1. (10 points) From the diffusion coefficient of ribonuclease, (a) determine how far a ribonuclease particle moves in one second, if it is trapped in a very small (molecular-sized) pore so that it can only move in one dimension.

According to the Handbook, the diffusion coefficient of ribonuclease is $11.9 \times 10^{-11} \text{ m}^2 \text{s}^{-1}$. One may use this value in the equation

$$\delta x = \sqrt{2Dt}$$

This gives the following result:

$$\delta x = \sqrt{2 \times 11.9 \times 10^{-11} \text{ m}^2 \text{s}^{-1} \times 1\text{s}}$$

$$= 1.54 \times 10^{-5} \text{ m} = 15.4 \text{ microns}$$

(b) Now, consider the movement of a ribonuclease particle in a three-dimensional fluid (the usual case). How far would it travel, on average, in that solution in one second?

This is somewhat tricky. One has to realize that the square of the distance in three dimensions is $x^2 + y^2 + z^2$. Each of these contributes $2Dt$ to the square of the distance, so that the total is $6Dt$. The distance traveled is the square root of that number:

$$\delta r = \sqrt{6Dt}$$

$$= \sqrt{6 \times 11.9 \times 10^{-9} \text{ m}^2 \text{s}^{-1} \times 1\text{s}}$$

$$= 2.67 \times 10^{-5} \text{ m} = 26.7 \text{ microns}$$
2. (15 points) Lysozyme was centrifuged at 55,000 min\(^{-1}\) in water at 20\(^\circ\)C. The following data were obtained. What is the sedimentation coefficient of lysozyme in water under these conditions? (Be sure to show all work clearly. HINT: A plot of appropriate functions may be helpful.)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>(X_b) (cm)</th>
<th>(X_b/X_b(0))</th>
<th>(\ln(X_b/X_b(0)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>6</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>30</td>
<td>6.07</td>
<td>1.01166</td>
<td>0.0115991</td>
</tr>
<tr>
<td>60</td>
<td>6.14</td>
<td>1.02333</td>
<td>0.0230653</td>
</tr>
<tr>
<td>90</td>
<td>6.21</td>
<td>1.035</td>
<td>0.0344014</td>
</tr>
<tr>
<td>120</td>
<td>6.28</td>
<td>1.04666</td>
<td>0.0456105</td>
</tr>
<tr>
<td>150</td>
<td>6.35</td>
<td>1.05833</td>
<td>0.0566953</td>
</tr>
</tbody>
</table>

This is Example Problem 24.11 in your text. A plot of the logarithm of the position of the boundary versus time should be linear, with the slope being \(s\omega^2\). The graph below shows that it is linear. The slope of this plot is \(3.78 \times 10^{-4}\) min\(^{-1}\). Converting units, this is \(6.3 \times 10^{-8}\) s\(^{-1}\). Now, convert the rotational speed from rotations per minute to radians per second.

\[
\omega = \frac{55000 \text{ min}^{-1}}{60 \text{ s min}^{-1}} \times \frac{2\pi \text{ radians}}{\text{rotation}} = \frac{5760 \text{ radians}}{s}
\]

Using this information and the slope, one finds the sedimentation coefficient:

\[
\bar{s} = \frac{s}{\omega^2} = \frac{6.3 \times 10^{-8} \text{ s}^{-1}}{(5760 \text{s}^{-1})^2} = 1.9 \times 10^{-13} \text{s} = 1.9 \text{Sv}
\]
3. **(20 points)** Insert the proper word or phrase into each of the following sentences to complete it appropriately.

a. Transport phenomena involve the evolution of a system property in response to a nonequilibrium distribution of the property.

b. The theoretical basis of diffusion is a statistical formulation called the theory of random walks.

c. The movement of counterions toward the opposite electrode sets up a charge current that opposes the motion of a charged macromolecules results in the electrophoretic effect.

d. The property that characterizes resistance to flow is viscosity.

e. In the equation \( \eta_{sp} = \nu \sum \nu' c_2 + \cdots \) is called the Simha (or asymmetric) factor.

f. In the method of initial rates, the concentration of a single reactant is changed while holding all other concentrations constant, and the early change in that concentration is determined.

g. For reactions that occur on timescales as short as 1 ms, stopped flow techniques provide a convenient method by which to measure solution-phase reactions.

h. It cannot be overemphasized that orders have no relation to stoichiometric coefficients.

i. The majority of modern experiments to determine the kinetics of a reaction involve physical methods for determining the concentrations of components.
4. **(10 points)** For the following reaction, give the stoichiometric coefficients of all components of the reaction:

\[ K_2\text{MnO}_4 + H_2O \rightarrow MnO_2 + 2 \text{KOH} + \frac{1}{2}O_2 \]

<table>
<thead>
<tr>
<th>Component</th>
<th>Stoichiometric Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>-1</td>
</tr>
<tr>
<td>$K_2\text{MnO}_4$</td>
<td>-1</td>
</tr>
<tr>
<td>KOH</td>
<td>+2</td>
</tr>
<tr>
<td>MnO$_2$</td>
<td>+1</td>
</tr>
<tr>
<td>O$_2$</td>
<td>+1/2</td>
</tr>
</tbody>
</table>
5. **(15 points)** Lactose can be decomposed into its constituent sugars, galactose and glucose. This decomposition is accomplished through acid-based hydrolysis, or by the enzyme lactase. The following data were obtained on the rate of lactose decomposition as a function of the acid and lactose concentrations. Using these data, determine the initial-rate-law expression for the acid-based hydrolysis of lactose. (Explain clearly how you were able to write down this law.)

<table>
<thead>
<tr>
<th>[Lactose] (Mole dm⁻³)</th>
<th>[H⁺] (Mole dm⁻³)</th>
<th>Initial Rate (Mole dm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.001</td>
<td>0.00116</td>
</tr>
<tr>
<td>0.02</td>
<td>0.001</td>
<td>0.00232</td>
</tr>
<tr>
<td>0.01</td>
<td>0.004</td>
<td>0.00464</td>
</tr>
</tbody>
</table>

In the procedure for determining orders by initial rates, one determines the power to which the ratio of concentrations must be raised to be in agreement with the ratio of rates for different experiments in which only one concentration is different. So, for example the first two experiments allow one to determine the order with respect to lactose:

\[
\frac{R_1}{R_2} = \left( \frac{[\text{Lactose}]_1}{[\text{Lactose}]_2} \right)^n
\]

\[
\frac{0.00116 \text{ mole dm}^{-3} \text{s}^{-1}}{0.00232 \text{ mole dm}^{-3} \text{s}^{-1}} = \left( \frac{0.01 \text{ mole dm}^{-3}}{0.02 \text{ mole dm}^{-3}} \right)^n
\]

\[
\frac{1}{2} = \left( \frac{1}{2} \right)^n
\]

It is obvious from this last relationship that the order, \( n \), must be 1.

Similarly, one may use the first and third experiments to determine the order with respect to hydrogen ion.

\[
\frac{R_1}{R_3} = \left( \frac{[\text{H}^+]_1}{[\text{H}^+]_3} \right)^n
\]

\[
\frac{0.00116 \text{ mole dm}^{-3} \text{s}^{-1}}{0.00464 \text{ mole dm}^{-3} \text{s}^{-1}} = \left( \frac{0.001 \text{ mole dm}^{-3}}{0.004 \text{ mole dm}^{-3}} \right)^n
\]

\[
\frac{1}{4} = \left( \frac{1}{4} \right)^n
\]

Once again, one sees that the appropriate order is \( n = 1 \). So, the initial-rate law looks like this:

\[
v = k[\text{Lactose}] [\text{H}^+]
\]
6. (15 points) The formation of hydrogen bromide is given by the equation:

\[ H_2 + Br_2 \rightarrow 2HBr \]

The reaction is quite complex. Max Bodenstein has shown that, over a wide range of conditions, the reaction velocity has the following form, where \( k \) and \( k' \) are constants, independent of concentrations:

\[
v = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr][Br_2]} \]

(a) In an experiment in which the reaction was observed in the very early stages of reaction, what would an experimenter give as the orders of reaction with respect to each of the following species:

<table>
<thead>
<tr>
<th>Component</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H_2 )</td>
<td>+1</td>
</tr>
<tr>
<td>( Br_2 )</td>
<td>+1/2</td>
</tr>
<tr>
<td>( HBr )</td>
<td>0</td>
</tr>
</tbody>
</table>

(b) Explain, in one or two sentences, how you determined the orders in part (a).

In the initial stages of reaction, the concentration of HBr is very small, so the second term in the denominator is negligible. That gives a form that is of the form of \( v = k[A]^a[B]^b \), from which the orders can be read directly.

(c) What are the units of the constant \( k \)?

The units the velocity are \( \text{mole dm}^{-3} \text{s}^{-1} \). Using the units of concentration of the reactants and that value allows one to determine the units of \( k \):

\[
\frac{\text{mole}}{\text{dm}^3 \text{s}} \quad [\equiv] \quad \text{(units of } k\text{)} \times \left(\frac{\text{mole}}{\text{dm}^3}\right)\left(\frac{\text{mole}}{\text{dm}^3}\right)^{1/2} \quad [\equiv] \quad \text{(units of } k\text{)} \times \left(\frac{\text{mole}}{\text{dm}^3}\right)^{3/2}
\]

By dividing through, one obtains

\[
\text{(units of } k\text{)} \quad [\equiv] \quad \frac{\text{mole}}{\text{dm}^3 \text{s}} \times \left(\frac{\text{dm}^3}{\text{mole}}\right)^{3/2} \quad [\equiv] \quad \frac{\text{dm}^{3/2}}{\text{mole}^{1/2} \text{s}}
\]
7. (15 points) (a) Write a balanced equation for the reaction of nitrogen dioxide with oxygen to form dinitrogen pentoxide.

\[ 2 \text{NO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{N}_2\text{O}_5 \]

or

\[ 4 \text{NO}_2 + \text{O}_2 \rightarrow 2 \text{N}_2\text{O}_5 \]

(b) Nitrogen dioxide, oxygen and dinitrogen pentoxide are all gases, so monitoring the reaction can be achieved by monitoring the total pressure. Let the initial pressures of nitrogen dioxide and oxygen be \( P_0 \) (i.e. they start out with equal pressures) and let the drop in the partial pressure of nitrogen dioxide at any time be \( x \). Write an equation for the partial pressure of nitrogen dioxide at any time in terms of the instantaneous total pressure, \( P \), and the initial pressure of either oxygen or nitrogen dioxide, \( P_0 \).

The easiest way to do this determination is to set up a table of the partial pressures initially and at any time:

<table>
<thead>
<tr>
<th>Time</th>
<th>Pressure (NO(_2))</th>
<th>Pressure (O(_2))</th>
<th>Pressure (N(_2)O(_5))</th>
<th>Total Pressure</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( P_0 )</td>
<td>( P_0 )</td>
<td>0</td>
<td>2( P_0 )</td>
</tr>
<tr>
<td>( t )</td>
<td>( P_0 - x )</td>
<td>( P_0 - x/4 )</td>
<td>( x/2 )</td>
<td>2( P_0 - 3x/4 )</td>
</tr>
</tbody>
</table>

From this table, one sees that \( x \) can be determined from the instantaneous total pressure and the initial partial pressure of nitrogen dioxide:

\[ P_{\text{total}} = 2P_0 - \frac{3x}{4} \]

Rearrangement gives an expression for \( x \):

\[ x = \frac{4}{3}(2P_0 - P_{\text{total}}) \]

Substitution of this value into the instantaneous partial pressure of nitrogen dioxide gives the result we seek:

\[ P_{\text{NO}_2}(t) = P_0 - x = P_0 - \frac{4}{3}(2P_0 - P_{\text{total}}(t)) \]

\[ = \frac{4}{3}P_{\text{total}}(t) - \frac{5}{3}P_0 \]

Thus, the appropriate parameter to monitor the reaction progress is this last difference, which can be calculated from the total pressure at the time and \( P_0 \), the initial partial pressure of nitrogen dioxide (which is also the initial partial pressure of oxygen).