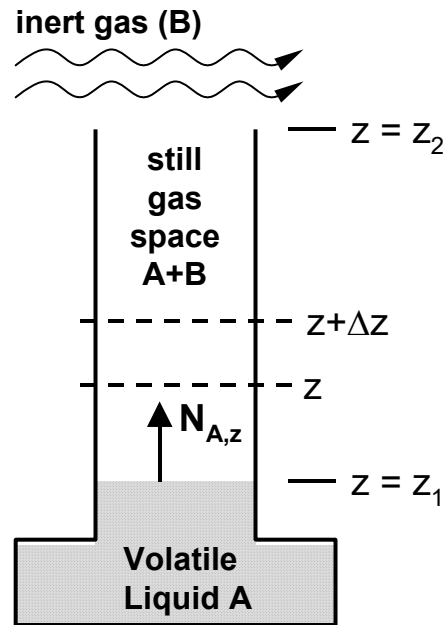# CHAPTER 26: STEADY-STATE MOLECULAR DIFFUSION

26.1 One-Dimensional Mass Transfer Independent of *Homogeneous* Chemical Reaction ($R_A = 0$)

Unimolecular Diffusion (UMD) vs. Equimolar Counter Diffusion (EMCD)

Unimolecular Diffusion (UMD)

SOURCE for A vapor: volatile liquid at the bottom of the cell
SINK for A vapor: flowing inert gas B outside of the cell

ASSUMPTIONS and BOUNDARY CONDITIONS

·   steady-state process, $\partial C_A / \partial t = 0$
·   quiescent gas space in diffusion cell above liquid
·   binary mixture of volatile vapor (A) and inert gas (B), $y_A + y_B = 1$
·   no homogeneous reaction of A or B in gas space, $R_A = 0$
·   one-dimensional flux along coordinate z
·   uniform cross-sectional area "S" for flux $N_{A,z}$
·   component B is not soluble in liquid A
·   constant T & P within diffusion cell (constant C and D_{AB})

$$z = z_1, y_A = y_{A1} = y_{As} = \frac{P_A}{P} \text{ (vapor pressure of A at liquid surface)}$$

$$z = z_2, y_A = y_{A2} \approx 0 \text{ (rapidly swept away once "A" is out of diffusion cell)}$$

CHE 333: Fundamentals of Mass Transfer

General Differential Equation for Mass Transfer (rectangular coordinates)

$$-\frac{\partial N_{A,z}}{\partial z} + R_A = \frac{\partial C_A}{\partial t}$$

reduces to $\dfrac{\partial N_{A,z}}{\partial z} = \dfrac{dN_{A,z}}{dz} = 0$ (N_A is constant along z)

Flux Equation

$$N_{A,z} = -CD_{AB}\frac{dy_A}{dz} + y_A\left(N_{A,z} + N_{B,z}\right)$$

For UMD within the diffusion cell, component B has NO SINK (it is not soluble in liquid A) but still occupies space (i.e. it is *stagnant*). Therefore, a concentration profile for B will exist but $N_{B,z} = 0$.

$$N_{A,z} = -CD_{AB}\frac{dy_A}{dz} + y_A\left(N_{A,z} + 0\right) \quad \text{or} \quad N_{A,z} = -\frac{CD_{AB}}{1-y_A}\frac{dy_A}{dz}$$

Since $N_{A,z}$ is constant along z, it is OK to separate dependent composition variable y_A from independent position variable z and then integrate directly

$$\int_{z_1}^{z_2} N_{A,z}dz = \int_{y_{A1}}^{y_{A2}} -CD_{AB}\frac{dy_A}{1-y_A}$$

If C and D_{AB} are also constant then integrate:

$$N_{A,z} = \frac{CD_{AB}}{(z_2 - z_1)}\ln\left(\frac{1-y_{A2}}{1-y_{A1}}\right)$$

Define $y_{B,lm}$ as the "log mean" mole fraction of B between z_1 and z_2

$$y_{B,lm} = \frac{y_{B2}-y_{B1}}{\ln\left(\dfrac{y_{B2}}{y_{B1}}\right)} = \frac{(1-y_{A2})-(1-y_{A1})}{\ln\left(\dfrac{1-y_{A2}}{1-y_{A1}}\right)} = \frac{y_{A1}-y_{A2}}{\ln\left(\dfrac{1-y_{A2}}{1-y_{A1}}\right)}$$

$$\therefore N_{A,z} = \frac{CD_{AB}}{(z_2 - z_1)}\frac{\left(y_{A1}-y_{A2}\right)}{y_{B,lm}}$$

"Concentration Profile" y_A vs. z

$$\frac{dN_{A,z}}{dz} = 0 = \frac{d}{dz}\left(-\frac{CD_{AB}}{1-y_A}\frac{dy_A}{dz}\right) = 0 \quad \text{(second order differential equation in } y_A)$$

Integrate twice with respect to z

$$\left(\frac{1}{1-y_A}\frac{dy_A}{dz}\right) = a_1 \qquad\qquad -\ln(1-y_A) = a_1 z + a_2$$

where a_1 and a_2 are integration constants. Apply BC to solve for a_1 and a_2

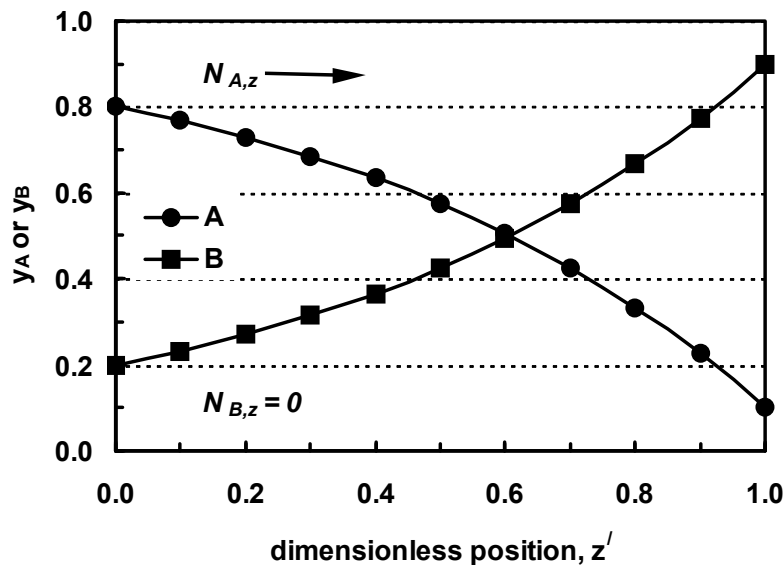at $z = z_1$, $y_A = y_{A1}$ at $z = z_2$, $y_A = y_{A2}$

$$\therefore \quad -\ln(1-y_{A1}) = a_1 z_1 + a_2 \qquad\qquad \therefore \quad -\ln(1-y_{A2}) = a_1 z_2 + a_2$$

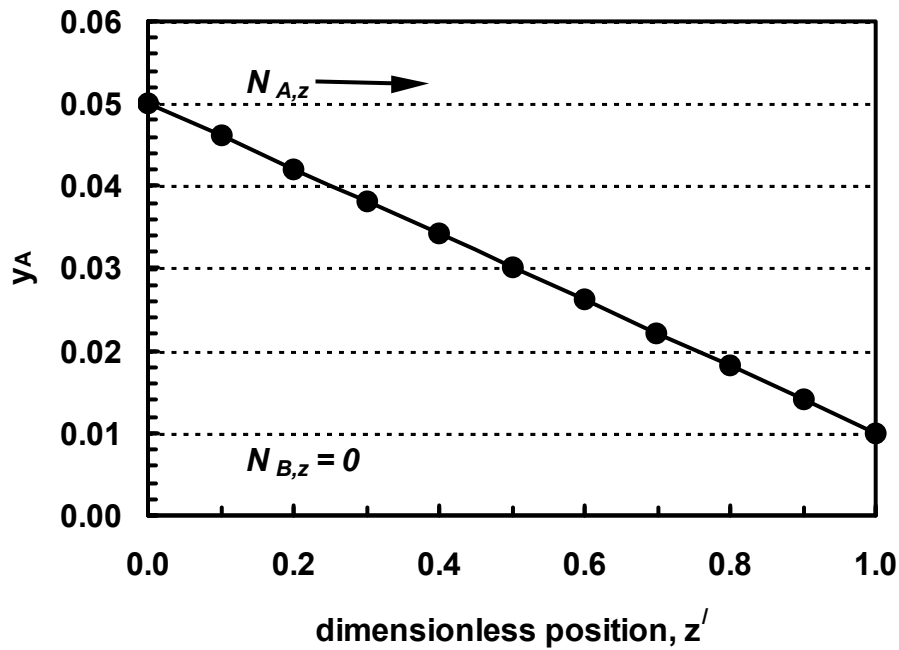Plug a_1 and a_2 back in and re-arrange

$$y_A(z) = 1 - (1-y_{A1})\left(\frac{1-y_{A2}}{1-y_{A1}}\right)^{\left[z'\right]} \qquad \text{where} \quad z' = \frac{z-z_1}{z_2-z_1} \quad (0 \le z' \le 1)$$

The concentration profile is "nonlinear" at high concentrations
(e.g. $y_{A1} = 0.8$, $y_{A2} = 0.1$)

CHE 333: Fundamentals of Mass Transfer

At lower concentrations (e.g. $y_{A1} = 0.05$, $y_{A2} = 0.01$), the concentration profile becomes nearly linear

If $y_A \ll 1$, then the Flux Equation Reduces to

$$N_{A,z} = -\frac{CD_{AB}}{1-y_A}\frac{dy_A}{dz} \cong \frac{-CD_{AB}}{1}\frac{dy_A}{dz}$$

and

$$\int_{z_1}^{z_2} N_{A,z}\,dz = \int_{y_{A1}}^{y_{A2}} -CD_{AB}\,dy_A$$

and

$$N_{A,z} = \frac{CD_{AB}}{(z_2 - z_1)}(y_{A1} - y_{A2}) \quad \text{with} \quad y_{B,lm} \to 1$$

Concentration Profile is linear (show derivation in your notes)

$$y_A = y_{A1} - (y_{A1} - y_{A2}) \cdot z'$$

Equimolar Counter Diffusion (EMCD)

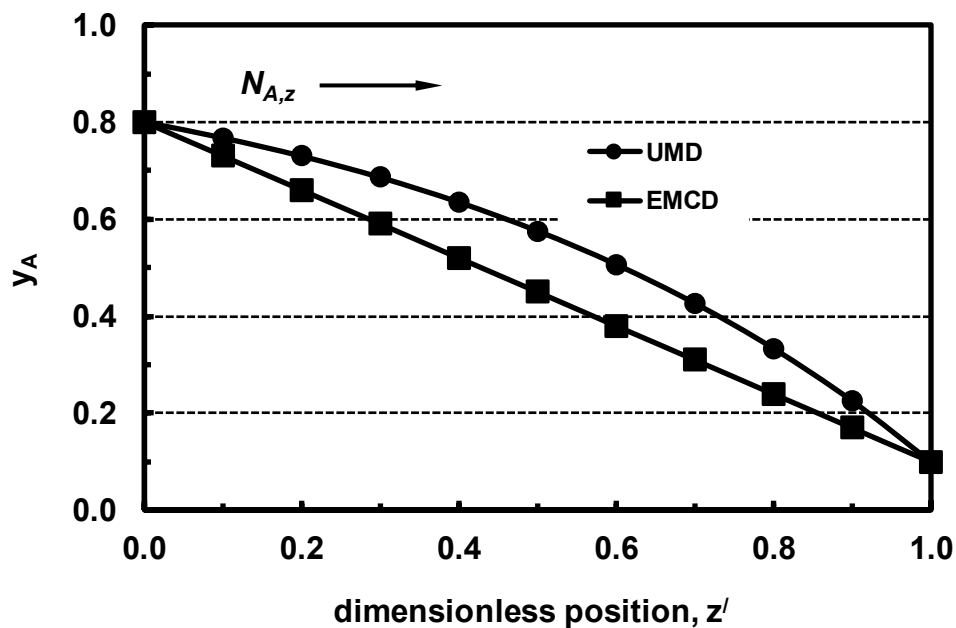Consider now $N_A = -N_B$ (many possible physical situations)

Flux Equation

$$N_{A,z} = -CD_{AB}\frac{dy_A}{dz} + y_A(N_{A,z} + N_{B,z}) = -CD_{AB}\frac{dy_A}{dz}$$

Consequently

$$\int_{z_1}^{z_2} N_{A,z}dz = \int_{y_{A1}}^{y_{A2}} -CD_{AB}\,dy_A \text{ and so } N_{A,z} = \frac{CD_{AB}}{(z_2 - z_1)}(y_{A1} - y_{A2})$$

Dilute UMD and **EMCD** yield the same mathematical result for N_A even though they are physically different processes

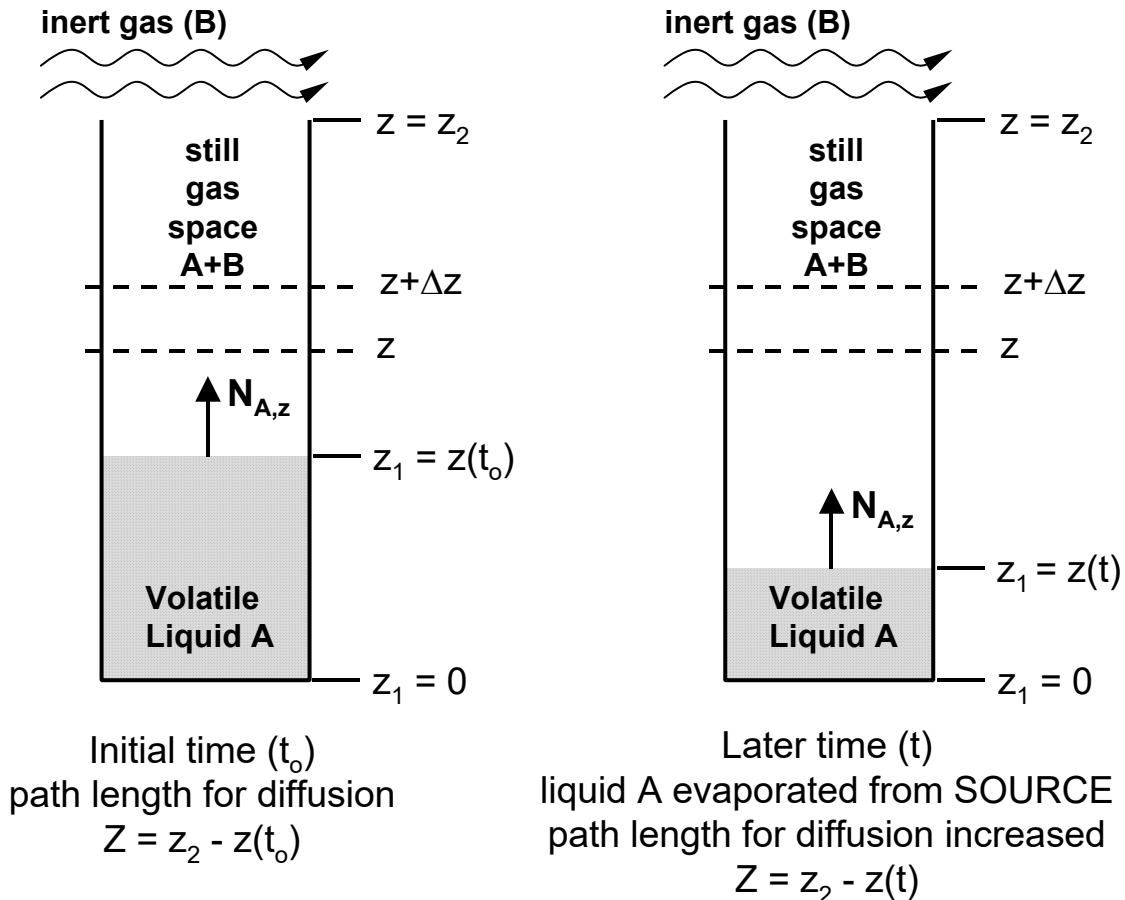UMD vs. EMCD concentration profile for same B.C.

26.1 (continued)

Pseudo Steady-State (PSS) Diffusion

In pseudo steady-state (PSS) diffusion, the SOURCE for A at the boundary is finite and is depleted over time. However, within the control volume for diffusion of A, the diffusion process is at steady state and " $\partial C_A / \partial t$ " term is zero. Define TWO systems, each with its own material balance.

SYSTEM I: control volume for diffusion of A (steady state material balance)

SYSTEM II: the SOURCE for A (unsteady state material balance)

Arnold Diffusion Cell

inert gas (B)

still gas space A+B

$z = z_2$

$z+\Delta z$

z

$N_{A,z}$

$z_1 = z(t_o)$

Volatile Liquid A

$z_1 = 0$

Initial time (t_o)
path length for diffusion
$Z = z_2 - z(t_o)$

inert gas (B)

still gas space A+B

$z = z_2$

$z+\Delta z$

z

$N_{A,z}$

$z_1 = z(t)$

Volatile Liquid A

$z_1 = 0$

Later time (t)
liquid A evaporated from SOURCE
path length for diffusion increased
$Z = z_2 - z(t)$

SOURCE for A vapor: volatile liquid at the bottom of the cell
SINK for A vapor: flowing inert gas B outside of the cell

SYSTEM I: quiescent gas space in diffusion cell (A + B)

SYSTEM II: pure liquid A in bottom of tube (FINITE SOURCE)

Assumptions and Boundary Conditions

·   steady-state process, $\partial C_A / \partial t = 0$ (PSS assumption)
·   quiescent gas space in diffusion cell above liquid
·   binary mixture of volatile vapor (A) and inert gas (B), $y_A + y_B = 1$
·   no homogeneous reaction of A or B in gas space, $R_A = 0$
·   no homogeneous reaction of liquid A
·   one-dimensional flux along coordinate z
·   uniform cross-sectional area "S" for flux $N_{A,z}$
·   component B is not soluble in liquid A
·   constant T & P within diffusion cell (constant C and D_{AB})

$$z = z_1 = z(t), y_A = y_{A1} = y_{As} = \frac{P_A^*}{P} \text{ (vapor pressure of A at liquid surface)}$$

$$z = z_2, y_A = y_{A2} \approx 0 \text{ (rapidly swept away once "A" is out of diffusion cell)}$$

SYSTEM I (material balance on A)

Recall

$$N_{A,z} = \frac{C D_{AB}}{(z_2 - z_1)} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right) = \frac{C D_{AB}}{Z(t)} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right)$$

The PSS Assumption: $z_1 = z(t)$ is decreasing with time so that $Z(t) = z_2 - z(t)$ increases with time. Consequently, the flux $N_{A,z}$ will also decrease since the path length for diffusion is increasing.   However, the time scale for $Z(t)$ is slow enough so that the "$\partial C_A / \partial t$" term is negligible, i.e. SYSTEM I can establish steady-state quickly even though Z is increasing.

SYSTEM II (material balance on A, moles A/time)

m_A = current mass of liquid A in bottom of tube

V = current volume of liquid A in bottom of tube, volume element $\Delta V = S\,\Delta z$

IN – OUT + GEN = ACC (moles A/time)

$$0 - N_{A,z} \cdot S + 0 = \frac{dm_{A,liq}}{dt} \qquad \text{with} \quad \frac{dm_{A,liq}}{dt} = \frac{d\left[\dfrac{\rho_{A,liq}}{M_A} V\right]}{dt} = \frac{\rho_{A,liq}}{M_A} \frac{dV}{dt} = \frac{\rho_{A,liq} S}{M_A} \frac{dz}{dt}$$

$$\therefore \quad -N_{A,z} \cdot S = \frac{\rho_{A,liq} S}{M_A} \frac{dz}{dt} \qquad \text{note:} \quad \frac{dZ}{dt} = \frac{[z_2 - z]}{dt} = -\frac{dz}{dt}$$

$$\therefore \frac{C D_{AB}}{Z(t)} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right) = \frac{\rho_{A,liq}}{M_A} \frac{dZ}{dt} \qquad y_{A1} \text{ and } y_{A2} \text{ are not functions of } t$$

Separate variables Z and t and integrate with respect to boundary conditions for Z

$$\int_{Z_o}^{Z} Z \cdot dZ = \frac{M_A C D_{AB}}{\rho_{A,liq}} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right) \int_{t_o}^{t} dt$$

$$Z_o = z_2 - z(t_o) \qquad Z = z_2 - z(t) \quad (Z > Z_o)$$

$$Z^2 - Z_o^2 = \frac{2 M_A C D_{AB}}{\rho_{A,liq}} \ln\left(\frac{1 - y_{A2}}{1 - y_{A1}}\right)(t - t_o)$$

Therefore, a plot of $Z^2 - Z_o^2$ vs. t should be linear.

Pseudo Steady State Problem Example with Arnold Diffusion Cell

A diffusion experiment was conducted within an Arnold Diffusion Cell maintained at the following conditions:

$$T = \quad 25\ ^\circ C$$
$$P = \quad 1.00\ \text{atm}$$
$$M_A = \quad 78\ \text{g/gmole}$$
$$\rho_{A,liq} = \quad 0.80\ \text{g/cm}^3$$
$$P_A = \quad 95\ \text{mm Hg (at 25 }^\circ C)$$
$$R = \quad 82.06\ \ \text{cm}^3\ \text{atm/gmole-K}$$

The total length of the diffusion cell is 15.0 cm. The initial depth of the liquid benzene is 5.0 cm. The data from the experiment are provided below:
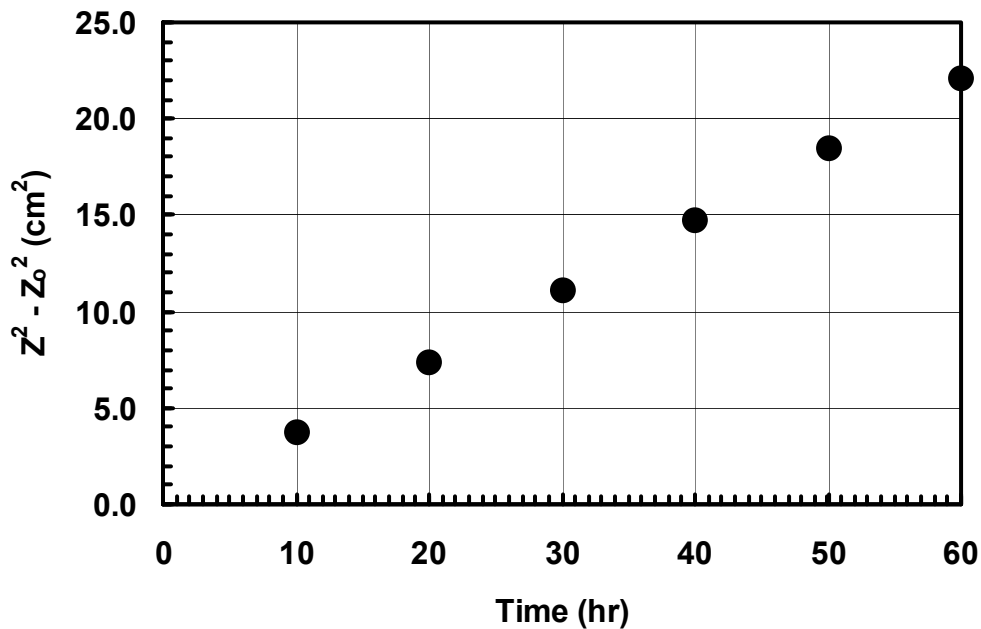
(a) Estimate the diffusion coefficient of benzene in air at 25 °C
(b) Estimate the flux of benzene vapor out of the diffusion cell after 10 hr and 50 hr.

26.1 Example: PSS Diffusion in SiO₂ Thin Film Formation on Solid Si

Problem statement. The formation of a silicon oxide (SiO₂) thin film on a silicon (Si) wafer surface is an important step in the fabrication of solid-state microelectronic devices. A thin film of SiO₂ serves as a barrier to dopant diffusion or as a dielectric insulator to isolate various devices being formed on the wafer. In one common process, silicon is oxidized by exposure to oxygen (O₂) gas at temperatures above 700 °C

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$
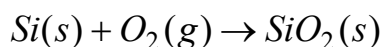
Molecular O₂ dissolves into the SiO₂ solid, diffuses through the SiO₂ film, and then reacts with Si the Si/SiO₂ interface, as shown below.

Assuming that the diffusion of O₂ through the SiO₂ film limits the oxidation process, predict the thickness of the SiO₂ layer (δ) as a function of time at 1000 °C.
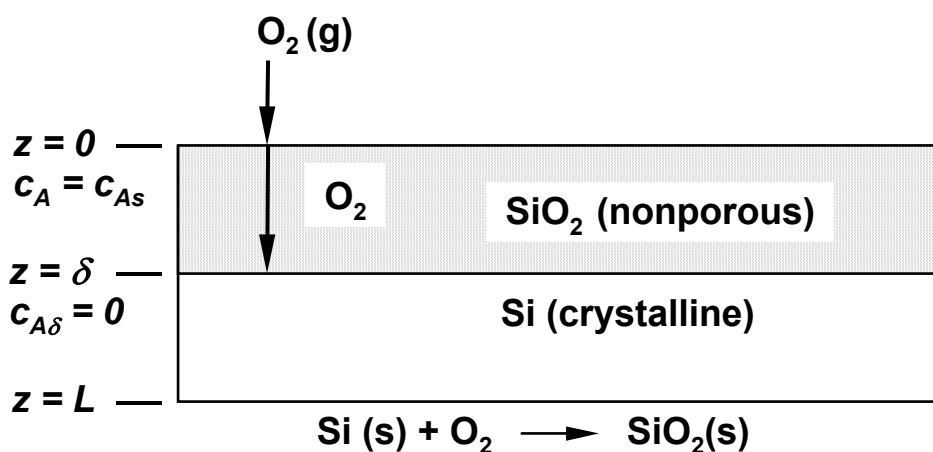
Thermal Oxidation of a Silicon Wafer

Physical System: SiO₂ solid layer (species B) containing "dissolved" O₂

SOURCE for O₂: 100% O₂ gas over SiO₂ solid film
SINK for O₂: unreacted Si at boundary surface

SYSTEM I: dissolved O₂ in SiO₂ film
SYSTEM II: unreacted Si

Assumptions & Conditions

1. The oxidation of Si to SiO_2 occurs only at the Si/SiO_2 interface. The unreacted Si at the interface serves as the sink for molecular mass transfer of O_2 through the film.

2. The O_2 in the gas phase above the wafer represents an infinite source for O_2 transfer. The O_2 molecules "dissolve" into the nonporous SiO_2 solid at the gas solid interface.

3. The rate of SiO_2 formation is controlled by the rate of molecular diffusion of O_2 (species A) through the solid SiO_2 layer (species B) to the unreacted Si layer. The reaction is very rapid, so that the concentration of molecular O_2 at the interface is equal to zero, i.e $C_{A\delta} = 0$. Furthermore, there are no mass transfer resistances in the gas film above the wafer surface, since O_2 is a pure component in the gas phase.

4. The flux of O_2 through the SiO_2 layer is one-dimensional along coordinate z.

5. The rate of SiO_2 film formation is slow enough so that at a given film thickness δ, there is no accumulation of reactants or products within the SiO_2 film. However, the thickness of the film will still increase with time (the PSS Assumption).

6. The overall thickness of the wafer does not change as the result of the formation of the SiO_2 layer.

7. The process is isothermal.

SYSTEM I

General Differential Equation for Mass Transfer

$$\frac{dN_{Az}}{dz} = 0 \quad (N_{A,z} \text{ is constant along z, therefore can integrate flux equation directly})$$

Fick's Flux Equation (UMD process, dilute system, $C_A << C$)

$$N_{Az} = -D_{AB}\frac{dC_A}{dz} + \frac{C_A}{C}(N_{Az} + N_{Bz}) = -D_{AB}\frac{dC_A}{dz} + \frac{C_A}{C}N_{Az} \cong -D_{AB}\frac{dC_A}{dz}$$

N_A is constant along z. Separate dependent variable c_A from independent variable z

$$\int_0^\delta N_{Az}\,dz = -D_{AB}\int_{c_{As}}^0 dC_A$$

Flux of O_2 through the SiO_2 layer of current thickness δ

$$N_{Az} = \frac{D_{AB}\,C_{As}}{\delta}$$

c_{As} = the concentration of O_2 dissolved in solid phase SiO_2 (mole O_2 / cm^3 solid)

D_{AB} = molecular diffusion coefficient of O_2 in SiO_2

SYSTEM II (PSS Analysis)

The unreacted Si is the SINK for O2 that is depleted over time. However, for convenience with setup, consider a material balance on the SiO_2 that is accumulated. Material Balance on SiO_2 (moles SiO_2/time) is

IN – OUT + GENERATION = ACCUMULATION

$$0-0+N_{A,z}\cdot S\cdot\frac{1.0\text{ mole SiO}_2\text{ (B)}}{1.0\text{ mole O}_2\text{ (A)}} = \frac{dm_B}{dt} \qquad \frac{dm_B}{dt} = \frac{d\left(\dfrac{\rho_B S\delta}{M_B}\right)}{dt}$$

ρ_B = density of solid SiO_2 (2.27 g/cm^3)

M_B = molecular weight of the SiO_2 layer (60 g/mole)

Combine with Flux Equation (Fick's Equation)

$$\frac{D_{AB}\,C_{As}}{\delta} = \frac{\rho_B}{M_B}\frac{d\delta}{dt}$$

Separate dependent variable δ from the independent variable t

$$\int_0^\delta \delta \, d\delta = \frac{M_B D_{AB} C_{As}}{\rho_B} \int_0^t dt \quad \text{or} \quad \delta = \sqrt{\frac{2M_B D_{AB} C_{As}}{\rho_B} t} \quad \text{note: } \delta \propto \sqrt{t}$$

Model Predictions vs. Process Data (SiO$_2$ film thickness δ vs. reaction time)

D_{AB} = 2.7 · 10^{-9} cm^2/s at 1000 °C
C_{As} = 9.6 10^{-8} mole O$_2$ / cm^3 solid at 1000 °C and 1.0 atm O$_2$ partial pressure
  (very very dilute)
ρ_B = 2.27 g/cm^3
M_B = 60 g/mole   note $C \approx C_B = \rho_B / M_B = 0.038$ mole/cm^3

Film is very thin (< 1 µm), but the D$_{AB}$C$_{As}$ term is very small. Initially the reaction is reaction-rate limited but quickly moves to diffusion limited (note the small value of D_{AB}).
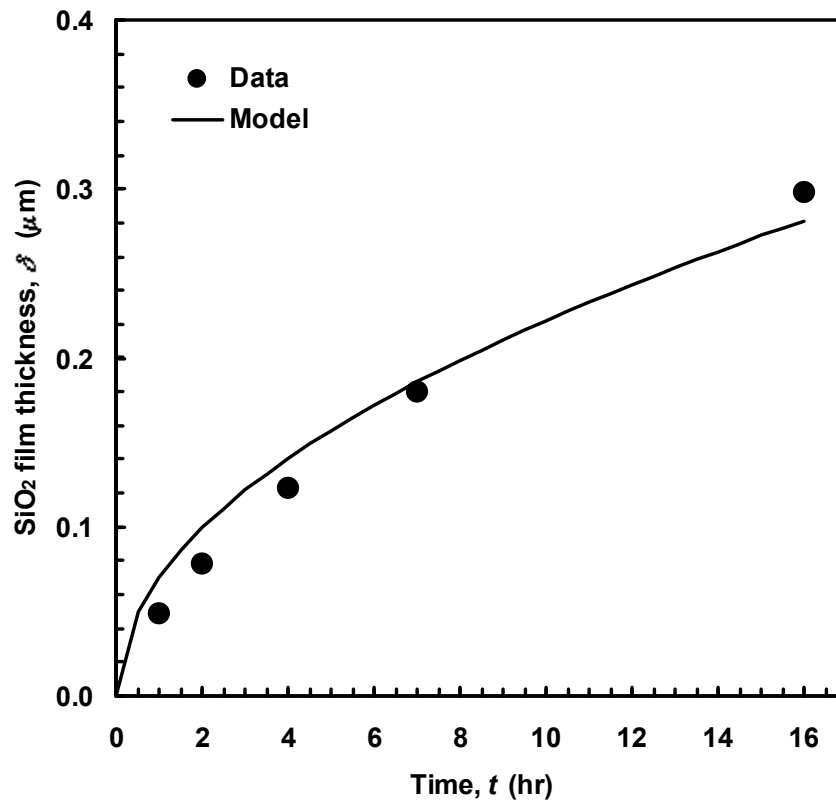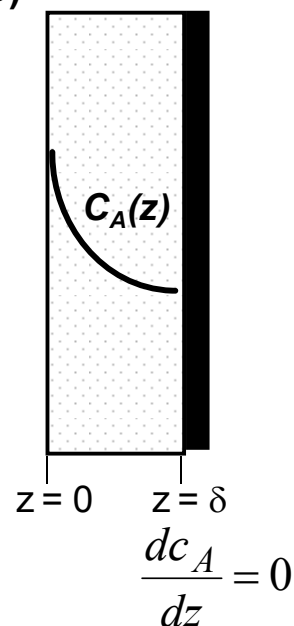
26.2 One-Dimensional Systems Associated with Chemical Reaction

Homogeneous vs. Heterogeneous Reactions

Homogeneous Reaction within Control Volume
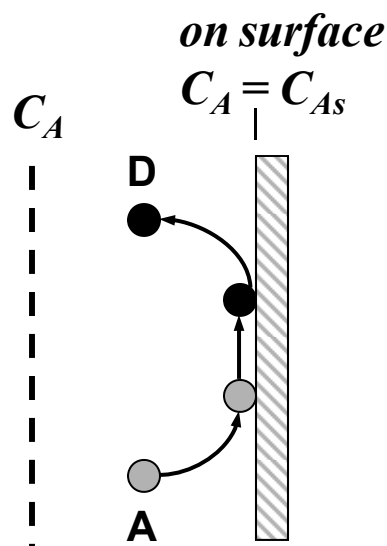## (units R_A mol/cm³-sec, A diffuses and reacts)

First Order Rxn	Second Order Rxn

$$A \xrightarrow{\ k\ } D \qquad\qquad A + B \xrightarrow{\ k\ } D$$
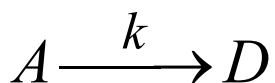
$$R_A = -k\,C_A \qquad\qquad R_A = -k\,C_A C_B$$
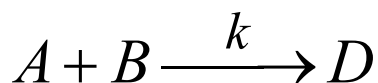
units of **k 1/sec** $\qquad\qquad$ units of **k cm³/mol-sec**

$C_A(z)$

z = 0 $\qquad$ z = δ

$$\frac{dc_A}{dz} = 0$$

First-Order Surface Reaction
(reaction only at a reaction surface)

on surface

$$C_A = C_{As}$$

C_A

D

**Flux at surface balanced
by surface reaction rate**

$$R'_A = -k_s\,C_{As} \quad \text{(mol/cm²-sec)}$$

$$N_A = -R'_A$$

units of **k_s cm/sec**

A

14

Diffusion within a Homogeneous, First-Order Chemical Reaction

26.2 Example: Diffusion with a Homogeneous First-Order Reaction within a Biofilm

Problem statement. Basic concepts for diffusion with a homogeneous reaction can be illustrated with the "biofilm" process described below.   Dilute concentrations of toxic organic solutes can often be degraded by a "biofilm" attached to an inert, nonporous solid surface. A biofilm consists of living cells immobilized in a gelatinous matrix. Biofilms are not very thick, usually less than a few millimeters. A toxic organic solute (species A) diffuses into the biofilm and is degraded to harmless products, hopefully CO_2 and water, by biological catalysts (either cells or enzymes) within the biofilm. For engineering applications, the biofilm itself can be approximated as a homogeneous substance

The concentration of species A in the bulk fluid phase over the biofilm is constant if the fluid phase is well mixed. However, the concentration of A within the biofilm will decrease along the depth of the biofilm z as species A is degraded. There are no resistances to convective mass transfer across the fluid boundary layer between the bulk fluid and the biofilm surface. Furthermore, phenol is equally soluble in both water and the biofilm, and the density difference between the biofilm and water can be neglected, so that the surface concentration of phenol in the aqueous phase equals the surface concentration of phenol in the gel phase just inside the biofilm, i.e. at $z = 0, C_{As} = C_{Ao}$.

biofilm cross section

$$\frac{dc_A}{dz} = 0$$
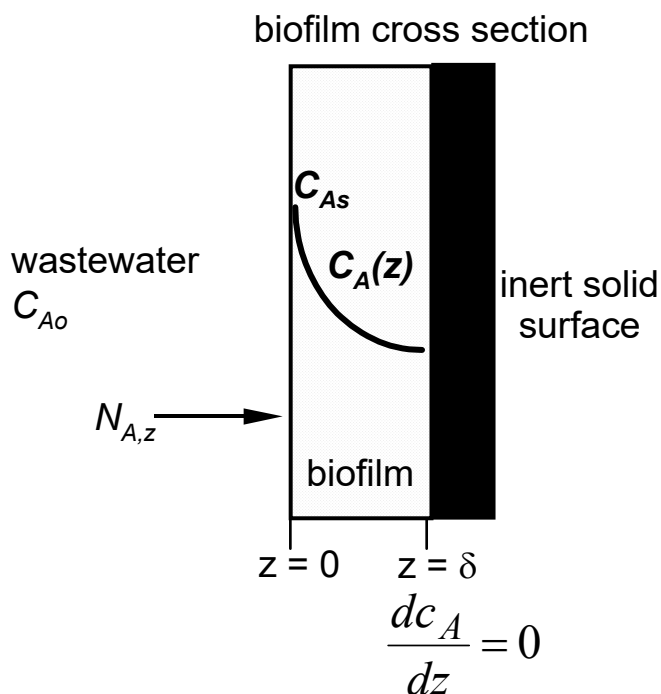
SYSTEM: *biofilm (material B) containing dilute solute A*
SOURCE: *solute A in liquid outside of biofilm*
SINK: *homogeneous consumption of A within biofilm (occurs within control volume, but control volume itself is not the sink)*

Assumptions (ongoing list)

- *Steady state process (constant SOURCE and SINK)*
- *1-D flux along z (note orientation of SOURCE and SINK)*
- Homogeneous "first-order" reaction, $R_A = -k_1 C_A$
- *Dilute system* $C_A \ll C$ (e.g. $C_A / C < 0.05$ *rule of thumb*)
- UMD process w.r.t. A
- *Pseudo binary mixture of A (solute) and B (biofilm)*
- $C_{Ao} = C_{As}$

Aside: the homogeneneous rate equation (R_A) for a biofilm

The rate of degradation of the toxic solute per unit volume of the biofilm is described by a "saturation" kinetic rate equation of the form

$$R_A = -\frac{R_{A,\max} C_A}{K_A + C_A}$$

$R_{A,max}$ = maximum possible (saturation) degradation rate of species A in the biofilm (mole/m^3-hr)

K_A = half-saturation constant for the degradation of species A within the biofilm (mole/m^3)

If $K_A \gg C_A$ (e.g. very low concentration),
R_A is a first-order reaction w.r.t. reactant "A"

$$R_A = -\frac{R_{A,\max} C_A}{K_A + C_A} \cong -\frac{R_{A,\max}}{K_A} C_A = -k_1 C_A \quad \text{with} \quad k_1 = \frac{R_{A,\max}}{K_A}$$

notes:

- the minus "-" sign indicates that A is consumed, as R_A is defined as the "rate of generation of A"

- first-order rate constant k_1 has units of inverse time (e.g. sec^{-1})

R_A vs. C_A for "saturation" kinetic rate equation common in enzyme-catalyzed homogeneous reactions (enzyme is homogeneously distributed throughout the biofilm)

$$K_A = \quad 0.3 \quad \text{gmole A/m}^3$$
$$R_{A,max} = \quad 5.70\text{E-}03 \quad \text{gmole A/m}^3\text{-sec}$$
$$k_1 = \quad 1.90\text{E-}02 \quad \text{sec}^{-1}$$
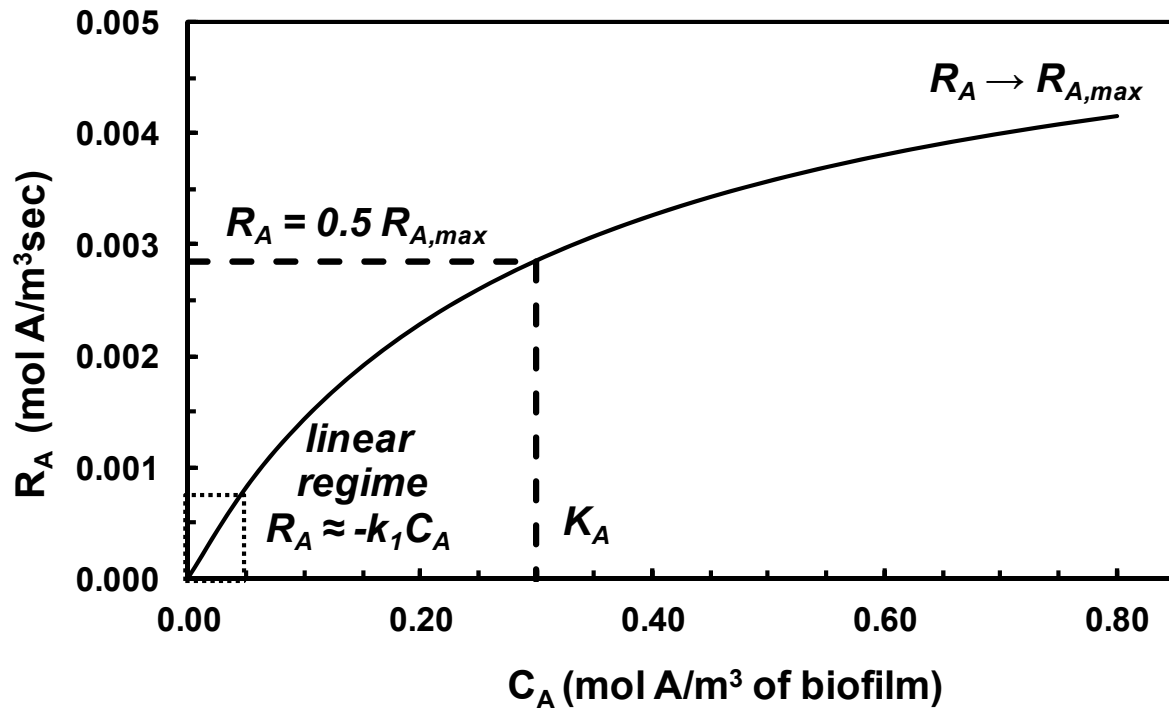
General Differential Equation for Mass Transfer (N_A form)

$$-\nabla N_A + R_A = \frac{\partial C_A}{\partial t}$$

Invoke assumptions

$$-\frac{dN_{A,z}}{dz} + R_A = 0 \quad (N_{A,z} \text{ is not constant along z})$$

Flux Equation

$$N_A = -D_{AB} \nabla C_A + \frac{C_A}{C}(N_A + N_B)$$

Invoke assumptions

$$N_{A,z} = -D_{AB}\frac{dC_A}{dz} + \frac{C_A}{C}\left(N_{A,z} + N_{B,z}\right) = -D_{AB}\frac{dC_A}{dz} + \frac{C_A}{C}\left(N_{A,z} + 0\right) \cong -D_{AB}\frac{dC_A}{dz}$$

Note $\nabla N_A \neq 0$. Therefore, must combine differential equation for mass transfer with flux equation, get concentration profile $C_A(z)$, then differentiate concentration profile back again to get $N_{A,z}$!

$$-\frac{d}{dz}\left(-D_{AB}\frac{dC_A}{dz}\right) + R_A = 0$$

Add in the first-order reaction $R_A = -k_1 C_A$

$$D_{AB}\frac{d^2 C_A}{dz^2} - k_1 C_A = 0 \quad \text{OR} \quad \frac{d^2 C_A}{dz^2} - \frac{k_1}{D_{AB}}C_A = 0$$

Boundary Conditions

$$z = \delta, \frac{dC_A}{dz} = 0 \qquad (N_{A,z} = 0 \text{ at impermeable wall; biofilm is immobilized on}$$

nonporous solid surface)

$$z = 0, C_A = C_{As} = C_{Ao} \qquad \text{(constant surface concentration in biofilm; see}$$

assumptions)

Solution to Differential Equations

General solution to second-order ordinary differential equation (a.k.a. MTH 256)

$$C_A(z) = a_1 \cosh\left(z\sqrt{k_1/D_{AB}}\right) + a_2 \sinh\left(z\sqrt{k_1/D_{AB}}\right)$$

where a_1 and a_2 are integration constants. Apply BC to get a_1 and a_2

at $z = 0$ (surface of biofilm exposed to waste water)

$$C_{As} = C_{Ao} = a_1 \cosh(0) + a_2 \sinh(0) \quad \therefore a_1 = C_{Ao}$$

at $z = \delta$ (wall)

$$\frac{dC_A}{dz} = \left(\sqrt{k_1/D_{AB}}\right)\left[C_{Ao} \sinh\left(z\sqrt{k_1/D_{AB}}\right) + a_2 \cosh\left(z\sqrt{k_1/D_{AB}}\right)\right]$$

$$\left.\frac{dC_A}{dz}\right|_{z=\delta} = 0 = \left(\sqrt{k_1/D_{AB}}\right)\left[C_{Ao} \sinh\left(\delta\sqrt{k_1/D_{AB}}\right) + a_2 \cosh\left(\delta\sqrt{k_1/D_{AB}}\right)\right]$$

$$\therefore a_2 = -C_{Ao} \tanh\left(\delta\sqrt{k_1/D_{AB}}\right)$$

FYI

$$\left.\frac{dC_A}{dz}\right|_{z=0} = -C_{Ao}\left(\sqrt{k_1/D_{AB}}\right)\left[\tanh\left(\delta\sqrt{k_1/D_{AB}}\right)\right]$$

Finally (after a few hyperbolic trig identities) the concentration profile $C_A(z)$ in the biofilm is

$$C_A(z) = \frac{C_{Ao} \cosh\left((\delta - z)\sqrt{k_1/D_{AB}}\right)}{\cosh\left(\delta\sqrt{k_1/D_{AB}}\right)}$$

Flux N_A into the biofilm at $z = 0$ ($N_{A,z}$ is not constant along z)

$$N_A|_{z=0} = -D_{AB}\left.\frac{dC_A}{dz}\right|_{z=0} = +\frac{D_{AB}\, c_{Ao}}{\delta}\left(\delta\sqrt{k_1/D_{AB}}\right)\tanh\left(\delta\sqrt{k_1/D_{AB}}\right)$$

Let $\phi = \delta\sqrt{k_1 / D_{AB}}$ the "Theile Modulus" (dimensionless group)

If $\phi < 0.1$ (i.e. ϕ is small) then $\tanh(\phi) \approx \phi$ and

$$N_A\big|_{z=0} = \frac{D_{AB}\, c_{Ao}}{\delta}\left(\delta\sqrt{k_1 / D_{AB}}\right)^2 \qquad \text{"reaction control"}$$
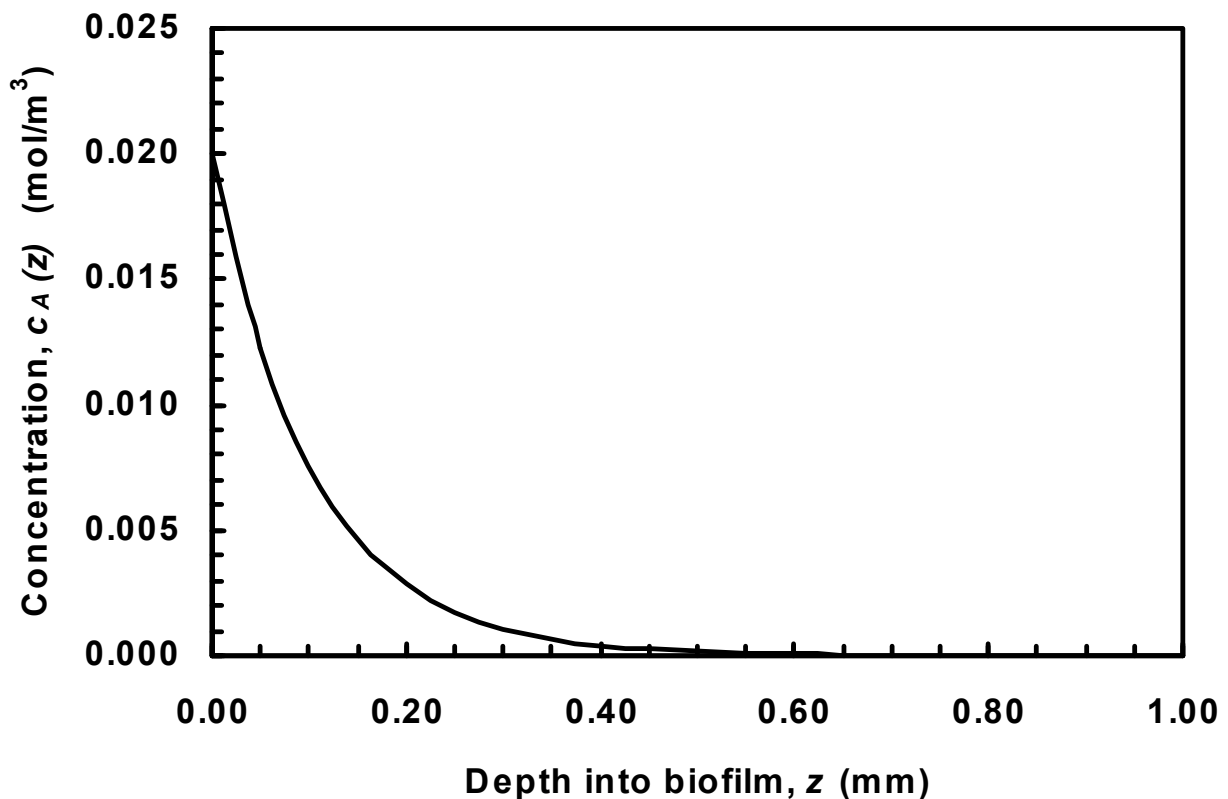
If $\phi > 5$ (i.e. ϕ is large) then $\tanh(\phi) \approx 1$ and

$$N_A\big|_{z=0} = \frac{D_{AB}\, c_{Ao}}{\delta}\left(\delta\sqrt{k_1 / D_{AB}}\right) \qquad \text{"diffusion control"}$$

Model Predictions for $C_A(z)$

D_{AB} $= 2.0 \cdot 10^{-10}$ m^2/sec (A = phenol in biofilm B)
C_{Ao} $= 0.02$ gmole A/m^3
k_1 $= 0.019$ sec^{-1}
δ $= 2$ mm (0.002 m thickness of biofilm)

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Effect of ϕ on $C_A(z)$

D_{AB} = 2.0 · 10^{-10} m²/sec (A = phenol in biofilm B)
C_{Ao} = 0.02 gmole A/m³
k_1 = 0.019 sec⁻¹
δ = 2 mm (0.002 m thickness of biofilm)
ϕ = 19.5

D_{AB} = 2.0 · 10^{-10} m²/sec (A = phenol in biofilm B)
C_{Ao} = 0.02 gmole A/m³
k_1 = 0.0038 sec⁻¹
δ = 2 mm (0.002 m thickness of biofilm)
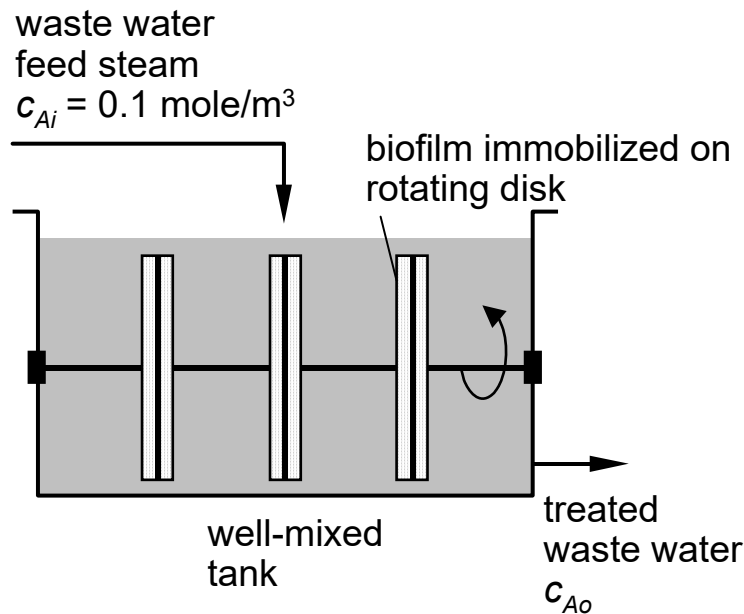ϕ = 8.7
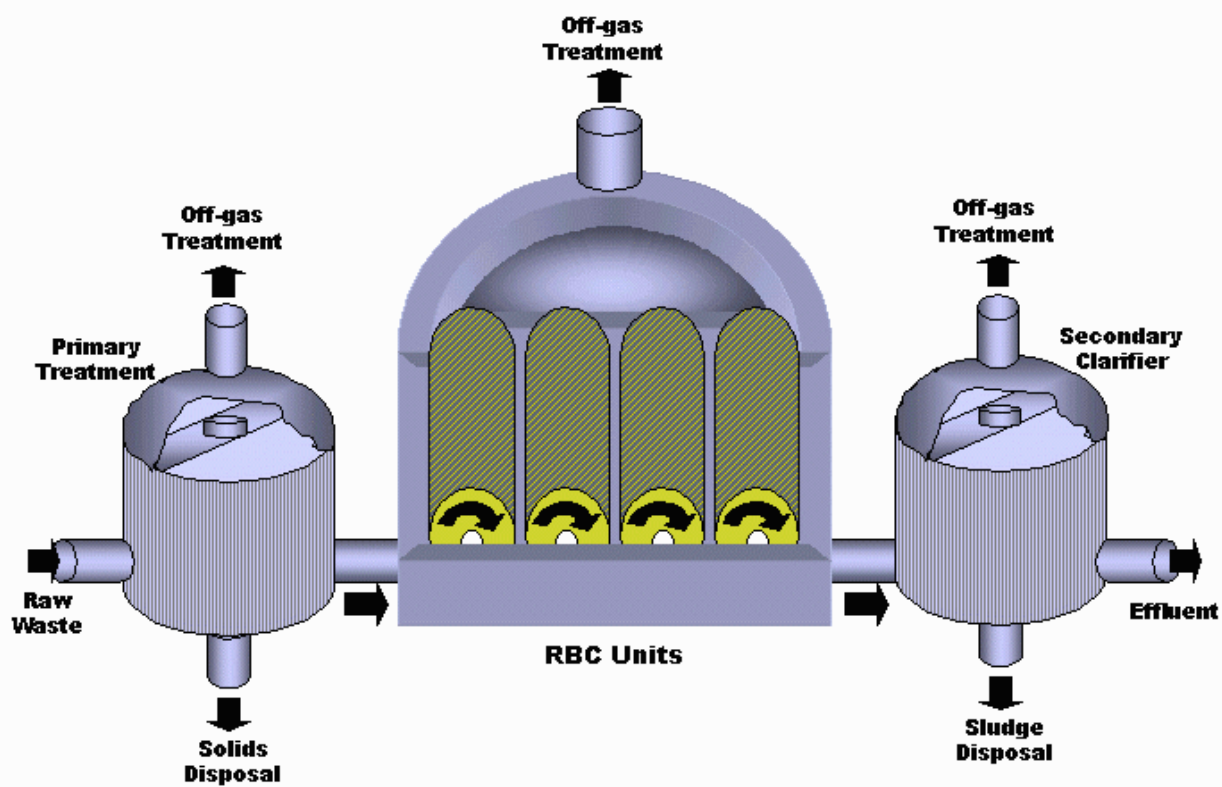
$$\phi = \delta\sqrt{\frac{k_1}{D_{AB}}}$$
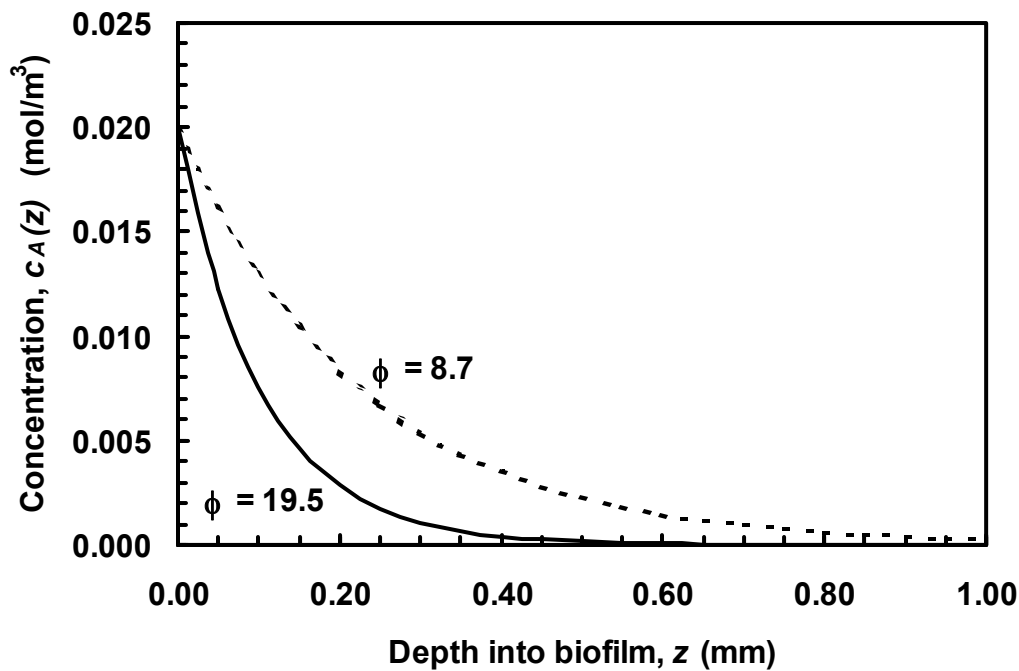
Extension of the Biofilm Process: Design of a Wastewater Treatment System

Problem statement. Consider the "rotating disk" process unit shown below for the treatment of phenol (species A) in waste water. The biofilm contains a microorganism rich in the enzyme peroxidase that oxidatively degrades phenol. It is desired to treat 0.1 m^3 per hour of wastewater containing 0.1 gmole/m^3 of the toxic substance phenol.

If the biofilm thickness is 2.0 mm (0.002 m), what is the required surface area (S) of the biofilm necessary to achieve the desired outlet concentration of 0.02 mole/m^3? The reaction kinetic and mass transport properties for the biofilm are: $K_A = 0.3$ gmole/m^3, $R_{A,max} = 5.7 \cdot 10^{-3}$ mol/m$^3 \cdot$ sec, and $D_{AB} = 2.0 \cdot 10^{-10}$ m^2/sec at the process temperature of 25 °C.

waste water
feed steam
$c_{Ai} = 0.1$ mole/m³

biofilm immobilized on
rotating disk

treated
waste water
c_{Ao}

well-mixed
tank

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Assumptions on process unit

- Steady state operation
- Well mixed holding tank (outlet conc. of A = conc. of A in liquid held in tank)

Material balance on process unit (species A)

IN - OUT + GEN = ACC

at Steady State operation

CONSUMPTION = IN - OUT

$$\begin{pmatrix} rate\ of\ phenol \\ degraded \end{pmatrix} = \begin{pmatrix} rate\ of\ phenol \\ added\ to\ process \end{pmatrix} - \begin{pmatrix} rate\ of\ phenol \\ exiting\ process \end{pmatrix}$$

or

$$W_A = v_i c_{Ai} - v_o c_{Ao} \cong v_o(c_{Ai} - c_{Ao}) = \frac{0.1\ m^3}{hr}(0.1 - 0.02)\frac{gmole}{m^3} = 8.0 \cdot 10^{-3} \frac{gmole}{hr}$$

v_i = inlet volumetric flowrate of waste water (e.g. m³/hr)

v_o = outlet volumetric flowrate of water water ($v_o = v_i$ if liquid, and dilute)

Total rate of degradation of A by biofilm:

$$W_A = S \cdot N_A\big|_{z=0}$$

S = *required* surface area of the biofilm to satisfy process unit material balance

Estimate N_A at z = 0 (flux of A into the biofilm)

$$N_A\big|_{z=0} = +\frac{D_{AB}\,c_{Ao}}{\delta}\left(\delta\sqrt{k_1/D_{AB}}\right)\tanh\left(\delta\sqrt{k_1/D_{AB}}\right)$$

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First, get k_1

$$k_1 = \frac{R_{A,\max}}{K_A} = \frac{5.7 \cdot 10^{-3} \frac{mole}{m^3 \cdot sec}}{0.3 \frac{mole}{m^3}} = 1.9 \cdot 10^{-2} \ sec^{-1}$$

Now get the dimensionless parameter

$$\delta \sqrt{\frac{k_1}{D_{AB}}} = 0.002 \, m \sqrt{\frac{1.9 \cdot 10^{-2} \frac{1}{sec}}{2 \cdot 10^{-10} \frac{m^2}{sec}}} = 19.49$$

Notes: in chemical engineering, ϕ is the "Thiele Modulus"
                    if $\phi \gg 1$, then diffusion has a strong effect on the reaction process

Finally

$$N_{Az} = \frac{\left(2 \cdot 10^{-10} \frac{m^2}{s}\right)\left(0.02 \frac{gmole}{m^3}\right)}{0.002 \, m} (19.49) \tanh(19.49) = 3.9 \cdot 10^{-8} \frac{mole}{m^2 \cdot s}$$

Now back out S, the required biofilm surface area to get the unit to work

$$S = \frac{W_A}{N_{Az}} = \frac{8.0 \cdot 10^{-3} \frac{gmole}{hr} \frac{1 \, h}{3600 \, sec}}{3.9 \cdot 10^{-8} \frac{gmole}{m^2 \cdot sec}} = 57.0 \, m^2$$