frac{1}{3 	imes 0.833} \right) \]
\[ = 0.736 \]

Example 10.13
A first-order chemical reaction takes place in a reactor in which the catalyst pellets are platelets of thickness 5 mm. The effective diffusivity \( D_e \) for the reactants in the catalyst particle is \( 10^{-5} \text{ m}^2/\text{s} \) and the first-order rate constant \( k \) is 14.4 s^{-1}.
Calculate:

(i) the effectiveness factor \( \eta \).
(ii) the concentration of reactant at a position half-way between the centre and the outside of the pellet (i.e. at a position one quarter of the way across the particle from the outside).

Solution
For the particle, the Thiele modulus \( \phi = \sqrt{\frac{k}{D_e}L} = \lambda L \)
\[ = \sqrt{\frac{14.4}{10^{-5}} \times (2.5 \times 10^{-3})} = 3 \]
From equation 10.202, the effectiveness factor, \( \eta = \frac{1}{\phi} \tanh \phi \)
\[ = \frac{1}{3} \tanh 3 = 0.332 \]
Thus \( \eta \lambda \approx 1 \), corresponding to the region where mass transfer effects dominate.
The concentration profile is given by equation 10.198 as:
\[ \frac{C_A}{C_{Ai}} = \frac{\cosh \lambda y}{\cosh \lambda L} \]
The concentration \( C_A \) at \( y = 1.25 \times 10^{-3} \text{ m} \)
\[ = 0.015 \frac{\cosh 1.5}{\cosh 3} = 0.035 \text{ kmol/m}^3 \]

10.7.4. Mass transfer and chemical reaction with a mass transfer resistance external to the pellet
When the resistance to mass transfer to the external surface of the pellet is significant compared with that within the particle, part of the concentration driving force is required to overcome this external resistance, and the concentration of reacting material at the surface of the pellet \( C_{Ai} \) is less than that in the bulk of the fluid phase \( C_{A0} \). In Sections 10.7.1–10.7.3, the effect of mass transfer resistance within a porous particle
is expressed as an effectiveness factor, by which the reaction rate within the particle is reduced as a result of this resistance. The reaction rate per unit volume of particle (moles/unit volume and unit time) for a first-order reaction is given by:

\[ \mathfrak{R}_v = \eta k C_{Ai} \]  

(10.217)

For a particle of volume \( V_p \), the reaction rate per unit time for the particle is given by:

\[ \mathfrak{R}_p = \eta k V_p C_{Ai} \]  

(10.218)

When there is an external mass transfer resistance, the value of \( C_{Ai} \) (the concentration at the surface of the particle) is less than that in the bulk of the fluid \( (C_{A0}) \) and will not be known. However, if the value of the external mass transfer coefficient is known, the mass transfer rate from the bulk of the fluid to the particle may be expressed as:

\[ \mathfrak{R}_p = h_D A_p (C_{A0} - C_{Ai}) \]  

(10.219)

giving:

\[ C_{Ai} = C_{A0} - \frac{\mathfrak{R}_p}{h_D A_p} \]  

(10.220)

Substituting in equation 10.219:

\[ \mathfrak{R}_p = \frac{k C_{A0}}{\frac{1}{\eta V_p} + \frac{k}{h_D A_p}} \]  

(10.221)

Then, dividing by \( V_p \) gives the reaction rate \( \mathfrak{R}_v \) (moles per unit volume of particle in unit time) as:

\[ \mathfrak{R}_v = \frac{k C_{A0}}{\frac{1}{\eta} + \frac{k}{h_D L}} \]  

(10.222)

where \( L = V_p/A_p \), the particle length term used in the normalised Thiele modulus. Information on external mass transfer coefficients for single spherical particle and particles in fixed beds is given in Section 10.8.4, and particles in fluidised beds are discussed in Volume 2.

**Example 10.14**

A hydrocarbon is cracked using a silica-alumina catalyst in the form of spherical pellets of mean diameter 2.0 mm. When the reactant concentration is 0.011 kmol/m\(^3\), the reaction rate is \( 8.2 \times 10^{-2} \) kmol/(m\(^3\) catalyst) s. If the reaction is of first-order and the effective diffusivity \( D_e \) is \( 7.5 \times 10^{-8} \) m\(^2\)/s, calculate the value of the effectiveness factor \( \eta \). It may be assumed that the effect of mass transfer resistance in the fluid external to the particles may be neglected.

**Solution**

Since the value of the first-order rate constant is not given, \( \lambda \) and \( \phi_L \) cannot be calculated directly. The reaction rate per unit volume of catalyst \( \mathfrak{R}_v = \eta k C_{Ai} \) (equation 10.217), and the Thiele modulus

\[ \phi_L = \sqrt{\frac{k}{D_e L}} = \sqrt{\frac{k}{\sqrt{7.5 \times 10^{-8} \times 3}}} = 1.217 \sqrt{k} \]  

(i)
The effectiveness factor $\eta$ is given by equation 10.215 as:

$$\eta = \frac{1}{\phi_L} \left( \coth 3\phi_L \frac{1}{3\phi_L} \right)$$

$\phi_L > 3$, and hence:

$$\eta = \phi_L^{-1}$$  \hspace{1cm} (ii)

It is assumed that the reactor is operating in this regime and the assumption is then checked.

Substituting numerical values in equation 10.217:

$$8.2 \times 10^{-2} = \eta k (0.011)$$  \hspace{1cm} (iii)

From equations (i) and (ii):

$$\eta = \phi_L^{-1} = 0.822 \frac{1}{\sqrt{k}}$$

From equation (iii):

$$8.2 \times 10^{-2} = 0.822 \frac{1}{\sqrt{k}} (0.011)$$

and:

$$k = 82.2 \text{ s}^{-1}$$

From equation (i):

$$\phi_L = 11.04 \text{ and } \eta = 0.0906$$

This result may be checked by using equation 10.215:

$$\eta = \frac{1}{11.04} \left( \coth 33.18 \frac{1}{3 \times 11.04} \right)$$

$$= 0.0878$$

This value is sufficiently close for practical purposes to the value of 0.0906, calculated previously. If necessary, a second iteration may be carried out.

### 10.8 PRACTICAL STUDIES OF MASS TRANSFER

The principal applications of mass transfer are in the fields of distillation, gas absorption and the other separation processes involving mass transfer which are discussed in Volume 2. In particular, mass transfer coefficients and heights of transfer units in distillation, and in gas absorption are discussed in Volume 2. In this section an account is given of some of the experimental studies of mass transfer in equipment of simple geometry, in order to provide a historical perspective.

#### 10.8.1. The $\phi$-factor of Chilton and Colburn for flow in tubes

**Heat transfer**

Because the mechanisms governing mass transfer are similar to those involved in both heat transfer by conduction and convection and in momentum transfer (fluid flow), quantitative relations exist between the three processes, and these are discussed in Chapter 12. There is generally more published information available on heat transfer than on mass transfer, and these relationships often therefore provide a useful means of estimating mass transfer coefficients.