

**Problem 1.**

You need to determine the rate law for a reaction  $A + B \rightarrow \text{products}$ . To do this, you measured the initial rate of the reaction at different starting concentrations of the reactants; the results are summarized in the table below.

[A], M	[B], M	Initial rate, M/s
0.8	0.5	$5.0 \cdot 10^{-5}$
0.8	0.2	$3.2 \cdot 10^{-6}$
0.8	0.1	$4.0 \cdot 10^{-7}$
0.6	0.5	$3.75 \cdot 10^{-5}$
0.2	0.5	$1.25 \cdot 10^{-5}$

(1) Based on these data, determine the rate law for this reaction (i.e. the reaction orders and the rate constant).

$$\text{the rate law: } (5 \cdot 10^{-4} \text{ M}^{-3} \text{ s}^{-1}) [A][B]^3$$

(2) Now you perform another experiment, with the initial concentrations  $[A]_0 = 0.1 \text{ M}$  and  $[B]_0 = 10 \text{ M}$ . What time does it take for the concentration of A to decrease to  $0.08 \text{ M}$ ? Assume that the reaction is irreversible. Note that the initial concentration of B is so much greater than [A] that the amount of B can be considered *constant* during the reaction.

Solution: Since  $[B] \approx \text{const} = [B]_0$ , the actual rate law is  $k' [A]$  (a pseudo-first order), where  $k' = (5 \cdot 10^{-4} \text{ M}^{-3} \text{ s}^{-1}) [B]_0^3 = 0.5 \text{ s}^{-1}$ . The integrated form of the first order kinetics is  $\ln([A]/[A]_0) = -k' t$ . From here we get  $t = -(1/k') \ln(0.8) = 0.446 \text{ s}$ .

**Problem 2.**

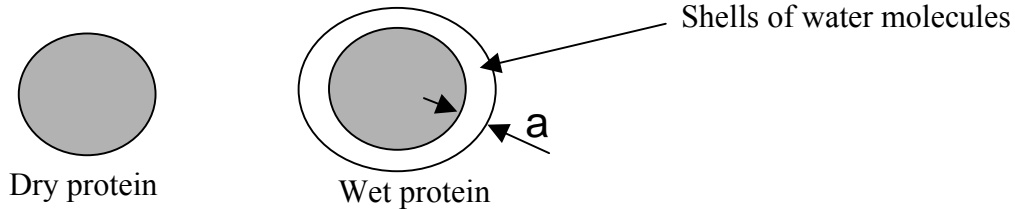
(1) Calculate the translational diffusion coefficient in water at  $20^\circ \text{C}$  for a protein with the molecular weight of  $10,000 \text{ Da}$ . Assume the protein can be approximated by a sphere (a so-called “dry-protein” model). The partial specific volume is  $0.7 \text{ cm}^3/\text{g}$ ; the viscosity of water  $\eta = 0.01 \text{ g cm}^{-1} \text{ s}^{-1}$ . [PAY ATTENTION TO THE UNITS!]

Solution:  $D = kT/f = kT/(6\pi\eta R)$ ; R can be found from the volume of the molecule,  $V = (4/3)\pi R^3 = vM_w/N_A$ , where  $M_w$  is the molecular weight ( $M_w = 10,000 \text{ grams}$ ),  $N_A$  is the Avogadro number, and  $v$  is the partial specific volume of the protein:  $R = \left( \frac{3vM_w}{4\pi N_A} \right)^{1/3} = 14.07 \cdot 10^{-8} \text{ cm}$ .

Then  $D = 1.5246 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ .

(2) In contrast with your predictions, the measurements give  $D = 1.27 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Trying to understand the possible reasons for this discrepancy, you now included in your calculations a hydration layer around the protein (This is the so-called “wet-protein” model, the hydration layer represents those solvent molecules that move together with the protein). What should be the thickness of the hydration shell  $a$  in order to account for the observed difference between the measured and the predicted diffusion coefficients? Compare your result with the diameter or

H<sub>2</sub>O molecule (2.8Å or 2.8 10<sup>-8</sup> cm) – this will tell you how many shells of water molecules are involved.

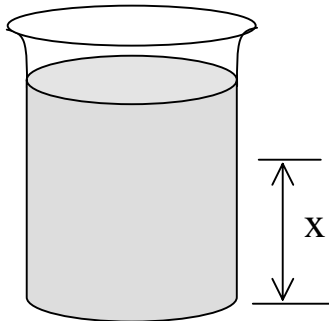


Solution: The molecular friction coefficient for the wet protein is  $f_{\text{wet}} = 6\pi\eta(R+a)$ . The ratio of the diffusion coefficients of the “dry” and “wet” molecules is

$D_{\text{dry}}/D_{\text{wet}} = f_{\text{wet}}/f_{\text{dry}} = (R+a)/R = (1.5246 \cdot 10^{-6} \text{ cm}^2\text{s}^{-1}/1.27 \cdot 10^{-6} \text{ cm}^2\text{s}^{-1}) = 1.2$ . From here we get  $a = 0.2 R = 2.8 \cdot 10^{-8} \text{ cm}$ , which means that a single layer of water molecules could account for the difference between the predicted (for a dry protein) and the measured diffusion coefficients.

### Problem 3.

You filled a beaker with a protein solution. Gravity will force the protein molecules toward the bottom, and thereby will create a concentration gradient. The molecular diffusion will counteract and create a flux (Fick’s law) that would drive the molecules upward, opposing the force of gravity. Considering that at the equilibrium the two fluxes (from the gravity and from the diffusion) balance each other, determine the relationship between the concentration  $C$  of protein molecules in a given layer and its distance  $x$  from the bottom. Note that the relationship  $C(x)$  might depend on the temperature, molecular friction coefficient, and the molecular weight of the protein. Assume that the gravity force does not change with the height.



### Solution:

The equation of motion (Newton’s second law) is

$$ma = mg\phi - fv$$

where  $\phi$  is the buoyancy factor:  $\phi = 1 - \nu\rho_{\text{H}_2\text{O}}$ .

In the steady-state regime (acceleration  $a = 0$ ), the velocity of the protein molecule is  $v = mg\phi/f$ , hence the gravity-associated flux is  $J_{\text{grav}} = -C v = -C mg\phi/f$ . The negative sign here indicates that this flux is oriented downwards, i.e. opposite to the direction of the  $x$ -axis (we measure the

height  $x$  from the bottom up).

According to the first Fick’s law, the diffusion-associated flux is  $J_{\text{diff}} = -D dC/dx$ . At the equilibrium, the net flux should be zero:  $J = J_{\text{grav}} + J_{\text{diff}} = 0$ , which gives:  $Cmg\phi/f = -DdC/dx$ . This equation can be rearranged:

$$\frac{1}{C} \frac{dC}{dx} = \frac{d \ln C}{dx} = -\frac{mg\phi}{Df} = -\frac{mg\phi}{kT} \quad \text{and then solved: } \ln C = -\frac{mg\phi}{kT} x + \text{const}, \text{ or}$$

$C = C_0 \exp\left(-\frac{mg\phi}{kT} x\right)$ , where the constant  $C_0$  is defined as the equilibrium concentration of the protein at the bottom of the beaker:  $C_0 = C(x = 0)$ .