To motivate looking into forced convection, we will quickly review concentration polarization. Consider the system shown in Figure 1.

![Diagram of concentration profile through a porous stagnant media](image)

Figure 1: Steady state concentration profile of diffusion through a porous stagnant media

The current per area is given by:

\[
\frac{I}{A} = -neD \frac{\partial c}{\partial x} (x = 0)
\]

At steady state the concentration profile is linear (as shown in Figure 1). The current is therefore given by:

\[
\frac{I}{A} = \frac{neD(\bar{c} - c_s)}{L}
\]

The limiting current occurs when \(c_s = 0\).

\[
\frac{I_{lim}}{A} = \frac{neD\bar{c}}{L}
\]
The I-V curve, Figure 2, shows the effects of polarization.

In order to reduce the losses due to concentration polarization, the limiting current, $I_{lim}$, should be increased. Two ways to increase the limiting current are to increase $\bar{c}$ or to use forced convection. Forced convection introduces a flow over the reacting surface. This flow leads to a boundary layer which is critical to the concentration profile and therefore the reaction. Figure 3 is a schematic of a boundary layer caused by flowing over a reacting surface.

Figure 3: Boundary layer caused by flowing over a reacting surface

The flux in the $y$-direction is given by the diffusion in the $y$-direction

$$F_y = -D \frac{\partial c}{\partial y}$$
The length scale in the y-direction is $\delta(x)$ so the flux can be approximated as:

$$F_y \sim -D \frac{\bar{c} - c_s}{\delta(x)}$$

Because $\delta(x) \ll L$, transport is typically faster in forced convection. In order to model the concentration we will examine the 2-D steady state species conservation equation.

$$u_x \frac{\partial c}{\partial x} + u_y \frac{\partial c}{\partial y} = D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right)$$

Applying that there is only flow in the x-direction, $u_y = 0$, and performing scaling analysis on the right hand side of the conservation equation:

$$\frac{\partial^2 c}{\partial x^2} \sim \frac{c}{L^2}, \quad \frac{\partial^2 c}{\partial y^2} \sim \frac{c}{\delta(x)^2}$$

Applying $\delta(x) \ll L$

Therefore:

$$\frac{\partial^2 c}{\partial x^2} \sim \frac{c}{L^2} \ll \frac{\partial^2 c}{\partial y^2} \sim \frac{c}{\delta(x)^2}$$

This simplifies the conservation equation to:

$$u_x \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}$$

We will now examine 2 flow profiles, the first is plug flow and the second is Poiseuille flow with the Leveque approximation. In plug flow the velocity profile is just given by a constant, $u_x = u_0$. In Poiseuille flow, the velocity profile can be solved by solving the Navier-Stokes equation with a channel of height, $H$ (shown in the appendix).

$$u_x = 6 \bar{u} \left( \frac{y}{H} - \left( \frac{y}{H} \right)^2 \right)$$
Applying the Leveque approximation using \( y \sim \delta(x) \ll H \), the quadratic term is negligible and therefore the velocity profile simplifies to:

\[
\frac{6\bar{u}}{H} y
\]

First we will scale the conservation equation with each of these velocity profiles to learn how the boundary layers scale with \( x \).

**Plug Flow**

\[
\begin{align*}
\frac{\partial c}{\partial x} &= D \frac{\partial^2 c}{\partial y^2} \\
\frac{\bar{c}}{x} &= D \frac{\bar{c}}{\delta(x)^2} \\
\delta(x)^2 &\sim \frac{Dx}{u_0} \\
\delta(x) &\sim \sqrt{\frac{Dx}{u_0}}
\end{align*}
\]

**Poiseuille Flow with Leveque Approx.**

\[
\begin{align*}
\frac{\partial c}{\partial x} &= D \frac{\partial^2 c}{\partial y^2} \\
\left(\frac{6\bar{u}}{H} y\right) \frac{\partial c}{\partial x} &= D \frac{\partial^2 c}{\partial y^2} \\
\left(\frac{\bar{u}}{H} \delta(x)\right) \frac{\bar{c}}{x} &\sim D \frac{\bar{c}}{\delta(x)^2} \\
\delta(x)^3 &\sim \frac{HDx}{\bar{u}} \\
\delta(x) &\sim 3 \sqrt[3]{\frac{HDx}{\bar{u}}}
\end{align*}
\]

For the plug flow case, the boundary layer scales with the square root of \( x \) but using Poiseuille flow with the Leveque approximation the boundary layer scales with the cube root of \( x \).

The analytical solution can also be found for each of these cases. There is not an intrinsic length scale for this PDE so a similarity variable should be used to solve each.

**Plug Flow**

\[
\begin{align*}
\frac{\partial c}{\partial x} &= D \frac{\partial^2 c}{\partial y^2} \\
c(x, 0) &= c_s = 0 \\
c(x, y \to \infty) &= \bar{c} \\
c(0, y) &= \bar{c}
\end{align*}
\]

**Poiseuille Flow with Leveque Approx.**

\[
\begin{align*}
\left(\frac{6\bar{u}}{H} y\right) \frac{\partial c}{\partial x} &= D \frac{\partial^2 c}{\partial y^2} \\
c(x, 0) &= c_s = 0 \\
c(x, y \to \infty) &= \bar{c} \\
c(0, y) &= \bar{c}
\end{align*}
\]
The similarity variable that should be chosen is:

\[ \eta = \frac{y}{2} \sqrt{\frac{u_0}{D x}} \]

Plugging this into the governing equation gives:

\[ 0 = \frac{\partial^2 c}{\partial \eta^2} + 2 \eta \frac{\partial c}{\partial \eta} \]

\[ c(\eta = 0) = 0 \]

\[ c(\eta \to \infty) = \bar{c} \]

See appendix for derivation

The solution to this differential equation is an error function:

\[ c = \bar{c} \text{erf}\left(\frac{x}{2} \sqrt{\frac{u_0}{D x}}\right) \]

Where

\[ \text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-s^2} ds \]

Now that the concentration profiles have been found, an estimate of the boundary layer thickness can be found. A good approximation for when the boundary layer ends is \( \frac{\bar{c}}{c} = 0.99 \). Applying the concentration ratio for the plug flow, the boundary layer comes out to:

\[ \delta = 3.643 \sqrt{\frac{D x}{u_0}} \]

For the Poiseuille Flow with Leveque approximation, the boundary layer comes out to:

\[ \delta = 1.607 \sqrt{\frac{1.5}{\overline{u}_2}} \]
Any time there is flow over a reactive surface there is a balance between fuel utilization and power density. As the velocity increases, the power density increases because there is less of an effect of concentration polarization but more fuel is unused. Conversely, when the velocity is small, the boundary layer is larger so more fuel is used but there is not as large a power density because concentration polarization diminishes the returns. Figure 4 shows this effect.

Figure 4: The figure on the right shows the boundary layer for two different velocities $u_2 > u_1$ and the figure on the left shows the corresponding I-V curve showing the effect of the velocity on the concentration polarization.
Appendix

Derivation of Poiseuille flow

\[ \frac{\partial^2 u_x}{\partial y^2} = \frac{1}{\mu} \frac{dP}{dx} \]

\[ u_x(y = 0) = 0 \]
\[ u_x(y = H) = 0 \]

Where \( P \) is the pressure and \( \mu \) is the viscosity and the boundary conditions come from no slip on the surface.

\[ \frac{dP}{dx} \] will be constant so the solution to the differential equation is:

\[ u_x = \frac{1}{2\mu} \frac{dP}{dx} y^2 + Ay + B \]

Applying \( u_x(y = 0) = 0 \), \( B = 0 \).

Applying \( u_x(y = H) = 0 \)

\[ A = -\frac{H}{2\mu} \frac{dP}{dx} \]

\[ u_x = \frac{1}{2\mu} \frac{dP}{dx} y^2 - \frac{H}{2\mu} \frac{dP}{dx} y \]

The average velocity is given by:

\[ \bar{u} = \frac{1}{H} \int_0^H u_x \, dy \]

\[ \bar{u} = \frac{1}{H} \int_0^H \left( \frac{1}{2\mu} \frac{dP}{dx} y^2 - \frac{H}{2\mu} \frac{dP}{dx} y \right) dy \]

\[ \bar{u} = \frac{1}{H} \left( \frac{1}{6\mu} \frac{dP}{dx} H^3 - \frac{H}{4\mu} \frac{dP}{dx} H^2 \right) \]

\[ \bar{u} = -\frac{1}{12} \frac{dP}{dx} H^2 \]
\[ \frac{dP}{dx} = -\frac{12 \mu}{H^2} \bar{u} \]

The velocity is therefore
Derivation of $\eta$ and the governing concentration profile for plug flow:

$$u_0 \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}$$

Assume a similarity variable exists in the form:

$$\eta = \frac{y}{g(x)}$$

Plugging this into the differential equation:

$$u_0 \frac{\partial c}{\partial \eta} \frac{\partial \eta}{\partial x} = D \frac{\partial^2 c}{\partial \eta^2} \left( \frac{\partial \eta}{\partial y} \right)^2$$

$$u_0 \frac{\partial c}{\partial \eta} \left( - \frac{y}{g(x)} g'(x) \right) = D \frac{\partial^2 c}{\partial \eta^2} \left( \frac{1}{g(x)} \right)^2$$

$$0 = \frac{\partial^2 c}{\partial \eta^2} + \left( \frac{u_0}{D} \right) g(x) g'(x) \eta \frac{\partial c}{\partial \eta}$$

For the similarity variable to exist neither $x$ nor $y$ can appear in the governing equation so $\left( \frac{u_0}{D} \right) g(x) g'(x)$ must be equal to a constant. To simplify the math later this value can be set to 2.

$$\left( \frac{u_0}{D} \right) g(x) g'(x) = 2$$

$$g(x) g'(x) = 2 \frac{D}{u_0}$$

$$\frac{g(x)^2}{2} = 2 \frac{D}{u_0} x$$

$$g(x) = 2 \sqrt{\frac{D}{u_0} x}$$

Therefore:

$$\eta = \frac{y}{2} \sqrt{\frac{u_0}{D x}}$$
\[
0 = \frac{\partial^2 c}{\partial \eta^2} + 2 \eta \frac{\partial c}{\partial \eta}
\]

Derivation of \( \eta \) and the governing concentration profile for Poiseuille flow with the Leveque approximation:

\[
\frac{6\bar{u}}{H} y \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial y^2}
\]

Assume a similarity variable exists in the form:

\[
\eta = \frac{y}{g(x)}
\]

Plugging this into the differential equation:

\[
\frac{6\bar{u}}{H} y \frac{\partial c}{\partial \eta} \frac{\partial \eta}{\partial x} = D \frac{\partial^2 c}{\partial \eta^2} \left( \frac{\partial \eta}{\partial y} \right)^2
\]

\[
\frac{6\bar{u}}{H} \frac{\partial c}{\partial \eta} \left( - \left( \frac{y}{g(x)} \right)^2 g'(x) \right) = D \frac{\partial^2 c}{\partial \eta^2} \left( \frac{1}{g(x)} \right)^2
\]

\[
0 = \frac{\partial^2 c}{\partial \eta^2} + \left( \frac{6\bar{u}}{HD} \right) g(x)^2 g'(x) \eta^2 \frac{\partial c}{\partial \eta}
\]

For the similarity variable to exist neither \( x \) nor \( y \) can appear in the governing equation so \( \left( \frac{6\bar{u}}{HD} \right) g(x)^2 g'(x) \) must be equal to a constant. To simplify the math later this value can be set to 3.

\[
\left( \frac{6\bar{u}}{HD} \right) g(x)^2 g'(x) = 3
\]

\[
g(x)^2 g'(x) = \frac{HD}{2\bar{u}}
\]

\[
g(x)^3 = \frac{HD}{2\bar{u}} x
\]

\[
g(x) = x \sqrt[3]{\frac{3HD}{2\bar{u}}}
\]

Therefore:

\[
\eta = y \sqrt[3]{\frac{2\bar{u}}{3HDx}}
\]
\[ 0 = \frac{\partial^2 c}{\partial \eta^2} + 3 \eta^2 \frac{\partial c}{\partial \eta} \]
10.626 Electrochemical Energy Systems
Spring 2014

For information about citing these materials or our Terms of Use, visit: http://ocw.mit.edu/terms.