
Homework 2

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1 Problem 1

Estimate the diffusivity of oxygen atoms (not O_2) in water at 25°C using the following relations:

- (a) Stokes–Einstein equation (assuming that oxygen is roughly spherical with an atomic diameter of 0.347 nm).

We are given the following values.

$$T = 25^\circ\text{C} = 298\text{ K}$$

$$R = (0.347\text{ nm})/2 = 0.174\text{ nm} = 1.74 \times 10^{-10}\text{ m}$$

$$\mu = 890.20\text{ }\mu\text{Pa s} = 890.20 \times 10^{-6}\text{ Pa s}$$

for temperature T , atomic radius R , and μ the dynamic viscosity of water (the solvent) at 25°C , given by [Kestin et al., 1978]. The Stokes–Einstein equation states that the diffusion coefficient may be estimated by the equation

$$D_{ij} = \frac{k_B T}{f} = \frac{k_B T}{6\pi\mu R} \quad (1.1)$$

where $k_B = 1.381 \times 10^{-23}\text{ J K}^{-1}$ is the Boltzmann constant, and $f = 6\pi\mu R$ is the drag coefficient when applied to a sphere of radius R . So, the diffusion coefficient is

$$D = \frac{(1.381 \times 10^{-23}\text{ J K}^{-1})(298\text{ K})}{6\pi(890.20 \times 10^{-6}\text{ Pa s})(1.74 \times 10^{-10}\text{ m})} = 1.41 \times 10^{-9}\text{ m}^2/\text{s} = \boxed{1.41 \times 10^{-5}\text{ cm}^2/\text{s}}$$

- (b) Wilke–Chang correlation (using an association parameter for water of 2.26 and a molar volume for oxygen of $25.6\text{ cm}^3\text{ mol}^{-1}$).

We are given the following values.

$$\phi = 2.26$$

$$V_0 = 25.6\text{ cm}^3\text{ mol}^{-1}$$

$$T = 25^\circ\text{C} = 298\text{ K}$$

$$M = 16.00\text{ g mol}^{-1} + 2(1.01\text{ g mol}^{-1}) = 18.02\text{ g mol}^{-1}$$

for association constant ϕ , molar volume for oxygen V_0 and molecular weight M of water (the solvent). Since $\text{Pa} \cdot \text{s} = \text{N} \cdot \text{s}/\text{m}^2 = \text{kg m}^{-1} \text{s}^{-1}$, we can easily convert the dynamic viscosity given in part (a) to units compatible with the other given values.

$$\begin{aligned}\mu &= 890.20 \times 10^{-6} \text{ Pa} \cdot \text{s} = 890.20 \times 10^{-6} \text{ kg m}^{-1} \text{s}^{-1} \\ &= 890.20 \times 10^{-6} \text{ kg m}^{-1} \text{s}^{-1} \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ m}}{10^2 \text{ cm}} = 890.20 \times 10^{-5} \text{ g cm}^{-1} \text{s}^{-1}\end{aligned}$$

The Wilke–Chang correlation states that the diffusion coefficient in $\text{cm}^2 \text{s}^{-1}$ is calculated empirically by

$$D = (7.4 \times 10^{-10}) \frac{T \sqrt{\phi M}}{\mu V_0^{0.6}} \quad (1.2)$$

which gives us

$$\begin{aligned}D &= (7.4 \times 10^{-10}) \frac{(298 \text{ K}) \sqrt{2.26(18.02 \text{ g mol}^{-1})}}{(890.20 \times 10^{-5} \text{ g cm}^{-1} \text{s}^{-1})(25.6 \text{ cm}^3 \text{mol}^{-1})^{0.6}} \\ &= \boxed{2.26 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}}\end{aligned}$$

(c) Now do some research to find the measured diffusion coefficient of oxygen atoms in water. Which method comes closest to the measured value? Why is the inferior method so far off? Be sure to cite the source from where you found the measure diffusion coefficient.

The diffusion coefficient of O_2 in pure water is $1.9\text{--}2.3 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ [Xing et al., 2014]. The Wilke–Chang correlation obtains a closer result of $D = 2.25 \times 10^{-5} \text{ cm}^2 \text{s}^{-1}$ rather than Stokes–Einstein’s value of $D = 1.41 \times 10^{-5} \text{ cm}^2/\text{s}$.

The Stokes–Einstein result is far off from the experimental range of D because: (1) Stokes–Einstein requires that the solute must be more than five times bigger than the solvent, while an oxygen atom is smaller than one water molecule, (2) the value is based on a spherical assumption of a singular oxygen atom rather than a diatomic molecule, and (3) Stokes–Einstein does not account for other factors such as intermolecular forces (solute–solvent interactions) and the volume of the solute unit.

2 Problem 2

Heat transfer and mass transfer are analogous transport phenomena and the conduction of heat and the diffusion of a solute are mathematically very similar. Solving either of these sorts of problems requires a good grasp of differential equations. In heat transfer, α is defined as the “diffusivity of temperature,” and is given by $\alpha = k/\rho C_P$, where k is the thermal conductivity of a medium, ρ is the medium density and C_P is the heat capacity. The 1D equation that relates temperature change in time and space is:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} \quad (2.3)$$

Let’s consider a patch of desert. The desert surface is at $z = 0$ and the temperature of the surface is the same temperature as the air above it. The z -axis points downward so that values of $z > 0$ are underground. Assume for the moment that the air temperature can be roughly modeled as oscillating with a period of 1 year, such that $\omega = 2\pi/\text{year}$. So, the temperature in the earth is a function of both time t and the depth z .

(a) Show that

$$T(t, z) = T_o(e^{-z/\delta}) \cos\left(\frac{z}{\delta} - \omega t\right) \quad (2.4)$$

where $\delta = \sqrt{2\alpha/\omega}$. Use the following boundary conditions:

- $T(t, z = 0) = T_o \cos \omega t$
- If you go deep enough into the earth (where z is very large), the temperature is constant and approximately equal to 0.

Our approach starts with an ansatz that $T(t, z)$ is a function whose variables t and z are separated as functions $X(t)$ and $Y(z)$ respectively. We then reexpress Equation (2.3) as a new differential equation that is both homogeneous first-order linear with respect to X and homogeneous second-order linear with respect to Y (Equation (2.6)).

$$T(t, z) = X(t)Y(z) \quad (2.5)$$

$$\frac{\partial T}{\partial t}(t, z) = X'(t)Y(z)$$

$$\frac{\partial^2 T}{\partial z^2}(t, z) = X(t)Y''(z)$$

$$X'(t)Y(z) = \alpha X(t)Y''(z) \quad (2.6)$$

Solving for $X(t)$, we simply integrate with respect to X as the equation is separable.

$$\begin{aligned}\frac{X'(t)}{X(t)} &= \alpha k = \frac{\alpha Y''(z)}{Y(z)} \\ \int \frac{X'(t)}{X(t)} dt &= \int \alpha k dt \\ \ln |X(t)| &= \alpha kt + \ln A \\ X(t) &= Ae^{\alpha kt}\end{aligned}\tag{2.7}$$

where $A \in \mathbb{R}$ is some constant and

$$k = \frac{X'(t)}{\alpha X(t)} = \frac{Y''(z)}{Y(z)}$$

Likewise, we attempt to obtain a solution for $Y(t)$ from the homogeneous second-order linear equation.

$$\begin{aligned}\alpha X(t)Y''(z) - X'(t)Y(z) &= 0 \\ Y''(z) - \frac{X'(t)}{\alpha X(t)}Y(z) &= 0 \\ Y''(z) - kY(z) &= 0\end{aligned}\tag{2.8}$$

The characteristic equation for this allows us to guess a solution form for Equation (2.8). Given two roots r_1 and r_2 , a possible solution can be formed as a linear combination of two basis solutions each derived from r_1 or r_2 .

$$r^2 - k = 0 \implies r_{1,2} = \pm k^{1/2}$$

Since r_1 and r_2 are distinct, we can guess that the solution to the differential equation (2.4) should come in the form

$$Y(z) = Be^{\sqrt{k}z} + Ce^{-\sqrt{k}z}\tag{2.9}$$

To make the solution “compatible” with the boundary condition $T(t, 0) = T_0 \cos \omega t$, we use Euler’s formula.

$$e^{i\theta} = \cos \theta + i \sin \theta\tag{2.10}$$

$$T(t, 0) = T_0 e^{-i\omega t}\tag{2.11}$$

since consequently $\Re(e^{-i\omega t}) = \cos -\omega t = \cos \omega t$. Setting this equal to $X(t)Y(z)$,

$$\begin{aligned}X(t)Y(z) &= Ae^{\alpha kt}(Be^{\sqrt{k}z} + Ce^{-\sqrt{k}z}) \\ X(t)Y(0) &= Ae^{\alpha kt}(B + C) = T_0 e^{-i\omega t}\end{aligned}\tag{2.12}$$

which comes from Equations (2.7) and (2.9). This gives us two new relations:

$$A(B + C) = T_0, \quad \alpha k = -i\omega \quad (2.13)$$

where the second relation gives $k = -i\omega/\alpha$. Plugging this back into Equation (2.12),

$$\sqrt{k} = (-i\omega/\alpha)^{1/2} = i^{3/2} \sqrt{\omega/\alpha}$$

Since $i^{3/2} = (e^{i\pi/2})^{3/2} = e^{3i\pi/4}$, then by Equation (2.10),

$$i^{3/2} = \cos \frac{3\pi}{4} + i \sin \frac{3\pi}{4} = \frac{1}{\sqrt{2}} - \frac{1}{\sqrt{2}}i = \frac{1}{\sqrt{2}}(i - 1)$$

If we set $\delta = \sqrt{2\alpha/\omega}$,

$$\sqrt{k} = \sqrt{\frac{\omega}{2\alpha}}(i - 1) = \frac{i - 1}{\delta} \quad (2.14)$$

Substituting (2.13) and (2.14) back into (2.12),

$$X(t)Y(z) = Ae^{-i\omega t}(Be^{(i-1)z/\delta} + Ce^{-(i-1)z/\delta}) \quad (2.15)$$

The second boundary condition states that as depth z increases, the temperature stabilizes to zero after arbitrarily large z . Symbolically,

$$T(t, \infty) = \lim_{z \rightarrow \infty} Ae^{-i\omega t}(Be^{(i-1)z/\delta} + Ce^{-(i-1)z/\delta}) = \lim_{z \rightarrow \infty} AB e^{-i\omega t} e^{(i-1)z/\delta} = 0$$

For this to be true, B has to be equal to zero (otherwise T diverges at infinite depth). Thus, by (2.13), $AC = T_0$, and we have the complex-valued form of the desired function.

$$\begin{aligned} T(t, z) &= ACe^{-i\omega t}e^{-(1-i)z/\delta} \\ &= T_0e^{-i\omega t}e^{-z/\delta}e^{iz/\delta} \\ &= T_0e^{-z/\delta}e^{i(z/\delta - \omega t)} \end{aligned}$$

Taking the real component of T , we have the desired solution by Equation (2.10).

$$\begin{aligned} \Re[T(t, z)] &= T_0e^{-z/\delta}\Re\left[e^{i(z/\delta - \omega t)}\right] \\ &= T_0e^{-z/\delta}\cos\left(\frac{z}{\delta} - \omega t\right) \end{aligned}$$

- (b) Note that δ is in units of length – it is a characteristic length of the problem, which ought to give you a good idea of how far the temperature changes on the surface penetrate into the earth. It is sometimes called the penetration depth, and for our desert limestone it has a value of ~ 3.2 m. At $z = \delta$ (in other words, if you measured the temperature 3.2 m below the surface of the desert), how long (in days) after the surface temperature had peaked would you record the maximum temperature at $z = \delta$?

At $z = \delta$, the temperature is

$$T(t, \delta) = T_0 e^{-\delta/\delta} \cos(\delta/\delta - \omega t) = T_0 e^{-1} \cos(1 - \omega t)$$

Suppose that the surface temperature peaks at the minimum time t_0 .

$$T(t_0, 0) = T_0 \cos \omega t_0 \implies \cos \omega t_0 = 1 \implies t_0 = 0$$

Now suppose the minimum time we want to record the maximum temperature is t_1 . T reaches its maximum when its sinusoidal component, $\cos(\cdot)$, equals one (i.e. $|\cos x| \leq 1$ for all x in the domain of interest).

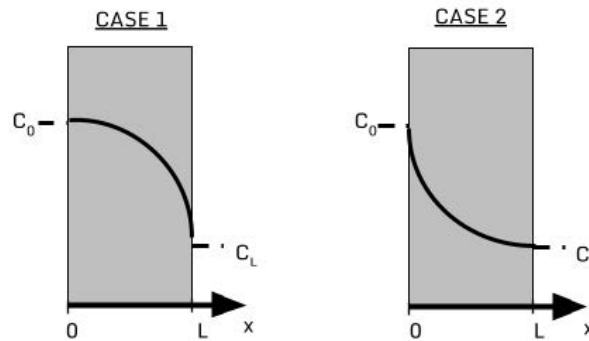
$$\cos(1 - \omega t_1) = 1 \implies 1 - \omega t_1 = 0 \implies t_1 = 1/\omega$$

So, the time after the surface temperature peaks would be

$$\Delta t = t_1 - t_0 = 1/\omega = (365 \text{ days})/(2\pi) = \boxed{58.1 \text{ days}}$$

3 Problem 3

Two membranes are shown below. The membranes separate two well-stirred baths so that the concentration of solute on either side of each membrane is constant. The concentration is C_0 on the left of the membrane and C_L on the right, $\phi = 1$, and $C(x)$ is drawn in the membrane. A chemical reaction is taking place within the membranes, yielding a non-zero rate of reaction R . Using Fick's 2nd law, derive the concentration function $C(x)$ inside the membrane in terms of D , C_0 , C_L , L , and R . For which case below is $R > 0$ and for which is $R < 0$. Explain your answer.



The two boundary conditions are that

$$C(x=0) = \phi C_0 = C_0 \quad C(x=L) = \phi C_L = C_L \quad (3.16)$$

Fick's second law states that for concentration $C(x, t)$, diffusivity D , and reaction rate R ,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} + R \quad (3.17)$$

and since the situation does not involve non-steady concentrations, then the concentration function is constant with respect to t . So, C should be expressed as $C(x)$ only, and

$$0 = D \frac{d^2 C}{dx^2} + R \quad (3.18)$$

Rearranging, we get a form that can be twice integrated to yield C .

$$\frac{d^2 C}{dx^2} = -\frac{R}{D} \quad (3.19)$$

Integrating,

$$\iint \frac{d^2 C}{dx^2} dx dx = \iint -\frac{R}{D} dx dx = \int \left(-\frac{R}{D}x + A \right) dx = -\frac{R}{2D}x^2 + Ax + B \quad (3.20)$$

where A and B are constants. From the boundary conditions (3.16), we have

$$\begin{aligned} C(0) &= C_0 = B \\ C(L) &= -\frac{R}{2D}L^2 + AL + B = C_L \end{aligned}$$

and so

$$\begin{aligned} AL &= C_L - C_0 + \frac{R}{2D}L^2 \\ A &= \frac{C_L - C_0}{L} + \frac{R}{2D}L \end{aligned}$$

Thus the concentration function is

$$\boxed{C(x) = -\frac{R}{2D}x^2 + \left(\frac{C_L - C_0}{L} + \frac{RL}{2D} \right)x + C_0} \quad (3.21)$$

We can determine each case by looking at the sign of $C''(x)$ from Equation (3.18).

1. In case 1, the graph of C is concave down, so $C''(x) = -R/D < 0$. Thus, $R > 0$.
2. In case 2, the graph of C is concave up, so $C''(x) = -R/D > 0$. Thus, $R < 0$.

4 Problem 4

Complete the Lab 02 protocol and fill out the following table.

The table below shows that the fluxes are consistent throughout the entire system regardless of concentration.

	Far left	1-2 interface	2-3 interface	Far right
c (mol m ⁻³)	0.80000	0.54684		
c_2 (mol m ⁻³)		0.13671	0.010127	
c_3 (mol m ⁻³)			0.050633	0.0000
Flux c (mol m ⁻¹ s ⁻¹)	1.2658×10^{-9}	1.2658×10^{-9}		
Flux c_2 (mol m ⁻¹ s ⁻¹)		1.2658×10^{-9}	1.2658×10^{-9}	
Flux c_3 (mol m ⁻¹ s ⁻¹)			1.2658×10^{-9}	1.2658×10^{-9}

References

- [Kestin et al., 1978] Kestin, J., Sokolov, M., and Wakeham, W. A. (1978). Viscosity of liquid water in the range -8°C to 150°C . *Journal of Physical and Chemical Reference Data*, 7(3):941–948.
- [Xing et al., 2014] Xing, W., Yin, M., Lv, Q., Hu, Y., Liu, C., and Zhang, J. (2014). 1 - oxygen solubility, diffusion coefficient, and solution viscosity. In Xing, W., Yin, G., and Zhang, J., editors, *Rotating Electrode Methods and Oxygen Reduction Electrocatalysts*, pages 1–31. Elsevier, Amsterdam.