Solutions to Exam #2

1. Imagine an experimental apparatus consisting of a very long cylindrical tube of cross–sectional area A. The tube is placed horizontally along the x–axis. Initially there is an impermeable membrane at $x = 0$. For $x < 0$, the tube if filled with a solutions containing a substance with concentration C_o (in number of particles per unit volume). For $x > 0$, the tube is filled with a solution in which the concentration of the substance is 0. At time $t = 0$, the membrane at $x = 0$ is removed and the substance on the left begins to disperse towards the right. At any x and time $t > 0$, let $C(x, t)$ denote the concentration of the substance at points on the cross–section at x and at time t. Assume that C is a C^2 function; that is, the second partial derivatives of C exist and are continuous for all x and all $t > 0$.

   (a) Write down a differential equation model that describes the evolution of $C(x, t)$ in time, subject to the initial condition described above.

   Solution: The function C satisfies the initial value problem

$$\begin{cases} \dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2}, & x \in \mathbb{R},\ t > 0; \\ C(x,0) = f(x), & x \in \mathbb{R}, \end{cases} \tag{1}$$

   where

$$f(x) = \begin{cases} C_o, & \text{if } x \leqslant 0; \\ 0, & \text{if } x > 0. \end{cases} \tag{2}$$

   □

   (b) Give a solution to the initial value problem formulated in part (a). Express the solution in terms of the Error function. ***Solution:*** A candidate for a solution is given by

$$C(x,t) = \int_{-\infty}^{\infty} p(x-y,t) f(y)\, dy, \quad \text{for } x \in \mathbb{R} \text{ and } t > 0, \tag{3}$$

   where

$$p(x,t) = \frac{e^{-x^2/4Dt}}{\sqrt{4\pi D t}}, \quad \text{for } x \in \mathbb{R} \text{ and } t > 0, \tag{4}$$

   is the heat kernel.

Next, use (2) and (4) to obtain from (3) that

$$C(x,t) = C_o \int_{-\infty}^{0} \frac{e^{-x^2/4Dt}}{\sqrt{4\pi Dt}}\ dy, \qquad \text{for } x \in \mathbb{R} \text{ and } t > 0. \tag{5}$$

Make the change variables $s = \dfrac{x-y}{\sqrt{4Dt}}$ in (5) to obtain

$$C(x,t) = \frac{C_o}{\sqrt{\pi}} \int_{\infty}^{x/\sqrt{4Dt}} e^{-s^2}\ ds, \qquad \text{for } x \in \mathbb{R} \text{ and } t > 0,$$

which can be written in terms of the Error function as

$$C(x,t) = \frac{C_o}{2}\left[1 - \text{Erf}\left(\frac{x}{\sqrt{4Dt}}\right)\right], \qquad \text{for } x \in \mathbb{R} \text{ and } t > 0. \tag{6}$$

□

(c) Use Fick's first law of diffusion to compute the flux, $J_x(x,t)$, of the substance in the solution. Give an interpretation for $J_x(0,t)$.

***Solution**:* Using Fick's first law of diffusion,

$$J_x(x,t) = -D\frac{\partial}{\partial x}[C(x,t)],$$

we obtain from (6) that

$$J_x(x,t) = \frac{DC_o}{\sqrt{4\pi Dt}} e^{-x^2/4Dt}, \qquad \text{for } x \in \mathbb{R} \text{ and } t > 0,$$

or

$$J_x(x,t) = \frac{C_o\sqrt{D}}{2\sqrt{\pi}} \frac{e^{-x^2/4Dt}}{\sqrt{t}}, \qquad \text{for } x \in \mathbb{R} \text{ and } t > 0.$$

The flux at $x = 0$,

$$J_x(0,t) = \frac{C_o\sqrt{D}}{\sqrt{\pi}} \frac{1}{2\sqrt{t}}, \qquad \text{for } t > 0, \tag{7}$$

is the number of particles of the substance per unit area that cross the cross–section at $x = 0$ in a unit of time. □

(d) Let M_t denote the number of particles of the substance in the solution that crossed the cross–section at $x = 0$ during the time interval $[0,t]$. Use the result from part (c) to derive the formula

$$M_t = \frac{AC_o\sqrt{D}}{\sqrt{\pi}}\ \sqrt{t}, \tag{8}$$

where D is the diffusivity of the medium in the tube.

***Solution**:* To compute M_t integrate $AJ_x(0,t)$, where $J_x(0,t)$ is given in (??) and A is the cross–sectional area, from 0 to t to obtain

$$\begin{aligned} M_t &= \int_0^t AJ_x(0,\tau)\, d\tau \\ &= \int_0^t \frac{AC_o\sqrt{D}}{\sqrt{\pi}} \frac{1}{2\sqrt{\tau}}\, d\tau \\ &= \frac{AC_o\sqrt{D}}{\sqrt{\pi}}\sqrt{t}, \end{aligned}$$

where we have used (7). We have therefore established (8). □

(e) Give an interpretation for (8) and explain how you can use the result in (8) to estimate the diffusivity of the medium.

***Solution**:* The expression in (8) implies that a plot of M_t versus $\sqrt{t}$ should yield a linear relation with slope $\dfrac{AC_o\sqrt{D}}{\sqrt{\pi}}$. Thus, if there is an experimental way to measure M_t for various times $t_1, t_2, \ldots, t_k$, we can plot the points $(\sqrt{t_i}, M_{t_i})$, for $t = 1, 2, \ldots, k$. We can then obtain the least–square linear fit of the points to get an estimate for the slope, m. Using the estimate

$$\frac{AC_o\sqrt{D}}{\sqrt{\pi}} = m, \tag{9}$$

we can solve for D in (9) to get the estimate

$$D = \pi\left(\frac{m}{AC_o}\right)^2$$

for the diffusivity, D, of the medium. □

2. *(Estimating the Diffusivity)* Suppose that the tube described in Problem 1 has total length L and that the equation in (8) holds true in this case as well. Assume also that the middle cross–section of the tube is located at $x = 0$.

   (a) Let M_o denote the number of particles to the left of $x = 0$ in the setup described in Problem 1 before the membrane at $x = 0$ is removed. Give a formula for computing M_o.

***Solution**:* At time $t = 0$, the concentration of to the left of 0 is C_o and the total volume of the solution in that region is $\frac{AL}{2}$. It then follows that the total number of particles to the left of $x = 0$ at time $t = 0$ is

$$M_o = \frac{C_o AL}{2}. \tag{10}$$

□

(b) Use your result from part (a) and the formula in (8) to derive the formula

$$\frac{M_t}{M_o} = 2\frac{\sqrt{D}}{\sqrt{\pi L^2}}\sqrt{t}. \tag{11}$$

***Solution**:* Combining (8) and (10) we get

$$\frac{M_t}{M_o} = \frac{AC_o\sqrt{D}}{\sqrt{\pi}}\sqrt{t}\cdot\frac{2}{C_o AL},$$

from which (11) follows. □

(c) The graph in Figure 1 on page 6 of this exam shows a plot of the ratio M_t/M_o versus $\sqrt{t}$ based on data collected in experiments[1] involving diffusion of bromophenol blue anions (series a) and KCL (series b). The lines in the plot in Figure 1 are the least–square regression lines. The length of the tube, L, in the bromophenol blue experiment is 8.7 cm and that in the KCl experiment is 9.3 cm. The time is measured in seconds.

Use (11) and the data in Figure 1 to estimate the diffusion coefficients for (i) bromophenol blue, and (ii) KCl.

***Solution**:* Let m denote the slope of the regression lines in Figure 1. Then, according to (11), m provides an estimate for $2\frac{\sqrt{D}}{\sqrt{\pi L^2}}$; so that

$$2\frac{\sqrt{D}}{\sqrt{\pi L^2}} = m. \tag{12}$$

Solving for D in (12) yields the estimate

$$D = \frac{\pi m^2 L^2}{4} \tag{13}$$

[1] Crooks, J. E., *Measurement of Diffusion Coefficients.* Journal of Chemical Education, 1989, **66**, pp. 614–615

for the diffusion coefficient D. Observe that, according to (11) and (12), m has units of 1 over square root of time. It then follows from (13) that D has unit of square length per time, as expected for a diffusion coefficient.

We can use the plot in Figure 1 to estimate the slopes of the regression lines for series a and b. For series a, we obtain the estimate

$$m_a \doteq 2.84 \times 10^{-4} \quad 1/\sqrt{\text{sec}}; \tag{14}$$

and for series b,

$$m_b \doteq 5.12 \times 10^{-4} \quad 1/\sqrt{\text{sec}}. \tag{15}$$

The length of the tube for series a is

$$L_a = 8.7 \text{ cm}; \tag{16}$$

and that for series b is

$$L_b = 9.3 \text{ cm}. \tag{17}$$

Using the formula in (13) for the diffusivity, D, with the values of m and L given in (14) and (16), respectively, we obtain the estimate

$$D_a \doteq 4.79 \times 10^{-6} \quad \text{cm}^2/\text{sec},$$

for the diffusion coefficient of bromophenol blue.

Similarly, using the estimates in (15) and (17), we obtain the estimate

$$D_b \doteq 1.78 \times 10^{-5} \quad \text{cm}^2/\text{sec},$$

for the diffusion coefficient of KCl. □

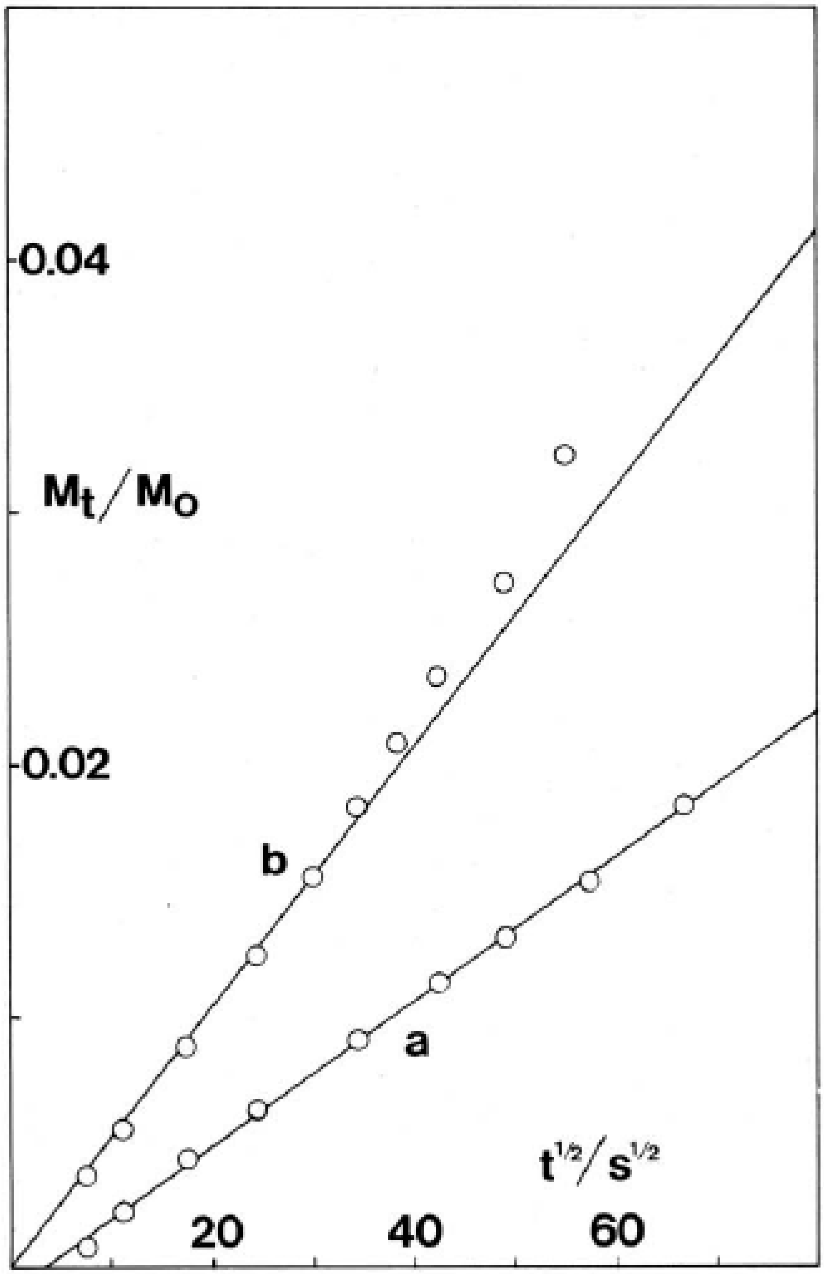

Figure 1: M_t/M_o versus $\sqrt{t}$. Series a: bromophenol blue anion. Series b: KCl