CHAPTER 25: DIFFERENTIAL EQUATIONS OF MASS TRANSFER

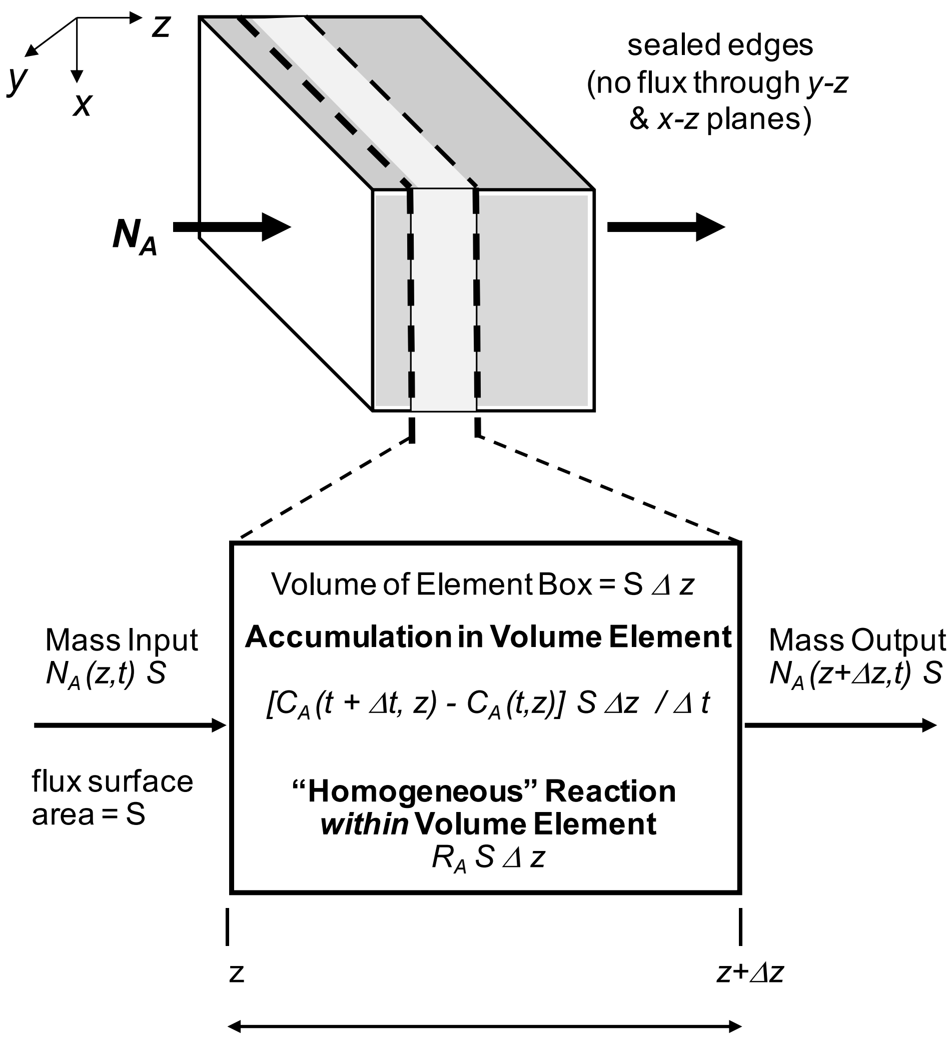
25.1 The Differential Equation for Mass Transfer

Model Development

Mass balance for species *"A"* on a rectangular volume element (Shell Balance)

$$\begin{bmatrix} rate\ of\ \ "A"\ into \\ volume\ element \end{bmatrix} - \begin{bmatrix} rate\ of\ \ "A"\ out\ of \\ volume\ element \end{bmatrix} + \begin{bmatrix} rate\ of\ \ generation\ of\ \ "A" \\ within\ volume\ element \end{bmatrix}$$
$$= \begin{bmatrix} rate\ of\ \ accumulation\ of\ \ "A" \\ within\ volume\ element \end{bmatrix}$$

the units of each term must be “moles A/time”

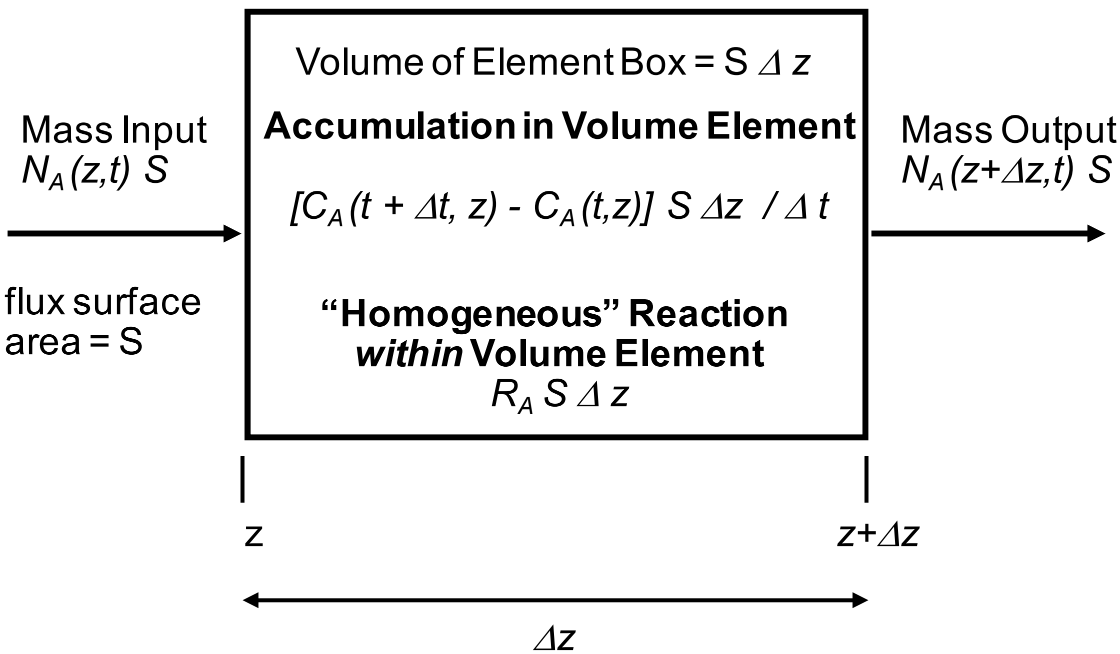


Consider the following conditions and assumptions:

- rectangular coordinates
- flux for species A directed along diffusion path length z
- fixed cross-sectional area "S"

IN - OUT + GENERATION = ACCUMATION (species A, moles A/time)

$$N_A(t,z)\,S \;-\; N_A(t,z+\Delta z)\,S \;+\; R_A\,S\,\Delta z \;=\; \frac{\left[C_A(t+\Delta t,z) - C_A(t,z)\right] S\,\Delta z}{\Delta t}$$



Divide by SΔ z, rearrange

$$-\left[\frac{N_A(t,z+\Delta z) \;-\; N_A(t,z)}{\Delta z}\right] + R_A \;=\; \frac{\left[C_A(t+\Delta t,z) - C_A(t,z)\right]}{\Delta t}$$

Take limit $\Delta z \rightarrow 0$ and $\Delta t \rightarrow 0$

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

In general (*x,y*, and *z*)

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

where "∇" is the Gradient Operator

"∇N_A" is the net flux gradient of A through the control volume, i.e. the **IN-OUT** term (mole A/m^3-sec)

"R_A" is the production rate of "*A*" within the control volume, i.e. the homogeneous reaction (**GENERATION**) term (mole A/m^3-sec)

"$\partial C_A/\partial t$" is the **ACCUMULATION** term for A within the control volume (mole A/m^3-sec)

If the diffusion coefficient D_{AB} is constant, then

$$D_{AB}\nabla^2 C_A - \nabla\cdot(C_A V) + R_A = \frac{\partial C_A}{\partial t}$$

If D_{AB} and total system density ρ is also constant, then

$$D_{AB}\nabla^2 C_A - \mathrm{v}\cdot\nabla C_A + \mathrm{R_A} = \frac{\partial \mathrm{C_A}}{\partial \mathrm{t}}$$

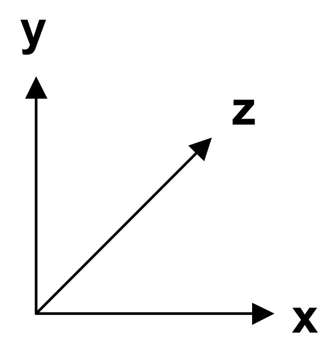
where V is the molar average velocity and $\boldsymbol{v}$ is the mass average velocity

Mass Conservation Equations in Standard Coordinate Systems (The Differential Equation of Mass Transfer)

Rectangular Coordinates (x, y, z)

$$-\left[\frac{\partial N_{A,x}}{\partial x}+\frac{\partial N_{A,y}}{\partial y}+\frac{\partial N_{A,z}}{\partial z}\right]+R_A=\frac{\partial C_A}{\partial t}$$

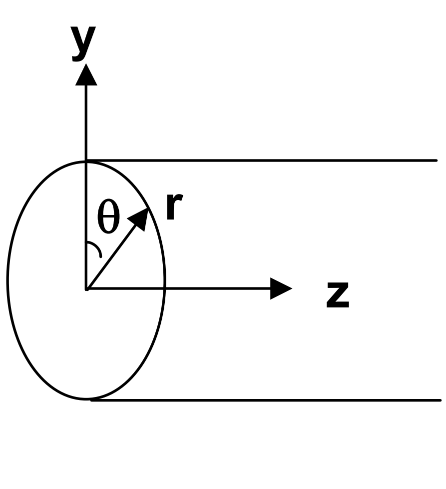
$$D_{AB}\left[\frac{\partial^2 C_A}{\partial x^2}+\frac{\partial^2 C_A}{\partial y^2}+\frac{\partial^2 C_A}{\partial z^2}\right]-\left[v_x\frac{\partial C_A}{\partial x}+v_y\frac{\partial C_A}{\partial y}+v_z\frac{\partial C_A}{\partial z}\right]+R_A=\frac{\partial C_A}{\partial t}$$



Cylindrical Coordinates (r, z only)

$$-\left[\frac{1}{r}\frac{\partial}{\partial r}\left(rN_{A,r}\right)+\frac{\partial N_{A,z}}{\partial z}\right]+R_A=\frac{\partial C_A}{\partial t}$$

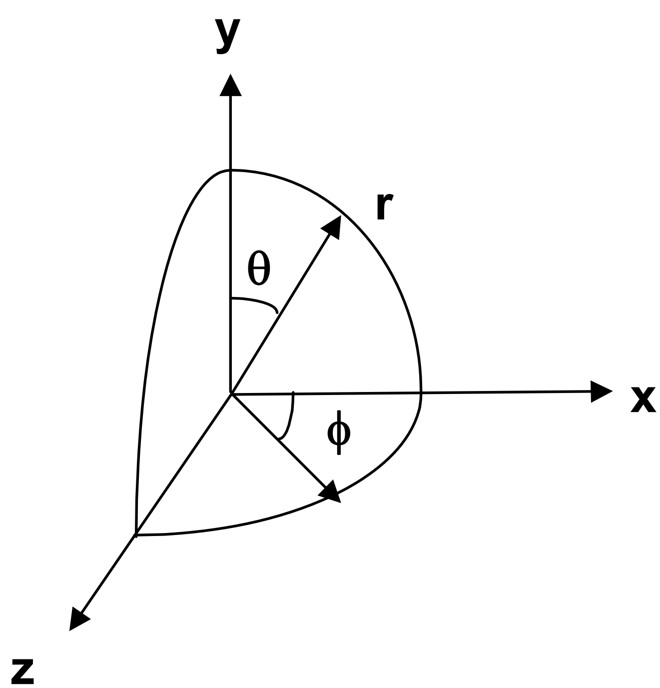
$$D_{AB}\left[\frac{\partial^2 C_A}{\partial r^2}+\frac{1}{r}\frac{\partial C_{A,r}}{\partial r}+\frac{\partial^2 C_{A,z}}{\partial z^2}\right]-\left[v_r\frac{\partial C_A}{\partial r}+v_z\frac{\partial C_A}{\partial z}\right]+R_A=\frac{\partial C_A}{\partial t}$$



Spherical Coordinates (r only)

$$-\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 N_{A,r}\right)\right] + R_A = \frac{\partial C_A}{\partial t}$$

$$D_{AB}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C_A}{\partial r}\right)\right] - v_r \frac{\partial C_A}{\partial r} + R_A = \frac{\partial C_A}{\partial t}$$



Definitions of the Laplacian Operator ∇^2 and Gradient ∇

Rectangular Coordinates

$$\nabla N_A = \frac{\partial N_{A,x}}{\partial x} + \frac{\partial N_{A,y}}{\partial y} + \frac{\partial N_{A,z}}{\partial z}$$

$$\nabla^2 C_A = \frac{\partial^2 C_A}{\partial x^2} + \frac{\partial^2 C_A}{\partial y^2} + \frac{\partial^2 C_A}{\partial z^2}$$

Cylindrical Coordinates

$$\nabla N_A = \frac{1}{r}\frac{\partial}{\partial r}(r\, N_{A,r}) + \frac{1}{r}\frac{\partial N_{A,\theta}}{\partial \theta} + \frac{\partial N_{A,z}}{\partial z}$$

$$\nabla^2 C_A = \frac{\partial^2 C_A}{\partial r^2} + \frac{1}{r}\frac{\partial C_{A,r}}{\partial r} + \frac{1}{r^2}\frac{\partial^2 C_{A,\theta}}{\partial \theta^2} + \frac{\partial^2 C_{A,z}}{\partial z^2}$$

Spherical Coordinates

$$\nabla N_A = \frac{1}{r^2}\frac{\partial}{\partial r}(r^2\, N_{A,r}) + \frac{1}{r\sin\theta}\frac{\partial}{\partial \theta}(N_{A,\theta}\sin\theta) + \frac{1}{r\sin\theta}\frac{\partial N_{A,\phi}}{\partial \phi}$$

$$\nabla^2 C_A = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial C_A}{\partial r}\right] + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left[\sin\theta\frac{\partial C_A}{\partial \theta}\right] + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 C_A}{\partial \phi^2}$$

Differential operations for the Gradient of a scalar quantity (e.g. concentration C_A) are given in Appendix B of W^3-R (5^{th}) or WRF (6^{th}, 7^{th} Ed.)

25.2 Special Forms of the Differential Mass Transfer Equation

Consider Three Common Levels of Simplification (binary mixture of A and B)

1. No bulk-phase reaction ($R_A = 0$) AND no net bulk flow ($v = 0$ or $N_A + N_B = 0$)

Differential Equation for Mass Transfer (N_A form)

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

Differential Equation for Mass Transfer (C_A form)

$$D_{AB}\nabla^2 C_A = \frac{\partial C_A}{\partial t}$$

2. One-dimensional (1-D) flux along rectilinear coordinate z constant total system density

Flux Equation

$$N_A = -D_{AB}\frac{\partial C_A}{\partial z} + y_A(N_A + N_B) \text{ OR}$$

$$N_A = -D_{AB}\frac{\partial C_A}{\partial z} + C_A V_z$$

Differential Equation for Mass Transfer (N_A form)

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

Differential Equation for Mass Transfer (C_A form)

$$D_{AB}\frac{\partial^2 C_A}{\partial z^2} - v_z\frac{\partial C_A}{\partial z} + R_A = \frac{\partial C_A}{\partial t}$$

3. No bulk phase reaction ($R_A = 0$) AND no net bulk flow ($v_z = 0$ or $N_A + N_B = 0$) AND one-dimensional flux along "z"

Flux Equation

$$N_A = -D_{AB}\frac{\partial C_A}{\partial z}$$

Differential Equation for Mass Transfer (N_A form)

$$-\frac{\partial N_A}{\partial z} = \frac{\partial C_A}{\partial t}$$

Differential Equation for Mass Transfer (C_A form)

$$D_{AB}\frac{\partial^2 C_A}{\partial z^2} = \frac{\partial C_A}{\partial t}$$

The above equation is commonly called

"Fick's Second Law of Diffusion"

25.3 Commonly Encountered Boundary Conditions

Number of Boundary and Initial Conditions

- Boundary conditions (BC) must be specified before the differential equation for mass transfer can be solved for flux N_A or the concentration profile C_A

- For unsteady state processes, initial condition(s) (IC) must also be specified

- For each order of differentiation on C_A with respect to a given coordinate (position or time), you must have one boundary or initial condition

For example, consider the differential equation for mass transfer in cylindrical coordinates (r and z direction)

$$D_{AB}\left[\frac{\partial^2 C_A}{\partial r^2}+\frac{1}{r}\frac{\partial C_{A,r}}{\partial r}+\frac{\partial^2 C_{A,z}}{\partial z^2}\right]-\left[v_r\frac{\partial C_A}{\partial r}+v_z\frac{\partial C_A}{\partial z}\right]+R_A=\frac{\partial C_A}{\partial t}$$

Specify 2 BCs for second-order C_A term in co-ordinate ***z*** (e.g. at z = 0 and $z = L$)
Specify 2 BCs for second-order C_A term in co-ordinate ***r*** (e.g. $r = 0$ and $r = R$)
Specify 1 IC for first-order C_A term with respect to time ***t*** (e.g. $t = 0$)

Total: 4 BC and 1 IC

Commonly Encountered Boundary Conditions

Known Concentration at a Boundary (Type I Boundary Condition)

e.g. for 1-D flux through a slab (z direction):

z = 0 (surface of slab) $C_A(z,t) = C_A(0,t) = C_{As}$

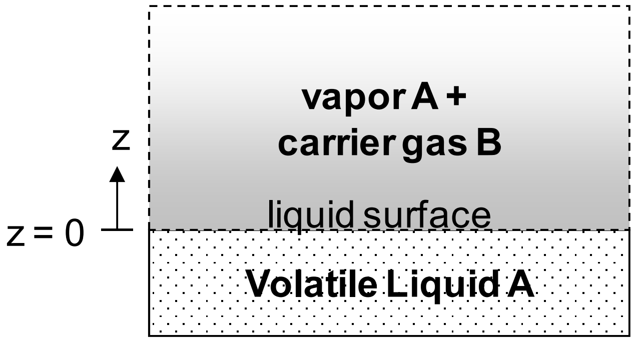
Typical physical situations include:

- known vapor pressure of a liquid surface in contact with a gas
- known solubility of a gas within a liquid or solid
- known solubility of a liquid in contact with a solid surface

known concentration at a chemically reacting surface (for diffusion-limited surface reactions, $C_{As} = 0$ if A is the stoichiometrically-limiting reagent)

Known Concentration at a Boundary (Type I Boundary Condition)cont.

Examples Where Equilibrium Constraints Set the Boundary Concentration

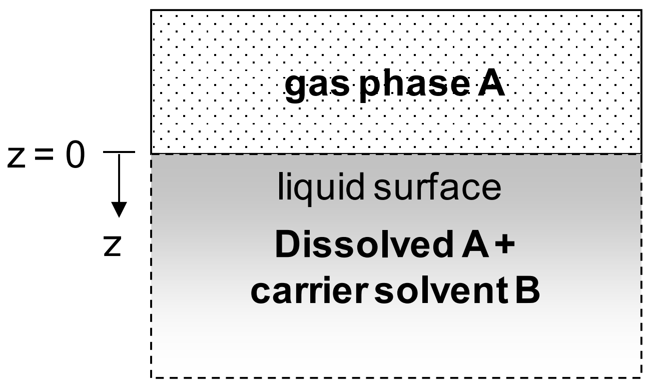


Vapor pressure of A in gas at surface

$$z = 0 \quad p_A = p_{As} = P_A$$

Conc. of A in gas at surface

$$C_{As} = \frac{p_{As}}{RT}$$



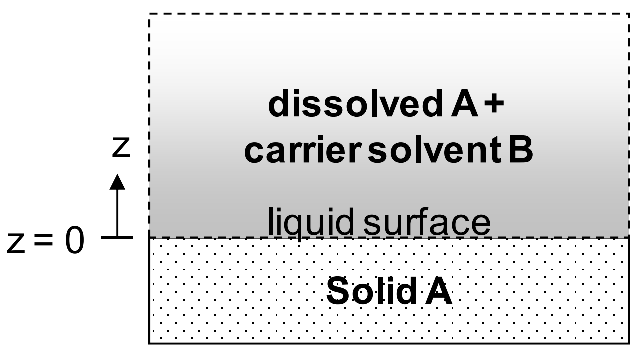
Partial pressure of A in gas at surface

$$z = 0 \quad p_A = p_{As}$$

Conc. of A dissolved in liq. at surface

$$C_{As} = \frac{p_{As}}{H}$$

H = Henry's law constant for dissolution of gas phase solute A in carrier solvent B



Solubility limit of A in liquid at surface

$$z = 0 \quad C_A = C_{As} = C_A^*$$

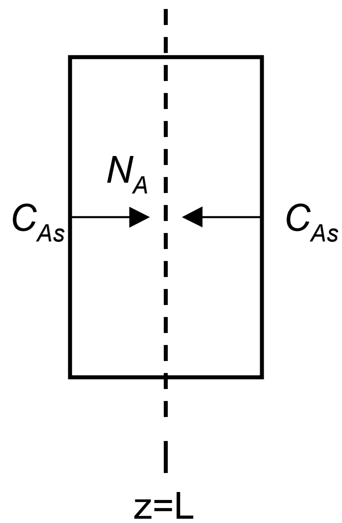
Known Flux at a Boundary (Type II Boundary Condition)

e.g. for 1-D flux through a slab (z direction):

Case 1 z = L (center of slab where both sides are available for flux)

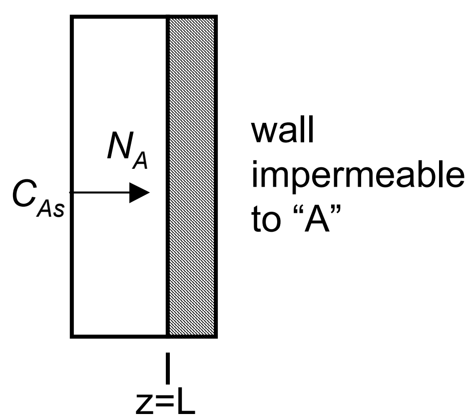
From symmetry considerations

$$\textit{net flux } N_A(L,t) = 0 \quad \therefore \frac{\partial C_A(L,t)}{\partial z} = 0$$



Case 2 z = L (one side of wall impermeable to "A", $N_A = 0$)

$$\textit{flux } N_A(L,t) = 0 \quad \therefore \frac{\partial C_A(L,t)}{\partial z} = 0$$



25.4 Steps for Modeling Processes Involving Molecular Diffusion

1. Draw a picture of the physical system undergoing mass transfer

   - Identify boundary conditions on the picture
   - Identify source and sink on the picture
   - Identify coordinate system on the picture

2. Make a list of assumptions particular to your physical system

   To get started, always ask yourself these three questions:

   - Steady state process vs. unsteady state process?
   - No homogeneous reaction in control volume vs. homogeneous reaction in control volume?
   - One-dimensional (1-D) flux vs. flux in more than one dimension?

3. Pick a coordinate system, then develop and simplify the Differential Equation for Mass Transfer and the Flux Equation based on your assumptions

4. Specify the Boundary Conditions and Initial Conditions

5. Solve the Differential Equation for Mass Transfer based on the BC and IC to arrive at an algebraic equation for concentration profile C_A or flux N_A

6. Plug in the numbers to your final model equation developed in Step 5 above.

25.4 Asides

Reduction of $\nabla N_A = 0$

If $\nabla N_A = 0$ (i.e. steady state, $R_A = 0$)

For one-dimensional flux, " $S{\cdot}N_A$ " is constant along the diffusion coordinate (continuity requirement for diffusion at steady state, $R_A = 0$)

Rectilinear coordinates (along z)

$$\frac{dN_{A,z}}{dz} = 0 \quad \therefore S(z)\cdot\frac{dN_{A,z}}{dz} = \frac{d}{dz}\left(S(z)\cdot N_{A,z}\right) = 0$$

$S(z){\cdot}N_{A,z}$ is constant along z *(surface area at position z)*

Cylindrical coordinates (along r)

$$\nabla N_A = \frac{1}{r}\frac{d}{dr}\left(r\cdot N_{A,r}\right) = 0 \quad \therefore \quad \frac{d}{dr}\left(r\cdot N_{A,r}\right) = 0$$

$r\cdot N_{A,r}$ or $S(r){\cdot}N_{A,r}$ is constant along r

$S(r) = 2\pi\, r\, L$ (surface area of cylinder at position r with length L)

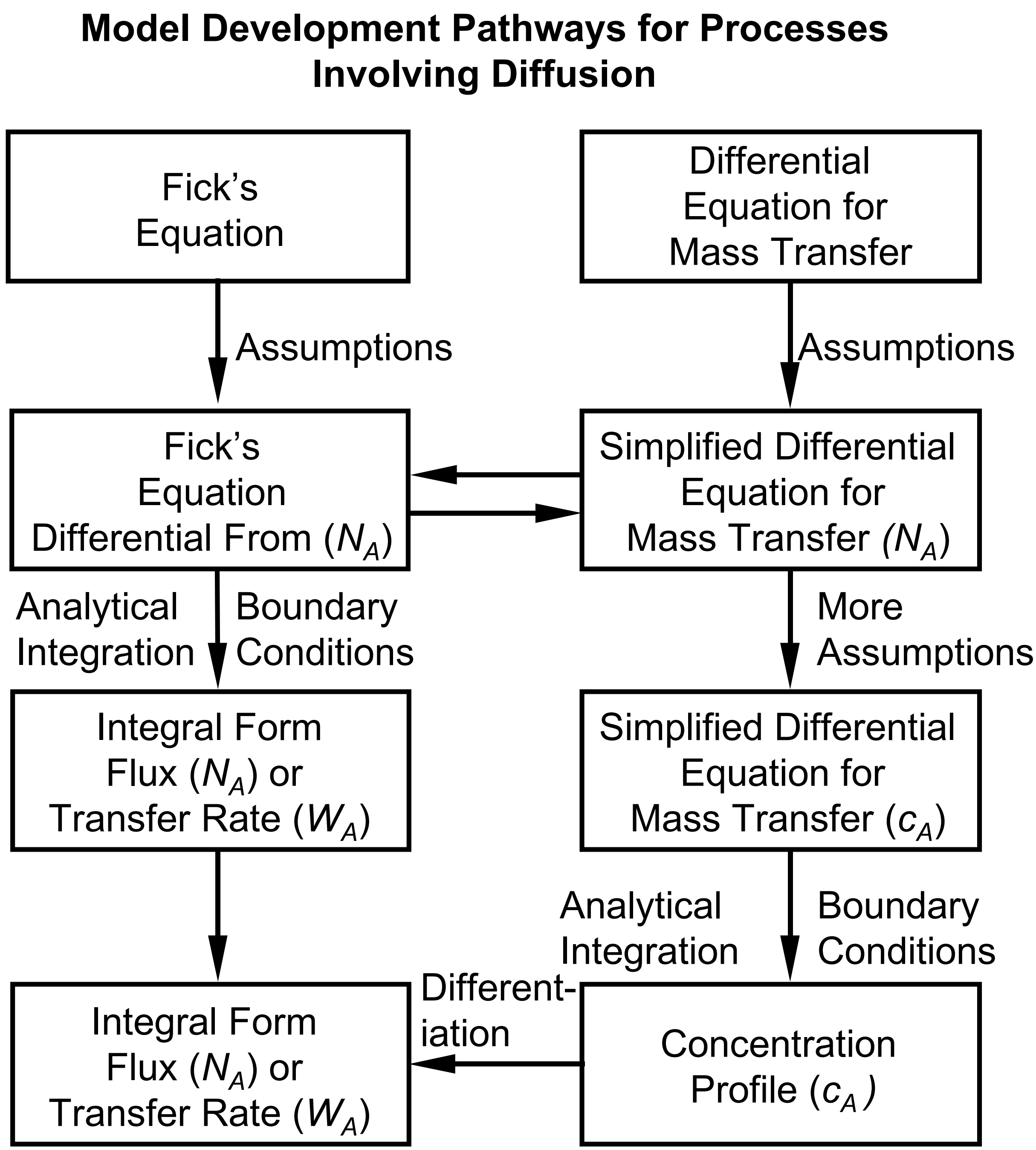
Spherical coordinates (along r)

$$\nabla N_A = \frac{1}{r^2}\frac{d}{dr}\left(r^2\cdot N_{A,r}\right) = 0 \quad \therefore \quad \frac{d}{dr}\left(r^2\cdot N_{A,r}\right) = 0$$

$r^2\cdot N_{A,r}$ or $S(r){\cdot}N_{A,r}$ is constant along r

$S(r) = 4\,\pi\, r^2$ (surface area of sphere at position r)

25.4 Asides

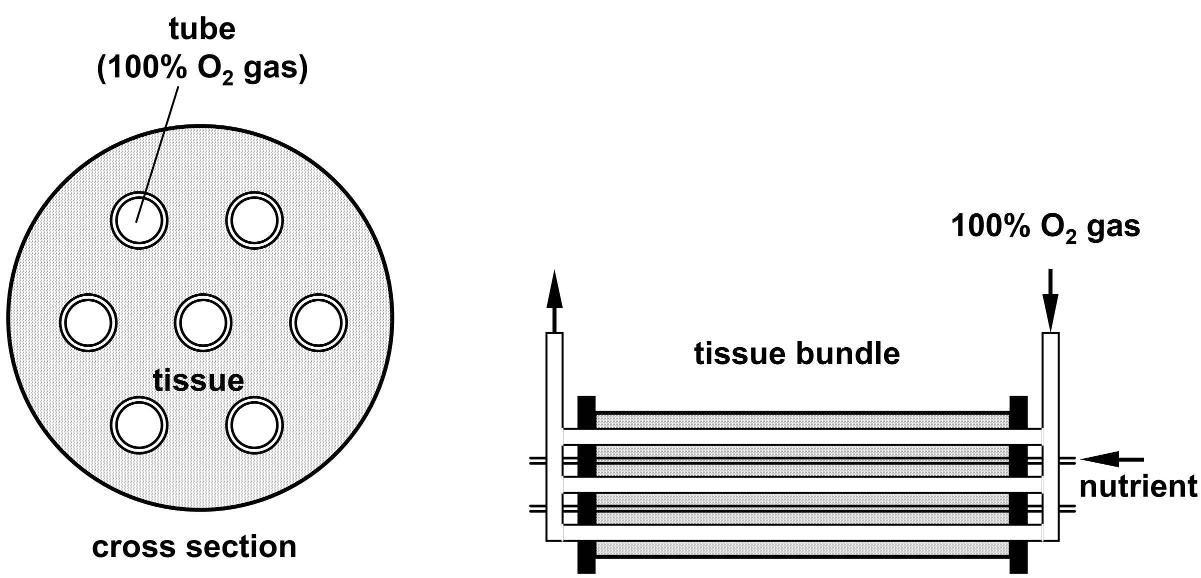


Model Development Pathways for Processes Involving Diffusion
Fick's Equation
Differential Equation for Mass Transfer
Assumptions
Assumptions
Fick's Equation Differential From (N_A)
Simplified Differential Equation for Mass Transfer (N_A)
Analytical Integration
Boundary Conditions
More Assumptions
Integral Form Flux (N_A) or Transfer Rate (W_A)
Simplified Differential Equation for Mass Transfer (c_A)
Analytical Integration
Boundary Conditions
Different-iation
Integral Form Flux (N_A) or Transfer Rate (W_A)
Concentration Profile (c_A)

Topic 25.4 Example: Engineered Tissue Bundle

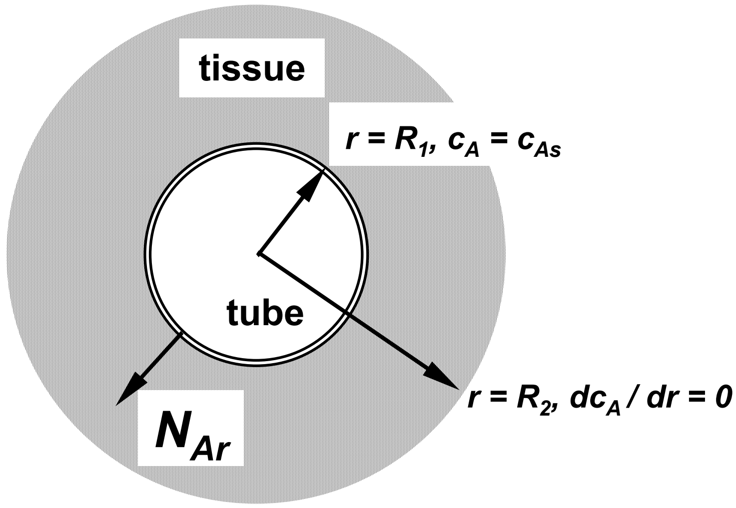
Problem statement. An emerging area of biotechnology called "tissue engineering" develops new processes to grow organized living tissues of human or animal origin. A typical configuration is the engineered tissue bundle. Engineered tissue bundles have several potential biomedical applications, including the production of replacement body tissue for transplantation into the human body, or in the future, may serve as artificial organs for direct implantation into the human body.

Living tissues require oxygen to stay alive. The mass transport of oxygen (O_2) to the tissue is an important design consideration. One potential system is schematically illustrated below:



Thin tubes pass longitudinally through the tissue bundle. The tubes serve as a "scaffold" for supporting the living tissue matrix and supply oxygen and nutrients to the tissue at the same time.

Let us simplify this situation down to a single O_2 delivery tube with tissue surrounding it, as illustrated below.



simplifed cross section

Pure oxygen (O_2) gas flows through the tube. The tube wall is extremely permeable to O_2, and the O_2 partial pressure through the porous tube wall can be taken as the O_2 partial pressure inside the tube.

Oxygen is only sparingly soluble in the tissue, which is mostly water. The concentration of dissolved O_2 at $r = R_1$, is

$$c_{As} = \frac{p_A}{H}$$

where H is the Henry' law constant for the dissolution of O_2 in living tissue at the process temperature, and p_A is the partial pressure of O_2 in the tube.

The dissolved O_2 diffuses through the tissue and is metabolically consumed. The metabolic consumption rate "m" of dissolved O_2 is described by a "zero order" kinetic rate equation of the form

$$R_A = -m \quad \left(\frac{\text{mol}\,\text{O}_2}{\text{cm}^3\text{tissue} - \text{sec}} \right)$$

If the dissolved oxygen concentration in the tissue gets too low, the tissue can be starved for oxygen. Therefore, it is important to know the radial concentration profile, $c_A(r)$ of dissolved O_2.

Determine:

(a) The differential equation for dissolved oxygen profile $c_A(r)$
(b) The integral equation for dissolved oxygen profile $c_A(r)$
(c) An equation to predict flux N_A

Model Development & Analysis

Assumptions and Conditions

The physical system: tissue surrounding the tube (A = dissolved O_2)

Coordinate system: cylindrical geometry

SOURCE for O_2 mass transfer: the pure O_2 gas inside the tube

SINK for O_2 mass transfer: metabolic consumption of dissolved oxygen by the tissue.

1. The O_2 transfer process is at steady state (constant SOURCE and SINK for O_2)

2. If the O_2 partial pressure p_A is maintained constant inside the tube along longitudinal coordinate z, then the flux of oxygen through the tissue is one-dimensional along the radial (r) direction, ***i.e. 1-D flux along r***

3. Consumption of dissolved O_2 within the tissue is a zero order process,

   i.e. $R_A = -m$ if $C_A > 0$, $R_A = 0$ if $C_A = 0$

4. Tissue remains viable and maintains constant physical properties

5. The tissue is stationary, and the dissolved O_2 concentration is dilute

6. At $r = R_1$, the tube material is thin and highly permeable to O_2 so that the dissolved O_2 concentration in the tissue is in equilibrium with the O_2 partial pressure in the tube

7. At $r = R_2$, there is no net flux of O_2

8. Constant system parameters: D_{AB}, R_1, R_2, C_{As}

Simplify General Differential Equation for Mass Transfer and Flux Equation

General differential equation for mass transfer in cylindrical coordinates

$$-\left(\frac{1}{r}\frac{\partial}{\partial r}\left(rN_{Ar}\right)+\frac{1}{r}\frac{\partial N_{A\theta}}{\partial \theta}+\frac{\partial N_{Az}}{\partial z}\right)+R_A=\frac{\partial c_A}{\partial t}$$

For steady-state one-dimensional flux along the r-direction, the general equation for mass transfer reduces to

$$-\frac{1}{r}\frac{\partial}{\partial r}\left(rN_{Ar}\right)+R_A=0$$

For a one-dimensional system, the partial derivatives can be replaced with ordinary derivatives.

Shell Balance

Alternatively, we can perform a material balance for dissolved O_2 on the differential element of volume $2\pi Lr\Delta r$

Specifically, for steady-state one-dimensional flux along the r-direction with a homogeneous reaction R_A within the differential volume element, we have

$$2\pi L\, rN_{Ar}\big|_{r=r}-2\pi\, L\, r\, N_{Ar}\big|_{r=r+\Delta r}+R_A\cdot 2\pi L\; r\cdot\Delta r=0$$

Diving through by $2\pi L\Delta r$, and rearranging, we get

$$-\left(\frac{rN_{Ar}\big|_{r=r+\Delta r}-r\,N_{Ar}\big|_{r=r}}{\Delta r}\right)+R_A\; r=0$$

Finally, taking the limit as $\Delta r\rightarrow 0$ yields

$$-\frac{1}{r}\frac{d}{dr}\left(rN_{Ar}\right)+R_A=0$$

Flux Equation

For one-dimensional flux of dissolved O_2 through the stagnant tissue in cylindrical coordinates along the *r*-direction, Fick's equation reduces to

$$N_{Ar} = -D_{AB}\frac{dc_A}{dr} + \frac{c_A}{c}(N_{Ar}) \cong -D_{AB}\frac{dc_A}{dr}$$

because O_2 is only sparingly soluble in the tissue so that $c_A << c$, where c is the total molar concentration of the tissue, which approximates the molar concentration of water.

In cylindrical geometry, N_{Ar} is not constant along diffusion path r, because (a) cross-sectional area for flux is increasing along increasing r, and (b) the R_A term is present. As a result, the flux equation cannot be integrated, as was the case in Example 1. It is now necessary to combine Fick's equation and the differential equation for mass transfer in order to get the concentration profile

$$-\frac{1}{r}\frac{d}{dr}\left(-rD_{AB}\frac{dc_A}{dr}\right) + R_A = 0$$

or

$$D_{AB}\frac{d^2c_A}{dr^2} + \frac{1}{r}\frac{dc_A}{dr} - m = 0$$

Boundary Conditions

The concentration profile $c_A(r)$ represents a second-order differential equation. Therefore, two boundary conditions on $c_A(r)$ must be specified:

$$r = R_1,\ c_A = c_{As} = \frac{p_A}{H}$$

$$r = R_2,\ \frac{dc_A}{dr} = 0$$ (net flux $N_A = 0$ at $r = R_2$)

Topic 25.4 Example: Engineered Tissue Bundle (cont.)

Analytical Solution to Model Equations for $C_A(r)$

Differential Equation for Mass Transfer

Type: Second-order, homogenous Ordinary Differential Equation (O.D.E.)

Dependent variable: c_A (dissolved O2 concentration in tissue)

Independent variable: r (radial position from tube wall into surrounding tissue)

$$D_{AB}\frac{d^2c_A}{dr^2}+\frac{1}{r}\frac{dc_A}{dr}-m=0 \quad \text{or} \quad \frac{d}{dr}\left(r\frac{dc_A}{dr}\right)=\frac{m}{D_{AB}}r$$

Boundary Conditions:

tube surface: $r=R_1,\, c_A=c_{As}=c_A{*}=\dfrac{p_A}{H}$

tissue bundle boundary: $r=R_2,\, \dfrac{dc_A}{dr}=0$ (net flux $N_A = 0$ at $r = R_2$)

Analytical Solution:

For this particular form of O.D.E., the general analytical solution for $c_A(r)$ is obtained by "integrating twice" with respect to r

First integration:

$$\frac{dc_A}{dr}=\frac{m}{2D_{AB}}r+\frac{\alpha_1}{r}$$

Second integration:

$$c_A(r)=\frac{m}{4D_{AB}}r^2+\alpha_1\ln(r)+\alpha_2 \qquad \text{(general solution to O.D.E.)}$$

Apply boundary conditions to solve for integration constants α_1 and α_2

at $r = R_2$ $\quad \alpha_1 = -\dfrac{mR_2^{\,2}}{2D_{AB}}$, at $r = R_1$, $\alpha_2 = c_{As} - \dfrac{mR_1^{\,2}}{4D_{AB}} + \dfrac{mR_2^{\,2}}{2D_{AB}}\ln(R_1)$

Plug integration constants α_1 and α_2 back into general solution of O.D.E.

$$c_A(r) = c_{As} + \frac{m}{4D_{AB}}(r^2 - R_1^{\,2}) - \frac{mR_2^{\,2}}{2D_{AB}}\ln\left(\frac{r}{R_1}\right)$$

valid $c_A(r) \geq 0$ and $R_1 \leq r < R_2$

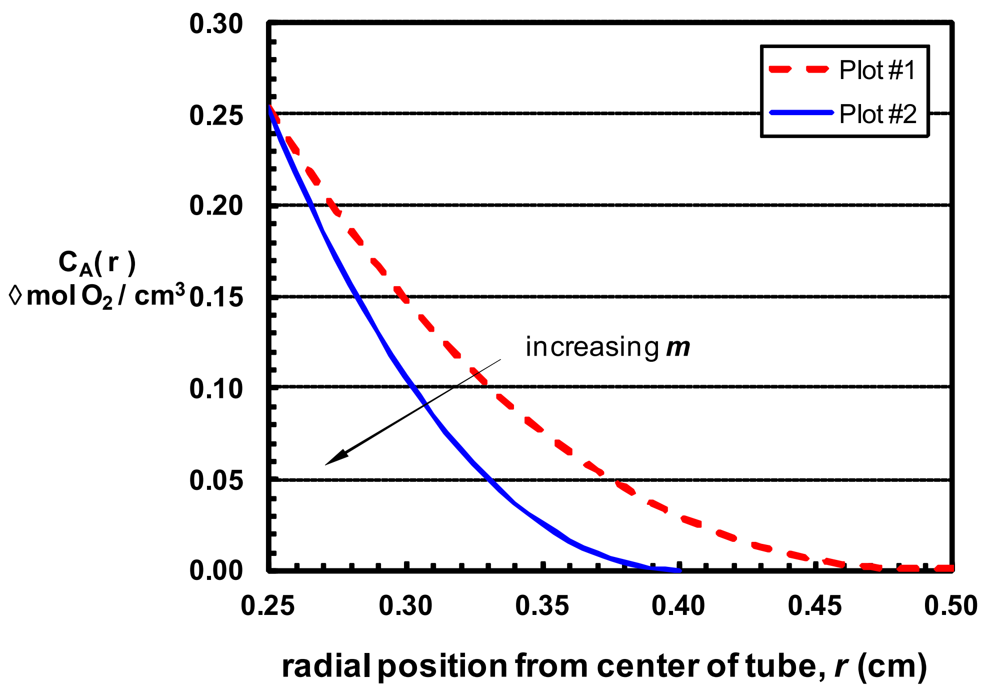
For a constant O_2 consumption rate m, at some point $c_A(r) = 0$. The critical radius" where $c_A(r) = 0$ is found at $R_2 = R_c$ and $r = R_c$

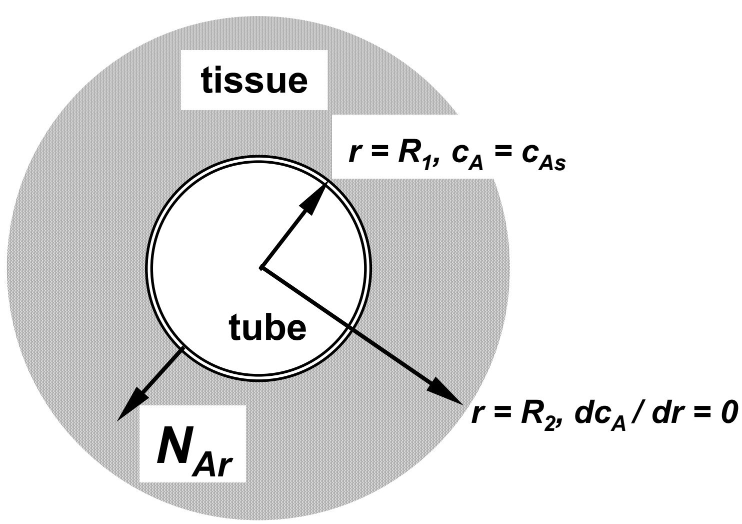
$$c_A(R_c) = 0 = c_{As} + \frac{m}{4D_{AB}}(R_c^{\,2} - R_1^{\,2}) - \frac{mR_c^{\,2}}{2D_{AB}}\ln\left(\frac{R_c}{R_1}\right)$$

R_c is found from the root of this nonlinear equation (m, R_1, D_{AB} known)

Topic 25.4 Example: Engineered Tissue Bundle (cont.) - Model Predictions

m =	1.50E-04	4.00E-04	μmol O_2/cm^3-sec
C_A^* =	0.254	0.254	μmol O_2/cm^3
D_{AB} =	2.10E-05	2.10E-05	cm^2/sec
R_1 =	0.25	0.25	cm
R_c =	0.49	0.40	cm
$f(R_c)$ =	0.0000	0.0000	





simplifed cross section