

3.185 Problem Set 2

Diffusion

Solutions

1. Decomposition of poly(vinyl chloride)

- (a) This time we have the conservation equation with generation, so the generation term is G times the volume of a shell between r and Δr . That volume is approximately $2\pi r L \Delta r$ (the cylinder area times the shell thickness), so we start with

$$0 = -(J_r \cdot 2\pi r L)_r + (J_r \cdot 2\pi r L)_{r+\Delta r} + G \cdot 2\pi r L \Delta r$$

Again we divide by $2\pi r L \Delta r$ and let Δr go to zero:

$$-\frac{\partial}{\partial r}(Jr) + Gr = 0$$

Substituting Fick's first law gives us the differential equation:

$$\frac{\partial}{\partial r} \left(rD \frac{\partial C}{\partial r} \right) + Gr = 0$$

This integrates to

$$rD \frac{\partial C}{\partial r} + \frac{Gr^2}{2} = A$$

for a constant A . Now divide by r and rearrange to give

$$\frac{dC}{dr} = -\frac{rG}{2D} + \frac{A}{Dr}$$

and integrate both sides for the general solution

$$C = -\frac{r^2 G}{4D} + A' \ln r + B$$

where once again $A' = \frac{A}{D}$.

- (b) Because the rod is symmetric about its axis, the concentration everywhere around the axis will be the same, so there will be no flux through the center. This means that at the center, the slope is zero:

$$\frac{dC}{dr} = -\frac{rG}{2D} + \frac{A'}{r} = 0$$

So $A' = 0$. You could also say that the concentration is finite at the center, therefore A' must be zero. On the surface:

$$C_{\text{HCl},s} = -\frac{R^2 G}{4D} + B$$

$$B = C_{\text{HCl},s} + \frac{R^2 G}{4D}$$

The solution is:

$$C = C_{\text{HCl},s} + \frac{G(R^2 - r^2)}{4D}$$

The maximum concentration is the concentration at $r = 0$:

$$C_{\text{max}} = C_{\text{HCl},s} + \frac{GR^2}{4D}$$

(c) If we divide the maximum concentration by the surface concentration, we get:

$$\frac{C_{\text{max}}}{C_{\text{HCl},s}} = 1 + \frac{GR^2}{4DC_{\text{HCl},s}}$$

This means that if $\frac{GR^2}{DC_{\text{HCl},s}}$ is small, $\frac{C_{\text{max}}}{C_{\text{HCl},s}}$ will be very close to one, so the HCl concentration will be very uniform. If it is large, the maximum concentration will be much larger than that at the surface of the rod.

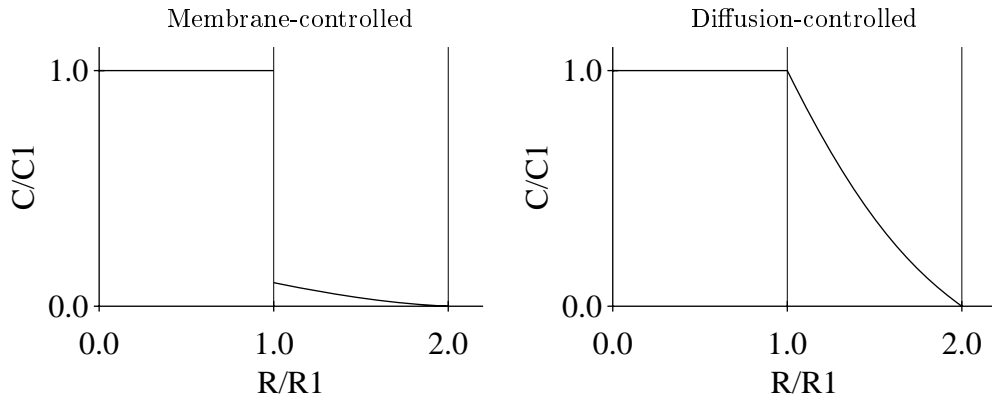
2. Encapsulated liposomes for long-term drug delivery

(a) The “thickness” of the encapsulant is $R_2 - R_1 = 0.01$ cm, so

$$\frac{\text{thickness}^2}{D} = \frac{(0.01\text{cm})^2}{10^{-7} \frac{\text{cm}^2}{\text{sec}}} = 1000\text{seconds}$$

This is short compared to the service life of the device (for any definition of “long-term”), so we can safely assume quasi-steady-state diffusion in the encapsulant.

(b) It’s worth pointing out that “lipid bilayer membrane” means two molecular layers, so the membrane is *really* thin (*i.e.* submicron, ask a biomat person for molecular details).



(c) The universal conservation equation:

$$\text{accumulation} = \text{in} - \text{out} + \text{generation}$$

Steady state indicates accumulation=0, there should be no generation term. We’ll use a spherical “shell” of thickness Δr :

$$0 = [A \cdot J_r]_r - [A \cdot J_r]_{r+\Delta r}$$

$$0 = [4\pi r^2 \cdot J_r]_r - [4\pi r^2 \cdot J_r]_{r+\Delta r}$$

Divide by $4\pi\Delta r$, let Δr go to zero:

$$0 = -\frac{d}{dr}(r^2 J_r)$$

Substitute $J_r = -D\frac{dC}{dr}$:

$$0 = \frac{d}{dr} \left(Dr^2 \frac{dC}{dr} \right)$$

For constant D , we divide by D and are left with:

$$0 = \frac{d}{dr} \left(r^2 \frac{dC}{dr} \right).$$

Note the similarity to the differential equation in problem 1a.

(d) Start from the equation in part 2c and integrate:

$$-A = r^2 \frac{dC}{dr}$$

(A is an arbitrary constant, negative here because we'll make it positive below.) Divide by r^2 and integrate again to yield the general solution:

$$C = \frac{A}{r} + B$$

Now apply the boundary conditions from above:

$$C_2 = \frac{A}{R_1} + B$$

$$0 = \frac{A}{R_2} + B$$

There are a couple of ways to go from here. I like to subtract the second from the first to eliminate B , this gives

$$C_2 = \frac{A}{R_1} - \frac{A}{R_2} = A \left(\frac{1}{R_1} - \frac{1}{R_2} \right)$$

$$A = \frac{C_2}{\frac{1}{R_1} - \frac{1}{R_2}}$$

Then from the second BC:

$$0 = \frac{C_2}{\frac{1}{R_1} - \frac{1}{R_2}} \frac{1}{R_2} + B$$

$$B = -\frac{C_2/R_2}{\frac{1}{R_1} - \frac{1}{R_2}}$$

Plugging this A and B into the general solution and dividing by C_2 gives:

$$\frac{C}{C_2} = \frac{\frac{1}{r} - \frac{1}{R_2}}{\frac{1}{R_1} - \frac{1}{R_2}}$$

(e) We begin with the flux:

$$J_r = -D \frac{dC}{dr} = -D \frac{d}{dr} \left[\frac{C_2}{\frac{1}{R_1} - \frac{1}{R_2}} \left(\frac{1}{r} - \frac{1}{R_2} \right) \right]$$

$$J_r = \frac{DC_2}{\frac{1}{R_1} - \frac{1}{R_2}} \cdot \frac{1}{r^2}$$

The area A is simply $4\pi r^2$, so when we multiply them the r^2 s cancel:

$$J_r A = \frac{4\pi DC_2}{\frac{1}{R_1} - \frac{1}{R_2}}$$

This is independent of r .

If this is diffusion-limited, then $C_2 \simeq C_1$, and:

$$J_r A = \frac{4\pi D C_1}{\frac{1}{R_1} - \frac{1}{R_2}}$$

Plugging in the problem parameters gives us:

$$J_r A = \frac{4\pi \cdot 10^{-7} \frac{\text{cm}^2}{\text{sec}}}{\frac{1}{0.01 \text{cm}} - \frac{1}{0.02 \text{cm}}} \cdot C_1 = 2.5 \times 10^{-8} \frac{\text{cm}^3}{\text{sec}} C_1$$

Since C_1 is in $\frac{\text{moles}}{\text{cm}^3}$ or $\frac{\text{mg}}{\text{cm}^3}$ etc., this gives the overall rate of drug delivery from the device—if it's diffusion-limited.

- (f) The flux equation was given, and here $C_2 = 0$ modifies it slightly:

$$J_r = h_D(C_1 - C_2) \simeq h_D C_1$$

Because the membrane is at R_1 , the relevant area A is $4\pi R_1^2$, which gives us:

$$J_r \cdot A = h_D C_1 \cdot 4\pi R_1^2 = 4\pi \cdot (0.01 \text{cm})^2 \cdot 1.4 \times 10^{-6} \frac{\text{cm}}{\text{s}} C_1 = 1.8 \times 10^{-9} \frac{\text{cm}^3}{\text{s}} C_1$$

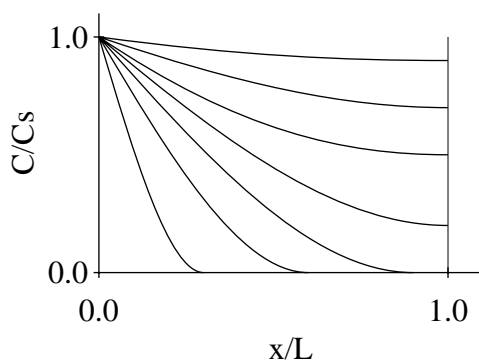
- (g) Because the answers to part 2f is so much lower than that to part 2e, the membrane definitely controls the rate of drug delivery. The actual rate of delivery will thus be close to what's predicted in part 2f, or about $2 \times 10^{-9} \frac{\text{cm}^3}{\text{s}} C_1$. That's the end of the story as far as 3.185 is concerned, and the answer this question was looking for.

However, if you read the reference given in the problem, you'll notice that the drug delivery rate for the encapsulated liposomes is actually *higher* than for the bare liposomes. This is because the encapsulation process weakens the membrane so that it is not as effective a barrier as without the encapsulant.

3. Nitriding of an iron thin film

Why would you want to make such a film? I've no idea...

- (a) This has a zero initial condition, and fixed concentration boundary condition at $x = 0$ (the exposed top surface of the film); so at least to start, it's an erfc. Then when the nitrogen in the tail of the erfc reaches the bottom of the film, it hits what we're assuming is an impermeable wall, a no-flux boundary condition. So the derivative is always zero there at the Fe-Si interface, and the concentration rises until reaching a steady-state with uniform nitrogen concentration across the iron.



Approximate nitrogen concentration profile in the iron film at several times.

- (b) As mentioned above, this is an erfc solution:

$$C = C_s \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right).$$

- (c) For this, we need to solve the erfc solution from part 3b for x , and set C to one-half of C_s to find at what depth the concentration has that value:

$$\frac{x}{2\sqrt{Dt}} = \text{erfc}^{-1}(0.5C_s/C_s).$$

$$x = 2\sqrt{Dt}\text{erfc}^{-1}(0.5).$$

From the erf table (in the diffusion handout), $\text{erfc}^{-1}(0.5)$ is about 0.48, so at $t = 1$ second, $x = 9.6 \times 10^{-5}$ cm, or just under one micron. At $t = 4$ seconds, $x = 1.92 \times 10^{-4}$ cm, just under two microns. So the depth of the top layer where $C \geq 0.5C_s$ gets thicker proportional to the square root of time.

- (d) This ceases to be valid when the film is no longer semi-infinite, so for film thickness L , the validity criterion is:

$$t \leq \frac{L^2}{16D}.$$

For $L = 10\mu\text{m} = 10^{-3}\text{cm}$ and $D = 10^{-8}\frac{\text{cm}^2}{\text{s}}$, this gives $t = 6.25$ seconds.

- (e) This is a bit tricky. We have a film of finite thickness, which right away suggests the Fourier series as a solution. But we've only seen that solution in lecture referring to finite systems with fixed concentration on both sides, using half of one square wave period; here we have one fixed concentration boundary condition and one zero-flux condition.

The solution is to use one-quarter of a square wave period, with $C_0 = C_s$ to get the surface concentration right, and $C_{max} = 0$ to get the initial condition, since it's below the surface concentration. The half-period is twice the film thickness $2L$ which is $20\mu\text{m}$ (since we're using one-quarter of the period for L).

At long times, the series terms with $n > 1$ decay rapidly, so we're left with the $n = 1$ term:

$$C = C_s - \frac{4C_s}{\pi} \exp\left(-\frac{\pi^2 Dt}{(2L)^2}\right) \sin\left(\frac{\pi x}{2L}\right)$$

- (f) We want to calculate t when $C(x = L = 10\mu\text{m}) = 0.9C_s$:

$$0.9C_s = C_s - \frac{4C_s}{\pi} \exp\left(-\frac{\pi^2 Dt}{(2L)^2}\right) \sin\left(\frac{\pi L}{2L}\right)$$

Note $\sin(\pi/2) = 1$ so that part drops out.

$$\frac{4}{\pi} \exp\left(-\frac{\pi^2 Dt}{(2L)^2}\right) = 0.1$$

$$\frac{\pi^2 Dt}{(2L)^2} = -\ln\left(\frac{0.1\pi}{4}\right) = \ln\left(\frac{40}{\pi}\right)$$

$$t = \frac{(2L)^2}{\pi^2 D} \ln\left(\frac{40}{\pi}\right) = \frac{(2 \times 10^{-3}\text{cm})^2}{\pi^2 \cdot 10^{-8}\frac{\text{cm}^2}{\text{s}}} \ln(12.7) = 103 \text{ seconds}$$