Mass Transfer

Boundary Layer Theory:
Mass and Heat/Momentum Transfer

Lecture 11, 28.11.2019, Dr. M.Reza. Kholghy
9. Basic Theories for Mass Transfer Coefficients

9.1 Fluid-Fluid Interfaces (lecture of 20.11.18)

Fluid-fluid interfaces are typically not fixed and are strongly affected by the flow leading to heterogeneous systems that make it difficult to develop a general theory behind the MT correlations (Cussler Table 8.3-2).

9.2 Fluid-Solid Interfaces

Solids typically have fixed and well-defined surfaces, allowing to develop theoretical foundations for the empirical MT correlations (Cussler Table 8.3-3). In contrast to fluid-fluid interfaces the models are far more rigorous but, unfortunately, computationally INTENSIVE.
In addition to this, fluid-solid interfaces have been investigated intensely with respect to heat transfer. We can make use of this due to the analogy between heat momentum and mass transfer.

### 9.2.1 MT from a plate (boundary layer theory)

Example: A sharp-edged, flat plate that is sparsely dissolvable is immersed in a rapidly flowing solvent.

MT correlation (Table 8.3-3):

\[
\text{Sh} = \frac{kL}{D} = 0.646 \left( \frac{L}{v} \right)^{1/2} \left( \frac{U_\infty}{v} \right)^{1/3} \left( \frac{v}{D} \right)
\]

L: plate length; \(U_\infty\): bulk fluid velocity
Prandtl first introduced the concept of boundary layers.

The transition from zero velocity at the plate to the velocity of the surrounding free stream takes place in the boundary layer.

**Goal:** Calculate the MTC for this fluid–solid interface

**Literature:**
(a) Fluid drag on a flat plate generates a "boundary layer"

(b) Slow dissolution of the plate also affects a thinner region near the plate
Procedure:

Rectangular coordinates

\[ \frac{\partial c_1}{\partial t} + v_x^0 \frac{\partial c_1}{\partial x} + v_y^0 \frac{\partial c_1}{\partial y} + v_z^0 \frac{\partial c_1}{\partial z} = D \left( \frac{\partial^2 c_1}{\partial x^2} + \frac{\partial^2 c_1}{\partial y^2} + \frac{\partial^2 c_1}{\partial z^2} \right) + r_1 \]

1. Calculate the velocity profile in the B.L.

2. Calculate the concentration profile in the B.L.

3. Calculate the flux at the interface 
   \[ j = -D \frac{\partial c}{\partial y} \bigg|_{y=0} \]
   and set it equal to \( k \Delta c \) to obtain \( k \).
The relative magnitude of the fluid flow (momentum) B.L. and the concentration B.L. is given by

\[ Sc = \frac{v}{D} = \frac{\text{kinematic viscosity}}{\text{diffusivity}} \]

- \( Sc > 1 \): Momentum B.L. > Concentration B.L. (typical)
- \( Sc = 1 \): Momentum B.L. = Concentration B.L.
- \( Sc < 1 \): Momentum B.L. < Concentration B.L. (rare case)
Laminar B.L.

Continuity equation:
\[
\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0
\]  
(1)

Momentum Balance in \( x \) and \( y \)

\[
\begin{align*}
    u \cdot \frac{\partial u}{\partial x} + v \cdot \frac{\partial u}{\partial y} &= -\frac{1}{\rho} \cdot \frac{\partial p}{\partial x} + v \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \\
    u \cdot \frac{\partial v}{\partial x} + v \cdot \frac{\partial v}{\partial y} &= -\frac{1}{\rho} \cdot \frac{\partial p}{\partial y} + v \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right)
\end{align*}
\]

at
\[
\begin{align*}
    y &= 0: & u &= 0 & \text{and} & v &= 0 \\
    y &= \infty: & u &= U_\infty
\end{align*}
\]
For flow over a flat plate \( \frac{\partial p}{\partial x} = \frac{\partial p}{\partial y} \approx 0 \)

as we are far from the entrance point (Prandtl assumption). Then,

Shear stress on plate \( \propto \frac{\partial u}{\partial x} \approx \text{const} \Rightarrow \frac{\partial^2 u}{\partial x^2} \approx 0 \)

\[
\begin{align*}
    u \cdot \frac{\partial u}{\partial x} + v \cdot \frac{\partial u}{\partial y} &= v \cdot \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right) \\
    \text{(2)}
\end{align*}
\]
Momentum equation in y (for steady flows):

\[ u \cdot \frac{\partial v}{\partial x} + v \cdot \frac{\partial v}{\partial y} = -\frac{1}{\rho} \cdot \frac{\partial p}{\partial y} + v \cdot \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} \right) \]

As \( v \) typically is small in the BL (for lam. case here =0), this reduces to:

\[ \frac{\partial p}{\partial y} = 0 \quad \text{(Negligible pressure changes in y (thin layer))} \quad (3) \]

Boundary conditions:

\[ y = 0: \quad u = 0 \quad \text{and} \quad v = 0 \quad \text{(fluid adheres to plate)} \]
\[ y = \infty: \quad u = U_{\infty} \]
Equations (1) and (2) are solved by introducing the variable 
\[ \eta = \frac{y}{\sqrt{v \cdot x / U_\infty}} \]

*Digression:* How did Prandtl come up with that?

The B.L. thickness, \( \delta \), is related to \( \text{Re} \) by
\[ \frac{\delta}{x} \sim \text{Re}^{-1/2} = \sqrt{\frac{v}{U_\infty \cdot x}} \]
\[ \frac{y}{\delta} \sim \frac{y}{x} \text{Re}^{1/2} = \frac{y}{\sqrt{v \cdot x / U_\infty}} = \eta \]
The two T-shirts are similar.

BL 1 and 2 are similar. They look the same after normalization.

\[ \eta = \frac{y}{\sqrt{v \cdot x / U_\infty}} \]

\[ \delta_1 \]

\[ \delta_2 \]
A stream function (with regard to 2 Dimensional Incompressible fluid flow) is an arbitrary function whose derivatives give velocity components of a particular flow situation.

The stream function is mathematically defined in such a way that lines of constant stream function are streamlines (hence the name stream function).

In other words, iso-stream function lines are streamlines in a fluid flow.

The stream function makes a lot of calculations and understanding of 2D Incompressible fluid flows easy.
Eq. (2) can be simplified by formulating it in terms of a stream function $\Psi$. In order to satisfy the continuity equation (1), the velocity components must be:

$$u = \frac{\partial \Psi}{\partial y} \quad v = -\frac{\partial \Psi}{\partial x}$$

$$u \cdot \frac{\partial u}{\partial x} + v \cdot \frac{\partial u}{\partial y} = v \cdot \frac{\partial^2 u}{\partial y^2} \quad \rightarrow \quad \frac{\partial \Psi}{\partial y} \cdot \frac{\partial^2 \Psi}{\partial x \partial y} - \frac{\partial \Psi}{\partial x} \cdot \frac{\partial^2 \Psi}{\partial y^2} = v \cdot \frac{\partial^3 \Psi}{\partial y^3}$$

The corresponding stream function is:

$$\Psi = \sqrt{vU_\infty x} \cdot f(\eta)$$

where $f(\eta)$ is the dimensionless stream function.

Thus,

$$u = \frac{\partial \Psi}{\partial y} = \frac{\partial \Psi}{\partial \eta} \cdot \frac{\partial \eta}{\partial y} = \sqrt{vU_\infty x} \cdot f' \cdot \frac{1}{\sqrt{v \cdot x/U_\infty}} = U_\infty \cdot f'$$
\[
\frac{\partial u}{\partial x} = -\frac{1}{2} U_\infty \frac{y}{\sqrt{\nu x^3}} \cdot f'' = -\frac{1}{2} \frac{U_\infty}{x} \eta \cdot f''
\]

\[
\frac{\partial u}{\partial y} = U_\infty \left( \frac{U_\infty}{\nu x} \right)^{1/2} f'' \quad \text{and} \quad \frac{\partial^2 u}{\partial y^2} = \left( \frac{U_\infty^2}{\nu x} \right) \cdot f''''
\]

\[
v = -\frac{\partial \Psi}{\partial x} = -\frac{1}{2} \left( \frac{\nu U_\infty}{x} \right)^{1/2} f + \sqrt{\nu U_\infty x} \cdot \frac{1}{2} \frac{y}{\left( \nu \cdot x^3 \right)^{1/2}} f'
\]

\[
v = -\frac{1}{2} \left( \frac{\nu U_\infty}{x} \right)^{1/2} f + \frac{1}{2} \left( \frac{\nu U_\infty}{x} \right)^{1/2} \eta \cdot f' = \frac{1}{2} \left( \frac{\nu U_\infty}{x} \right)^{1/2} (\eta \cdot f' - f)
\]
Now the equation of motion (2) becomes:

\[ 2f'' + f'' \cdot f = 0 \]

at

\[ \eta = 0: \quad f = 0 \quad \text{and} \quad f' = 0 \]

\[ \eta = \infty: \quad f' = 1 \quad (\text{see Table}) \]

This is a third order nonlinear ordinary differential equation. A solution in form of Blasius series expansion is available.

See attached Table from H. Schlichting ("Boundary Layer Theory"), which gives the complete values of u and v for every x and y. The velocity profiles have been calculated.
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<th>$\eta = y \sqrt{\frac{U_\infty}{\nu x}}$</th>
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<th>$f' = \frac{u}{U_\infty}$</th>
<th>$f''$</th>
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Source: H. Schlichting, "Boundary Layer Theory"
Blasius similarity solution of the velocity distribution in a laminar boundary layer on a flat plate.

Mass Transfer in Boundary Layers

The diffusion equation in the B.L. is:

\[ u \frac{\partial c_1}{\partial x} + v \frac{\partial c_1}{\partial y} = D \left[ \frac{\partial^2 c_1}{\partial x^2} + \frac{\partial^2 c_1}{\partial y^2} \right] \]  \hspace{1cm} (4)

B.C.’s: \( y = 0: \ c_1 = c_{10} \)
\( y = \infty: \ c_1 = c_{1\infty} \)

Introduce dimensionless variables:

\[ c_1^* = \frac{c_1 - c_{10}}{c_{1\infty} - c_{10}}, \quad u^* = \frac{u}{U_{\infty}}, \quad v^* = \frac{v}{U_{\infty}} \]

\[ \Rightarrow u^* \frac{\partial c_1^*}{\partial x} + v^* \frac{\partial c_1^*}{\partial y} = D \frac{\partial^2 c_1^*}{\partial x^2} + \overbrace{\frac{\partial^2 c_1^*}{\partial y^2}}^{\text{usually negligible}} \]  \hspace{1cm} (5)

B.C.s: \( y = 0: \ c_1^*=0 \)
\( y = \infty: \ c_1^*=1 \)
Compare to the momentum equation (2):

\[
\frac{u^*}{U_\infty} \frac{\partial u^*}{\partial x} + \frac{v^*}{\partial y} = \nu \left[ \frac{\partial^2 u^*}{\partial x^2} \right] \quad \text{B.C.'s: } y = 0: \quad u^* = 0 \quad \text{and} \quad v^* = 0
\]

\[
y = \infty: \quad u^* = 1
\]

\[
\text{The two equations have the same form!}
\]

\[
\text{Sc} = 1: \quad \text{In this special case where} \quad \frac{\nu}{U_\infty} = \frac{D}{U_\infty} \quad \text{or} \quad \nu = D
\]

\[
\text{the solution to the concentration profile is given by} \quad c_1^* = u^*
\]

\[
\text{The boundary layers for flow and concentration are IDENTICAL.}
\]
For this case we write Fick’s first law $j = -D \cdot \frac{\partial c_1}{\partial y} \bigg|_{y=0}$ with $c_1^*$:

$$j = -D \cdot \frac{\partial c_1^*}{\partial y} \bigg|_{y=0} (c_{1\infty} - c_{10})$$

$$j = -\nu \cdot \frac{\partial u^*}{\partial y} \bigg|_{y=0} (c_{1\infty} - c_{10}) = -\frac{\nu}{U_{\infty}} \frac{\partial u}{\partial y} \bigg|_{y=0} (c_{1\infty} - c_{10})$$

$$j = -\frac{\nu}{U_{\infty}} U_{\infty} \left( \frac{U_{\infty}}{\nu x} \right)^{1/2} \left( \frac{\partial^2 f}{\partial \eta^2} \right)_{\eta=0} (c_{1\infty} - c_{10})$$

$$j = -\left( \frac{\nu U_{\infty}}{x} \right)^{1/2} \cdot 0.332 \cdot (c_{1\infty} - c_{10})$$

Table from $f''$ from Table
As $j = k (c_{10} - c_{1\infty})$, $k = 0.332 \cdot \left(\frac{\nu U_{\infty}}{x}\right)^{1/2}$

\[
Sh = \frac{k \cdot x}{D} = 0.332 \cdot \frac{\nu}{\nu D} \cdot \left(\frac{\nu \cdot U_{\infty}}{x}\right)^{1/2}
\]

\[
= 0.332 \cdot \left(\frac{\nu}{D}\right) \cdot \left(\frac{U_{\infty} x}{\nu}\right)^{1/2} = 0.332 \cdot Sc \cdot Re^{1/2}
\]

Here, $Sc = 1$: \(Sh = 0.332 \cdot Re^{1/2}\)

**This is the Local Mass Transfer Coefficient** to be distinguished from the average MTC over a plate of length $L$ (Cussler Table 8.3-3):

\[Sh = 0.646 \cdot Re^{1/2} \cdot Sc^{1/3}\]
A more realistic case is with $Sc \gg 1$ which is typical in liquids and particle / gas systems.

$Sc \gg 1$: (S.K. Friedlander, “Smoke, Dust and Haze”, 1st ed., 1977)

Examples: Dissolution of solid compounds in flowing liquid streams. Flow (deposition) of pollutants over lakes or leaves
More specifically, if the B.L. (displacement) thickness is:

\[ \delta^* = 1.72 \cdot \left( \frac{x \nu}{U_\infty} \right)^{1/2} \]  

(Blasius, Schlichting)

For a wind blowing at a speed of 10 km/h, \( \delta \approx 0.56 \) mm. E.g., at 2 cm from the leading edge of the flat surface:

\[ \delta^* = 1.72 \cdot \left( 0.02 \cdot \frac{15 \cdot 10^{-6} \text{Pa s}}{1 \text{kg/m}^3} \right) = 1.72 \cdot 0.33 \cdot 10^{-3} \text{m} = 0.56 \text{mm} \]

**Goal:** To obtain the mass transfer coefficient
Again at steady-state

\[
u^* \frac{\partial c_1^*}{\partial x} + v^* \frac{\partial c_1^*}{\partial y} = \frac{D}{U_\infty} \frac{\partial^2 c_1^*}{\partial y^2}\tag{5}\]

Expand \(u^* = \frac{U}{U_\infty} = f'(\eta)\) and \(v^* = \frac{v}{U_\infty} = \frac{1}{2} \left( \frac{v}{xU_\infty} \right)^{1/2} (\eta \cdot f'(\eta) - f(\eta))\)

near the wall \((\eta \rightarrow 0)\) into Taylor series:

\[
u^* = \frac{U}{U_\infty} = f'(0) + f''(0) \cdot \eta + f'''(0) \cdot \frac{\eta^2}{2} + \ldots \approx 0 + 0.332 \eta = a\eta
\]

disregard higher order terms because \(\eta \leq 1\)

\[
v^* = \frac{v}{U_\infty} = \frac{1}{2} \left( \frac{v}{xU_\infty} \right)^{1/2} \left[ f(0) + \frac{1}{2} f''(0) \eta^2 + \frac{1}{3} f'''(0) \eta^3 + \ldots \right]
\]

\[
= \frac{1}{2} \left( \frac{v}{xU_\infty} \right)^{1/2} \left[ 0 + \frac{0.332}{2} \eta^2 \right] = \frac{a}{4} \left( \frac{v}{xU_\infty} \right)^{1/2} \eta^2
\]
Substitution in the above differential equation (5) gives:

\[ a \eta \frac{\partial c_1^*}{\partial x} + \frac{a}{4} \left( \frac{v}{x \cdot U_\infty} \right)^{1/2} \eta^2 \frac{\partial c_1^*}{\partial y} = \frac{D}{U_\infty} \frac{\partial^2 c_1^*}{\partial y^2} \quad \text{with} \quad \eta = \left( \frac{U_\infty}{\nu x} \right)^{1/2} \cdot y \]

Assume that \( c_1^* \) is a function only of \( \eta \): \( c_1^* = g(\eta) \)

Then:

\[ \frac{\partial c_1^*}{\partial y} = \frac{\partial g}{\partial \eta} \frac{\partial \eta}{\partial y} = \left( \frac{U_\infty}{\nu x} \right)^{1/2} \cdot g' \]

\[ \frac{\partial^2 c_1^*}{\partial y^2} = \left( \frac{U_\infty}{\nu x} \right) \cdot g'' \]

\[ \frac{\partial c_1^*}{\partial x} = -\frac{1}{2} \frac{\eta}{x} \cdot g' \]
Introducing the above variables in the diffusion equation:

\[
\begin{align*}
& a \left[ -\frac{\eta^2}{2x} g' \right] + \frac{a}{4} \left( \frac{v}{x \cdot U_\infty} \right)^{1/2} \eta^2 \left( \frac{U_\infty}{\nu x} \right)^{1/2} g' = \frac{D}{U_\infty} \frac{U_\infty}{\nu x} g'' \\
\text{or} \quad & g'' + \frac{a}{4} \left( \frac{v}{D} \right) \cdot \eta^2 \cdot g' = 0 \\
\text{with} \quad & \eta = 0 \quad g = 0 \\
& \eta = \infty \quad g = 1
\end{align*}
\]

Solution: Set \( P = g' \) \( \Rightarrow \frac{\partial P}{\partial \eta} + \frac{a}{4} \eta^2 \cdot \text{Sc} \cdot P = 0 \)

Integrate: \( \ln \left( \frac{P}{P_0} \right) = -\frac{a}{12} \eta^3 \cdot \text{Sc} \)

where \( P_0 = \left( \frac{\partial g}{\partial \eta} \right)_{\eta=0} \)

Reduce it to a boundary value problem

Seperate variables and integrate
\[
\frac{\partial g}{\partial \eta} = P = P_0 \cdot \exp\left[-\frac{a}{12} \eta^3 \text{Sc}\right]
\]

From the B.C.'s.: at \( \eta = 0, g = 0 \):
\[
g = P_0 \int_0^\eta \exp\left[-\frac{a}{12} \text{Sc} \cdot r^3\right] \, dr
\]

From the B.C.'s.: at \( \eta = \infty, g = 1 \), hence:
\[
P_0 = \left(\int_0^\infty \exp\left[-\frac{a}{12} \text{Sc} \cdot r^3\right] \, dr\right)^{-1}
\]

\[
\eta = \left(\frac{U_\infty}{\nu X}\right)^{1/2} \cdot y
\]

\[
c_1^* = \frac{c_1 - c_{10}}{c_{1\infty} - c_{10}},
\]

\[
c_1^* = g(\eta)
\]

\[
dm = \left(\frac{a}{12 \text{Sc}}\right)^{1/3} d\eta
\]
and

\[ \left( \frac{\partial g}{\partial \eta} \right)_{\eta=0} = \frac{\left( \frac{a}{12 \cdot \text{Sc}} \right)^{1/3}}{\int_0^1 \exp \left[ -m^3 \right] \, dm \bigg/ 1/3 \Gamma(1/3)} = \frac{\left( \frac{a}{12 \cdot \text{Sc}} \right)^{1/3}}{0.89} \]

Remember (Gamma function): \( \Gamma(z) = (z-1)\Gamma(z-1) = \int_0^\infty \exp[-x] x^{z-1} \, dx \)

\[ x = m^3 \rightarrow dx = 3m^2 \, dm \]

\[ \Gamma(z) = \int_0^\infty m^{3(z-1)} \exp\left[ -m^3 \right] 3m^2 \, dm = 3 \int_0^\infty m^{(3z-1)} \exp\left[ -m^3 \right] \, dm \]
\[
c_1^* = g(\eta)
\]
\[
g = P_0 \int_{0}^{\eta} \exp \left[ - \frac{a}{12} \text{Sc} \cdot r^3 \right] \, dr
\]
\[
P_0 = \left( \frac{\partial g}{\partial \eta} \right)_{\eta=0} = \left( \frac{a \cdot \text{Sc}}{12} \right)^{1/3} \frac{1}{0.89}
\]
\[ j = -D \cdot \frac{\partial c_1}{\partial y} \bigg|_{y=0} = D \cdot (c_{10} - c_{1\infty}) \cdot \left( \frac{\partial c_1^*}{\partial y} \right) \bigg|_{y=0} \]

\[ = D \cdot (c_{10} - c_{1\infty}) \cdot \left( \frac{U_{\infty}}{\nu X} \right)^{1/2} \left( \frac{\partial g}{\partial \eta} \right)_{\eta=0} \]

\[ = \frac{D}{\nu} \left( \frac{\nu}{U_{\infty} X} \right)^{1/2} \frac{U_{\infty}}{0.89} \left( \frac{a}{12 \text{Sc}} \right)^{1/3} (c_{10} - c_{1\infty}) \]

\[ = \text{Sc}^{-2/3} \cdot \text{Re}^{-1/2} \cdot \frac{U_{\infty}}{0.89} \left( \frac{0.332}{12} \right)^{1/3} (c_{10} - c_{1\infty}) \]
So \[ k = 0.34 \cdot U_\infty \text{Sc}^{-2/3} \text{Re}^{-1/2} \]

This is the local mass transfer coefficient while the overall is found by:

\[
\overline{j_{Av}} = -\frac{1}{L} \int_0^L D \frac{\partial c_1}{\partial y} \bigg|_{y=0} \, dx
\]

\[
= 0.68 \cdot U_\infty \text{Sc}^{-2/3} \text{Re}^{-1/2} \cdot (c_{10} - c_{1\infty})
\]
Let's calculate $Sh$ to compare it with our Table of correlations (Table 8.3-3)

$$\frac{kL}{D} = 0.68 \frac{L}{D} Sc^{-2/3} Re^{-1/2} U_{\infty}$$

$$= 0.68 \frac{L}{D} D^{2/3} \frac{D^{2/3}}{v^{1/2}} \frac{v^{1/2}}{u^{1/2}L^{1/2}} u$$

$$= 0.68 \left( \frac{v}{D} \right)^{1/3} \left( \frac{uL}{v} \right)^{1/2}$$

$$= 0.68 \cdot Sc^{1/3} Re^{1/2}$$

So we obtained the mass transfer coefficient from theory! Very rare.

Another example is MTC for laminar flow through a short circular tube (look at section 9.4.1 of Cussler book)
In general

\[
\frac{j}{U_\infty \Delta c} = \frac{k}{U_\infty} = \text{const} \cdot \text{Sc}^{-2/3} \text{Re}^{-1/2}
\]

Applicable for flow around spheres, cylinders etc.

Mass transfer correlation over a wide range of \( Re \):

\[
\text{Sh} = 2 + 0.6 \text{Re}^{1/2} \text{Sc}^{1/3}
\]
9.3 Theories for concentrated solutions

The MTC’s are based typically on dilute solutions but they are VERY successful even in concentrated ones as, typically, the volume average velocity normal to the fluid-fluid interface is rather small.

When the MTC’s fail, it is observed typically that “the k depends strongly on concentration” especially when mass transfer is fast.

The flux is written as

\[ N_1 = k(c_{1i} - c_1) + c_{1i}v^0 \]

\[ = k(c_{1i} - c_1) + c_{1i}(\overline{V}_1N_1 + \overline{V}_2N_2) \]
This framework can be used to build new film, penetration and surface-renewal theories.

However, this is difficult and we also have the previous unknowns again (film thickness, contact or residence times). Instead we are looking for corrections to the dilute mass transfer coefficient by the film theory:

\[
\frac{k}{k^0} = \frac{\text{MTC in concentrated solution}}{\text{MTC in dilute solution}}
\]
Dilute

Concentrated
The total flux for a concentrated solution across a film:

\[ n_1 = -D \frac{dc_1}{dz} + c_1 v^0 \quad \text{with B.C.'s:} \quad z = 0: \quad c_1 = c_{1i} \]

\[ z = L: \quad c_1 = c_1 \]

For concentrated solutions, \( n_1 \) and \( v^0 \) are constant, so the above equation can be integrated from \( z=0 \) to \( L \) to give

\[ \frac{c_1 - n_1 / v^0}{c_{1i} - n_1 / v^0} = \exp \left[ v^0 \cdot \frac{L}{D} \right] \]

Rearranging:

\[ n_1 \bigg|_{z=0} = N_1 = \frac{v^0}{\exp[v^0 \cdot L/D] - 1} \left( c_{1i} - c_1 \right) + c_{1i} v^0 \]

Compare:

\[ N_1 = k \left( c_{1i} - c_1 \right) + c_{1i} v^0 \]
Then the mass transfer coefficient is

\[ k = \frac{v^0}{\exp[v^0 \cdot L / D] - 1} \]

For dilute solutions:

\[ k^0 = \frac{D}{L} \]

Taking the ratio \( k / k^0 \), we eliminate the dependency in \( L \):

\[ \frac{k}{k^0} = \frac{v^0 / k^0}{\exp[v^0 / k^0] - 1} \]
k can be smaller or larger than $k^0$ depending the $v^0$ direction