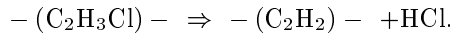# 3.185 Problem Set 2

Diffusion

Due Monday September 15, 2003

1. Decomposition of poly(vinyl chloride) (20)

   Poly(vinyl chloride), or PVC, like many other polymers, is subject to degredation reactions at high temperatures. In the case of PVC, HCl is evolved when a monomer in the chain undergoes the reaction

   $$- (C_2H_3Cl) - \Rightarrow - (C_2H_2) - + HCl.$$

   This takes place throughout the polymer body at a constant rate G which is independent of HCl concentration, and we'll assume the back-reaction occurs at a negligible rate even at maximum HCl concentration.

   A PVC rod of radius R is held at high temperature for a long time, so that the concentration of HCl reaches a steady state. On the surfaces, the rod reaches equilibrium with its surroundings at a fixed HCl concentration $C_{HCl,s}$. Since the properties of PVC are affected by the presence of dissolved HCl, we want to know the concentration profile of HCl in the rod.

   (a) Write down the differential equation for steady state diffusion and homogeneous chemical reaction at constant reaction rate G in a cylindrical rod. What is the general form of the solution to this equation? (9)

   (b) For the boundary conditions at the center and on the surface of the rod given above, what is the solution? What is the maximum concentration of HCl? (6)

   (c) Consider the dimensionless quantity $\frac{GR^2}{DC_{HCl,s}}$. What does the value of this quantity tell you about the uniformity of concentration of HCl throughout the rod? (5)

2. Encapsulated liposomes for long-term drug delivery (40)

"Liposomes" are small spherical lipid bilayer membranes which can be used to enclose high-molecular weight drugs in aqueous solution (MW $> 1000\frac{\text{g}}{\text{mol}}$) and deliver them at a controlled rate. Unfortunately, they interact with the immune system, and so must be surrounded with a protective "encapsulant" material, such as poly-L-lysine.
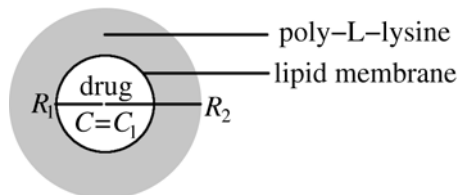
This device is a spherical system with the lipid membrane at radius R_1 and the encapsulant between R_1 and R_2. Transport of the drug will be in the radial direction and limited by one of two mechanisms:

- Transport through the very thin lipid membrane, which we'll model using a mass transfer coefficient: $J_r = h_D(C_1 - C_2)$ where C_1 is the concentration inside the membrane and C_2 is the concentration between the membrane and the encapsulant.

- Diffusion through the encapsulant material with diffusivity D.

You may assume the concentration outside the encapsulant is zero, and that the "equilibrium constant" k_{eq} for the drug entering the encapsulant is 1.

Data: $R_1 = 0.01$ cm, $R_2 = 0.02$ cm, $D = 10^{-7}\frac{\text{cm}^2}{\text{s}}$. Note that as the drug leaves the device, C_1 and C_2 will both slowly fall (*very* slowly, so we can assume quasi-steady-state below), so they are not constant.

(a) Approximately how long does it take to establish a steady-state diffusion profile across the encapsulant? (4)

(b) Sketch the concentration profile assuming transport is completely controlled by the membrane, and make a separate sketch assuming complete control by diffusion through the encapsulant. (6)

(c) Starting from a mass balance in the radial direction, derive the differential equation for steady-state diffusion of the drug through the encapsulant. (8)

(d) Solve the differential equation from part 2c, and using the boundary conditions $r = R_1 \Rightarrow C = C_2$ and $r = R_2 \Rightarrow C = 0$, express the concentration of the drug in the encapsulant as a function of r. (7)

(e) Use the solution from part 2d to write expressions for the flux J_r and sphere area A as a function of r. The product $J_r \cdot A$ should be independent of r. Suppose the drug transport is limited by diffusion through the encapsulant, so $C_2 = C_1$. In this case, what is that product $J_r \cdot A$, in terms of the concentration C_1? (7)

(f) If the drug delivery is purely limited by transport through the membrane, so $C_2 = 0$, what will be the product $J_r \cdot A$ in terms of the concentration C_1? Use $h_D = 1.4 \times 10^{-6}\frac{\text{cm}}{\text{s}}$. (5)

(g) Based on your answers to parts 2e and 2f, is the rate-limiting mechanism here the membrane or the encapsulant? Which part therefore gives the more correct rate of drug delivery $J_r \cdot A$? (3)

Reference: S. Cohen, P.G. Kibat, M.B. Chow, R.S. Langer, "Microencapsulated liposomes for the pulsed release of biologically-active materials," Polymer Preprints, ACS Books & Journals Div., Washington, DC (Science stacks QD281.P6.A511), v 30 n 1 pp. 478-479.

3. Nitriding of an iron thin film (40)

An iron film is vapor-deposited on a silicon wafer with a thickness of 10 μm ($=10^{-3}$ cm). The film is then exposed (at time $t = 0$, naturally) to a nitriding atmosphere which fixes the nitrogen concentration in the iron on the exposed surface at $C = C_s$. You would like to know the nitrogen concentration in the iron film as a function of position and time.

Nitriding atmosphere
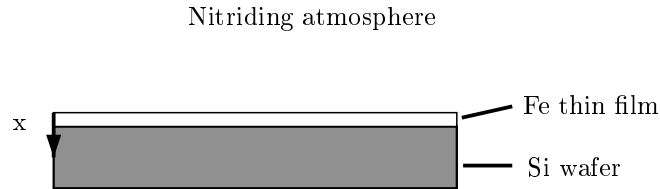
You may assume:

- C_s is much higher than the nitrogen solubility in the silicon, that is, there is no nitrogen in the silicon, and the flux of nitrogen from the iron into the silicon is zero.
- C_s is sufficiently low that there are no phase transformations here, and no significant volume change, just nitrogen diffusing into iron.

Datum: $D_{\text{N}-\text{Fe}} = 10^{-8} \frac{\text{cm}^2}{\text{s}}$

(a) Sketch the concentration profile of nitrogen at the start of the process (with no nitrogen), and for several times leading to steady-state. (7)

(b) Write the simple (one-term) solution of the diffusion equation which is valid for a short time after the nitriding atmosphere is introduced. (5)

(c) What is the thickness of the sublayer in which nitrogen concentration is at least half of the surface concentration at 1 second, and at four seconds? (5)

(d) At what time t does your solution in part 3b cease to be valid? (6)

(e) Write the simple (one-term) solution of the diffusion equation which is valid a long time after the nitriding atmosphere is introduced. (7)

(f) At what time t does the nitrogen concentration on the iron side of the iron-silicon interface reach $0.9C_s$? (10)