1. Consider a cylindrical vessel of inner radius \( R_1 \) and outer radius \( R_2 \). The oxygen concentration inside the vessel is uniform and equal to \( c_1 \). The oxygen concentration outside the vessel is \( c_2 \). Find the flux of oxygen through the vessel as a function of the geometry and coefficient of diffusion \( D \). Under what condition can we assume that the vessel wall behaves like a flat membrane?

2. Show that the following function is solution to the diffusion equation:

\[
c(x,t) = \frac{1}{2\sqrt{\pi Dt}} e^{-x^2/4Dt}
\]

Show that it satisfies the initial condition \( c(x,0) = \delta(x) \), where \( \delta(x) \) is the 1D delta function.

This function is essentially the probability of finding a particle at a distance \( x \) away from its original position after a time \( t \). Show that the mean square displacement of the particle \( \langle x^2 \rangle \) scales like \( Dt \).

Hint: prove first that

\[
\frac{\partial c}{\partial x} = \frac{1}{2\sqrt{\pi Dt}} \frac{-x}{2Dt} e^{-x^2/4Dt}
\]

\[
\frac{\partial^2 c}{\partial x^2} = \frac{1}{2\sqrt{\pi Dt}} \frac{x^2}{4Dt^2} e^{-x^2/4Dt} - \frac{1}{4\sqrt{\pi(Dt)^{3/2}}} e^{-x^2/4Dt}
\]

\[
\frac{\partial c}{\partial t} = \frac{1}{2\sqrt{\pi Dt}} \frac{x^2}{4Dt^2} e^{-x^2/4Dt} - \frac{1}{4\sqrt{\pi Dt^{3/2}}} e^{-x^2/4Dt}
\]

3. Polymers are synthesised from monomers with two reactive ends that self-assemble with each other. It is usually difficult to estimate the length of the polymer chains after the synthesis. One knows the total number \( N_m \) of monomers we put in before the reaction, but ignore the final number of chains \( N_p \) and their individual length, represented by the number of monomers \( n \) per chain. We just know that, in average, \( N_m = nN_p \).

To find \( n \), chemists extract these polymers, and measure, in different solvents, the evolution of their osmotic pressure as a function of their concentration (expressed in monomers/L).

(a) Explain why all the curves shown in figure 1 are converging at vanishingly small concentration.

(b) Without calculating it explicitly, say how we could use this measurement to evaluate the average number of monomers per chain.

(c) Why did the chemists use several solvents?

4. Partial pressure and ideal gas law

We consider a mixture of gases of molecular mass \( m_i \). Gases are enclosed in a container of volume \( V \), and the number of molecules of each gas is \( n_i \). We want to calculate from
first principles the partial pressure of the gas $i$ by calculating the momentum transfer to a surface due to the molecules of the gas species $i$ only.

Consider a simple 1D description, where particles only move at a velocity $v_i$ directed along the normal to the surface. Half of them move toward the surface, and half of them away from it. The only prior knowledge we use comes from statistical physics. The energy associated with each degree of freedom originates from thermal energy and is at the equilibrium $k_B T/2$. Assuming we are dealing with a perfect gas (no interaction between molecules), the only energy is kinetic, leading to the following result:

$$E_c = \frac{1}{2} m_i v_i^2 = \frac{1}{2} k_B T$$

(a) Find the number of particles hitting the surface during $\delta t$, over a surface area $a$.
(b) Calculate the momentum transfer per unit of time and area, assuming that particles hitting the surface simply bounce back elastically.
(c) Show that the partial pressure $P_i$ is then given by: $P_i = k_B T n_i / V$.
(d) Hence, show that $P_i = \frac{\mu_i}{\mu} P = x_i P$ where $P$ is the total pressure.

5. A solution of pure water has a free interface with air. Find the concentrations of nitrogen and oxygen in the solution. Use solubility values from the lecture notes (provided for blood plasma) or from the internet if required.

Nitrogen narcosis is a common condition caused by a large amount of nitrogen dissolved in the body. If a scuba diver is breathing air at a depth of 30 meters for a long time, what would be the equilibrium concentration of nitrogen in the body?
6. CO₂ equilibrium in water.

Consider a solution of pure water in contact with a large quantity of carbon dioxide gas at a controlled pressure $P_g = 1$ atm. The following thermodynamical relationships are provided:

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad \text{with} \quad K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 4.30 \cdot 10^{-7} \text{mol L}^{-1}$$

$$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \quad \text{with} \quad K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 2.5 \cdot 10^{-4} \text{mol L}^{-1}$$

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad \text{with} \quad K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 5.61 \cdot 10^{-11} \text{mol L}^{-1}$$

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \quad \text{with} \quad K_d = [\text{H}^+][\text{OH}^-] = 10^{-14} \text{mol}^2\text{L}^{-2}$$

(a) Find the concentrations of CO₂ and H₂CO₃ at the equilibrium. The solubility of carbon dioxide in water is $\sigma = 3.3 \cdot 10^{-5}$ Molar/mMg.

(b) Considering the electroneutrality of the solution (i.e. the fact that no net charge is created during chemical reactions), show that: $[\text{H}^+] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-]$. From this assumption, it follows that $[\text{H}^+] \approx [\text{HCO}_3^-]$. This assumption about the relative values of the concentrations has to be verified once numbers have been calculated.

(c) Using assumptions about the relative values of the various species concentrations, find then the pH and concentrations of HCO₃⁻ and CO₃²⁻ in the solution after equilibrium with the gas.

(d) Repeat (a) and (c) for smaller carbon dioxide partial pressure $P_g$ respectively equal to $10^{-2}$, $10^{-4}$, $10^{-6}$ and $10^{-8}$ atm. Assumptions that were true earlier might not be valid any more...

7. Inhibitors and activators: Establish the results of the sections 4.3.2 and 4.3.3.

Solutions/Hints

4.a: $\frac{1}{2} a v_i \delta t n_i / V$ with $v_i^2 = k_B T / m_i$.

6: Because the concentration of carbon dioxide is relatively large at 1 atm, it is useful to assume first that $[\text{HCO}_3^-] >> [\text{CO}_3^{2-}]$ and $[\text{H}^+] >> [\text{OH}^-]$. From this assumption, it follows that $[\text{H}^+] \approx [\text{HCO}_3^-]$. This assumption about the relative values of the concentrations has to be verified once numbers have been calculated.