Chapter 14 - Kinetics
Additional Practice Problems

1) A hypothetical reaction A ----> products is second order in A. The half-life of a reaction that was initially 1.66 M in A is 310 min. What is the value of the rate constant, \( k \)?

2) A reaction shows the same half-life regardless of the starting concentration of the reactant. Is it a zero-order, first-order or second-order reaction?

3) In three different experiments the following results were obtained for the reaction A ----> products: \([A]_0 = 1.00 \text{ M}, t_{1/2} = 50 \text{ min}; [A]_0 = 2.00 \text{ M}, t_{1/2} = 25 \text{ min}; [A]_0 = 0.50 \text{ M}, t_{1/2} = 100 \text{ min}\). Write the rate equation for this reaction and indicate the value of \( k \).

4) Ammonia decomposes on the surface of a hot tungsten wire. Following are the half-lives that were obtained at 1100 °C for different initial concentrations of NH₃:
\([\text{NH}_3]_0 = 0.0031 \text{ M}, t_{1/2} = 7.6 \text{ min}; 0.0015 \text{ M, 3.7 min; 0.00068 M, 1.7 min}\). For this decomposition reaction, what is (a) the order of the reaction; (b) the rate constant \( k \)?

5) The gas-phase reaction of chlorine with carbon monoxide to form phosgene,
\( \text{Cl}_2 (g) + \text{CO} (g) \rightarrow \text{COCl}_2 (g) \), obeys the following rate law:
\[
\text{Rate} = \frac{\Delta [\text{COCl}_2]}{\Delta t} = k [\text{Cl}_2]^{3/2} [\text{CO}] \\
\text{(exp. rate law)}
\]

A mechanism involving the following series of steps is consistent with the rate law:

\[
\text{Cl}_2 \rightleftharpoons 2\text{Cl} \quad \text{Cl} + \text{CO} \rightleftharpoons \text{COCl} \quad \text{COCl} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2 + \text{Cl}
\]

Assuming that this mechanism is correct, which of the steps above is the slow, or rate-determining, step? Explain.

Hint: try making each step the slowest step (rate-det. step) and see what rate law you get and if it agrees with the experimental rate law given.
Ch. 14 - Additional Practice Problems - Solutions

14.26) \( A \rightarrow \) products is 2nd order in \( A \)

\[ r = k[A]^2 \] rate law for 2nd order rx.

The half-life for a 2nd order rx is:

\[ t_{1/2} = \frac{1}{k[A]_0} \quad t_{1/2} = 310 \text{ min} \quad [A]_0 = 1.66 \text{ M} \]

\[ k = \frac{1}{t_{1/2}[A]_0} \]

\[ k = \frac{1}{(310 \text{ min})(1.66 \text{ M})} \]

\[ k = 1.943 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1} \]

\[ = 1.94 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1} \]

\[ t_{1/2} = 310 \text{ min} \text{ to 1st half-life} \]

\[ [A]_{1/2,t_{1/2}} = \frac{1}{2}[A]_0 = \frac{1}{2}(1.66 \text{ M}) = 0.83 \text{ M} \]

What is the 2nd half-life?

In this case, \( [A]_0 = [A]_{1/2,t_{1/2}} = \frac{1}{2}[A]_{\text{start}} = 0.83 \text{ M} \)

\[ t_{2,1/2} = \frac{1}{k[A]_{1/2,t_{1/2}}} = \frac{1}{(1.943 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1})(0.83 \text{ M})} \]

\[ t_{2,1/2} = 620 \text{ min} \]

The half-life for a 2nd order rx increases (gets longer) as the reaction proceeds (as conc. of reactant dec.).
\[14.07\]

1st order \( t_\frac{1}{2} \) life

\[ t_\frac{1}{2} = \frac{0.693}{k} \]

2nd order \( t_\frac{1}{2} \) life

\[ t_\frac{1}{2} = \frac{1}{k[A]_0} \]

\( t_\frac{1}{2} \) is constant (independent of the initial conc.)

\( t_\frac{1}{2} \) depends on the initial conc. (inc. as rx. proceeds)

Since the problem states that the rx. shows the same \( t_\frac{1}{2} \) life regardless of \([A]_0\), the rx. must be first order.

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<table>
<thead>
<tr>
<th>Exp</th>
<th>([A]_0 ) (a)</th>
<th>( t_\frac{1}{2} ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp 1</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Exp 2</td>
<td>2.00</td>
<td>0.50</td>
</tr>
<tr>
<td>Exp 3</td>
<td>0.50</td>
<td>1.00</td>
</tr>
</tbody>
</table>

\( t_\frac{1}{2} \) varies w. \([A]_0\), so \( t_\frac{1}{2} \) can't be a 1st order rx.

Could be zero order or 2nd order.

\[ t_\frac{1}{2} = \frac{[A]_0}{2k} \]

\[ t_\frac{1}{2} = \frac{1}{k[A]_0} \]

From these eqns. can see that for a

1) zero order rx.; \( t_\frac{1}{2} \) dec. as rx. proceeds (Exp 1, Exp 2);
2) 1st order rx.; \( t_\frac{1}{2} \) constant
3) 2nd order rx.; \( t_\frac{1}{2} \) inc. as rx. proceeds \( (t_\frac{1}{2} \text{ increases}) \)

From above data you can see as \([A]_0 \text{ decreases}\), \( t_\frac{1}{2} \text{ decreases}\) per a 2nd order rx.

In fact, as \([A]_0 \text{ is cut in half}\), \( t_\frac{1}{2} \text{ doubles}\).
50) (cont.)
\[ r = \frac{K[SAT]^2}{L_0^2} \quad \text{where} \quad L_0 = \frac{K[SA]}{L} \]

\[ k = \frac{L_0[A]}{L_0[A]_0} = \frac{(5.0 \text{ min})(1.00)}{0.02 \text{ M min}^{-1}} \]

- using exp. 1 data

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51) Similar to previous question.

\[ LN3 \text{H}_2\text{O} (M) \quad L_0 (\text{min}) \]

<table>
<thead>
<tr>
<th>exp</th>
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<td>0.0015</td>
<td>3.7</td>
</tr>
<tr>
<td>exp3</td>
<td>0.00068</td>
<td>1.7</td>
</tr>
</tbody>
</table>

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a) order of rx.

\[ \text{can see } t_{1/2} \text{ dec. as } [\text{NH}_3\text{H}_2\text{O}] \text{ dec. as} \]

\[ \text{zero order rx.} \]

\[ \text{as a matter of fact as } [\text{A}]_0 \text{ is cut in half, } t_{1/2} \text{ is cut in half} \]

\[ [\text{A}]_0, \text{exp} = \frac{1}{2} [\text{A}]_0, \text{exp} \]

\[ t_{1/2, \text{exp}} = \frac{[\text{A}]_0, \text{exp}}{k} \]

\[ t_{1/2, \text{exp}} = \frac{[\text{A}]_0, \text{exp}}{k} = \frac{1}{2} \cdot t_{1/2, \text{exp}} \]

\[ \text{zero order rx.} \]

\[ r = k \]

b) \[ t_{1/2} = \frac{[\text{NH}_3\text{H}_2\text{O}]}{2K} \]

\[ K = \frac{[\text{NH}_3\text{H}_2\text{O}]}{2t_{1/2}} = \frac{0.0031 \text{ M}}{2 \cdot (0.6 \text{ min})} = 0.033 \times 10^{-4} = 2.0 \times 10^{-5} \text{ M min}^{-1} \]
For the reaction:

\[ \text{Cl}_2(g) + \text{CO}(g) \rightarrow \text{COCl}_2(g) \]

rate = \( k\left[\text{Cl}_2\right] \left[\text{CO}\right] \)

\[ \begin{align*}
(1) & \quad \text{Cl}_2 \overset{k_1}{\rightarrow} 2\text{Cl} \quad \text{(fast) \ initiation \ step} \\
(2) & \quad \text{Cl} + \text{CO} \overset{k_2}{\rightarrow} \text{COCl} \quad \text{(fast) \ chain \ propagation} \\
(3) & \quad \text{COCl} + \text{Cl}_2 \overset{k_3}{\rightarrow} \text{COCl}_2 + \text{Cl} \quad \text{(slow) \ steps}
\end{align*} \]

This is a chain rxn in which step (1) is an initiation step. Get Cl radical only need a few of Cl radicals from this step to get the rxn started. Once started Cl is generated in step (3) from Cl_2. Steps (2) & (3) are the chain propagation steps and essentially happen an infinite number of times compared to step (1). This is often true of chain rxns.

Thus, the overall rxn results from adding steps (2) + (3).

Base rate on 3rd step (rate determining).

(if you assume step 2 is slow step you don't get proper rate law)

\[ r = k_3 \left[\text{COCl}\right] \left[\text{Cl}_2\right] \]

\[ \left[\text{COCl}\right] \text{ is intermediate - use (5) to obtain} \]

\[ r = k_3 \left(k_2\right) \left[\text{Cl}_2\right] \left[\text{CO}\right] \left[\text{COCl}\right] \]

\[ \left[\text{Cl}_2\right] \text{ is intermediate - use (1) to obtain} \]

\[ k_1 \left[\text{Cl}_2\right] = k_4 \left[\text{CO}\right]^2 \Rightarrow \left[\text{Cl}_2\right] = \left(\frac{k_4}{k_1}\right)^{1/2} \left[\text{CO}\right]^{1/2} \]

\[ r = k_3 \left(k_2\right) \left(k_4\right) \left[\text{CO}\right] \left(\frac{k_4}{k_1}\right)^{1/2} \left[\text{CO}\right]^{1/2} \]

\[ = k_3 \left(k_2\right) \left(k_4\right) \left[\text{CO}\right]^{3/2} \]