Lecture 10

Mass transfer coupled with homogeneous reaction

Intended Learning Outcome

- To be able to construct and analyze the case of mass transfer with homogeneous reaction.
- To analyze the mass-transfer controlled as well as reaction controlled cases to been tasked to set up a packed bed in mass transfer.
- To analyze and contrast the trends in mass transfer upon rapid flow/stirring for homogeneous and heterogenous reaction cases.

Diffusion with homogeneous reaction

Heterogeneous vs. Homogeneous reactions:

Heterogeneous reactions occur only on surface

$$\text{rate per unit area} = \kappa_1(\text{concentration per unit area})$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}$$

Reaction term appears in the boundary condition

Homogeneous reactions occur throughout the volume

$$\text{rate per unit volume} = \kappa_1(\text{concentration per unit volume})$$

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2} + r_1$$

Diffusion with irreversible homogeneous reaction

In case, there is no reaction, we have linear concentration profile at steady-state

$$\overset{o}{Accumulation} * (Adz) = \overset{o}{Flux}\,|_{in} * A - \overset{o}{Flux}\,|_{out} * A + \overset{o}{Generation} * (Adz) - \overset{o}{Consumption} * (Adz)$$

$$0 = AJ_1\,|_z - AJ_1\,|_{z+dz} + 0 \;\; (no\ generation) - 0 \;\; (no\ consumption)$$

$$\Rightarrow \frac{dJ_1}{dz} = 0 \qquad\qquad \Rightarrow -D\frac{d^2c_1}{dz^2} = 0$$

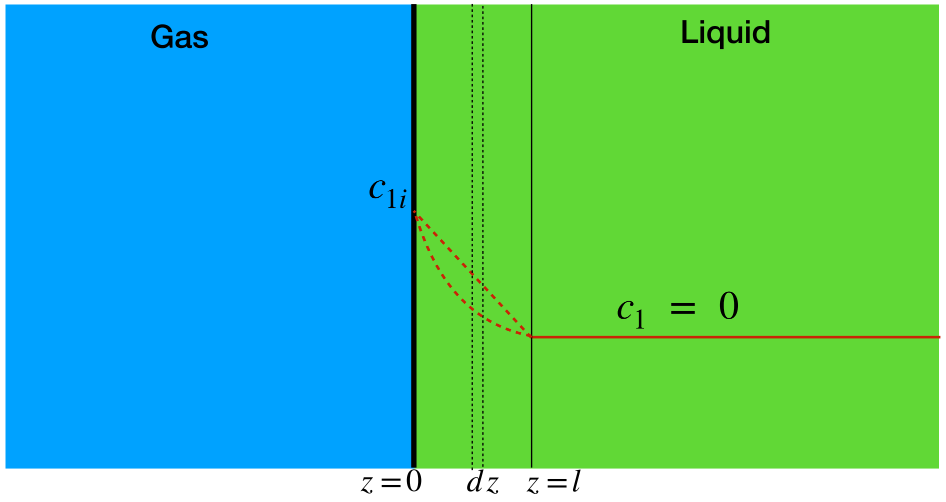
- Flux does not change with z.
- Constant flux.
- Linear concentration profile.

A gas is diffusing and reacting (homogenous, irreversible)

The concentration profile should be different than the case of no reaction!

$$0 = AJ_1\,|_z - AJ_1\,|_{z+dz} + 0 \;\; (no\ generation) - rAdz$$

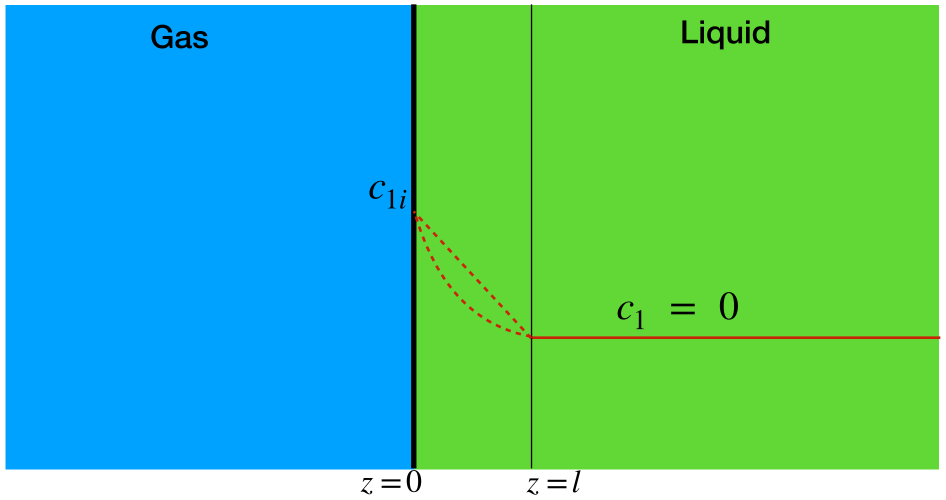
$$\Rightarrow \frac{dJ_1}{dz} = -r \qquad\qquad \Rightarrow J_1 = J_{1i} - \int r dz$$



Plot of gas concentration, c_1

- Flux decreases with z.
- Slope of concentration will decrease with z.

Will mass transfer from gas to interface increase or decrease due to homogeneous reaction?



Flux from gas to liquid interface = flux @z=0

When there is no reaction,

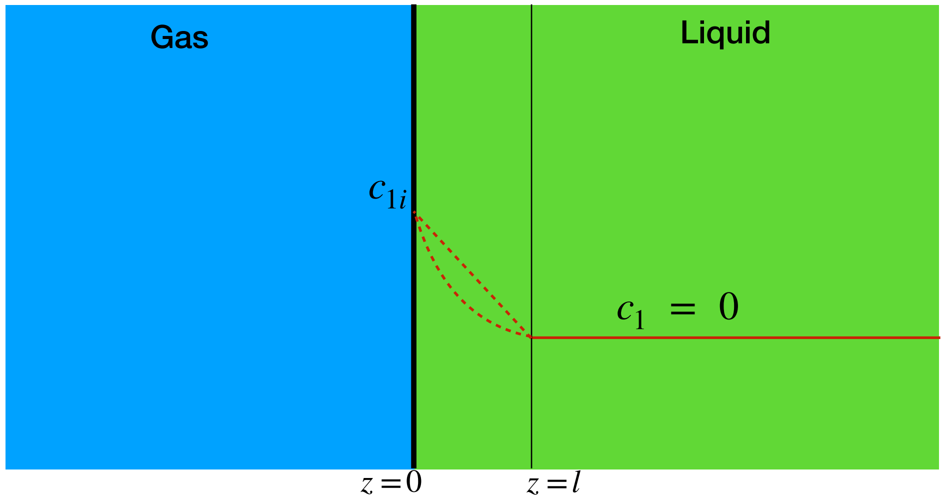
$$J_1\,|_{z=0} = J_1 = D\frac{(c_{1i}-0)}{l} = D\frac{c_{1i}}{l}$$

When there is reaction,

$$J_1\,|_{z=0} \text{ corresponds to the slope at z} = 0$$

Homogeneous reaction increases the flux at the interface

How the mass transfer coefficient change due to reaction?



Since we know that the flux increases at the interface, will the mass transfer coefficient increase?

- So far, we dealt with constant flux:
- But with reaction, flux is no longer constant:

Correct definition of mass transfer coefficient:

$$k = \frac{J_{1,interface}}{(c_{1,interface} - c_{1,bulk})}$$

$$J_{1,interface} = k(c_{1,interface} - c_{1,bulk})$$

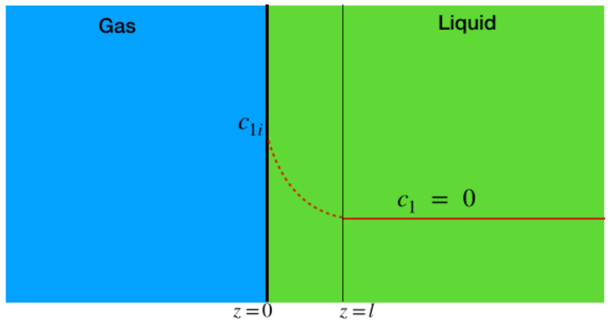
$$J_1 \,|_{z=0} = k(c_{1i} - 0) = kc_{1i}$$

Homogeneous reaction increases mass transfer coefficient

Goal: to calculate enhancement in mass transfer due to irreversible reaction

Calculation of enhancement in mass transfer: case of irreversible first-order reaction

Diffusion with irreversible first-order homogeneous reaction



$$\frac{dJ_1}{dz} = -r \qquad \Rightarrow -D\frac{d^2c_1}{dz^2} = -\kappa c_1 \qquad \Rightarrow \frac{d^2c_1}{dz^2} = \frac{\kappa}{D}c_1$$

Solution to 2nd order differential equation

$$c_1 = A\ \exp\left(\sqrt{\frac{\kappa}{D}}z\right) + B\exp\left(-\sqrt{\frac{\kappa}{D}}z\right)$$

A and B are constant

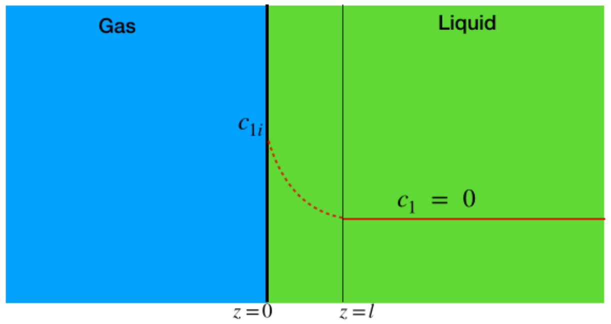
Check if solution is accurate: differentiate twice

$$\frac{dc_1}{dz} = A\sqrt{\frac{\kappa}{D}}\ \exp\left(\sqrt{\frac{\kappa}{D}}z\right) - B\sqrt{\frac{\kappa}{D}}\exp\left(-\sqrt{\frac{\kappa}{D}}z\right)$$

$$\Rightarrow \frac{d^2c_1}{dz^2} = A\frac{\kappa}{D}\ \exp\left(\sqrt{\frac{\kappa}{D}}z\right) + B\frac{\kappa}{D}\exp\left(-\sqrt{\frac{\kappa}{D}}z\right) = \frac{\kappa}{D}\left[A\ \exp\left(\sqrt{\frac{\kappa}{D}}z\right) + B\exp\left(-\sqrt{\frac{\kappa}{D}}z\right)\right]$$

$$\Rightarrow \frac{d^2c_1}{dz^2} = \frac{\kappa}{D}c_1$$

Calculation of enhancement in mass transfer: case of irreversible first-order reaction



$$c_1 = A\exp\left(\sqrt{\frac{\kappa}{D}}z\right) + B\exp\left(-\sqrt{\frac{\kappa}{D}}z\right)$$

Boundary condition:

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

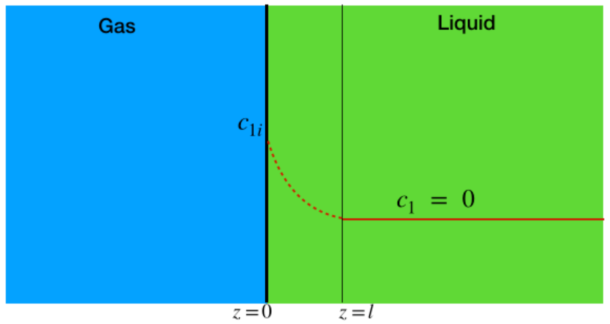
$z = l,\ c_1 = 0$

$$A = -\frac{\exp\left(-\sqrt{\frac{\kappa}{D}}l\right)}{\exp\left(\sqrt{\frac{\kappa}{D}}l\right) - \exp\left(-\sqrt{\frac{\kappa}{D}}l\right)}c_{1i} \qquad B = \frac{\exp\left(\sqrt{\frac{\kappa}{D}}l\right)}{\exp\left(\sqrt{\frac{\kappa}{D}}l\right) - \exp\left(-\sqrt{\frac{\kappa}{D}}l\right)}c_{1i}$$

$$\Rightarrow c_1 = -\frac{\exp\left(-\sqrt{\frac{\kappa}{D}}l\right)\exp\left(\sqrt{\frac{\kappa}{D}}z\right)}{\exp\left(\sqrt{\frac{\kappa}{D}}l\right) - \exp\left(-\sqrt{\frac{\kappa}{D}}l\right)}c_{1i} + \frac{\exp\left(\sqrt{\frac{\kappa}{D}}l\right)\exp\left(-\sqrt{\frac{\kappa}{D}}z\right)}{\exp\left(\sqrt{\frac{\kappa}{D}}l\right) - \exp\left(-\sqrt{\frac{\kappa}{D}}l\right)}c_{1i}$$

$$c_1 = \frac{\exp\left(\sqrt{\frac{\kappa}{D}}(l-z)\right) - \exp\left(-\sqrt{\frac{\kappa}{D}}(l-z)\right)}{\exp\left(\sqrt{\frac{\kappa}{D}}l\right) - \exp\left(-\sqrt{\frac{\kappa}{D}}l\right)}c_{1i} \qquad c_1 = \frac{\sinh\left(\sqrt{\frac{\kappa}{D}}(l-z)\right)}{\sinh\left(\sqrt{\frac{\kappa}{D}}l\right)}c_{1i}$$

Calculation of enhancement in mass transfer



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

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

$$J_1 = -D\frac{dc_1}{dz}$$

$$\Rightarrow J_1 = D\sqrt{\frac{\kappa}{D}} \frac{\cosh\left(\sqrt{\frac{\kappa}{D}}(l-z)\right)}{\sinh\left(\sqrt{\frac{\kappa}{D}}l\right)} c_{1i}$$

$$\Rightarrow J_1 = \sqrt{\kappa D} \frac{\cosh\left(\sqrt{\frac{\kappa}{D}}(l-z)\right)}{\sinh\left(\sqrt{\frac{\kappa}{D}}l\right)} c_{1i}$$

At the interface: z = 0

$$\Rightarrow J_{1i} = \sqrt{\kappa D} \frac{\cosh\left(\sqrt{\frac{\kappa}{D}}l\right)}{\sinh\left(\sqrt{\frac{\kappa}{D}}l\right)} c_{1i}$$

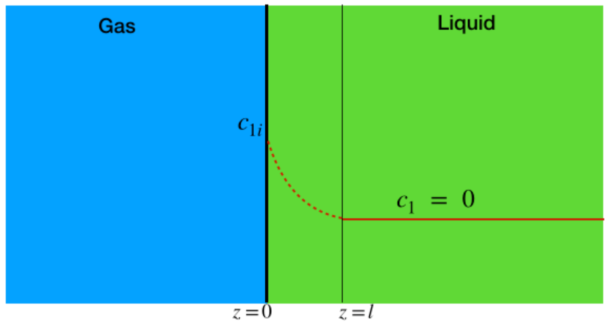
$$\Rightarrow J_{1i} = \sqrt{\kappa D} \coth\left(\sqrt{\frac{\kappa}{D}}l\right) c_{1i}$$

$$k = \frac{J_{1,interface}}{(c_{1,interface} - c_{1,bulk})}$$

$$\Rightarrow k = \frac{J_{1,i}}{(c_{1,i} - 0)} = \frac{J_{1,i}}{c_{1,i}}$$

$$\boxed{\Rightarrow k = \sqrt{\kappa D} \coth\left(\sqrt{\frac{\kappa}{D}}l\right)}$$

Calculation of enhancement in mass transfer



$$\boxed{\Rightarrow k = \sqrt{\kappa D}\ \coth\left(\sqrt{\frac{\kappa}{D}}l\right)}$$

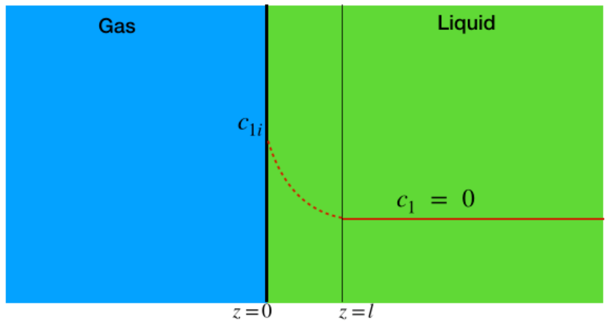
$$\text{enhancement factor} = \varepsilon = \frac{\text{mass transfer coefficient with reaction}}{\text{mass transfer coefficient without reaction}} = \frac{k}{k^0}$$

Using film theory: $k^0 = \dfrac{D}{l}$

$$\varepsilon = \frac{\sqrt{\kappa D}}{D/l}\ \coth\left(\sqrt{\frac{\kappa}{D}}l\right)$$

$$\boxed{\Rightarrow \varepsilon = \sqrt{\frac{\kappa}{D}}l\ \coth\left(\sqrt{\frac{\kappa}{D}}l\right)}$$

Enhancement factor



$$\boxed{\varepsilon = \sqrt{\frac{\kappa}{D}}l \ \coth\left(\sqrt{\frac{\kappa}{D}}l\right)}$$

$$\frac{\kappa}{D}l^2 = \frac{l^2/D}{1/\kappa} = \frac{\text{Diffusion time}}{\text{Reaction time}}$$

is known as second Damköhler number

Sometime *l* is not known, and you want to eliminate it

$$l = \frac{D}{k^0}$$

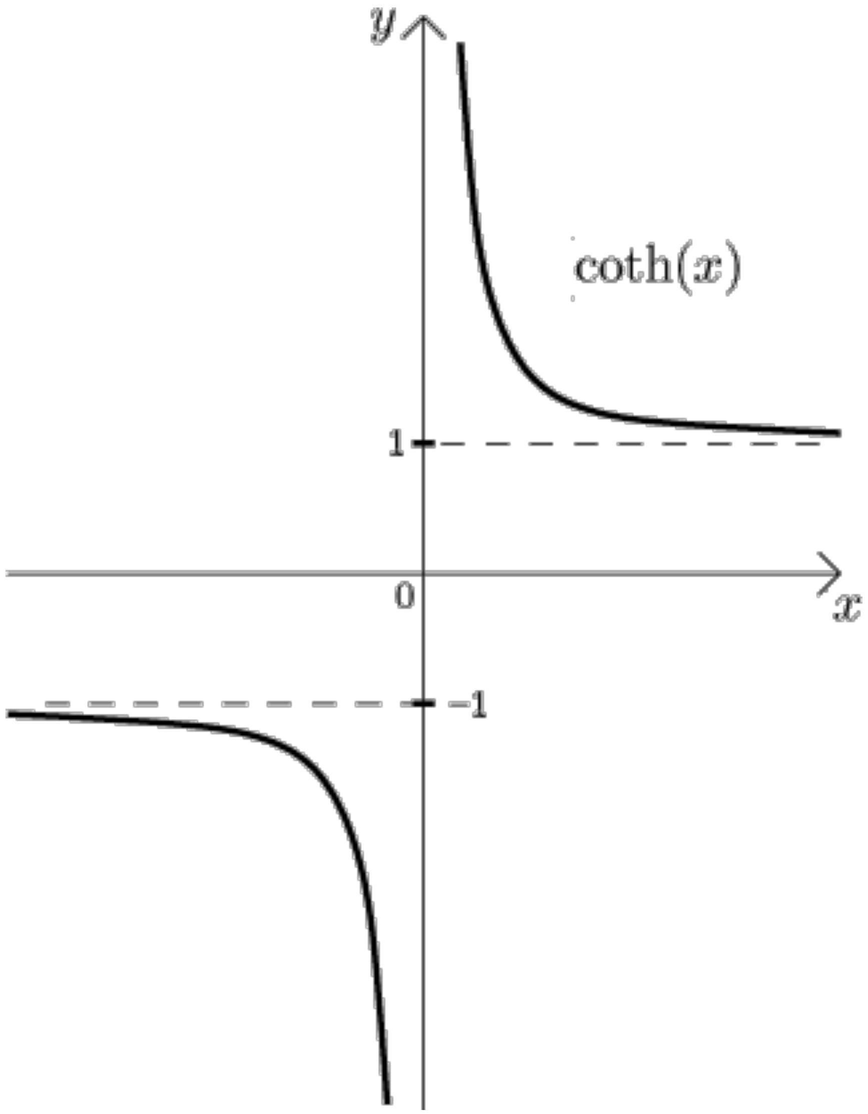
$$\Rightarrow \varepsilon = \frac{\sqrt{\kappa D}}{k^0} \ \coth\left(\sqrt{\frac{\kappa}{D}}\frac{D}{k^0}\right)$$

$$\boxed{\Rightarrow \varepsilon = \frac{\sqrt{\kappa D}}{k^0} \ \coth\left(\frac{\sqrt{\kappa D}}{k^0}\right)}$$

Enhancement factor:
What happens when $\sqrt{\frac{\kappa}{D}}l$ is small ?

$$\boxed{\varepsilon = \sqrt{\frac{\kappa}{D}}l \ \coth\left(\sqrt{\frac{\kappa}{D}}l\right)}$$

$$\boxed{\varepsilon = \frac{\sqrt{\kappa D}}{k^0} \ \coth\left(\frac{\sqrt{\kappa D}}{k^0}\right)}$$



$$\lim_{x \to 0} \coth x \approx \frac{1}{x}$$

$$\lim_{x \to \text{large}} \coth x \approx 1$$

$$\varepsilon = x * \frac{1}{x}$$

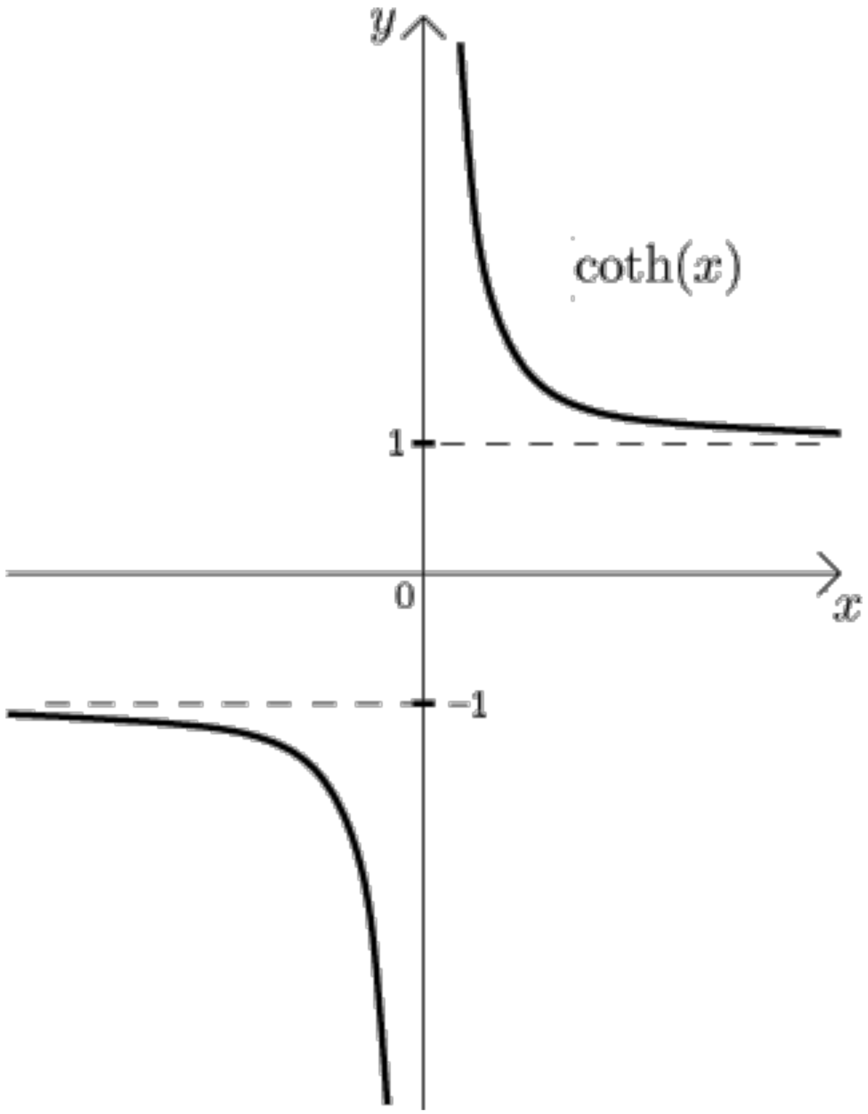
$$\varepsilon = 1$$

No enhancement !

Enhancement factor: What happens when $\sqrt{\frac{\kappa}{D}}l$ is large ?

$$\boxed{\varepsilon = \sqrt{\frac{\kappa}{D}}l \; \coth\left(\sqrt{\frac{\kappa}{D}}l\right)}$$

$$\boxed{\varepsilon = \frac{\sqrt{\kappa D}}{k^0} \; \coth\left(\frac{\sqrt{\kappa D}}{k^0}\right)}$$



$$\lim_{x\to 0} \coth x \approx \frac{1}{x}$$

$$\lim_{x\to \text{large}} \coth x \approx 1$$

$$\varepsilon = \sqrt{\frac{\kappa}{D}}l = \frac{\sqrt{\kappa D}}{k^0}$$

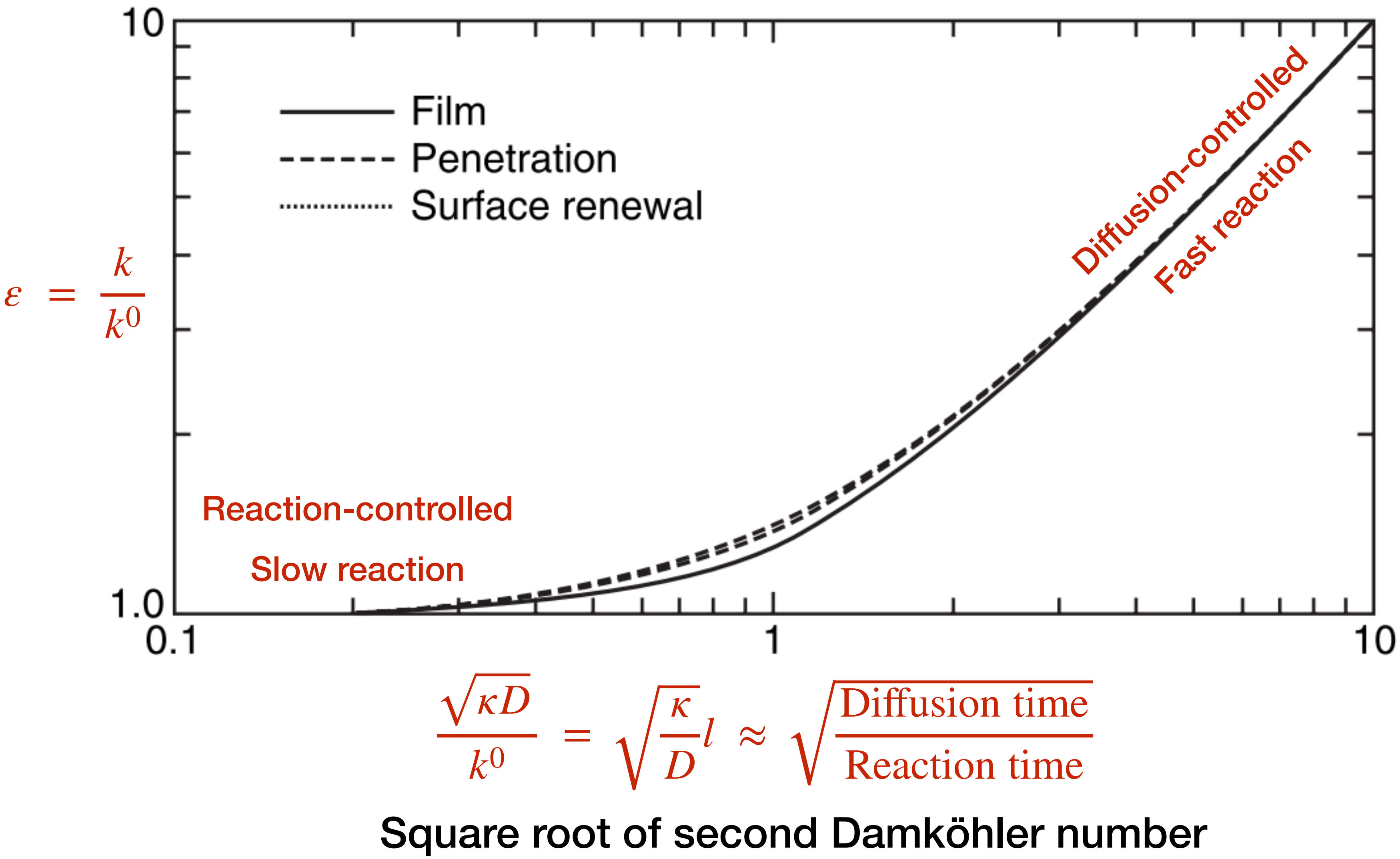
Enhancement factor

Slow reaction

$$\varepsilon = 1$$

Fast reaction

$$\varepsilon = \frac{\sqrt{\kappa D}}{k^0} = \sqrt{\frac{\kappa}{D}}\, l$$



Square root of second Damköhler number

k as a function of flow/stirring

$$k = \sqrt{\kappa D}\ \coth\left(\sqrt{\frac{\kappa}{D}}l\right) \qquad \Rightarrow k = \sqrt{\kappa D}\ \coth\left(\frac{\sqrt{\kappa D}}{k^0}\right) \qquad k^0 = \frac{D}{l}$$

The following correlation will give us k^0 (in absence of reaction)

Example: reaction between gas and liquid in a stirred tank

Pure gas bubbles in a stirred tank

$$\frac{kd}{D} = 0.13\left(\frac{(P\,/\,V)\,d^4}{\rho\nu^3}\right)^{1/4}\left(\frac{\nu}{D}\right)^{1/3}$$

d = bubble diameter
P/V = stirrer power per volume

Falling film

Falling films

$$\frac{kz}{D} = 0.69\left(\frac{zv^0}{D}\right)^{0.5}$$

z = position along film
v^0 = average film velocity

What is the fate of k^0 as a function of stirring (velocity) ??

It increases with stirring, or increasing the velocity

k as a function of flow/stirring

$$k = \sqrt{\kappa D} \coth\left(\frac{\sqrt{\kappa D}}{k^0}\right)$$

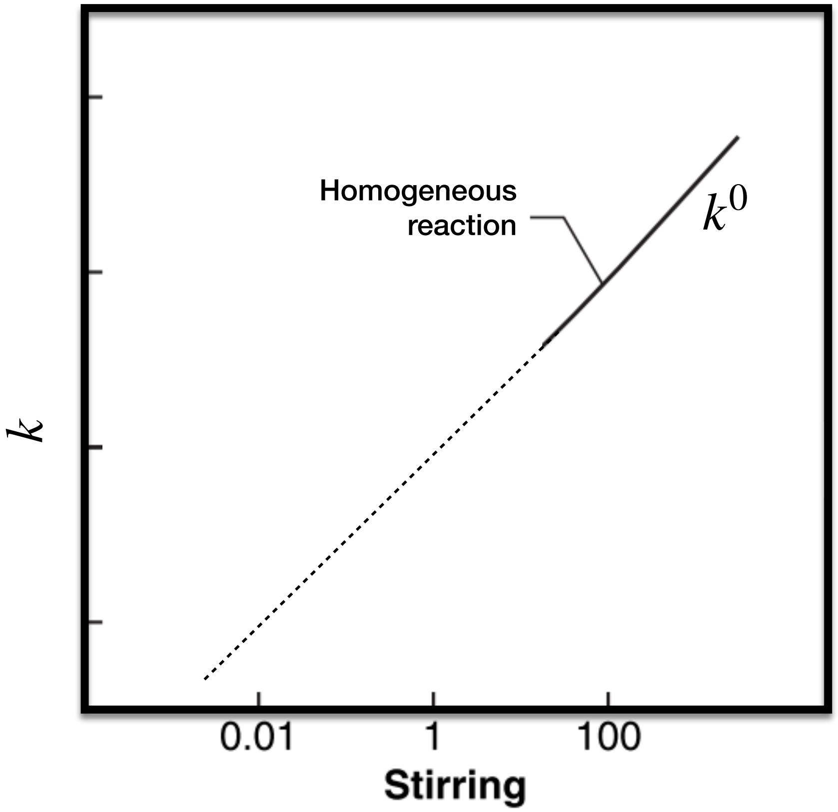
k^0 increases with stirring, or increasing the velocity

at high k^0,

$$\coth\left(\frac{\sqrt{\kappa D}}{k^0}\right) = \frac{k^0}{\sqrt{\kappa D}}$$

$$\Rightarrow k = k^0$$

Reaction controlled regime (no enhancement)



at low k^0,

$$\coth\left(\frac{\sqrt{\kappa D}}{k^0}\right) = 1$$

$$\Rightarrow k = \sqrt{\kappa D}$$

Diffusion controlled regime (enhancement)

Comparison with heterogeneous reaction

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{\kappa_2} + \frac{1}{k_3 K_2}$$

At fast stirring,

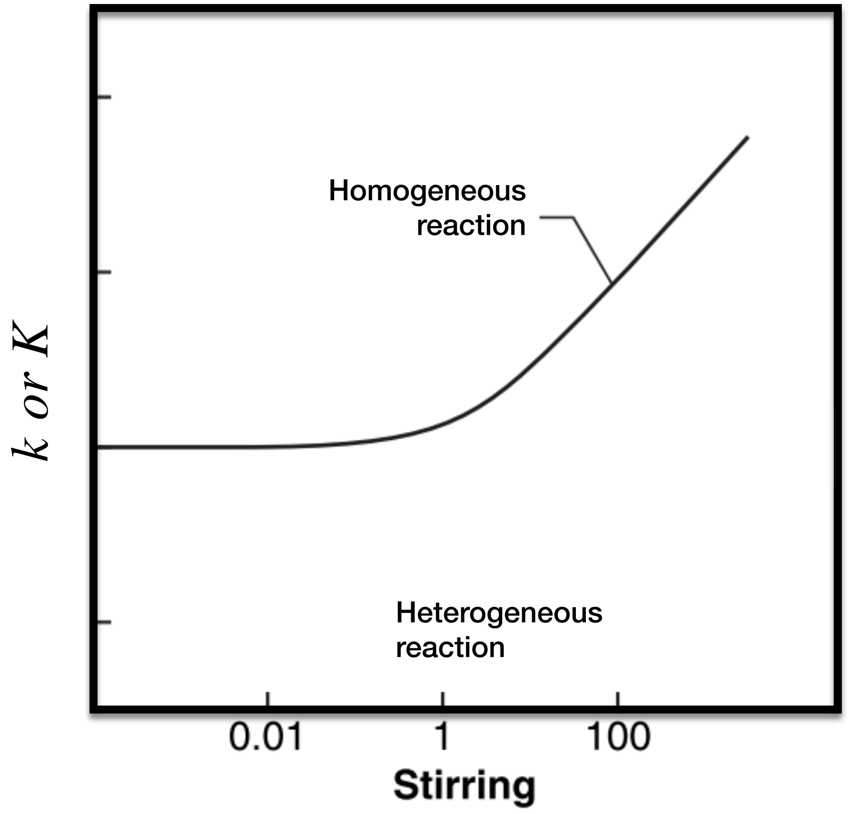
$$K = \kappa_2$$

K is independent of stirring

At slow stirring,

$$\frac{1}{K} = \frac{1}{k_1} + \frac{1}{k_3 K_2}$$

K is small and increases as a function of stirring

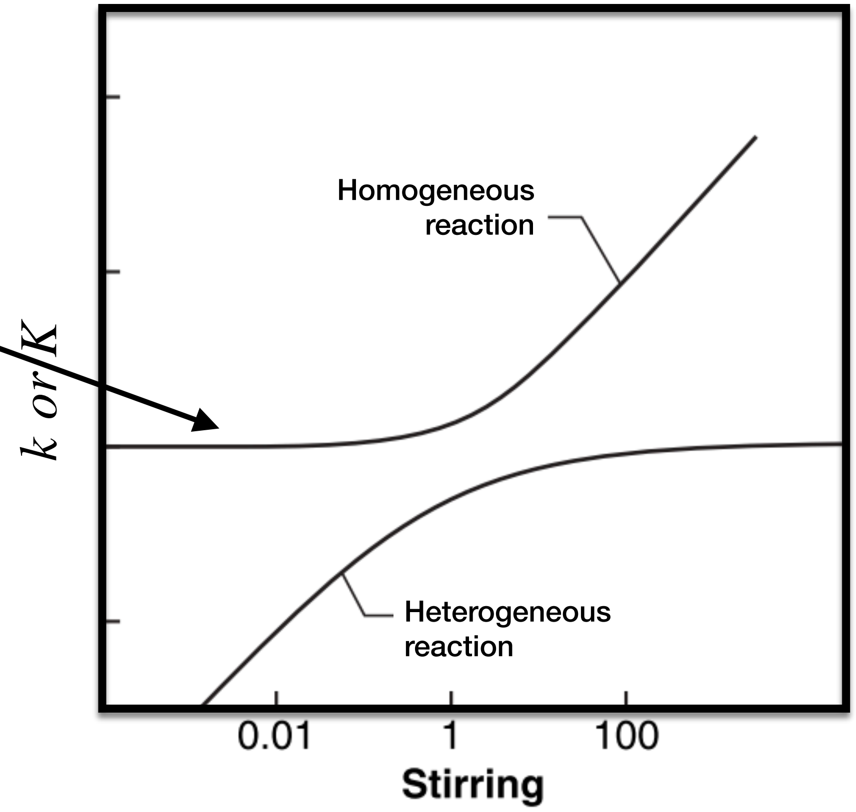


Is the reaction below heterogeneous or homogeneous ?

In an experiment, you are carrying a reaction without stirring (small mass transfer coefficient). When you just started to stir, the mass transfer did not increase.

A. Homogeneous

B. Heterogeneous

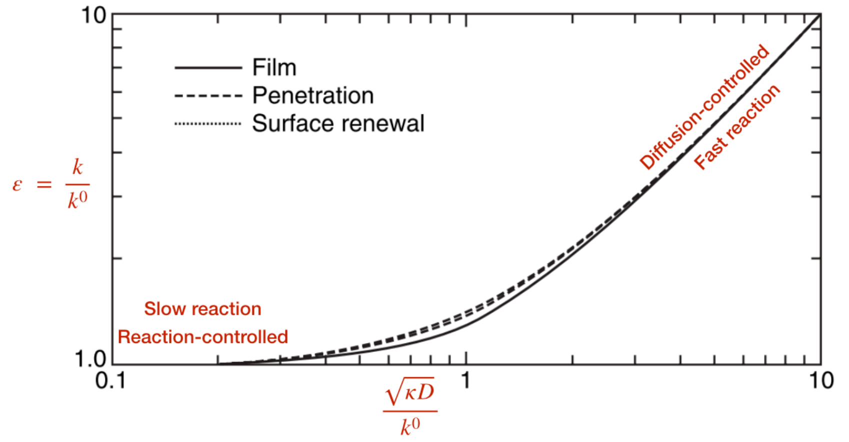


In-class exercise: calculate enhancement

Calculate the enhancement in mass transfer rate when

$$D = 10^{-5}\,\frac{\text{cm}^2}{\text{sec}} \qquad l = 100\ \mu\text{m}$$

(a) $\kappa = 10^{-3}\,\dfrac{1}{\text{sec}}$ **(b)** $\kappa = 10\,\dfrac{1}{\text{sec}}$



$$\varepsilon = \frac{\sqrt{\kappa D}}{k^0}\,\coth\left(\frac{\sqrt{\kappa D}}{k^0}\right)$$

$$k^0 = \frac{D}{l} = \frac{10^{-5}}{100 * 10^{-4}} = 10^{-3}\,\frac{\text{cm}}{\text{sec}}$$

(a) $\dfrac{\sqrt{\kappa D}}{k^0} = \dfrac{\sqrt{10^{-3} * 10^{-5}}}{10^{-3}} = 0.1$ $\qquad \varepsilon = 0.1\coth(0.1) = 0.1 * 10 = 1$

(b) $\dfrac{\sqrt{\kappa D}}{k^0} = \dfrac{\sqrt{10 * 10^{-5}}}{10^{-3}} = 10$ $\qquad \varepsilon = 10\coth(10) = 10 * 1 = 10$

In class exercise problem 2

You are dissolving NH_3 in a solution of HCl by bubbling NH_3 in a stirred HCl tank. Assuming an irreversible reaction between NH_3 and HCl, and bubble diameter of 1 mm, calculate the minimum stirring power per unit volume (in W/liter) needed to make sure that the reaction is not controlled by mass transfer.

Pure gas bubbles in a stirred tank

$$\frac{kd}{D} = 0.13\left(\frac{(P/V)\,d^4}{\rho\nu^3}\right)^{1/4}\left(\frac{\nu}{D}\right)^{1/3}$$

d = bubble diameter
P/V = stirrer power per volume

$$\mathrm{D} = 10^{-6}\ \mathrm{cm^2/s},\ \ \nu = 10^{-8}\ \mathrm{cm^2/s},\ \ \rho = 1\ \mathrm{g/cm^3},\ \ \kappa = 100\ \mathrm{s^{-1}}$$

We have diffusion controlled regime when

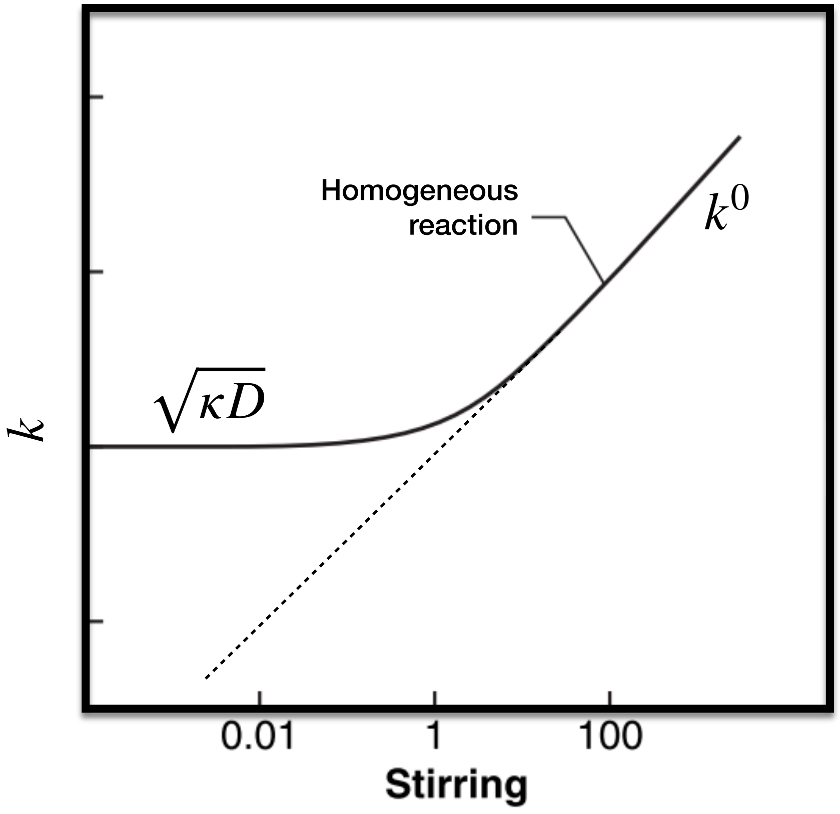
$$k \ = \ \sqrt{\kappa D}$$

To operate outside this regime, we need k such that

$$k > \sqrt{\kappa D} = 0.01\ \mathrm{cm/s}$$

Plugging k = 0.01 cm/s in the mass transfer correlation

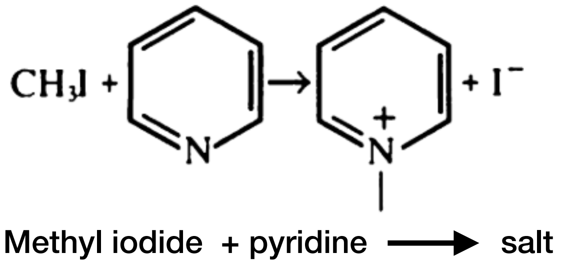
$$\Rightarrow P/V > 162.5\ \mathrm{W/liter}$$



Exercise 1: measuring reaction kinetics

You are planning to measure reaction rate constant for this pseudo first-order reaction where pyridine is in excess:

$$\text{expected rate} = \left[1.5 * 10^{-5}\ \frac{1}{\text{sec}}\right] c_{\mathrm{CH_3I}}$$



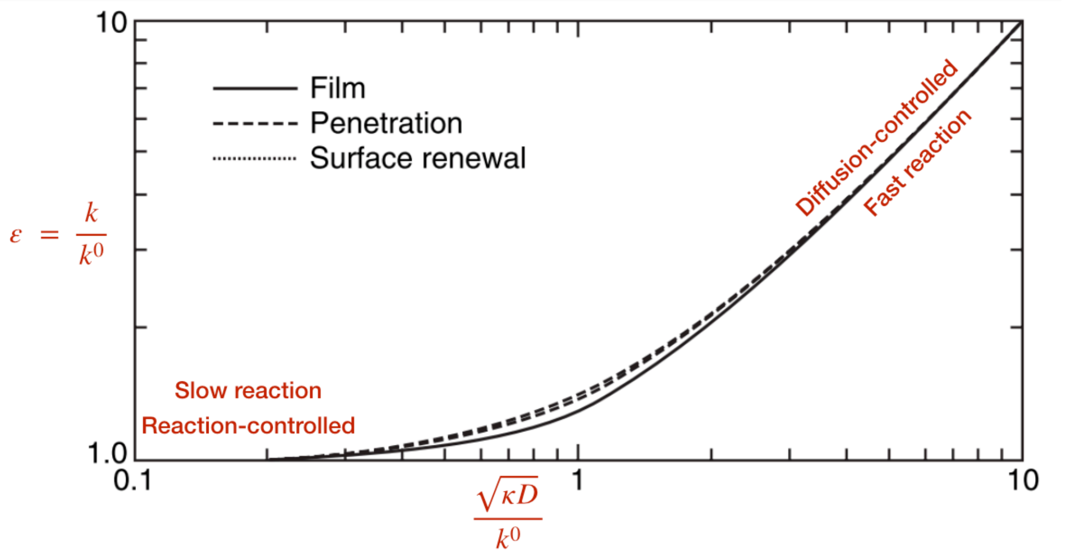
For the reaction, you are bubbling methyl iodide in solution containing excess pyridine. Calculate the range of mass transfer coefficient for methyl iodide such that we can reliably measure the reaction rate. Diffusion coefficient for methyl-iodide in pyridine is

$$D_{CH_3I} = 2 * 10^{-5}\ \frac{\text{cm}^2}{\text{sec}}$$

To correctly measure reaction rate-constant, you will want to operate in reaction-controlled regime.

$$\frac{\sqrt{\kappa D}}{k^0} < 1$$

$$k^0 > \sqrt{\kappa D} = 1.7 * 10^{-5}\ \frac{\text{cm}}{\text{sec}}$$

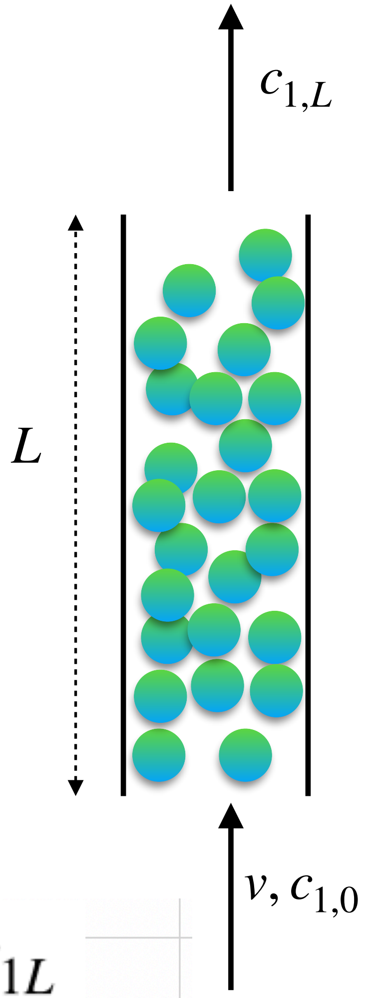


Exercise 2:
Screening of amines for chemisorbing CO_2

Chemisorption in this case is irreversible. You have been tasked to setup a packed bed based absorption column with max height of L=10 m (due to engineering reasons). The best available packing has a = 40 cm^{-1}. You have to choose between three amines for your column such that

$$\frac{c_{1L}}{c_{10}} < 0.2$$

$$\text{Assume } \mathrm{k}^0 = 10^{-3}\ \mathrm{cm/s}, \mathrm{D} = 10^{-5}\ \mathrm{cm^2/s}, \text{velocity} = 100\ \mathrm{cm/s}$$



Which of the following amine will be optimal in performance and cost. Cost goes up for higher rate constant.

(a) $\kappa = 1\ \mathrm{s}^{-1}$ (b) $\kappa = 10\ \mathrm{s}^{-1}$ (c) $\kappa = 100\ \mathrm{s}^{-1}$

$$c_{1L} = c_{10}\ \exp\left(-\frac{kaL}{v}\right)$$

$$k = \sqrt{\kappa D}\ \coth\left(\frac{\sqrt{\kappa D}}{k^0}\right)$$

with no enhancement, $\mathrm{c_{1L} = 0.67c_{10}}$

$$\frac{c_{1L}}{c_{10}} = 0.67$$

κ	k	$\frac{c_{1L}}{c_{10}}$
	1.00E-03	6.7E-01
1	3.17E-03	2.8E-01
10	1.00E-02	1.8E-02
100	3.16E-02	3.2E-06