

Questions

1. Fick's first law says that the flux of a solute is down its concentration gradient. Concentration gradients are well defined for continuous quantities. However, matter is not continuous. The point of this exercise is to understand whether the discrete nature of matter invalidates our formulation of Fick's first law.

a. Assume that the sodium concentration in physical saline is 150 mmol/L. Estimate the dimensions of a cube of physical saline that contains one million sodium molecules.

⇒ **Solution :**

One million sodium ions can be expressed in moles by dividing by Avogadro's number: $\frac{10^6}{6.022 \times 10^{23}}$ = 1.66×10^{-18} mol. A concentration of 150 mmol/L is equivalent to 150 mol/m³. Therefore the volume that contains 1.66×10^{-18} mol is

$$\frac{1.66 \times 10^{-18} \text{ mol}}{150 \text{ mol/m}^3} \approx 1.1 \times 10^{-20} \text{ m}^3 \approx (0.23 \mu\text{m})^3$$

A quarter- μ m cube of physiological saline contains approximately one million sodium ions.

b. With a few well-chosen sentences, describe how the result in Part a can be used to understand how the discrete nature of matter limits our application of Fick's first law.

⇒ **Solution :**

There could be 1,000,000 particles in a quarter- μ m cube of physiological saline, or 1,000,001 particles, but there could not be 1,000,000.17354 particles. Thus, possible values of the concentration of sodium ions in a quarter- μ m cube of physiological saline are limited by the discrete nature of matter. However, the difference between 1,000,000.17354 and 1,000,000 is such a small fraction of the number of particles that it can be ignored with little error (1 part in 1,000,000).

2. Measurements show that the diffusivity of potassium ions in aqueous solutions of KCl changes very little with the concentration of KCl. The diffusivities in 10, 100, and 1000 mmol/L solutions are 1.917×10^{-5} , 1.844×10^{-5} , and 1.892×10^{-5} cm²/s. Is this consistent or inconsistent with the Random

Walk Model of diffusion. Explain with a few well-chosen sentences.

⇒ **Solution :**

According to the Random Walk Model of diffusion, solute particles are in constant random motion because of collisions with solvent molecules. The idea is that solvent molecules so greatly outnumber solute particles that interactions between solute particles can be ignored (much as in the ideal gas approximation). If we assume that solute particles never collide with other solute particles, then the mean free path and mean free time between collisions of one particular solute particle and solvent molecules does not depend on how many other solute particles are present. Thus, the Random Walk Model of diffusion is consistent with the observation that potassium diffusivity should not depend on potassium concentration.

3. According to the random walk model, diffusion occurs because thermal agitations cause random motions of solute particles. It is therefore clear that the diffusivity of a solute should depend on temperature. However, diffusivity also depends on the solvent. Is the dependence of diffusivity on solvent consistent or inconsistent with the Random Walk Model of diffusion. Explain.

⇒ **Solution :**

Consistent. According to the random walk model, solutes diffuse because of collisions with solvent molecules. Therefore, it isn't surprising that diffusivity should depend on what the solvent molecules are. For example, we should expect very different patterns of collisions when helium diffuses through air and water

4. A variable $n(t)$ is described by a first-order linear differential equation with constant coefficients

$$\tau \frac{dn(t)}{dt} + n(t) = n_{\infty}$$

where τ and n_{∞} are constants. Let $n(0) = n_0$.

a. For $t \geq 0$, determine an expression for $n(t)$ in terms of n_0 , τ and n_{∞} .

⇒ **Solution :**

A first-order, linear differential equation with constant coefficients and a constant inhomogeneous (drive or input) term has an exponential solution. Therefore, the solution can be written in the form

$$n(t) = n_{\infty} + (n_0 - n_{\infty})e^{-t/\tau}$$

where $n_0 = n(0)$ is the initial value of $n(t)$ and $n_\infty = \lim_{t \rightarrow \infty} n(t)$

b. Plot $n(t)$ versus t for the following two cases and explain the difference between the two plots:

- $n_0 = 0, n_\infty = 10, \text{ and } \tau = 1$
- $n_0 = 0, n_\infty = 10, \text{ and } \tau = 10$

⇒ **Solution :**

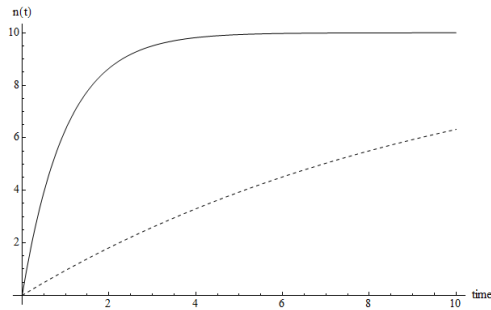


Figure 1: Plot of $n(t)$ for $\tau = 1$ (solid line) and $\tau = 10$ (dashed)

c. Plot $n(t)$ versus t for the following two cases and explain the difference between the two plots:

- $n_0 = 10, n_\infty = 0, \text{ and } \tau = 1$
- $n_0 = 10, n_\infty = 10, \text{ and } \tau = 1$

⇒ **Solution :**

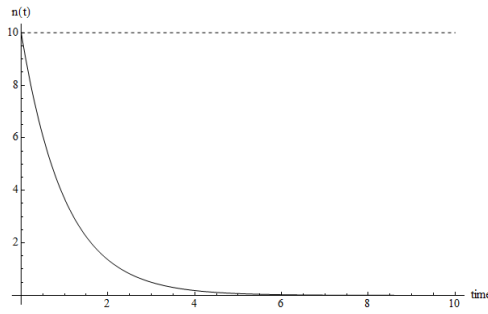


Figure 2: Plot of $n(t)$ for $n_{\infty} = 0$ (solid line) and $n_{\infty} = 10$ (dashed)

d. Plot $n(t)$ versus t for the following two cases and explain the difference between the two plots:

- $n_0 = 10$, $n_{\infty} = 0$, and $\tau = 1$
- $n_0 = -10$, $n_{\infty} = 10$, and $\tau = 1$

⇒ **Solution :**

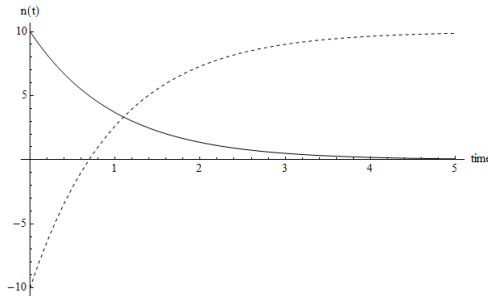


Figure 3: Plot of $n(t)$ for $n_0 = 10$ (solid line) and $n_0 = -10$ (dashed)

e. For the above generated graphs, describe a physical system that can be characterized by said plots. Ensure that you explain what each axis represents.

⇒ **Solution :**

For Figure 1, 2, and 3, the y-axis can represent the concentration of a given substance diffusing into/out of a solvent (respectively), whereas the x-axis can represent time (in arbitrary units - as the system is allowed to stabilize over infinite amount of time, the given substance's concentration will reach its equilibrium value).

Figure 1: for the solid line, it can be stated that the substance reaches a concentration of 10 units per volume, whereas for the dashed line, the substance reaches a concentration of 6 units per volume; the dashed line represents a system where the substance is less soluble in comparison with the solid line.

Figure 2: for the solid line, it can be stated that the substance in a solvent starts at a concentration of 10 units per volume, and completely diffuses out of the solvent, whereas the dashed line can represent the substance in a solvent which renders the solute indiffusible.

Figure 3: for the solid line, it can be stated that the substance in a solvent starts at a concentration of 10 units per volume, and completely diffuses out of the solvent. For the dashed line, the concentration quantity cannot be negative; therefore, it can be stated that the dashed line represents an unphysical system.

5. A general solution to a first-order linear differential equation with constant coefficients can be written as

$$n(t) = n_{\infty} + (n_0 - n_{\infty})e^{-t/\tau}$$

a. Determine the slope $m_0 = dn/dt$ at $t = 0$ in terms of n_0 , τ and n_{∞} .

⇒ **Solution :**

The initial slope of $n(t)$ with respect to t can be obtained from the solution or directly from the differential equation. The latter gives

$$m_0 = \left(\frac{dn(t)}{dt} \right)_{t=0} = \frac{n_{\infty} - n_0}{\tau}$$

b. If this slope were extended for $t > 0$ (i.e., $n^*(t) = n_0 + m_0t$), for what value of t will $n^*(t) = n_{\infty}$?

⇒ **Solution :**

Substitution for the slope in $n^*(t)$ gives

$$n^*(t) = n_0 + m_0t = n_0 + (n_{\infty} - n_0)\left(\frac{t}{\tau}\right)$$

Examination of this equation reveals that $n^*(t) = n_{\infty}$ when $t = \tau$. Thus, a line that has the same slope as the initial slope of the exponential intersects the final value of the exponential at a time that equals the time constant.

c. Plot $n(t)$ and $n^*(t)$ when $n_0 = -10$, $n_\infty = 10$, and $\tau = 1$.

⇒ **Solution :**

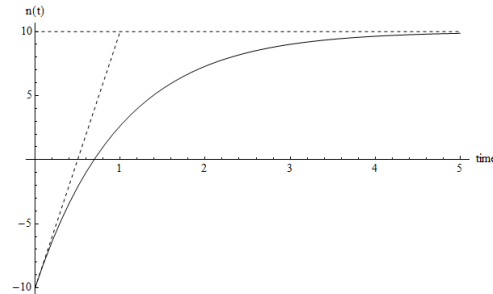
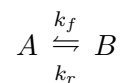


Figure 4: Plot of $n(t)$ (solid) and $n^*(t)$ (dashed)

6. For the chemical reaction



c_A is the concentration of the reactant A , c_B is the concentration of the product B , and the k s are rate constants for the chemical reaction. Then

$$\frac{dc_A}{dt} = k_r c_B - k_f c_A$$

and

$$\frac{dc_B}{dt} = k_f c_A - k_r c_B$$

The total quantity of product plus reactant is conserved in this reaction so that

$$C = c_A(t) + c_B(t)$$

a. Find the differential equation satisfied by $c_A(t)$.

⇒ **Solution :**

Substitution for $c_B(t)$ yields

$$\frac{dc_A(t)}{dt} = k_r(C - c_A(t)) - k_f c_A(t)$$

which can be rewritten as

$$\frac{dc_A(t)}{dt} + (k_r + k_f)c_A(t) = k_r C$$

b. If the initial concentration of A is $c_A(0) = c_{A0}$, determine c_A and c_B for $t \geq 0$ and sketch the results.

⇒ **Solution :**

The solution has the form

$$c_A(t) = c_{A\infty} + (c_{A0} - c_{A\infty})e^{-\frac{t}{\tau}}$$

where $c_{A\infty} = \frac{k_r C}{k_r + k_f}$ is the final value of $c_A(t)$ and is gotten from the differential equation by setting the derivative to 0 and solving for c_A . The time constant $\tau = \frac{1}{k_r + k_f} \cdot c_B(t)$ is found as follows

$$c_B(t) = C - c_A(t) = (C - c_{A\infty}) - (c_{A0} - c_{A\infty})e^{-\frac{t}{\tau}}$$

Both $c_A(t)$ and $c_B(t)$ are shown in Figure 5. The plots show that at each point in time $c_A(t) + c_B(t) = C$.

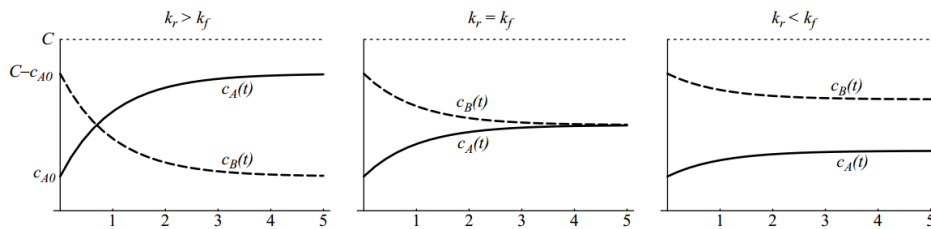


Figure 5: Plot of $c_A(t)$ and $c_B(t)$, which are drawn for the case $c_{A0} < c_{A\infty}$.

7. A 10 m^3 tank filled with water contains 0.05 m^3 of sand. A substance is added to the tank such that its concentration in the water is 10 M . The partition coefficient between the sand and water is $K_n = C_{sand}/C_{water} = 30$.

a. Given the partition coefficient of the system, what does this tell us about the tank? What is expected to happen to the added substance? (i.e in which compound is the added substance more soluble?)

⇒ Solution :

Since a given substance will distribute itself according to its partition coefficient, it can be stated that at equilibrium, the ratio of the concentration of the added substance in the sand and in the water will equal the partition coefficient for the given substance. Therefore, given the partition coefficient, it can be seen that the added substance is approximately 30 times more soluble in sand than it is in water.

b. Allowing the system to reach equilibrium, what will the concentration of the added substance be in the sand?

⇒ Solution :

$$K_n = \frac{C_{\text{in water}}}{C_{\text{in sand}}} = \frac{\# \text{ mol in water} \cdot V_{\text{sand}}}{V_{\text{water}} \cdot \# \text{ mol in sand}} = \frac{\text{mass in water} \cdot V_{\text{sand}} \cdot M}{M \cdot V_{\text{water}} \cdot \text{mass in sand}}$$

where the molecular mass M of the added substance can be cancelled out using the following formula:

$$\# \text{ mol} = \frac{\text{mass}}{\text{molar mass}}$$

Knowing that the initial added mass of the substance must always be conserved, the following can be shown:

$$\text{total mass} = \text{mass in sand} + \text{mass in water} = \frac{1 \text{ g}}{\text{m}^3} \cdot 10 \text{ m}^3 = 10 \text{ g}$$

Rearrange the partition coefficient equation to solve for the mass in water:

$$\text{mass in water} = \frac{V_{\text{water}} \cdot \text{mass in sand}}{V_{\text{sand}} \cdot K_n}$$

Substitute the given equation above into the equation for the total mass of the added substance; solve for the mass of the added substance in sand:

$$\text{mass in sand} = \frac{V_{\text{sand}} \cdot K_n \cdot \text{total mass}}{(V_{\text{sand}} \cdot K_n) + V_{\text{water}}}$$

The concentration of the substance in the sand once the system reaches equilibrium can therefore be represented by the following equation:

$$C_{\text{in sand}} = \frac{\text{mass in sand}}{V_{\text{sand}}} = \frac{K_n \cdot \text{total mass}}{(V_{\text{sand}} \cdot K_n) + V_{\text{water}}} = \frac{30 \cdot 10 \text{ g}}{(0.05 \text{ m}^3 \cdot 30) + 10 \text{ m}^3} \approx 26.09 \frac{\text{g}}{\text{m}^3}$$

c. Sketch a graph depicting the concentration of the added substance in the sand as a function of time. Make sure to label the graph accordingly.

⇒ **Solution :**

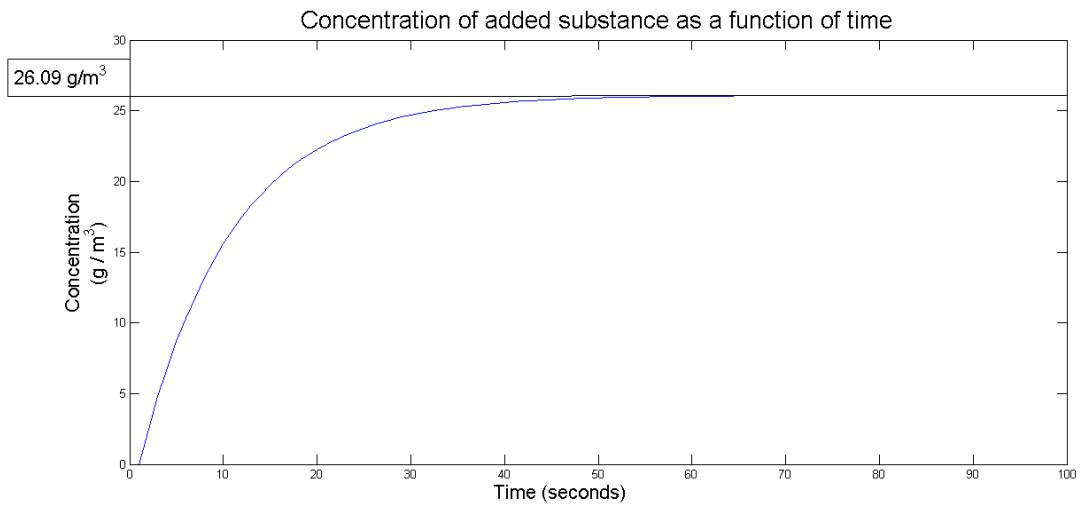


Figure 6: Plot of the concentration of the added substance in the sand as a function of time (note: the time axis is arbitrary; it is assumed that as t approaches ∞ , the concentration of the added substance in the sand will reach its equilibrium value)