Show your work on numerical problems to receive credit. This homework is due on Monday, February 5, 2007 at class time.

(6) 1. For the following reactions, relate how the disappearance of other reactants and the appearance of products is related to the disappearance of the bold-faced reactant. For example, in the first one what are the expressions for the changes in concentration of O\(_2\) and SO\(_3\) in terms of?

\[
\frac{\Delta [SO_2]}{\Delta t} = \frac{-\Delta [O_2]}{\Delta t} = \frac{\Delta [SO_3]}{\Delta t}
\]

\[
2 SO_2 (g) + O_2 (g) \rightarrow 2 SO_3 (g)
\]

Rate = \(-\frac{\Delta [SO_2]}{2\Delta t}\) = \(-\frac{\Delta [O_2]}{\Delta t}\) = \(
\frac{\Delta [SO_3]}{2\Delta t}\) so \(\frac{\Delta [O_2]}{\Delta t} = \frac{\Delta [SO_3]}{2\Delta t}\) and \(\frac{\Delta [SO_2]}{\Delta t} = -\frac{\Delta [SO_2]}{\Delta t}\)

\[
N_2 (g) + 3 H_2 (g) \rightarrow 2 NH_3 (g)
\]

Rate = \(-\frac{\Delta [N_2]}{\Delta t}\) = \(-\frac{\Delta [H_2]}{3\Delta t}\) = \(
\frac{\Delta [NH_3]}{2\Delta t}\) so \(\frac{\Delta [H_2]}{\Delta t} = \frac{3\Delta [N_2]}{\Delta t}\) and \(\frac{\Delta [NH_3]}{\Delta t} = -\frac{2\Delta [N_2]}{\Delta t}\)

\[
2 H_2 (g) + O_2 (g) \rightarrow 2 H_2O (g)
\]

Rate = \(-\frac{\Delta [H_2]}{2\Delta t}\) = \(-\frac{\Delta [O_2]}{\Delta t}\) = \(
\frac{\Delta [H_2O]}{2\Delta t}\) so \(\frac{\Delta [O_2]}{\Delta t} = \frac{\Delta [H_2]}{2\Delta t}\) and \(\frac{\Delta [H_2O]}{\Delta t} = -\frac{\Delta [H_2]}{\Delta t}\)
2. Given the following initial rate information, find the rate law and rate constant (including units) for the reaction $A + B \rightarrow \text{products}$.

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>$[A]$ (/M)</th>
<th>$[B]$ (/M)</th>
<th>Rate (M/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.20</td>
<td>0.20</td>
<td>0.10</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
<td>0.20</td>
<td>0.05</td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td>0.40</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Consider Experiments #1 and #2. The $[B]$ remains the same so the change in rate is only due to $[A]$. In going from Exp. 2 to Exp. 1, $[A]$ doubles and the rate doubles also so the order with respect to $[A]$ is 1. The order with respect to $[B]$ is a little more challenging because we haven’t kept $[A]$ constant in any two experiments. However, from the first part we know it is first order in $[A]$ so we can separate out the effects of $[A]$ on the rate.

Consider Experiment 1 and Experiment 2. The $[A]$ doubles from Exp. 1 to Exp. 3 so we would expect the rate to double ($2^1 = 2$) since we already know it is first order in $[A]$. That means we would expect the rate from Experiment 1 to double in going to Experiment 3, or go from 0.10 M/min to 0.20 M/min. The actual rate in Experiment 3 is 0.80 M/min – the difference between the expected 0.20 M/min and the actual 0.80 M/min must be due to the effect of $[B]$. Since $[B]$ doubles between Experiment 1 and 3 and the rate, adjusted for the effect of $[A]$, quadruples, the order with respect to $[B]$ must be 2 ($2^2=4$).

The rate law is: \( \text{Rate} = k [A][B]^2 \)

The rate constant is: \( k = \frac{\text{Rate}}{([A][B]^2)} \) which must be true for any of the experiments. Using Experiment #1:

\[
k = \frac{\text{Rate}}{[A][B]^2} = \frac{0.10 \text{ M/min}}{(0.20 \text{ M})(0.20 \text{ M})^2} = 12.5 \text{ M}^{-2} \text{s}^{-1}
\]
A particular reaction is first-order in A and first-order overall with a rate constant of \(1.45 \times 10^{-3} \text{ s}^{-1}\) and has the stoichiometry:

\[
A \rightarrow \text{Products}
\]

a. Find the concentration of reactant A 300 s into a reaction in which the initial concentration of A was 0.15 M.

\[
[A]_0 = 0.15 \text{ M} \quad k = 1.45 \times 10^{-3} \text{ s}^{-1} \quad t = 300 \text{ s}
\]

\[
\ln \frac{[A]_0}{[A]} = kt \quad \Rightarrow \quad \ln \frac{0.15M}{[A]} = 1.45 \times 10^{-3} \text{ s}^{-1} (300 \text{ s}) \quad \Rightarrow \quad \ln \frac{0.15}{[A]} = 0.435 \quad \Rightarrow
\]

\[
\frac{0.15}{[A]} = e^{0.435} \quad \Rightarrow \quad \frac{0.15}{[A]} = 1.545 \quad \Rightarrow \quad [A] = \frac{0.15M}{1.545} \quad \Rightarrow \quad 9.71 \times 10^{-2} \text{ M}
\]

b. What is the half-life of the reaction?

\[
t_{\frac{1}{2}} = \frac{\ln 2}{k} = \frac{\ln 2}{1.45 \times 10^{-3} \text{ s}^{-1}} = 478 \text{ s}
\]
A reaction is second-order in A and second-order overall. It has a rate constant of $4.2 \times 10^{-1} \text{ M}^{-1}\text{min}^{-1}$ at a particular temperature and the stoichiometry:

$$A \rightarrow \text{Products}$$

a. If the starting concentration of A is 0.25 M, how much A will remain after 10 minutes of reaction?

$$\frac{1}{[A]} - \frac{1}{[A]_o} = kt \quad \Rightarrow \quad \frac{1}{[A]} - \frac{1}{0.25} = 4.2 \times 10^{-1} \text{ M}^{-1}\text{min}^{-1} (10 \text{ min}) \quad \Rightarrow \quad \frac{1}{[A]} - 4M^{-1} = 4.2M^{-1} \quad \Rightarrow$$

$$\frac{1}{[A]} = 8.2M^{-1} \quad \Rightarrow \quad [A] = \frac{1}{8.2M^{-1}} \quad \Rightarrow \quad 0.122M$$

b. What is the half-life of the reaction if the starting concentration is 0.25M?

$$t_{1/2} = \frac{1}{k[A]_o} = \frac{1}{4.2 \times 10^{-1} \text{ M}^{-1}\text{min}^{-1} (0.25M)} = 9.52 \text{ min}$$

c. **OMIT** How would your answer change to part a, if at all, if the stoichiometry was $2A \rightarrow \text{Products}$? Explain your reasoning.

A qualitative answer would be to say more A would be consumed. The quantitative answer is a little more involved. Basically it uses an equation you have not seen but which is similar to the second order.

$$\frac{1}{[A]} - \frac{1}{[A]_o} = 2kt.$$ If you are curious:

$$\frac{1}{[A]} - \frac{1}{[A]_o} = 2kt \quad \Rightarrow \quad \frac{1}{[A]} - \frac{1}{0.25M} = 2(4.2 \times 10^{-1} \text{ M}^{-1}\text{min}^{-1})(10 \text{ min}) \quad \Rightarrow \quad \frac{1}{[A]} - 4M^{-1} = 8.4M^{-1} \quad \Rightarrow$$

$$\frac{1}{[A]} = 12.4M^{-1} \quad \Rightarrow \quad [A] = 8.06 \times 10^{-2}M$$