Chem 6 Sample Exam 1 brief answers

1. a. Consider the first 2 columns. Doubling \([HI]\) quadruples the rate, so it must be second order in HI. Note that you get the same result by considering columns 2 and 3. So the rate law must be \(\text{rate} = k[HI]^2\).
   
   b. To get the rate constant, plug in some numbers. I used column 1:
   \[\text{rate} = 7.5 \times 10^{-4} \text{Ms}^{-1} = k(0.005 \text{M})^2\]
   \[k = 30 \text{M}^{-1}\text{s}^{-1}\]
   c. Plug in \([HI] = 0.0020\text{M}\) to get
   \[\text{rate} = 30\text{M}^{-1}\text{s}^{-1}(0.0020\text{M})^2\]
   \[= 1.2 \times 10^{-4} \text{Ms}^{-1}\]

2. These sketches are not to scale, and my drawing program is not good at making curves, but you should be able to get the idea from these pictures......
   
   (a) \(\Delta E = 10, E_a = 25\)  
   (b) \(\Delta E = -10, E_a = 50\)  
   (c) \(\Delta E = -50, E_a = 50\)

   Reaction (a) (the left-hand one) will be the fastest, since it has the lowest activation energy, and \(k = Ae^{-Ea/RT}\)

3. Michaelis-Menten. From class discussion of the Lineweaver-Burk plot, we saw that the maximum possible rate is \(k_2[E]_0\). So half of that is \(k_2[E]_0/2\). Set this equal to the rate expression to get
   \[k_2[E]_0/2 = \frac{k_2[\text{E}_0][S]}{[S]} + K_M\]
   You can already see that this works when \([S] = K_M\)
   
   Or chug through the algebra:
   \[1/2 = [S]/[S] + K_M\]
   \[1/2[S] + 1/2K_M = [S]\]
   \[1/2K_M = 1/2[S]\]
   \[K_M = [S]\]
4. (a) Here are the steps labeled as initiation, propagation and termination.

\[
\text{C}_2\text{H}_6 + \text{I}_2 \rightarrow \text{C}_2\text{H}_5\text{I} + \text{HI}
\]

proposed mechanism

\[
\begin{array}{c}
\text{I} & \overset{k_1}{\longrightarrow} & 2\text{I} \\
\text{P} & \overset{k_2}{\longrightarrow} & \text{C}_2\text{H}_5 + \text{HI} \\
\text{P} & \overset{k_3}{\longrightarrow} & \text{C}_2\text{H}_5\text{I} + \text{I} \\
\text{T} & \overset{k_{-1}}{\longrightarrow} & \text{I}_2
\end{array}
\]

(b) The rate is given by \(-\frac{d}{dt}[\text{C}_2\text{H}_6] = k_2[\text{C}_2\text{H}_6][\text{I}]\)

But [I] is an intermediate so we need to get rid of its concentration. Do this from steps 1 and 4, which define an equilibrium: \([\text{I}]^2/[\text{I}_2] = K_{\text{eq}} = k_1/k_{-1}\)

So \([I] = \{[I_2]K_{\text{eq}}\}^{1/2}\)

Plug in to get

\[
\text{Rate} = k_2[\text{C}_2\text{H}_6][[I_2]K_{\text{eq}}]^{1/2}
\]

Another approach to find [I] also works: doing the steady-state approximation on the concentrations of both the intermediates \(\text{C}_2\text{H}_5\) and I. It would look like this, where the factors of 2 arise since you're either making or destroying 2 equivalents of I in steps 1 and 4.

\[
\begin{align*}
\frac{d}{dt}[\text{I}_2] &= 0 = 2k_1[I_2] - 2k_{-1}[I] \\
\frac{d}{dt}[\text{C}_2\text{H}_5] &= 0 = k_2[I][\text{C}_2\text{H}_6] - k_3[\text{C}_2\text{H}_5][I_2]
\end{align*}
\]

Add these up; several terms will cancel out nicely, to give

\[
0 = 2k_1[I_2] - 2k_{-1}[I]^2
\]

\([I] = \{[I_2]K_{\text{eq}}\}^{1/2}\) where \(K_{\text{eq}} = k_1/k_{-1}\), exactly the result from above.

5. a. The product ratio is given by the relative rates of formation of C and D. Thus \(\frac{d}{dt}[\text{C}] = k_2[\text{A}]\) and \(\frac{d}{dt}[\text{D}] = k_3[\text{B}]\), so

\[
\text{product ratio} = \frac{k_2[\text{A}]}{k_3[\text{B}]}
\]

But from the equilibrium, \([\text{B}]/[\text{A}] = K_{\text{eq}}\)

Or, \([\text{B}] = [\text{A}]K_{\text{eq}}\)

Plug this in to the product ratio expression to get

\[
\text{product ratio} = k_2[\text{A}]/k_3[\text{A}]K_{\text{eq}}
\]

\[
\text{product ratio} = k_2/k_3K_{\text{eq}}
\]
b. **FALSE.** You can reach this conclusion in 2 ways. From the product ratio result of part a, even if $K_{eq}$ is very small (favoring A), you can still get D as the major product if $k_3$ is bigger than $k_2$. Here are some numbers, for example. Suppose $K_{eq} = 0.01$ (i.e., a 100:1 mixture of A and B at equilibrium, $k_2$ is 1, and $k_3$ is 1000. This gives a product ratio of 0.1 (10:1 mixture of D and C).

Or, consider le Chatelier's principle. If an equilibrium mixture of A and B is perturbed by formation of D from B (which occurs faster than formation of C from A), you will drive the equilibrium from A to form B. If B continues to be drained by rapid formation of D, it should be clear this will be the major product even if the original equilibrium favored A.

6. For a 2\textsuperscript{nd}-order reaction, the rate law is
\[ \text{rate} = k [C_2F_4]^2 \]
and we're given the value of $k = 0.0896 M^{-1} s^{-1}$

Use the integrated form of the rate law:
\[ \frac{1}{[C_2F_4]} = \frac{1}{[C_2F_4]_0} + kt \]

Plug in the numbers provided
\[ \frac{1}{[C_2F_4]} = \frac{1}{0.100M} + (0.0896 M^{-1} s^{-1})(205s) \]
\[ [C_2F_4] = 3.53 \times 10^{-2} M \]

7. I've reproduced the data table here and added columns for $\ln[N_2O_5]$ and $\frac{1}{[N_2O_3]}$ needed to see if it's first or 2\textsuperscript{nd} order in $N_2O_5$.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>$[N_2O_3]$ (M)</th>
<th>$\ln[N_2O_5]$</th>
<th>$\frac{1}{[N_2O_3]}$</th>
<th>$[N_2O_3]$ (M)</th>
<th>$\ln[N_2O_5]$</th>
<th>$\frac{1}{[N_2O_3]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00x10^{-1}</td>
<td>-2.30</td>
<td>10</td>
<td>1.00x10^{-1}</td>
<td>-2.30</td>
<td>10</td>
</tr>
<tr>
<td>100</td>
<td>6.14x10^{-2}</td>
<td>-2.79</td>
<td>16.3</td>
<td>9.54x10^{-2}</td>
<td>-2.35</td>
<td>10.5</td>
</tr>
<tr>
<td>300</td>
<td>2.33x10^{-2}</td>
<td>-3.76</td>
<td>42.9</td>
<td>8.63x10^{-2}</td>
<td>-2.45</td>
<td>11.6</td>
</tr>
<tr>
<td>600</td>
<td>5.41x10^{-3}</td>
<td>-5.22</td>
<td>185</td>
<td>7.43x10^{-2}</td>
<td>-2.60</td>
<td>13.5</td>
</tr>
<tr>
<td>900</td>
<td>1.26x10^{-3}</td>
<td>-6.68</td>
<td>794</td>
<td>6.39x10^{-2}</td>
<td>-2.75</td>
<td>15.6</td>
</tr>
</tbody>
</table>

By inspection, $\ln[N_2O_3]$ data vs time is linear (this is most easily seen from the 318K data, where it goes up by 0.05 every 100 seconds) and the $\frac{1}{[N_2O_3]}$ points are not linear. You didn't need to do this for both sets of data, but it's a nice check to confirm you're doing it right.

The linearity of the plot means it's first-order in $N_2O_5$. Now we extract the first-order rate constant from the equation
\[ \ln[N_2O_3] = \ln[N_2O_3]_0 - kt \]

Plug in data at 338K, with time = 0 and 100 seconds (of course, other choices should give the same answer, or plotting $\ln[N_2O_3]$ vs time and getting the slope of the line.)
\[ \ln(6.14x10^{-2}M) = \ln(1.00x10^{-1}M) - k(100s) \]
\[ -2.79 = -2.30 - k(100s) \]
\[ -0.49 = -k(100s) \]
\[ k = 4.9 \times 10^{-3} \text{s}^{-1} \]
A similar analysis for the 318K data (same times) gives:
\[-2.35 = -2.30 - k(100\text{s})\]
\[ k = 5 \times 10^{-4} \text{s}^{-1} \]
Now, to find \( E_a \), apply one of the several forms of the Arrhenius equation. Most conveniently,
\[
\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]
\[
\ln\left(\frac{4.9 \times 10^{-3} \text{s}^{-1}}{5 \times 10^{-4} \text{s}^{-1}}\right) = \frac{E_a}{8.314 \text{J/molK}} \{1/318\text{K} - 1/338\text{K}\}
\]
\[2.28 = 2.24 \times 10^{-5} \text{J/mol}(E_a)\]
\[E_a = 1.02 \times 10^5 \text{ J/mol} = 102 \text{ kJ/mol}\]

8. Photoelectric effect: \( KE_{\text{electron}} = h\nu - h\nu_o \)
Here instead of the usual work function \( h\nu_o \), we have the ionization energy. To see if the light can remove the electron, we just have to find out if its energy \( h\nu \) is greater than the ionization energy \( h\nu_o \); thus it will work if \( h\nu > h\nu_o \).
So, plug in the numbers, being careful with units.
\[ h\nu = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{Js})(3 \times 10^8 \text{m/s})}{(225 \text{ nm} \times 1 \text{m}/10^9 \text{nm})} = 8.84 \times 10^{-19} \text{J} \]
Convert to kJ/mol:
\[8.84 \times 10^{-19} \text{J}(1\text{kJ}/1000\text{J})(6.02 \times 10^{23}/\text{mol}) = 532 \text{kJ/mol}\]
Is \( h\nu > h\nu_o \)? Nope, not even close. So the answer is NO.

9. a. It can’t go faster than the speed of light, so the biggest uncertainty must be just that, \( c = 3 \times 10^8 \text{ m/s} \). To make this more clear, possible speeds range from \( c \) to almost zero. How big an error could you get? Suppose you thought it had a velocity of zero, but it was really traveling at speed \( c \). Then the uncertainty is \( c \).

b. From the Heisenberg uncertainty principle, \( \Delta x \Delta p \geq \hbar/2 \). We want to find \( \Delta x \) and we have \( \Delta v \). Plug in the electron mass to get
\[ \Delta p = m\Delta v = (9.11 \times 10^{-31} \text{kg})(3 \times 10^8 \text{m/s}) = 2.73 \times 10^{-22} \text{ kgm/s} \]
Since \( \Delta x \Delta p \geq \hbar/2 \), then \( \Delta x \geq (\hbar/2)/\Delta p \)
\[ \Delta x \geq \frac{(6.626 \times 10^{-34} \text{Js}/2\pi)/2}{(2.73 \times 10^{-22} \text{kgm/s})} = 1.93 \times 10^{-13} \text{Js/kgm} \]
since \( 1 \text{J} = 1 \text{kgm}^2/\text{s}^2 \)
\[= 1.93 \times 10^{-13} \text{ m}, \text{ or, since there are } 10^9 \text{ nm in a meter, } 1.93 \times 10^{-4} \text{nm is the minimum uncertainty in position.} \]

10. 1. 268 hours is 4 half-lives. After 1 half-life, the initial 1 gram will decay to 0.5g; after 2, it’s down to 0.25g, after 3, to 0.125g, and after 4, 0.0625g. Thus the correct answer is c.

2. d
3. The slope of the lnk vs 1/T plot is \(-E_a/R\). The steeper the slope, the bigger \( E_a \), so B has a larger activation energy.

4. a

5. b