

University of Washington
Department of Chemistry
Chemistry 453
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Lecture 23 3/11/15

A. Diffusion of Macromolecules

- To understand diffusion-controlled kinetics we have to first quantify our notion of diffusion.
- Assume a solute (labeled subscript 2) has a concentration gradient $C_2(x)$. Then the chemical potential is also dependent on x and has the form:

$$\mu_2(x) = \mu_2^0 + k_B T \ln C_2(x) \quad (23.1)$$

- The gradient in the chemical potential gives rise to a transport force which effectively moves solvent molecules from the region in solution where the concentration of solute is high to regions where the solute concentration is low. This force has the form:

$$F_{transport} = -\frac{d\mu_2(x)}{dx} = -k_B T \frac{d \ln C_2(x)}{dx} = -\frac{k_B T}{C_2(x)} \frac{dC_2(x)}{dx} \quad (23.2)$$

- The transport force is opposed by the frictional force which has the opposite sign relative to the transport force:

$$F_f = f v_2 \quad (23.3)$$

where f is the coefficient of friction and v_2 is the velocity of solute transport.

- At steady state these two forces are in balance so solute moves through the solvent at a constant velocity:

$$-\frac{k_B T}{C_2(x)} \frac{dC_2(x)}{dx} = f v_2 \Rightarrow -\frac{k_B T}{f} \frac{dC_2(x)}{dx} = v_2 C_2(x) \quad (23.4)$$

- The quantity $v_2 C_2(x) = J_2(x)$ is called the solute flux, and has the interpretation as the amount of solute that passes through a unit area per unit time.
- The quantity $\frac{k_B T}{f} = D$ is called the diffusion coefficient. With these two definitions equation 23.4 becomes:

$$J_2(x) = -D \frac{dC_2(x)}{dx} \quad (23.5)$$

- Equation 23.5 is called Fick's First Law. It basically relates the solute flux to the solute concentration gradient with D the constant of proportionality. The negative sign indicates that the flux of particles occurs against the concentration gradient. See Figure 23.2. In other words solute molecules will move in to regions where the solute concentration is lower.

- We can differentiate both side of 21.13 to get

$$\frac{dJ_2(x)}{dx} = -\frac{\partial C_2(x,t)}{\partial t} \quad (23.6)$$

- The left hand side of equation 23.14 $\frac{dJ_2(x)}{dx}$ is called a flux gradient. With reference to Figure 23.3, depending on the sign of the flux gradient the concentration of solute will increase or decrease within a given volume.

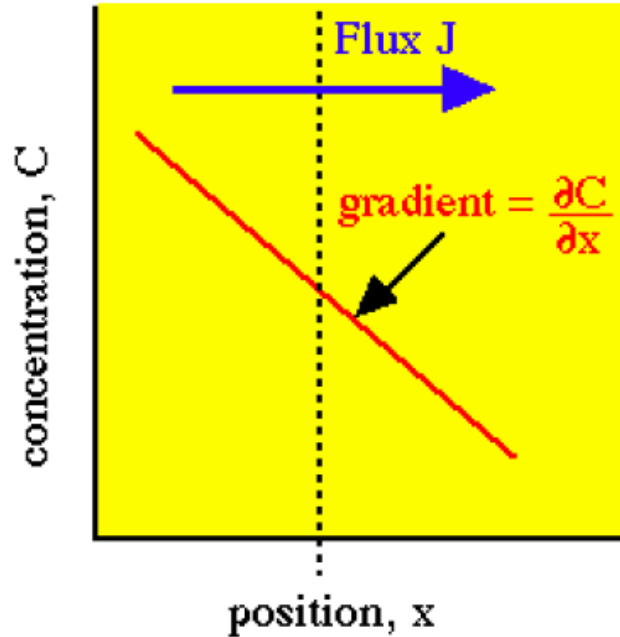


Figure 23.2: Illustration of Fick's First Law. The flux (blue arrow) occurs against the concentration gradient (red line). Solute particles diffuse from the area of high concentration to the area of low concentration.

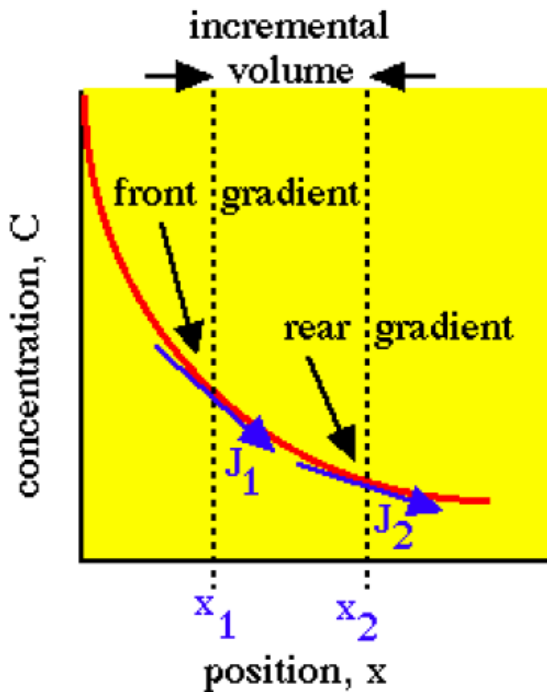


Figure 23.3: This is an illustration of Fick's Second Law. Consider the region defined by $x_1 < x < x_2$. If the flux coming into this region J_1 is greater than J_2 , the outgoing flux, the solute concentration in the region increases. If $J_1 < J_2$ the concentration decreases giving us equation 23.14

- Differentiate both sides of equation 23.13 and substitute in equation 23.14 to obtain. The diffusion equation:

$$\frac{\partial C_2(x,t)}{\partial t} = D \frac{\partial C_2(x,t)}{\partial x} \quad (23.7)$$

- The solution to 23.15 is

$$C_2(x,t) = \frac{C_0}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad (23.8)$$

- Like the solution to the random walk problem equation 23.6, this is a Gaussian or “bell-shaped” curve which spreads out as time increases, see Figure 23.4.

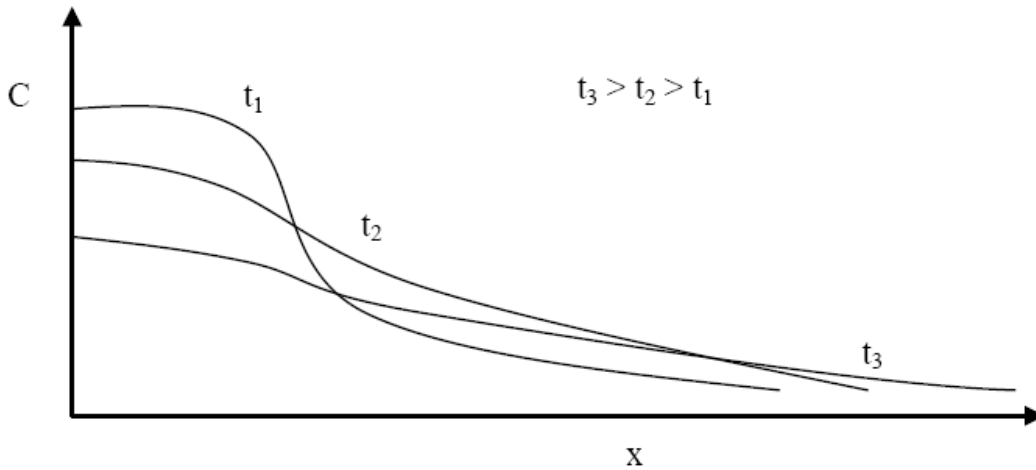


Figure 23.4: The diffusion profile $C_2(x,t)$ from equation 23.8 plotted for three values of t and for $x > 0$. Initially all solute was concentrated in a band at the left position, i.e. $x=0$.

- Because diffusing particles do not move in straight lines we can only calculate their mean displacements and their mean-squared displacements.

$$\langle x \rangle = \int_{-\infty}^{+\infty} x C_2(x,t) = \frac{C_0}{\sqrt{4\pi Dt}} \int_{-\infty}^{+\infty} x e^{-x^2/4Dt} = 0$$

$$\langle x^2 \rangle = \int_{-\infty}^{+\infty} x^2 C_2(x,t) = \frac{C_0}{\sqrt{4\pi Dt}} \int_{-\infty}^{+\infty} x^2 e^{-x^2/4Dt} = 2Dt \quad (23.9)$$

$$\therefore x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{2Dt}$$

- Equation 23.9 means that although the net displacement of particles in diffusion is zero, the rms displacement of a particle undergoing Brownian motion is dependent on the square root of time and the diffusion coefficient. Assuming displacements in the x , y , and z directions occur with equivalent probability the three dimensional displacement is:

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 2Dt + 2Dt + 2Dt = 6Dt \quad (23.10)$$

- The coefficient of translation diffusion D can be calculated for specific experimental conditions and molecular properties. For a spherical macromolecule of radius R :

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta R} \quad (23.11)$$

where $f = 6\pi\eta R$ is called Stokes' Law.

- The radius R is the radius of a hydrated macromolecule...a molecule coated with a layer of water molecules that move with the macromolecule. R is called for this reason a hydrodynamic radius.
- The quantity η is the solution viscosity. The viscosity has units of $\text{kg m}^{-1} \text{s}^{-1}$. The viscosity of water at $T=298\text{K}$ is about $0.891 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} = 1.00 \text{ centiPoise (cP)}$.
- Example: Calculation of D .

Suppose a spherical macromolecule has a hydrodynamic radius $R=4.00\text{nm}$. Assume the solution is very dilute so at $T=298\text{K}$ the solution viscosity is $\eta=0.891 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$. Calculate D .

$$\begin{aligned} D &= \frac{k_B T}{6\pi\eta R} = \frac{(1.38 \times 10^{-23} \text{ JK}^{-1})(298\text{K})}{(18.84)(0.891 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1})(4.00 \times 10^{-9} \text{ m})} \\ &= \frac{4.11 \times 10^{-21} \text{ J}}{6.71 \times 10^{-11} \text{ kg s}^{-1}} = 6.13 \times 10^{-11} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

Translational diffusion coefficients for macromolecules are frequently in the 10^{-11} - $10^{-12} \text{ m}^2 \text{ s}^{-1}$ range.