Problem Set 4

9.6

(a) \[ k = \ln 2 / t_{1/2} = \ln 2 / 5720 \text{ yr} = 1.21 \times 10^{-4} \text{ yr}^{-1} \]

(b) We assume that the natural abundance of $^{14}$C has remained constant over time, $[^{14}\text{C}]_0$. As long as an organism is alive, it can exchange material with its environment and its $[^{14}\text{C}]$ remains constant, or $[^{14}\text{C}] = [^{14}\text{C}]_0$. When it dies, it no longer takes in $^{14}$C, and the concentration decays according to first-order kinetics,

\[
[^{14}\text{C}]/[^{14}\text{C}]_0 = e^{kt}
\]

where the time of decay is $t$. Using the rate constant from (a), $[^{14}\text{C}]_0 = 1.1 \times 10^{-13}$ mol% and $[^{14}\text{C}] = 0.89 \times 10^{-14}$ mol% at present,

\[
t = -(1/k) \ln \left( \frac{[^{14}\text{C}]}{[^{14}\text{C}]_0} \right) = -(1/1.21 \times 10^{-4} \text{ yr}^{-1}) \ln \left( \frac{0.89 \times 10^{-14}}{1.1 \times 10^{-13}} \right)
\]

\[
t = 2.1 \times 10^4 \text{ yr}
\]

9.9

The absorbance of a reactant is proportional to its concentration, so from the data we know how the concentration varies with time. There are several ways we can use the data to find out the order of the reaction. One way would be to plot out the concentration (or absorbance) against time. For example, we can plot the following:

(a) $\ln \left( \frac{A}{A_0} \right)$ vs. time. If we get a straight line, then the reaction is first-order.

(b) $1/A$ vs. time. If we get a straight line, then the reaction is second-order.

(A is the absorbance at a particular time, and $A_0$ is the absorbance at $t = 0$.)

Trying (a) first:

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0</th>
<th>54</th>
<th>171</th>
<th>390</th>
<th>720</th>
<th>1010</th>
<th>1190</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln(A/A_0)$</td>
<td>0.000</td>
<td>-0.100</td>
<td>-0.298</td>
<td>-0.679</td>
<td>-1.251</td>
<td>-1.713</td>
<td>-2.045</td>
</tr>
</tbody>
</table>

Plotting this, we get a straight line with slope $-1.71 \times 10^{-3} \text{ s}^{-1}$. Since the line is straight, the reaction is first-order, and from the slope we know that $k = 1.71 \times 10^{-3} \text{ s}^{-1}$. 
Another way to find the reaction order is to plot A vs time and determine the half-life, which is the time where \( A = A_0/2 \).

The half-life is about 400 s. We can see how this value depends on initial concentration by determining the time it takes for this new concentration (or absorbance) to reach half its value. So if we now start with \( A_0 = 0.83 \), the next (or second) half-life is found where \( A = 0.42 \). From the figure, we see this occurs at about 800 s, or about 400 s after the first half-life. This means that the second half-life is again about 400 s. So each half-life is about 400 s, and does not depend on initial concentration of reactant, as we would expect for a first-order reaction. (For a second-order reaction, the half-life varies as \( A_0^{-1} \).

9.23

The first step involves rapid equilibration, so forward and reverse reactions in step 1 are much faster than the second step. The reaction rates in the first step are

Forward rate = \( k_1[O_3] \)

Reverse rate = \( k_{-1}[O_2][O] \)

If they are in equilibrium, then \( k_1[O_3] = k_{-1}[O_2][O] \)

Solving for \([O]\): \( [O] = k_1[O_3]/k_{-1}[O_2] \)

The rate of the second step: \( \text{rate} = k_2[O_3][O] = k_2k_1[O_3]^2/k_{-1}[O_2] = k[O_3]^2/[O_2] \), where \( k = k_2k_1/k_{-1} \).

The rate law shows that higher concentrations of \( O_2 \) will decrease the reaction rate. This is due to the reverse reaction in the first step. If more \( O_2 \) is present, this drives the first step towards reactant, or \( O_3 \), slowing down its depletion.
(a) The sum of the reactions,

$$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$$

$$\text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2$$

gives

$$\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2$$

(b) Cl is a catalyst; ClO is an intermediate.

(c) The C-F bond is stronger than the C-Cl bond, so that Cl is formed more easily than F.

(d) Ethane removes the Cl atom through the reaction

$$\text{C}_2\text{H}_6 + \text{Cl} \rightarrow \text{C}_2\text{H}_5 + \text{HCl}$$

(e) We know that O$_2$ is the most stable form of oxygen, so more stable than O or O$_3$.
   This means it is going from less stable reactants to more stable products, so is exothermic. Using the data from Appendix 2 for the enthalpy of formation of each of these compounds confirms this.

If reaction is not catalyzed,

![Reaction coordinate diagram](image)

If reaction is catalyzed,

![Reaction coordinate diagram](image)
9.27

If the rate doubles, then the rate constant doubles, too.

\[
\ln \left( \frac{k_{315}}{k_{305}} \right) = -\left( \frac{E_a}{R} \right) \left( \frac{1}{315 \, \text{K}} - \frac{1}{305 \, \text{K}} \right)
\]

\[
\ln 2 = -\left( \frac{E_a}{8.314 \, \text{J \ K}^{-1} \ \text{mol}^{-1}} \right) \left( \frac{1}{315 \, \text{K}} - \frac{1}{305 \, \text{K}} \right)
\]

\[
E_a = 5.54 \times 10^4 \, \text{J \ mol}^{-1}
\]

9.57

(a) Rate of formation of \( \text{HbO}_2 \) = \( \frac{\text{d[HbO}_2\text{]}}{\text{dt}} = k \ [ \text{Hb} \ ] \ [ \text{O}_2\] \)

\[
= (2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}) (8.0 \times 10^{-6} \text{ M}) (1.5 \times 10^{-6} \text{ M})
\]

\[
= 2.5 \times 10^{-5} \text{ M s}^{-1}
\]

(b) The rate of consumption of \( \text{O}_2 \) is the same as the rate of formation of \( \text{HbO}_2 \), so = 2.5 \times 10^{-5} \text{ M s}^{-1}

(c) Rate of formation of \( \text{HbO}_2 \) = \( k \ [ \text{Hb} \ ] \ [ \text{O}_2\]

\[
[ \text{O}_2\] = \text{Rate of formation of HbO}_2 / k \ [ \text{Hb} \]
\]

\[
= \left( 1.4 \times 10^{-4} \text{ M s}^{-1} \right) / \left( 2.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1} \right) (8.0 \times 10^{-6} \text{ M})
\]

\[
= 8.3 \times 10^{-6} \text{ M}
\]

The concentration of \( \text{O}_2 \) required to sustain the increase in metabolism during exercise is thus 5.6 times higher than is typically found in the blood.