Model 1   **Mathematical statement of Fick's First Law**

$$J_X = -D\frac{\partial c}{\partial x}$$

1. In the equation above, J is the flux in the x-direction with units of mole/m³-sec. Define the term flux.

2. In the equation above, D is the diffusion coefficient (not to be confused with the distribution coefficient, D), which is a property of a compound that is proportional to its rate for diffusion. D depends on size, shape and the solvent medium. What are the units of D? Would D generally increase or decrease as molecular size increases?

3. Does a positive net flux means that more moles enter a given area or leave a given area per unit time. Explain the negative sign conceptually by the direction of the flux relative to the direction of the diffusing particles.

4. The first law model is static in time. However, as the flux gradient builds up in space, the concentration with time changes as given below. According to this equation, does the concentration increase or decrease as the flux gradient increases? Explain what this means.

$$-\left(\frac{\partial J}{\partial x}\right)_t = \left(\frac{\partial c}{\partial t}\right)_X$$

Model 2   Fick's Second Law

$$\left(\frac{\partial c}{\partial t}\right)_x = -D\left(\frac{\partial^2 c}{\partial x^2}\right)_t$$

For a thin layer of solution that can be viewed as our sample applied to a separation in a quantity w (g/cm^2), Fick's Second Law can be used to derive a new expression for concentration as a function of time.

$$c = \frac{w}{\left(4\pi Dt\right)^{1/2}} e^{\frac{-x^2}{4Dt}}$$

1. Write the equation of a Gaussian distribution (from Harris Chapter 4) next to the equation above. Which term is equal to 4Dt in the concentration function on the left?

2. Qualitatively, how will the concentration function above change in magnitude and shape as a function of time? Draw the shapes of a thin Gaussian peak at some initial time t_i and some later time t_f. Think about the derivative and what it looks like relative to the function.

3. Mathematically, an infinitely thin solvent zone (called a δ function) will diffuse to form a Gaussian peak. How would we use Fick's second law to predict how wide the peak will be after a give time, t?

4. For his PhD thesis, Albert Einstein derived an equation relating the mean square displacement, $\left\langle x^2 \right\rangle$, to time.

$$\left\langle x^2 \right\rangle = 2Dt \qquad\qquad \left\langle x^2 \right\rangle^{1/2} = \sqrt{2Dt}$$

How do these equations follow from Model 2?

MODEL 3   Stokes Equation

Force is the product of an object's mass and acceleration. In solution any force (such as an electric field acting upon a molecule) is opposed by the frictional force exerted by the solution opposed to the direction of motion of the molecule. This leads to a situation in which the net force on the molecule is zero and the molecule travels at constant velocity. The frictional force on a molecule is proportional to its size, shape and the solvation state. When a molecule reaches its terminal velocity (no acceleration), the diffusion coefficient is simply related to the frictional coefficient: $D = kT/f$

1. In the equation, f = frictional coefficient. What factors might lead to an increase in f in solution?

2. The numerator term is the product of Boltzmann's constant (1.3807×10^{-23} J/K) and the absolute temperature. What is the familiar constant derived from the product $k * N_A$ (Avogadro's number)? What is the meaning of this all-too-familiar numerator term for one mole of a substance?

3. For a sphere, Stokes derived a relation between the radius, r, and the frictional coefficient, f:

$$f = 6\pi\eta r$$

In this expression, η = viscosity of the solution. What is viscosity? Give an example of a viscous solution.

4. The viscosity of a solution is commonly measured in a unit called poise, where 1 poise = 1 g/cm-sec. The viscosity of water is 1 centiPoise (cP) = 1.00×10^{-2} g/cm-sec at 20°C. What is the friction of a molecule of 1 nm diameter in water?

5. For a spherical molecule the relation between the measured diffusion coefficient and the radius is given below. Estimate a value of a typical of D in water at 25°C. How would this change at 50°C? 5°C?

$$D = kT/6\pi\eta r$$

MODEL 4   Relation of Diffusion to Chromatography

Statistics deals with moments about the mean of Gaussian peaks to obtain information about the distribution and about the relative areas under the distribution. The second moment about the mean is called the variance, σ^2. The square root of the variance is called the standard deviation and is a measure of the width of the Gaussian zone. In statistics, the standard deviation indicates how widely spread our data is from a mean value. In chromatography, the standard deviation is an indication of how widely spread molecules are from the mean position of the average of all molecules migrating through the separation column. For a Gaussian zone, $W_{1/2} = 2.35\ \sigma$ and $W = 4\sigma$.

1. The relation between the width of a peak and time is due to diffusion along the column. The longer the time a concentrated zone is allowed to sit, the greater its distribution over space (Fick's second law!). The Einstein relation indicates the relation between variance and the amount of time on the column.

$$\sigma^2 = 2Dt$$

How wide a peak would be observed for a typical molecule in 1 second? 1 minute? 1 hour?

2. Diffusion is manifest through several mechanisms in a chromatographic separation:

   1) Longitudinal diffusion: analytes diffuse along the column axis toward either end of the column.

   2) Eddy diffusion: different analytes take different paths along a column due to obstructions in the flow profile such as solid particles.

   3) Lateral diffusion: analytes diffuse in a radial direction at different rates.

   4) Mass transfer: two analytes exchange at different rates with a liquid or quasi-liquid phase in the column.

If two processes contribute to diffusion *independently*, the total variance is the sum of the variances for each process.

$$\sigma_{tot}^2 = \sigma_1^2 + \sigma_2^2 + \sigma_3^2 + ... + \sigma_n^2$$

From the Einstein relation, how do diffusion coefficients (D) add?

3. The distance a compound migrates is simply related to its velocity and the length of the column. Substituting into the Einstein provide a relation between σ^2 and D in terms of v and L.

4. The plate height, H, is defined by $\sigma^2 = H \bullet L$. What is the relation between H, D and v?

5. The parameter H is commonly called the height equivalent to a theoretical plate or the plate height. It is a measure of the efficiency of a separation. Does a smaller H imply less diffusion or more? What factors are likely to increase H? Reduce H?

6. Historically, chromatographers used a quantity called the number of theoretical plates defined below. The modern term for N is the efficiency of a column. Does a large value of efficiency imply better or worse separations? How do we increase the efficiency, N, in a real chromatography experiment?

$$N = \frac{L}{H}$$

7. You have already measured N from a chromatogram using the equation below. What information would you need to calculate D from a chromatogram?

$$N = 5.55 \left(\frac{t_r}{W_{1/2}} \right)^2$$