Homework 5

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BIOENG 104 Biological Transport Phenomena | Aaron Streets

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1 Problem 1

At the Streets Lab, we are investigating the dynamic diffusion process of a novel therapeutic agent, *Azulene*, across a specialized synthetic membrane in a controlled laboratory setting. Initially, at $t < 0$, the Azulene concentration throughout the membrane's structure is maintained at zero to ensure experimental accuracy. At the precise moment when $t = 0$, both faces of the membrane find themselves simultaneously exposed to a uniformly stirred bath containing Azulene at a steadfast concentration of $5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$. The partition coefficient is $\Phi_M = 0.9$, indicating the equilibrium distribution of Azulene between the membrane and the surrounding bath. The membrane itself, a product of advanced synthetic engineering, measures a total thickness of $1.8\,\mathrm{cm}$. Azulene's movement through this medium is characterized by a diffusivity constant of $6.2 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$.

Consider that the laboratory's ambient temperature is controlled at $25\,°\mathrm{C}$, although the temperature's effect on the diffusion process is assumed negligible for the scope of this problem. Also, the membrane's surface is treated with a non-reactive, hydrophobic coating to minimize external variables, although this treatment does not alter the partition coefficient or diffusivity of Azulene.

a) Calculate t_{critical} where $\eta = 3$ for treating the membrane from either side as a semi-infinite medium under these conditions.

The solution for the semi-infinite membrane is

$$\theta(\eta) = 1 - \operatorname{erf}(\eta) = 1 - \frac{2}{\sqrt{\pi}} \int_0^\eta \mathrm{e}^{-z^2}\,\mathrm{d}z \tag{1.1}$$

where

$$\eta = \frac{x}{\sqrt{4D_{ij}t}} \tag{1.2}$$

we can rearrange Equation (1.2) to calculate η in terms of x and t.

$$4D_{ij}t = (x/\eta)^2$$
$$t = \frac{x^2}{4D_{ij}\eta^2}$$

Since the system is composed symmetrically with the two halves each acting as a semi-infinite membrane, the length we need to substitute in must be half of the membrane's total length. Substituting $x = 1.8\,\mathrm{cm}/2 = 0.9\,\mathrm{cm}$, the diffusivity $D_{ij} = 6.2 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}}$, and $\eta = 3$,

$$t_{\text{critical}} = \frac{(0.9\,\mathrm{cm})^2}{4(6.2 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}})(3)^2} = \boxed{3.6 \times 10^3\,\mathrm{s}}$$

> b) Assuming a semi-infinite medium, determine the concentration (in mol/L) of Azulene precisely 0.15 mm from the membrane edges in contact with the baths at specific moments: 4.0 minutes and 8.0 minutes. Disregard the hydrophobic coating's presence for these calculations as it has no effect on Azulene's diffusion.

The concentration for the semi-infinite membrane can be found implicitly from Equation (1.1). When $x = 0.15\,\mathrm{mm}$ and $t = 240\,\mathrm{s}$,

$$\begin{aligned}
\eta &= \frac{x}{\sqrt{4D_{ij}t}} = \frac{0.015\,\mathrm{cm}}{\sqrt{4(6.2 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}})(240\,\mathrm{s})}} = 0.194 \\
\theta(\eta) &= 1 - \operatorname{erf}(\eta) = 0.783
\end{aligned}$$

Let the outside concentration be $C_0 = 0\,\mathrm{mol\,L^{-1}}$ and the concentration within the membrane be $C_1 = 5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}$. Since $\theta = (C - C_0)/(\Phi_M C_1 - C_0)$, then

$$\begin{aligned}
\theta(\eta) &= \frac{C}{\Phi_M C_1} \\
C(0.15\,\mathrm{mm}, 4.0\,\mathrm{min}) &= \theta(\eta)\Phi_M C_1 \\
&= [1 - \operatorname{erf}(\eta)]\Phi_M C_1 \\
&= 0.783(0.9)(5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}) \\
&= \boxed{3.52 \times 10^{-7}\,\mathrm{mol\,L^{-1}}}
\end{aligned}$$

We repeat the same calculation for the concentration of Azulene at $t = 8.0\,\mathrm{min} = 480\,\mathrm{s}$.

$$\begin{aligned}
\eta &= \frac{x}{\sqrt{4D_{ij}t}} = \frac{0.015\,\mathrm{cm}}{\sqrt{4(6.2 \times 10^{-6}\,\mathrm{cm^2\,s^{-1}})(480\,\mathrm{s})}} = 0.137 \\
C(0.15\,\mathrm{mm}, 8.0\,\mathrm{min}) &= [1 - \operatorname{erf}(\eta)]\Phi_M C_1 \\
&= (0.846)(0.9)(5 \times 10^{-7}\,\mathrm{mol\,L^{-1}}) \\
&= \boxed{3.81 \times 10^{-7}\,\mathrm{mol\,L^{-1}}}
\end{aligned}$$

c) Under the semi-infinite medium assumption, estimate the total amount of Azulene permeating into a membrane section with a surface area of $20\,\mathrm{cm}^2$ during the initial 24-hour exposure period to the bath (expressed in mol). Consider the membrane's advanced synthetic nature and hydrophobic treatment as non-factors in this calculation.

The total amount of Azulene permeating through the membrane section can be estimated by

$$n_{\text{Azulene}} = 2\int_0^{t_0}\iint_{\text{area}} J_x\,\mathrm{d}A\,\mathrm{d}t = 2A\int_0^{t_0} J_x\,\mathrm{d}t$$

where J_x is the diffusive flux along the x-direction (across the membrane), $A = 20\,\mathrm{cm}^2$ is the surface area, and $t_0 = 24\,\mathrm{h} = 86\,400\,\mathrm{s}$. Since Azulene goes through both sides of the membrane section, we multiply by a factor of two. We can find J_x using Fick's first law.

$$J_x = -D_{ij}\frac{\partial C}{\partial x} \tag{1.3}$$

Since $C = \theta(\eta)(\Phi_M C_1 - C_0) + C_0$,

$$\begin{aligned}\frac{\partial C}{\partial x} &= (\Phi_M C_1 - C_0)\frac{\partial \theta}{\partial x}\\ &= (\Phi_M C_1 - C_0)\frac{\partial \theta}{\partial \eta}\frac{\partial \eta}{\partial x}\\ &= (\Phi_M C_1 - C_0)\frac{\partial \theta}{\partial \eta}\frac{1}{\sqrt{4D_{ij}t}}\end{aligned} \tag{1.4}$$

since $\eta = x/\sqrt{4D_{ij}t}$. We then solve for $\partial\theta/\partial\eta$.

$$\frac{\partial \theta}{\partial \eta} = \frac{\partial}{\partial \eta}\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{\eta} \mathrm{e}^{-z^2}\,\mathrm{d}z\right) = -\frac{2}{\sqrt{\pi}}\mathrm{e}^{-\eta^2}$$

as follows from the Fundamental Theorem of Calculus. Substituting this back into Equations (1.3) and (1.4),

$$\begin{aligned}\frac{\partial C}{\partial x} &= \frac{\Phi_M C_1 - C_0}{\sqrt{4D_{ij}t}}\cdot -\frac{2}{\sqrt{\pi}}\mathrm{e}^{-\eta^2}\\ J_x &= 2(\Phi_M C_1 - C_0)\sqrt{\frac{D_{ij}}{4\pi t}}\mathrm{e}^{-\eta^2}\end{aligned}$$

At $x = 0$ ($\eta = 0$), the flux is

$$J_x = (\Phi_M C_1 - C_0)\sqrt{\frac{D_{ij}}{\pi t}}$$

So, the amount of Azulene is

$$
\begin{aligned}
n_{\text{Azulene}} &= 2A(\Phi_M C_1 - C_0)\sqrt{\frac{D_{ij}}{\pi}} \int_0^{t_0} \frac{1}{\sqrt{t}}\,\mathrm{d}t \\
&= 2A(\Phi_M C_1 - C_0)\sqrt{\frac{D_{ij}}{\pi}} 2\sqrt{t_0} \\
&= 4A(\Phi_M C_1 - C_0)\sqrt{\frac{D_{ij}}{\pi}} \sqrt{t_0} \\
&= \boxed{1.49 \times 10^{-5}\,\text{mol}}
\end{aligned}
$$

[d)] Establish the theoretical maximum quantity of Azulene that the membrane could absorb. Evaluate whether the semi-infinite medium assumption leads to an overestimation or underestimation in your answer for part (c). In a concise explanation of no more than 80 words, justify your reasoning, taking into account the advanced engineering and surface treatment of the membrane as elements that do not materially impact the diffusion process's fundamental principles.

The maximum concentration that the membrane could absorb is $\Phi_M C_1$. By definition of volume concentration,

$$
\begin{aligned}
n_{\text{Azulene}} &= \Phi_M C_1 V \\
&= \Phi_M C_1 \ell A \\
&= (0.9)(5 \times 10^{-10}\,\text{mol}\,\text{mL}^{-1})(1.8\,\text{cm})(20\,\text{cm}^2) \\
&= \boxed{1.62 \times 10^{-8}\,\text{mol}}
\end{aligned}
$$

which means that the semi-infinite medium assumption leads to an underestimation of the maximum theoretical quantity.

The semi-infinite assumption ignores that the diffusion behavior can be affected by the center of the membrane, where the two diffusions from each half-membrane meet each other. Even if we wait for 24 hours, which is much longer than t_{critical}, we cannot reach the maximum concentration because the solute is assumed to be not affected when it reaches a boundary.

2 Problem 2

Consider a spherical "absorber." This is a sphere of radius a such that any solute particles that reach the surface of the sphere are gobbled up. In other words, $C(a) = 0$. Assuming this sphere is dropped into an infinite bath of initial concentration C_0 at $t = 0$, solve for $C(r, t)$ for $r > a$ in spherical coordinates.

Assumptions: The bath is not well mixed. The partition coefficient is equal to 1. There is no reaction.
Hints: Substitute C with the dimensionless variable $\theta = (C - C_0)/(C_1 - C_0)$ and write Fick's second law in spherical coordinates in terms of θ, r, and t. Then define a new variable:

$$\chi = \theta r$$

in order to derive the following integral:

$$\chi = A \int_0^{\eta} \mathrm{e}^{-z^2}\,\mathrm{d}z + B$$

where η is defined as $(r-a)/(4Dt)^{1/2}$ and A and B are integration constants. Solve for A and B to get a specific solution for $C(r, t)$ using the necessary boundary conditions.

From the generalized form of Fick's second law, we wish to solve for the concentration C, or a dimensionless form of it, such that

$$\frac{\partial C}{\partial t} = D_{ij}\nabla^2 C + R_i = D_{ij}\nabla^2 C \tag{2.5}$$

since the reaction rate R_i equals zero. Then, we fully evaluate the Laplacian in terms of spherical coordinates (r, θ, φ). Since the concentration can be assumed to have no gradient over φ and θ, we can eliminate some terms containing the partial derivatives of C with respect to those variables. It is thus also implied that $C = C(r, t)$.

$$\frac{\partial C}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r^2\frac{\partial C}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial C}{\partial\theta}\right) + \frac{1}{r^2\sin\theta}\frac{\partial C}{\partial\varphi^2}\right] = \frac{D}{r}\frac{\partial}{\partial r^2}\left(r^2\frac{\partial C}{\partial r}\right) \tag{2.6}$$

We also bring up the following boundary and initial conditions. We can infer that at the initial state, the concentration is originally constant at C_0 everywhere outside the spherical absorber. As given, we can state that the concentration is zero at the edge of the absorber after the initial state, and as one goes further and further away from the absorber's edge, the concentration converges to C_0. Restating this mathematically,

Original boundary conditions:
- $C(r, 0) = C_0$ for all $r > a$ at $t = 0$ (initial)
- $C(a, t) = 0$ for all $t > 0$ at $r = a$ (boundary)
- $C(r, t) \to C_0$ for all $t > 0$ as $r \to \infty$ (boundary)

We first express Equation (2.6) in terms of the quantity χ defined

$$\chi = \theta r = \frac{C - C_0}{C_1 - C_0} r \quad \Longleftrightarrow \quad C = \frac{\chi}{r}(C_1 - C_0) + C_0 \tag{2.7}$$

First re-expressing the left-hand side of Equation (2.6) in terms of χ,

$$\frac{\partial C}{\partial t} = \frac{\partial C}{\partial \chi}\frac{\partial \chi}{\partial t} = \frac{C_1 - C_0}{r}\frac{\partial \chi}{\partial t}$$

Expressing the right-hand side of Equation (2.6) in terms of χ,

$$\begin{aligned}
\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) &= \frac{D}{r^2}\frac{\partial}{\partial r}\left[r^2\left(-\frac{\chi}{r^2}(C_1 - C_0) + \frac{1}{r}(C_1 - C_0)\frac{\partial \chi}{\partial r}\right)\right] \\
&= \frac{D}{r^2}(C_1 - C_0)\frac{\partial}{\partial r}\left(-\chi + r\frac{\partial \chi}{\partial r}\right) \\
&= \frac{D}{r^2}(C_1 - C_0)\left(-\frac{\partial \chi}{\partial r} + \frac{\partial \chi}{\partial r} + r\frac{\partial^2 \chi}{\partial r^2}\right) \\
&= \frac{D}{r}(C_1 - C_0)\frac{\partial^2 \chi}{\partial r^2} \qquad (2.8)
\end{aligned}$$

Equating Equation (2.7) and Equation (2.8) together yields

$$\begin{aligned}
\frac{C_1 - C_0}{r}\frac{\partial \chi}{\partial t} &= \frac{D}{r}(C_1 - C_0)\frac{\partial^2 \chi}{\partial r^2} \\
\frac{\partial \chi}{\partial t} &= D\frac{\partial^2 \chi}{\partial r^2} \qquad (2.9)
\end{aligned}$$

We can additionally express a new dimensionless radial parameter η, which is defined

$$\eta = \frac{r - a}{\sqrt{4Dt}}$$

Then, we express our differential equation (2.9) in terms of χ and η, which will serve as our new differential equation to solve. First, we determine the left-hand side of Equation (2.9),

$$\frac{\partial \chi}{\partial t} = \frac{\partial \chi}{\partial \eta}\frac{\partial \eta}{\partial t} = \frac{\partial \chi}{\partial \eta}(r - a)(4Dt)^{-3/2}(-1/2)(4D) = -\frac{1}{2}\frac{\partial \chi}{\partial \eta}\frac{r - a}{\sqrt{4Dt}} \cdot \frac{1}{t} = -\frac{\eta}{2t}\frac{\partial \chi}{\partial \eta} \tag{2.10}$$

and then we determine the right-hand side of Equation (2.9).

$$\begin{aligned} D\frac{\partial^2\chi}{\partial r^2} &= D\frac{\partial}{\partial r}\left(\frac{\partial\chi}{\partial\eta}\frac{\partial\eta}{\partial r}\right) \\ &= D\frac{\partial}{\partial r}\left(\frac{\partial\chi}{\partial\eta}\frac{1}{\sqrt{4Dt}}\right) \\ &= D\frac{1}{\sqrt{4Dt}}\frac{\partial\eta}{\partial r}\frac{\partial}{\partial\eta}\left(\frac{\partial\chi}{\partial\eta}\right) \\ &= D\frac{1}{\sqrt{4Dt}}\frac{1}{\sqrt{4Dt}}\frac{\partial^2\chi}{\partial\eta^2} \\ &= \frac{1}{4t}\frac{\partial^2\chi}{\partial\eta^2} \end{aligned} \tag{2.11}$$

Equating Equation (2.10) and Equation (2.11) together, we have

$$-\frac{\eta}{2t}\frac{\partial\chi}{\partial\eta} = \frac{1}{4t}\frac{\partial^2\chi}{\partial\eta^2} \implies \boxed{\frac{\partial^2\chi}{\partial\eta^2} = -2\eta\frac{\partial\chi}{\partial\eta}} \tag{2.12}$$

Our initial and boundary conditions must be reworked to fit our new differential equation. From the initial condition, since $t = 0$ and $r > a$, then $\eta = (r-a)/\sqrt{4Dt}$ will "equal" infinity; the value of θ, and therefore χ, will be zero, since the concentration at that moment is $C = C_0$ and r is positive.

From the boundary condition when $r = a$ for positive t, the value of η will be zero immediately, since η is proportional to the value of $r - a$. The quantity χ will be $\chi = -C_0 a/(C_1 - C_0) = a$ by the definition of χ and θ (C_1 in this case equals zero). The boundary condition when r approaches infinity for positive t implies that η will also approach infinity, by definition of η. The value of χ in this condition is equal to zero, since C approaches C_0. To summarize our restrictive conditions so far,

New boundary conditions:

- $\chi = 0$ for $\eta \to \infty$ (initial)
- $\chi = a$ at $\eta = 0$ (boundary)
- $\chi \to 0$ as $\eta \to \infty$ (boundary; **redundant**)

We can simplify this down to just the first two initial/boundary conditions, since the third listed condition is redundant. Solving Equation (2.12), we substitute $u = \partial\chi/\partial\eta$.

$$\begin{aligned} \frac{\partial u}{\partial\eta} &= -2\eta u \\ \int \frac{1}{u}\frac{\partial u}{\partial\eta}\,\mathrm{d}\eta &= \int -2\eta\,\mathrm{d}\eta \\ \ln|u| &= -\eta^2 + \ln A \\ u = \frac{\partial\chi}{\partial\eta} &= A\mathrm{e}^{-\eta^2} \end{aligned}$$

for some constant of integration $A \in \mathbb{R}$. Solving further,

$$\chi(\eta) = \int_0^\eta A\mathrm{e}^{-z^2}\,\mathrm{d}z + B$$

for constant of integration $B \in \mathbb{R}$. Now we plug in our initial and boundary conditions to solve for A and B.

The boundary condition states that at η equals zero, the value χ is equal to a.

$$\chi(\eta = 0) = \int_0^0 A\mathrm{e}^{-z^2}\,\mathrm{d}z + B = a \implies B = a$$

The initial condition states that as η approaches infinity, then χ is equal to zero.

$$\begin{aligned}\chi(\eta \to \infty) &= \int_0^\infty A\mathrm{e}^{-z^2}\,\mathrm{d}z + a = 0\\ &= A\sqrt{\pi}/2 + a = 0 \qquad \implies A = -2a/\sqrt{\pi}\end{aligned}$$

Therefore, the final solution is

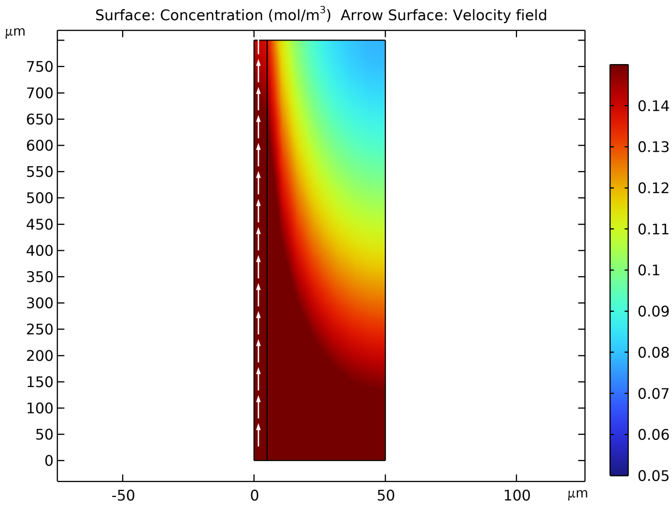
$$\chi(\eta) = -\frac{2a}{\sqrt{\pi}}\int_0^\eta \mathrm{e}^{-z^2}\,\mathrm{d}z + a$$

$$\boxed{C(r,t) = \frac{a}{r}(C_1 - C_0)\left(1 - \frac{2}{\sqrt{\pi}}\int_0^{(r-a)/\sqrt{4Dt}} \mathrm{e}^{-z^2}\,\mathrm{d}z\right) + C_0}$$

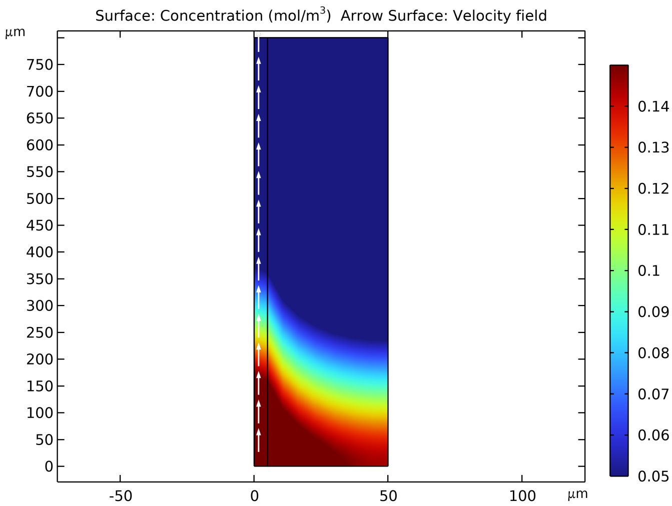
$$\boxed{= \frac{a}{r}(C_1 - C_0)\left[1 - \operatorname{erf}\left(\frac{r-a}{\sqrt{4Dt}}\right)\right] + C_0}$$

3 Lab Question: Problem 3

Include printouts of your Lab 05 model with and without hemoglobin.



with hemoglobin



without hemoglobin