1. Two well-mixed solutions are separated by a membrane of thickness \( \delta \). The membrane is permeable to NaCl. Two separate experiments are conducted with membranes of different thicknesses, but with NaCl solutions at the same concentrations, as shown below. Assume the diffusion coefficient of NaCl in both membranes is the same. In which case is the diffusive flux larger and why? Relate your answer explicitly to terms in Fick’s First Law of diffusion.

\[
J_m = -D \frac{dc}{dx} = -D \frac{(c' - c)}{\delta}
\]

For the same concentration difference, the thinner membrane has the larger concentration gradient and therefore the larger diffusive flux. The diffusion coefficient through the membrane remains the same for the two thicknesses.

2. Organisms require iron for survival. Reduced iron in the form of Fe\(^{2+}\) is readily available for acquisition by living systems. However, Fe\(^{2+}\) is rapidly oxidized by oxygen in air. The oxidation of Fe\(^{2+}\) follows the rate law:

\[
- \frac{d[Fe^{2+}]}{dt} = k_{\text{eff}} [Fe^{2+}]^2
\]

where \( k_{\text{eff}} = 7.30 \times 10^{-4} \text{ mol}^{-1} \text{ L hr}^{-1} \). Assume an initial concentration of 0.100 M Fe\(^{2+}\). How long would it take for the concentration of Fe\(^{2+}\) to drop to 0.0100 M?

for a second order reaction: 
\[
\frac{1}{[A]} - \frac{1}{[A]_o} = k_2 t \quad \text{or in this case:}
\]

\[
\frac{1}{0.0100 \text{ mol L}^{-1}} - \frac{1}{0.100 \text{ mol L}^{-1}} = 7.30 \times 10^{-4} \text{ mol}^{-1} \text{ L hr}^{-1} t
\]

890 mol\(^{-1}\) L = 7.30 \times 10^{-4} mol\(^{-1}\) L hr\(^{-1}\) t

\[
t = 1.23 \times 10^5 \text{ hr}
\]
3. Assume two well-mixed compartments with volumes $V_1$ and $V_2$ are separated by a membrane. Substance X diffuses through the membrane, which has cross-sectional area $A$:

![Diagram of two compartments separated by a membrane with substance X diffusing through it.]

Prove for diffusion of substance X across a membrane that the rate of concentration change in compartment 1 is given by:

$$\frac{d[X]}{dt} = \frac{dc_X}{dt} = J_m \left( \frac{A}{V_1} \right)$$

The flux is the amount per unit time per unit area and $\frac{dn_X}{dt} = J_m A$. The change in concentration is in moles per liter, which is just the last equation divided by the volume of compartment 1:

$$\frac{d[X]}{dt} = \frac{dc_X}{dt} = \frac{1}{V_1} \frac{dn_X}{dt} = J_m \frac{A}{V_1}.$$ The units are mol L$^{-1}$ s$^{-1}$.

4. From a thermodynamic perspective, are spontaneous processes always irreversible? Explain.

Yes: Returning a spontaneous process to its initial state requires energy input from the surroundings in the form of heat and work. The reverse of a spontaneous process is not the exact reverse of the change for the original forward process. The forward spontaneous process is irreversible. Equilibrium processes are reversible (always). The only way for a process to be reversible is for the system to be at equilibrium.

5. What role do gradients play in flux-force relationships?

For a general flux-force relationship, $J_i = L_i X_i$, the generalized force is given by a gradient. The gradient is the force for transport.

**Part 2:** Answer 4 of the following 6 questions. If you answer more than 5 cross out the ones you wish not to be graded. Otherwise only the first 5 will be graded. 16 points each.

6. For the reaction $O + NO + M \rightarrow NO_2 + M$, k at 300.0 K is $6.00 \times 10^9$ L$^2$ mol$^{-2}$ s$^{-1}$, and k at 1000.0 K is $3.00 \times 10^{10}$ L$^2$ mol$^{-2}$ s$^{-1}$. Calculate the activation energy.

$$\ln \frac{k_{T_2}}{k_{T_1}} = \frac{-E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{3.00 \times 10^{10}}{6.00 \times 10^9} = \frac{-E_a}{R} \left( \frac{1}{1000.0 \text{ K}} - \frac{1}{300.0 \text{ K}} \right)$$

$$1.609 = \frac{-E_a}{R} (-2.3333 \times 10^{-3} \text{ K}^{-1})$$

or $E_a = 5.73$ kJ mol$^{-1}$
7. The limiting molar conductivities of KCl, KNO₃, and AgNO₃ are 14.99 mS m² mol⁻¹, 14.50 mS m² mol⁻¹, and 13.34 mS m² mol⁻¹, respectively. What is the limiting molar conductivity of AgCl?

\[ \Lambda_m^0 (\text{AgCl}) = \Lambda_m^0 (\text{AgNO}_3) + \Lambda_m^0 (\text{KCl}) - \Lambda_m^0 (\text{KNO}_3) \]
\[ = 13.34 + 14.99 - 14.50 \text{ mS m}^2 \text{ mol}^{-1} = 13.83 \text{ mS m}^2 \text{ mol}^{-1} \]

8. A 2.32x10⁻⁵ M solution of a substance is placed outside in a 10.0 cm path length cell with an irradiated cross sectional area of 1.00x10⁻² m². The molar absorption coefficient of the solution at 500 nm is 3410. M⁻¹ cm⁻¹. Assume that the solar flux at this wavelength is 4.96 mol m⁻² day⁻¹ (in other words, moles of photons per meter squared per day). Calculate the number of moles of photons absorbed by the solution in one day.

\[ J_a = J_o (1 - e^{-2.303 \varepsilon_l [A]}) \]
\[ = 2.303 \varepsilon_c = 1.82 \]
\[ \text{giving } (1 - e^{-2.303 \varepsilon_l [A]}) = 0.838 \]
\[ n_{\text{photons}} = J_a \ A \Delta t = 4.96 \text{ mol m}^{-2} \text{ day}^{-1} (0.8383) (1.00x10^{-2} \text{ m}^2) (1 \text{ day}) = 0.0416 \text{ mol photons} \]

9. Calculate the uncertainty in \( \ln(k_2/k_1) \) if \( k_2 = 4.65 \times 10^7 \pm 0.23 \times 10^7 \text{ s}^{-1} \) and \( k_1 = 1.35 \times 10^7 \pm 0.08 \times 10^7 \text{ s}^{-1} \).

\[ k_2/k_1 = 3.444 \ \text{and } \ln(k_2/k_1) = 1.237 \]
\[ (\text{relative uncertainty in } k_2/k_1) = \sqrt{(0.23/4.65)^2 + (0.08/1.35)^2} = 0.0772 \ \text{(or 7.7%)} \]

<table>
<thead>
<tr>
<th>How does the error propagate for ( \ln x )? Remember ( \delta^2 x ) is the variance in ( x ) and:</th>
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<tbody>
<tr>
<td>( \delta^2 f = \left( \frac{\delta f}{\delta x} \right)^2 \delta^2 x ) or for a single error term: ( \delta f = \left( \frac{\delta f}{\delta x} \right) \delta x )</td>
</tr>
<tr>
<td>For ( \ln x ): ( \delta \ln x = \frac{x}{\delta x} )</td>
</tr>
<tr>
<td>absolute = relative error \</td>
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So the absolute error in \( \ln(k_2/k_1) \) = relative error in \( k_2/k_1 \): \( \ln(k_2/k_1) = 1.237 \pm 0.077 \)
10. Consider the following proposed mechanism for the decomposition of ozone. M is an unreactive gas molecule that collides with the ozone to break the ozone apart:

\[
\begin{align*}
\text{O}_3 + M & \overset{k_2}{\rightarrow} \text{O}_2 + \text{O} + M \\
\text{O} + \text{O}_3 & \overset{k_{-2}}{\rightarrow} 2 \text{O}_2
\end{align*}
\]

Assume \( k'_{2} \gg k_2 \). Show that the rate law that corresponds to this mechanism is:

\[
\frac{d[O_2]}{dt} = \frac{3 k'_2 k_2 [O_3]^2[M]}{k_2[O_2][M] + k'_2[O_3]}
\]

For the formation of product: \( \frac{d[O_2]}{dt} = k_2 [O_3][M] - k_{-2} [O_2][O][M] + 2 k'_2 [O][O_3] \)

Use the steady-state approximation for the reactive intermediate, [O]:

\[
\frac{d[O]}{dt} = k_2 [O_3][M] - k_{-2} [O_2][O][M] - k'_2 [O][O_3] = 0
\]

Subtract Eq. 2 from Eq. 1 to cancel terms, eliminating the explicit dependence on [M]:

\[
\frac{d[O_2]}{dt} = 3 k'_2 [O][O_3]
\]

Solve Eq. 2 for the concentration of the reactive intermediate:

\[
[O] = \frac{k_2 [O_3][M]}{k_2 [O_2][M] + k'_2 [O_3]}
\]

Substitute this result for [O] into Eq. 3: \( \frac{d[O_2]}{dt} = \frac{3 k'_2 k_2 [O_3]^2[M]}{k_2 [O_2][M] + k'_2 [O_3]} \)

11. Consider the bidirectional reaction:

\[
\begin{align*}
\text{A} & \overset{k_{f}}{\rightleftharpoons} \text{B} \\
\text{B} & \overset{k_{r}}{\rightleftharpoons} \text{C}
\end{align*}
\]

The initial rate law for the reaction, starting with A only, is experimentally determined to be:

\[
\frac{d[A]}{dt} = - k_{\text{obs},f} [A]_0
\]

[only valid far from equilibrium]

If the reverse reaction is run starting with C only, the initial rate law is determined to be:

\[
\frac{d[C]}{dt} = - k_{\text{obs},r} [C]_0
\]

[only valid far from equilibrium]

Why isn’t the equilibrium constant for the overall reaction given by the ratio of the forward to the reverse rate constants, \( k_{\text{obs},f}/k_{\text{obs},r} \)?

\text{Answer:} \text{The given rate laws are only valid far from equilibrium. At equilibrium, detailed balance holds, the forward and reverse rates are equal for each mechanistic step:}
$A \underset{k_1}{\overset{k_2}{\rightleftharpoons}} B \underset{k_{-1}}{\overset{k_{-2}}{\rightleftharpoons}} C$

with $K_{c,1} = \frac{k_1}{k_{-1}}$ and $K_{c,2} = \frac{k_2}{k_{-2}}$

For the overall reaction: $K_c = K_{c,1} K_{c,2} = \frac{k_1 k_2}{k_{-1} k_{-2}}$

For the given initial reaction rate laws the correspondence of the observed rate constants to the mechanistic rate constants in Eq 1 is: $k_{obs,f} = k_1$ and $k_{obs,r} = k_{-2}$.

The equilibrium constant for the reaction is given by the product of the forward rate constants divided by the product of the reverse rate constants (not just $k_{obs,f}/k_{obs,r} = k_1/k_{-2}$).

Literature Cited:
1. This solar flux is the flux averaged over a day in summer at 40°N latitude in a 10 nm band centered on 500 nm: A. Leifer, The Kinetics of Environmental Aquatic Photochemistry, American Chemical Society, Washington, D.C., 1988. p. 261