Diffusion rates altered by chemical reaction

Example: NH_3 absorption in water

pH of water can be changed by adding small amount of HCl, so that NH_3 gets converted to NH_4^+ in water.

$\Rightarrow$ Reduced local concentration of NH_3 in water near the interface, which increases the concentration gradient, and hence flux.

$\Rightarrow$ Prediction of flux enhancement utilizing the mass transfer correlations, available ~~this~~ ~~will~~ and widely used, and merely suggesting a correction factor due to reaction will be explored here.

Experimental observation
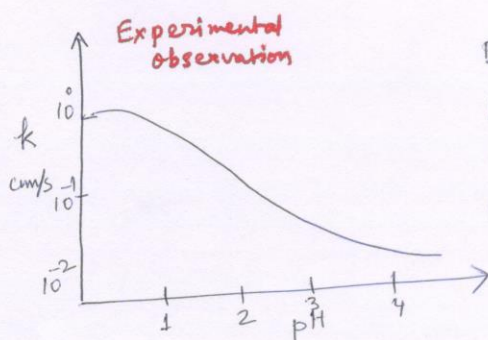
Below pH 4, k rises sharply by orders of magnitude. Below pH 1, Mass transfer in the liquid film is no longer rate limiting. Overall coefficient is limited by diffusion in the gas in that case.
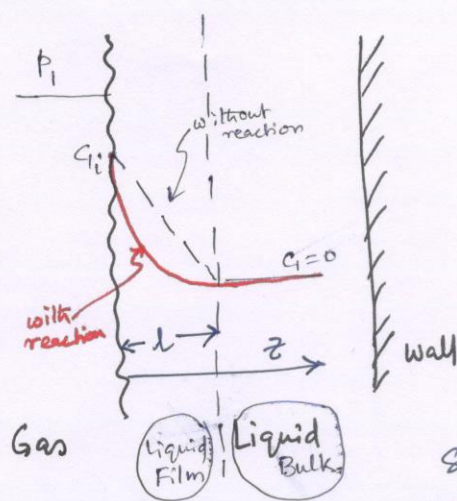
In this model, liquid is considered in contact with well-mixed gas. Gas contains solute vapour to be absorbed in the liquid.

Liquid is not well-mixed. Considering "FILM THEORY", a thin film exists near the interface on the liquid side. Absorbed species 1 has to diffuse through the film under steady state.

At gas liquid interface, concentration of species 1 in liquid $c_1 = c_{1i}$, which is in equilibrium with partial pressure p_1 of species 1 in gas side.

If c_1 at the transition face between liquid film and bulk liquid is zero, subject to boundary condition

$$\frac{\partial c_1}{\partial t} = D \nabla^2 c_1 \quad \Rightarrow \quad \text{For 1-D case} \quad D\frac{d^2 c_1}{dz^2} = 0$$

(steady state assumption)

@ $z = 0$, $c_1 = c_{1i}$

@ $z = l$, $c_1 = 0$

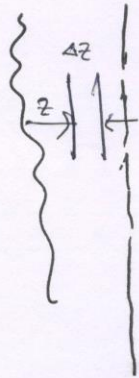Upon integration

$$c_1 = c_{1i}\left(1 - \frac{z}{l}\right)$$

Linear relation is shown by blue-dotted line in the figure

$$\text{Flux} = -D\frac{dc}{dz} = D\frac{c_{1i}}{l} = \frac{D}{l}(c_{1i} - 0) = k_0(c_{1i} - 0)$$

subscript '0' on k implies no chemical reaction.

If there is first order chemical reaction with rate given by $k_1 c_1$

(this includes pseudo first order reactions also, particularly when the reactant in liquid phase is in excess. This is a typical case for absorption with chemical reaction).

$$\left(-D\frac{\partial c_1}{\partial z}\Big|_z A\,\Delta t\right) - \left(-D\frac{\partial c_1}{\partial z}\Big|_{z+\Delta z} A\,\Delta t\right) = A\,\Delta z\,\Delta c_1 + \left(k_1 c_1\right)A\,\Delta z\,\Delta t$$

$$D\frac{\partial^2 c_1}{\partial z^2} = \underbrace{\frac{\partial c_1}{\partial t}}_{0\ \text{at steady state}} + k_1 c_1$$

$$\Rightarrow \quad D\frac{d^2 c_1}{dz^2} - k_1 c_1 = 0$$

Upon integration,

$$c_1 = a\,e^{\sqrt{\frac{k_1}{D}}\,z} + b\,e^{-\sqrt{\frac{k_1}{D}}\,z}$$

Once again, the boundary conditions are

@ $z=0$, $\quad c_1 = c_{1i}$ $\Bigg\}\Rightarrow$ $\boxed{a+b = c_{1i}}$

@ $z=\ell$, $\quad c_1 = 0$

$$a\,e^{\sqrt{\frac{k_1}{D}}\,\ell} + b\,e^{-\sqrt{\frac{k_1}{D}}\,\ell} = 0$$

or $\boxed{\dfrac{a}{b} = -e^{-2\sqrt{\frac{k_1}{D}}\,\ell}}$

$$a - a\,e^{2\sqrt{\frac{k_1}{D}}\,\ell} = c_{1i}$$

or $\boxed{a = \dfrac{c_{1i}}{1 - e^{2\sqrt{\frac{k_1}{D}}\,\ell}}}$

and $b = -a\,e^{2\sqrt{\frac{k_1}{D}}\,\ell}$

$$= -\frac{c_{1i}}{1 - e^{2\sqrt{\frac{k_1}{D}}\,\ell}}\,e^{2\sqrt{\frac{k_1}{D}}\,\ell}$$

$$= -\frac{c_{1i}}{e^{-2\sqrt{\frac{k_1}{D}}\,\ell} - 1}$$

$$\Rightarrow \boxed{b = \dfrac{c_{1i}}{1 - e^{-2\sqrt{\frac{k_1}{D}}\,\ell}}}$$

$$\frac{c_1}{c_{1i}} = \frac{e^{\sqrt{\frac{k_1}{D}}\,z}}{1 - e^{2\sqrt{\frac{k_1}{D}}\,\ell}} + \frac{e^{-\sqrt{\frac{k_1}{D}}\,z}}{1 - e^{-2\sqrt{\frac{k_1}{D}}\,\ell}}$$

$$= \frac{e^{-\sqrt{\frac{k_1}{D}}\,\ell}\,e^{\sqrt{\frac{k_1}{D}}\,z}}{e^{-\sqrt{\frac{k_1}{D}}\,\ell}\left(1 - e^{2\sqrt{\frac{k_1}{D}}\,\ell}\right)} + \frac{e^{\sqrt{\frac{k_1}{D}}\,\ell}\,e^{-\sqrt{\frac{k_1}{D}}\,z}}{e^{\sqrt{\frac{k_1}{D}}\,\ell}\left(1 - e^{-2\sqrt{\frac{k_1}{D}}\,\ell}\right)}$$

$$= \frac{e^{\sqrt{\frac{k_1}{D}}(\ell - z)} - e^{-\sqrt{\frac{k_1}{D}}(\ell - z)}}{e^{\sqrt{\frac{k_1}{D}}\,\ell} - e^{-\sqrt{\frac{k_1}{D}}\,\ell}}$$

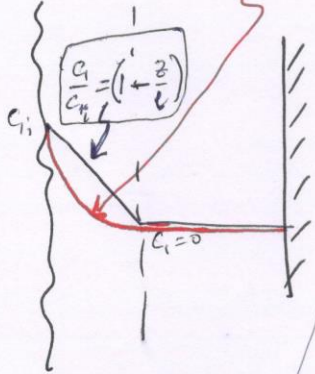$$= \frac{\sinh\left[\sqrt{\frac{k_1}{D}}(\ell - z)\right]}{\sinh\left[\sqrt{\frac{k_1}{D}}\,\ell\right]}$$

Recall $\sinh x = \dfrac{e^x - e^{-x}}{2}$

and $\cosh x = \dfrac{e^x + e^{-x}}{2}$

Therefore

$$\frac{C_1}{C_{1i}} = \frac{\sinh\left[\sqrt{\frac{k_1}{D}}(l-z)\right]}{\sinh\left[\sqrt{\frac{k_1}{D}}\,l\right]}$$ is the equation for curved line

When the reaction is slow, the curved line should approach the straight line. This is evident as follows (expanding Sinh in series).

$$\lim_{k_1 \to 0} \frac{C_1}{C_{1i}} = \frac{\sqrt{\frac{k_1}{D}}(l-z) + \cdots}{\sqrt{\frac{k_1}{D}}\,l} = 1 - \frac{z}{l}$$

Flux in presence of reaction at any location z

$$= -D\frac{dC_1}{dz} = -D\left(-\sqrt{\frac{k_1}{D}}\right)C_i\,\frac{\cosh\left[\sqrt{\frac{k_1}{D}}(l-z)\right]}{\sinh\left[\sqrt{\frac{k_1}{D}}\,l\right]}$$

$$\Rightarrow \quad -D\frac{dC_1}{dz}\bigg|_{z=0} = \sqrt{Dk_1}\,\frac{\cosh\left(\sqrt{\frac{k_1}{D}}\,l\right)}{\sinh\left(\sqrt{\frac{k_1}{D}}\,l\right)}C_{1i}$$

$$= \sqrt{Dk_1}\,\coth\left(\sqrt{\frac{k_1}{D}}\,l\right)\{C_{1i} - 0\} = k(C_i - 0)$$

$$\Rightarrow \quad k = \sqrt{Dk_1}\,\coth\left(\sqrt{\frac{k_1}{D}}\,l\right)$$

Here, l is thickness of film which is not measurable. Accordingly, l is replaced by $\frac{D}{k_0}$ assuming the thickness of the film is same for with-reaction and without-reaction cases.
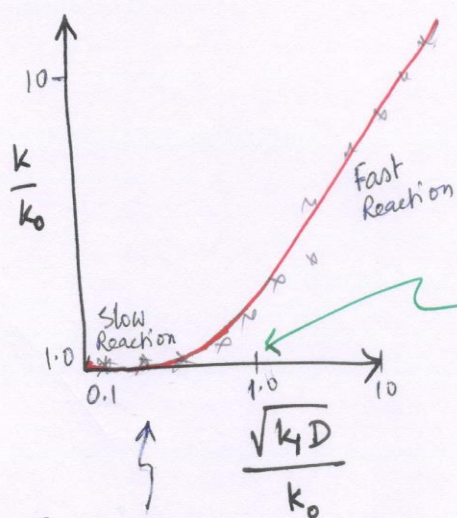
$$\Rightarrow \quad \frac{k}{k_0} = \sqrt{\frac{Dk_1}{(k_0)^2}}\,\coth\left(\sqrt{\frac{Dk_1}{k_0^2}}\right)$$ can be treated as the correction factor.

Two limits

(i) Slow Reaction $\Rightarrow k_1 \downarrow \Rightarrow \frac{k}{k_0} = 1 + \frac{Dk_1}{3(k_0)^2} + \cdots$

(ii) Fast Reaction $\Rightarrow k_1 \uparrow \Rightarrow k = \sqrt{Dk_1}$

Transition from usual mass transfer to the reaction-limited case

$$\frac{D k_1}{(k_0)^2} = 1$$

Both axes in log-scale

$\sqrt{k_1 D}$ over k_0

Experimental data points in the figure follows

$$\frac{k}{k_0} = \sqrt{\frac{D k_1}{(k_0)^2}} \, Coth\left(\sqrt{\frac{D k_1}{k_0^2}}\right)$$

demonstrating the assumption of film theory, and use of same film thickness for with and without reaction cases to be valid.

The correction factor can be used with any approved correlation of mass transfer ξ or Sherwood No.

For example, for a spinning disc of Reagent 1, immersed in a dilute solution containing Reagent 2, Sherwood No. depends on Reynold's No. as per following relation.

$$\frac{k_0 d}{D} = a \left(\frac{d \, v \rho}{\mu}\right)^{1/2}$$

where d = diameter of the disc.

when Reaction with first order rate constant k_1 with reference to Reagent 1 occurs,

$$k = \sqrt{D k_1} \; Coth\left[\sqrt{\frac{D k_1}{\frac{a^2 D^2}{d^2}\left(\frac{d v \rho}{\mu}\right)}}\right] = \sqrt{D k_1} \; Coth\left[\frac{1}{a}\sqrt{\frac{k_1 d \mu}{D v \rho}}\right]$$

Expressions of Sherwood No. in several other cases (with fluid flow) are tabulated in Mass Transfer text books;

Table 8.3-2 Selected mass transfer correlations for fluid–fluid interfaces[a]

Physical situation	Basic equation[b]	Key variables	Remarks
Liquid in a packed tower	$k\left(\dfrac{1}{vg}\right)^{1/3} = 0.0051 \left(\dfrac{v^0}{av}\right)^{0.67} \left(\dfrac{D}{v}\right)^{0.50} (ad)^{0.4}$	a = packing area per bed volume d = nominal packing size	Probably the best available correlation for liquids; tends to give lower values than other correlations.
	$\dfrac{kd}{D} = 25 \left(\dfrac{dv^0}{v}\right)^{0.45} \left(\dfrac{v}{D}\right)^{0.5}$	d = nominal packing size	The classical result, widely quoted; probably less successful than above.
	$\dfrac{k}{v^0} = \alpha \left(\dfrac{dv^0}{v}\right)^{-0.3} \left(\dfrac{D}{v}\right)^{0.5}$	d = nominal packing size	Based on older measurements of height of transfer units (HTU's); α is of order one.
Gas in a packed tower	$\dfrac{k}{aD} = 3.6 \left(\dfrac{v^0}{av}\right)^{0.70} \left(\dfrac{v}{D}\right)^{1/3} (ad)^{-2.0}$	a = packing area per bed volume d = nominal packing size	Probably the best available correlation for gases.
	$\dfrac{kd}{D} = 1.2(1-\epsilon)^{0.36} \left(\dfrac{dv^0}{v}\right)^{0.64} \left(\dfrac{v}{D}\right)^{1/3}$	d = nominal packing size ϵ = bed void fraction	Again, the most widely quoted classical result.
Pure gas bubbles in a stirred tank	$\dfrac{kd}{D} = 0.13 \left(\dfrac{(P/V)d^4}{\rho v^3}\right)^{1/4} \left(\dfrac{v}{D}\right)^{1/3}$	d = bubble diameter P/V = stirrer power per volume	Note that k does not depend on bubble size.
Pure gas bubbles in an unstirred liquid	$\dfrac{kd}{D} = 0.31 \left(\dfrac{d^3 g \Delta\rho/\rho}{v^2}\right)^{1/3} \left(\dfrac{v}{D}\right)^{1/3}$	d = bubble diameter $\Delta\rho$ = density difference between gas and liquid	For small swarms of bubbles rising in a liquid.
Large liquid drops rising in unstirred solution	$\dfrac{kd}{D} = 0.42 \left(\dfrac{d^3 \Delta\rho g}{\rho v^2}\right)^{1/3} \left(\dfrac{v}{D}\right)^{0.5}$	d = bubble diameter $\Delta\rho$ = density difference between bubbles and surrounding fluid	Drops 0.3-cm diameter or larger.
Small liquid drops rising in unstirred solution	$\dfrac{kd}{D} = 1.13 \left(\dfrac{dv^0}{D}\right)^{0.8}$	d = drop diameter v^0 = drop velocity	These small drops behave like rigid spheres.
Falling films	$\dfrac{kz}{D} = 0.69 \left(\dfrac{zv^0}{D}\right)^{0.5}$	z = position along film v^0 = average film velocity	Frequently embroidered and embellished.

Notes: [a] The symbols used include the following: D is the diffusion coefficient; g is the acceleration due to gravity; k is the local mass transfer coefficient; v^0 is the superficial fluid velocity; and v is the kinematic viscosity.
[b] Dimensionless groups are as follows: dv/v and v/av are Reynolds numbers; v/D is the Schmidt number; $d^3 g (\Delta\rho/\rho)/v^2$ is the Grashof number; kd/D is the Sherwood number; and $k/(vg)^{1/3}$ is an unusual form of Stanton number.

| Physical situation	Basic equation[b]	Key variables	Remarks
Membrane	$\dfrac{kl}{D} = 1$	l = membrane thickness	Often applied even where membrane is hypothetical.
Laminar flow along flat plate[c]	$\dfrac{kL}{D} = 0.646 \left(\dfrac{Lv^0}{v}\right)^{1/2} \left(\dfrac{v}{D}\right)^{1/3}$	L = plate length v^0 = bulk velocity	Solid theoretical foundation, which is unusual.
Turbulent flow through horizontal slit	$\dfrac{kd}{D} = 0.026 \left(\dfrac{dv^0}{v}\right)^{0.8} \left(\dfrac{v}{D}\right)^{1/3}$	v^0 = average velocity in slit d = [$2/\pi$] (slit width)	Mass transfer here is identical with that in a pipe of equal wetted perimeter.
Turbulent flow through circular tube	$\dfrac{kd}{D} = 0.026 \left(\dfrac{dv^0}{v}\right)^{0.8} \left(\dfrac{v}{D}\right)^{1/3}$	v^0 = average velocity in tube d = pipe diameter	Same as slit, because only wall regime is involved.
Laminar flow through circular tube	$\dfrac{kd}{D} = 1.62 \left(\dfrac{d^2 v^0}{LD}\right)^{1/3}$	d = pipe diameter L = pipe length v^0 = average velocity in tube	Very strong theory and experiment
Flow outside and parallel to a capillary bed	$\dfrac{kd}{D} = 1.25 \left(\dfrac{d_e^2 v^0}{vl}\right)^{0.93} \left(\dfrac{v}{D}\right)^{1/3}$	d_e = 4 area/wetted perimeter v^0 = superficial velocity	Not reliable because of channeling in bed.
Flow outside and perpendicular to a capillary bed	$\dfrac{kd}{D} = 0.80 \left(\dfrac{dv^0}{v}\right)^{0.47} \left(\dfrac{v}{D}\right)^{1/3}$	d = capillary diameter v^0 = velocity approaching bed	Reliable if capillaries evenly spaced.
Forced convection around a solid sphere	$\dfrac{kd}{D} = 2.0 + 0.6 \left(\dfrac{dv^0}{v}\right)^{1/2} \left(\dfrac{v}{D}\right)^{1/3}$	d = sphere diameter v^0 = velocity of sphere	Very difficult to reach $(kd/D) = 2$ experimentally; no sudden laminar-turbulent transition.
Free convection around a solid sphere	$\dfrac{kd}{D} = 2.0 + 0.6 \left(\dfrac{d^3 \Delta\rho g}{\rho v^2}\right)^{1/4} \left(\dfrac{v}{D}\right)^{1/3}$	d = sphere diameter g = gravitational acceleration	For a 1-cm sphere in water, free convection is important when $\Delta\rho = 10^{-9}$ g/cm^3.
Packed beds	$\dfrac{k}{v^0} = 1.17 \left(\dfrac{dv^0}{v}\right)^{-0.42} \left(\dfrac{D}{v}\right)^{2/3}$	d = particle diameter v^0 = superficial velocity	The superficial velocity is that which would exist without packing.
Spinning disc	$\dfrac{kd}{D} = 0.62 \left(\dfrac{d^2 \omega}{v}\right)^{1/2} \left(\dfrac{v}{D}\right)^{1/3}$	d = disc diameter ω = disc rotation (radians/time)	Valid for Reynolds numbers between 100 and 20,000.

Note: [a] The symbols used include the following: D is the diffusion coefficient of the material being transferred; k is the local mass transfer coefficient; ρ is the fluid density; v is the kinematic viscosity. Other symbols are defined for the specific situation.
[b] The dimensionless groups are defined as follows: (dv^0/v) and $(d^2\omega/v)$ are the Reynolds number; v/D is the Schmidt number; $(d^3 \Delta\rho g/\rho v^2)$ is the Grashof number; kd/D is the Sherwood number; k/v is the Stanton number.
[c] The mass transfer coefficient given here is the value averaged over the length L.
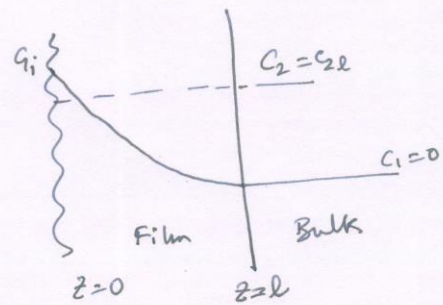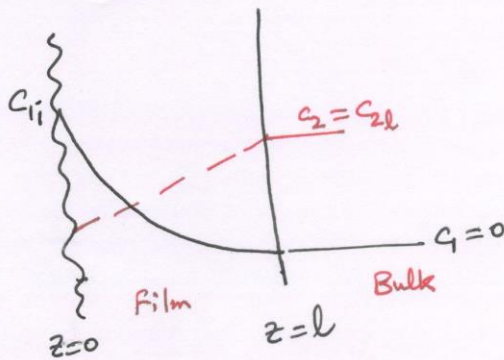
As species 1 from gas phase reacts with Species 2 in liquid phase, the concentrations of both the species are less than that of bulk. When species 2 is in excess, the concentration of species 2 remains same as C_{2l} all over the film (Right figure), and the reaction can be treated as pseudo first order. In that case, the enhancement factor $\frac{k}{k_0}$, defined earlier applies.

For the schematic on the left, mass balance has to be drawn for both species separately.

$$\frac{\partial c_1}{\partial t} = 0 = D_1 \frac{d^2 c_1}{dz^2} - k_1 c_1 c_2$$

$$\frac{\partial c_2}{\partial t} = 0 = D_2 \frac{d^2 c_2}{dz^2} - k_1 c_1 c_2$$

with typical boundary conditions as

@ $z=0$, $c_1 = c_{1i}$, $\frac{dc_2}{dz} = 0$

@ $z=l$, $c_1 = 0$, $c_2 = c_{2l}$

stoichiometric coefficient is to be incorporated in the reaction term appropriately.

Requires numerical Solution

A limiting case is when the reaction is VERY FAST and IRREVERSIBLE then finite concentrations of the two species cannot coexist, but simultaneously disappear at the reaction front ($z = z_c$)

Reaction Front $z = z_c$

Stoichiometry

$$(\text{Species 1}) + \gamma \, (\text{Species 2}) \rightarrow \text{Products}$$
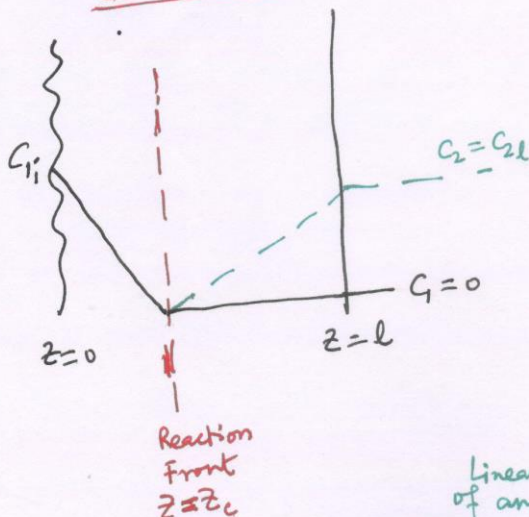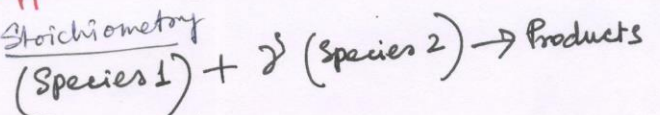
Flux of species 1
$$n_1 = \frac{D_1}{z_c} \left[c_{1i} - 0 \right]$$
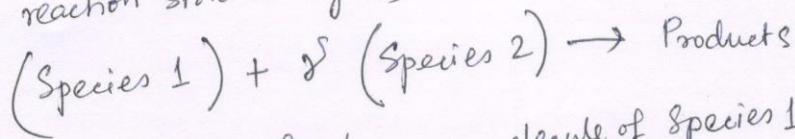
Flux of Species 2
$$n_2 = - \frac{D_2}{l - z_c} \left[c_{2l} - 0 \right]$$

Linearity in both concentration profiles is due to lack of any reaction on the two sides of reaction front. All reactions restricted to precisely at $z = z_c$ location.

$(-)$ sign of n_2 suggests species 1 travelling in negative z direction.

The reaction stoichiometry is

$$(\text{Species 1}) + \gamma \, (\text{Species 2}) \longrightarrow \text{Products}$$

$\Rightarrow$ At the reaction front, one molecule of Species 1 reacts with γ molecules of Species 2 at a time

$\Rightarrow$ Rate at which Species 2 reaches the reaction front must be γ times the rate at which Species 1 reaches the reaction front.

$\Rightarrow$ $\qquad \gamma n_1 + n_2 = 0$

$\Rightarrow$ $\qquad \gamma \dfrac{D_1}{z_c} c_{1i} - \dfrac{D_2 c_{2l}}{l - z_c} = 0$

$\Rightarrow$ $\qquad \dfrac{\gamma D_1}{z_c} c_{1i} = \dfrac{D_2 c_{2l}}{l - z_c}$

$\Rightarrow$ $\qquad \dfrac{l - z_c}{z_c} = \dfrac{D_2 c_{2l}}{\gamma D_1 c_{1i}}$

$\Rightarrow$ $\qquad \dfrac{l}{z_c} - 1 = \dfrac{D_2 c_{2l}}{\gamma D_1 c_{1i}}$

$\Rightarrow$ $\qquad \dfrac{1}{z_c} = \dfrac{1}{l}\left[1 + \dfrac{D_2 c_{2l}}{\gamma D_1 c_{1i}}\right]$

$$n_1 = \frac{D_1}{z_c}\left(c_{1i} - 0\right)$$
$$= \left[\frac{D_1}{l}\left(1 + \frac{D_2 c_{2l}}{\gamma D_1 c_{1i}}\right)\right]\left(c_{1i} - 0\right)$$
$$= k\left(c_{1i} - 0\right)$$

The mass transfer coefficient without reaction is as before
$$k_0 = \frac{D_1}{l}$$

$$\Rightarrow \quad \frac{k}{k_0} = 1 + \frac{D_2 c_{2l}}{\gamma D_1 c_{1i}}$$

Therefore, this becomes the enhancement factor for fast reaction (~~higher~~ second order). The enhancement factor for first order reaction (including pseudo first order reaction was derived earlier as

$$\frac{k}{k_0} = \sqrt{\frac{D k_1}{k_0^2}} \, \coth\left(\sqrt{\frac{D k_1}{k_0^2}}\right).$$

The above analysis is based on film theory. Enhancement factor can also be conceptualized based on penetration/ surface renewal theory with added complexities in the formulation.