Exam I

Rate Laws
Activation Energies
Mechanisms
Radioactive Decay
**Kinetics and Activation Energy**

1) Rate information was obtained for the following reaction at 25°C and 33°C:

\[
\text{Cr(H}_2\text{O)}_6^{3+} + \text{SCN}^- \rightarrow \text{Cr(H}_2\text{O)}_5\text{NCS}^{2+} + \text{H}_2\text{O(l)}
\]

<table>
<thead>
<tr>
<th>Initial Rate</th>
<th>[Cr(H₂O)₆³⁺]</th>
<th>[SCN⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0x10⁻¹¹</td>
<td>1.0x10⁻⁴</td>
<td>0.10</td>
</tr>
<tr>
<td>2.0x10⁻¹⁰</td>
<td>1.0x10⁻³</td>
<td>0.10</td>
</tr>
<tr>
<td>9.0x10⁻¹⁰</td>
<td>2.0x10⁻³</td>
<td>0.15</td>
</tr>
<tr>
<td>2.4x10⁻⁹</td>
<td>3.0x10⁻³</td>
<td>0.20</td>
</tr>
</tbody>
</table>

@ 33°C

<table>
<thead>
<tr>
<th>Initial Rate</th>
<th>[Cr(H₂O)₆³⁺]</th>
<th>[SCN⁻]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4x10⁻¹⁰</td>
<td>1.0x10⁻⁴</td>
<td>0.20</td>
</tr>
</tbody>
</table>

   a) Write a rate law consistent with the experimental data.

   b) What is the value of the rate constant at 25°C?

   c) What is the value of the rate constant at 33°C?

   d) What is the activation energy for this reaction?

   e) What is the reverse rate law?

2) The mechanism for the decomposition of phosgene

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

is thought to be,

fast eq. \[ \text{Cl}_2(g) \rightleftharpoons 2 \text{Cl(g)} \]
slow \[ \text{COCl}_2(g) + \text{Cl(g)} \rightarrow \text{COCl(g)} + \text{Cl}_2(g) \]
fast eq. \[ \text{COCl(g)} \rightleftharpoons \text{CO(g)} + \text{Cl(g)} \]

Based on this mechanism, what is the rate law for this reaction?
3) The following experimental data were obtained for the reaction at 250 K,

\[ \text{F}_2 + 2 \text{ClO}_2 \rightarrow 2 \text{FCIO}_2 \]

<table>
<thead>
<tr>
<th>[F\textsubscript{2}]/M</th>
<th>[ClO\textsubscript{2}]/M</th>
<th>Rate/(M/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>0.010</td>
<td>1.2x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>0.10</td>
<td>0.040</td>
<td>4.8x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>0.20</td>
<td>0.010</td>
<td>4.8x10\textsuperscript{-3}</td>
</tr>
</tbody>
</table>

3a) Write a rate law consistent with this data.

Rate =

3b) What is the value and units of the rate constant?

4) The bromination of acetone is acid catalyzed;

\[ \text{CH}_3\text{COCH}_3 + \text{Br}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{Br} + \text{H}^+ + \text{Br}^- \]

The rate of disappearance of bromine was measured for several different concentrations of acetone, bromine and hydrogen ions;

<table>
<thead>
<tr>
<th>Rate/Msec\textsuperscript{-1}</th>
<th>[Acetone]/M</th>
<th>[Br\textsubscript{2}]/M</th>
<th>[H\textsuperscript{+}]/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>6x10\textsuperscript{-5}</td>
<td>0.30</td>
<td>0.050</td>
<td>0.050</td>
</tr>
<tr>
<td>6x10\textsuperscript{-5}</td>
<td>0.30</td>
<td>0.100</td>
<td>0.050</td>
</tr>
<tr>
<td>1.2x10\textsuperscript{-4}</td>
<td>0.30</td>
<td>0.050</td>
<td>0.100</td>
</tr>
<tr>
<td>3.2x10\textsuperscript{-4}</td>
<td>0.40</td>
<td>0.050</td>
<td>0.200</td>
</tr>
<tr>
<td>8x10\textsuperscript{-5}</td>
<td>0.40</td>
<td>0.050</td>
<td>0.050</td>
</tr>
</tbody>
</table>

a) What is the forward rate law for this reaction?

b) What is the value and units of the forward rate constant?

c) What is the reverse rate law?

d) If the equilibrium constant is 1.3x10\textsuperscript{3}, what is the value of the reverse rate constant?
5) At low temperatures, the rate law for the reaction,

\[ \text{CO}(g) + \text{NO}_2(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \]

can be determined by the following data:

<table>
<thead>
<tr>
<th>[NO]/10^{-3} M</th>
<th>[CO]/10^{-3} M</th>
<th>[NO_2]/10^{-3} M</th>
<th>Initial Rate/10^{-4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.20</td>
<td>1.50</td>
<td>0.80</td>
<td>3.60</td>
</tr>
<tr>
<td>1.20</td>
<td>3.00</td>
<td>0.80</td>
<td>7.20</td>
</tr>
<tr>
<td>1.20</td>
<td>0.75</td>
<td>0.40</td>
<td>0.90</td>
</tr>
<tr>
<td>2.40</td>
<td>1.50</td>
<td>0.40</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Write a rate law in agreement with the data.

Which of the following mechanisms is consistent with this rate law? (Circle A, B, or C)

A) CO + NO_2 ---> CO_2 + NO slow

B) NO_2 <---> NO + O equil.
   O + CO --> CO_2 slow

C) 2 NO_2 <---> 2 NO + O_2 equil.
   CO + O_2 ---> CO_2 + O slow
   O + NO ---> NO_2 fast

D) None of the above
6) The following experimental data were obtained for the reaction:

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

<table>
<thead>
<tr>
<th>Initial Rate/10^-5</th>
<th>[NO]/10^-2 M</th>
<th>[H_2]/10^-2 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>0.50</td>
<td>0.20</td>
</tr>
<tr>
<td>2.40</td>
<td>1.00</td>
<td>0.20</td>
</tr>
<tr>
<td>0.30</td>
<td>0.25</td>
<td>0.40</td>
</tr>
</tbody>
</table>

a) Write a rate law in agreement with the data.

Rate =

b) What is the value of the rate constant?

c) What is the new rate when [NO] = 3x10^-2 M and [H_2] = 1.2x10^-2 M?

d) Which of the following mechanisms are consistent with the rate law above?

i) \(2 \text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}\) (slow)

ii) \(2 \text{NO} \leftrightharpoons \text{N}_2\text{O}_2\) (equil)
    \(\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}\) (slow)

iii) \(\text{NO} + \text{H}_2 \leftrightharpoons \text{H}_2\text{O} + \text{N}\) (equil)
    \(\text{N} + \text{NO} \rightarrow \text{N}_2\text{O}\) (slow)

e) Platinum acts as a catalyst for this reaction. What term must be added to the rate law to account for the presence of the catalyst?

f) Would platinum be a homogeneous or heterogeneous catalyst for this reaction?

g) If the temperature is increased by 6.8°C the reaction rate increases 1.65 times. What is the activation energy of the reaction?
7) The following experimental data were obtained for the reaction at 25°C,

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

<table>
<thead>
<tr>
<th>Initial [NO] /10^{-3} M</th>
<th>Initial [H\textsubscript{2}] /10^{-3} M</th>
<th>Initial Rate /10^{-5} Msec\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.40</td>
<td>2.20</td>
<td>2.60</td>
</tr>
<tr>
<td>12.8</td>
<td>1.10</td>
<td>5.20</td>
</tr>
<tr>
<td>6.40</td>
<td>4.40</td>
<td>5.20</td>
</tr>
</tbody>
</table>

Which of the following mechanisms are consistent with the rate law for this reaction?

a) \(2 \text{ NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}\) (slow)

b) \(2 \text{ NO} \rightleftharpoons \text{N}_2\text{O}_2\) (equil)
\(\text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}\) (slow)

c) \(\text{NO} + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{N}\) (equil)
\(\text{N} + \text{NO} \rightarrow \text{N}_2\text{O}\) (slow)

8) At low temperatures, the rate law for the reaction,

\[
\text{CO(g)} + \text{NO}_2(g) \rightarrow \text{CO}_2(g) + \text{NO(g)}
\]

is;

\[
\text{Rate} = k [\text{NO}_2]^2
\]

Which of the following mechanisms is consistent with this rate law? (Circle A, B, or C)

a) \(\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}\) slow

b) \(2 \text{ NO}_2 \rightarrow \text{N}_2\text{O}_4\) fast equil.
\(\text{N}_2\text{O}_4 + 2 \text{ CO} \rightarrow 2 \text{ CO}_2 + 2 \text{ NO}\) slow

c) \(2 \text{ NO}_2 \rightarrow \text{N}_2\text{O}_4\) slow
\(\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{ NO} + \text{O}_2\) fast equil.
\(\text{O}_2 + \text{CO}_2 \rightarrow 2 \text{ CO}_2\) fast
9) Given the following rate data, calculate the rate law at 25°C.

<table>
<thead>
<tr>
<th>@ 25°C</th>
<th>Rate/10⁻⁴</th>
<th>[I⁻]/M</th>
<th>[OCI⁻]/M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.10</td>
<td>0.20</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>12.2</td>
<td>0.40</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>36.6</td>
<td>0.60</td>
<td>0.100</td>
</tr>
<tr>
<td>@ 33°C</td>
<td>14.4</td>
<td>0.20</td>
<td>0.050</td>
</tr>
</tbody>
</table>

What is the rate law?

Rate =

What is the value of the rate constant at 25°C and at 33°C?

What is the activation energy for this reaction?

What is the half-life of this reaction at 45°C if [I⁻] = [OCI⁻] = 0.25 M?

10) Thiosulfate (S₂O₃²⁻) can react with triiodide (I₃⁻) according to the following reaction at 25°C,

\[ 2 \text{S}_2\text{O}_3^{2-} + \text{I}_3^- \rightleftharpoons \text{S}_4\text{O}_6^{2-} + 3 \text{I}^- \quad \text{Keq} = 3.75 \times 10^5 \]

Experimentally the forward rate law can be determined from the following data,

<table>
<thead>
<tr>
<th>Rxn</th>
<th>Rate/Msec⁻¹</th>
<th>[S₂O₃²⁻]/M</th>
<th>[I₃⁻]/M</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>2.56x10⁻⁴</td>
<td>0.040</td>
<td>0.12</td>
</tr>
<tr>
<td>#2</td>
<td>1.28x10⁻⁴</td>
<td>0.020</td>
<td>0.12</td>
</tr>
<tr>
<td>#3</td>
<td>1.92x10⁻⁴</td>
<td>0.060</td>
<td>0.06</td>
</tr>
</tbody>
</table>

a) What is the rate law?
b) What is the value of the rate constant? (Include units)
c) What are the minimum number of steps required in the mechanism of the forward rate law? Circle one

1          2            3

d) If reaction #1 is heated to 35°C the rate increases to 4.8x10^-4 M/sec. What is the activation energy of this reaction?

e) At what temperature would the reaction rate double from 25°C?

11) A cook finds that it takes 30 minutes to boil potatoes at 100°C in an open sauce pan and only 12 minutes to boil them in a pressure cooker at 110°C. Estimate the activation energy for cooking potatoes, which involves the conversion of cellulose into starch. Remember that there is an inverse relationship between time and the rate constant.

12) When N₂O₄ decomposes it forms NO₂,

\[ \text{N}_2\text{O}_4 \rightarrow 2 \text{NO}_2 \]

If the half-life of this reaction is 1386 seconds, how much of a 10 gram sample would be left after 1500 seconds? (Is the reaction first or second order?)

13) An archaeologist measured the amount of radioactivity of a piece of cloth used to wrap an Egyptian mummy. The cloth was found to have a decay rate of 9.1 dpm. If the decay rate is 15.3 dpm in living tissue, how old is the mummy? t1/2 = 5730 years.

14) Uranium is radioactive and decays into lead. This process can be used to date rocks. A piece of zirconium was dated using this process and it was found that this rock contained 3.2x10^-³ grams of uranium and 2.2x10^-⁵ grams of lead. If the half-life of uranium is 4.41x10⁹ years how old is the rock?

15) Assuming that the loss of ability to recall learned material is a first-order process with a half-life of 35 days. Compute the number of days required to forget 90% of the material that you learned in preparation for this exam.
16a) Under acidic conditions sucrose (table sugar) can be broken down into its individual sugars, glucose and fructose. At 27°C it takes 54.5 minutes to convert half the sucrose to glucose and fructose and at 37°C it takes 13.7 minutes. Estimate the activation energy for the breakdown of sucrose.

16b) The above reaction is known to second order which means that the half-life is dependent on the initial concentration. Will this fact effect your calculation of the activation energy above? Why or why not. (Hint: What must you assume about the initial concentration of [A] when using the Arrhenius equation?)

17) A 10 gram sample of $^{131}$I was sent from a pharmaceutical company to a hospital for use in the treatment of hyperthyroidism. If the half life of $^{131}$I is 8.07 days, how much of the sample would be left after a 2 day mail delivery?

18) The denaturation of the virus that causes the rabbit disease Myxomatosis can be followed by heating the virus under a microscope. It is observed that the reaction is first-order and that it takes 22.35 minutes at 50°C and 0.35 minutes at 60°C for the virus to denature. Estimate the activation energy for the denaturation of the Myxomatosis virus.
Answer Key - Kinetics and Activation Energy

1a) \[ \text{Rate} = k \left[ \text{Cr(H}_2\text{O)}_6^{3+} \right] \left[ \text{SCN}^- \right]^2 \]

1b) \[ 2 \times 10^{-11} = k \left[ 1 \times 10^{-4} \right] \left[ 0.1 \right]^2 \quad k = 2 \times 10^{-5} \ @ \ 25°C \]

1c) \[ 1.4 \times 10^{-10} = k \left[ 1 \times 10^{-4} \right] \left[ 0.2 \right]^2 \quad k = 3.5 \times 10^{-5} \ @ \ 33°C \]

1d) \[ \ln \left( \frac{2 \times 10^{-5}}{3.5 \times 10^{-5}} \right) = \frac{\text{Ea}}{8.314} \left( \frac{298 - 306}{298 \times 306} \right) \quad \text{Ea} = 53,033 \text{ J/mol} \]

1e) \[ k_F \left[ \text{Cr(H}_2\text{O)}_6^{3+} \right] \left[ \text{SCN}^- \right] = k_R \left[ X \right] \]

\[ \text{Keq} = \frac{k_F}{k_R} = \frac{[X]}{\left[ \text{Cr(H}_2\text{O)}_6^{3+} \right] \left[ \text{SCN}^- \right]^2} = \frac{\left[ \text{Cr(H}_2\text{O)}_5 \text{SCN}^{2+} \right]}{\left[ \text{Cr(H}_2\text{O)}_6^{3+} \right] \left[ \text{SCN}^- \right]} \]

\[ [X] = \left[ \text{Cr(H}_2\text{O)}_5 \text{SCN}^{2+} \right] \left[ \text{SCN}^- \right] \quad \text{rate}_R = k_R \left[ \text{Cr(H}_2\text{O)}_5 \text{SCN}^{2+} \right] \left[ \text{SCN}^- \right] \]

2) Start with the slow step

rate = k \left[ \text{COCl}_2 \right] \left[ \text{Cl} \right]

Get rid of [Cl] using the equilibrium,

\[ \frac{[\text{Cl}]}{[\text{Cl}_2]} = \text{Keq} \Rightarrow [\text{Cl}] = \sqrt{\text{Keq}[\text{Cl}_2]} \]

\[ \text{rate} = k \sqrt{\text{Keq}[\text{Cl}_2]} \left[ \text{COCl}_2 \right] = k \text{Keq}^{1/2} \left[ \text{Cl}_2 \right]^{1/2} \left[ \text{COCl}_2 \right] = k \left[ \text{Cl}_2 \right]^{1/2} \left[ \text{COCl}_2 \right] \]

3a) \[ \text{rate} = k[F_2]^2 \left[ \text{ClO}_2 \right] \]

3b) \[ 1.2 \times 10^{-3} \text{ M/s} = k \left[ 0.1 \text{ M} \right]^2 \left[ 0.01 \text{ M} \right] \quad k = 12 \text{ 1/M}^2\text{s} \]

4a) rate = k \left[ \text{Acetone} \right] \left[ \text{H}^+ \right]

4b) \[ 6 \times 10^{-5} \text{ M/s} = k \left[ 0.3 \text{ M} \right] \left[ 0.05 \text{ M} \right] \quad k = 4 \times 10^{-3} \text{ 1/Ms} \]
4c) \( k_F [\text{Acetone}] [H^+] = k_R [X] \)

\[
\frac{k_F}{k_R} = \frac{[X]}{[\text{Acetone}][H^+]} = \frac{[\text{AcetoneBr}][H^+][Br^-]}{[\text{Acetone}][Br_2]}
\]

\([X] = \frac{[\text{AcetoneBr}][H^+]^2[Br^-]}{[Br_2]} \) so, \( r_{rate} = k_R \frac{[\text{AcetoneBr}][H^+]^2[Br^-]}{[Br_2]} \)

5a) \( r = k \frac{[\text{CO}][\text{NO}_2]}{[\text{NO}]} \)

5b) A) \( r = k [\text{CO}][\text{NO}_2] \) No, doesn’t match

B) \( r = k [\text{O}][\text{CO}] \) and \( \text{Keq} = \frac{[\text{NO}][\text{O}]}{[\text{NO}_2]} \) so, \( [\text{O}] = \text{Keq} \frac{[\text{NO}_2]}{[\text{NO}]} \)

Substituting, we get \( r = k\text{Keq} \frac{[\text{CO}][\text{NO}_2]}{[\text{NO}]} \) or \( r = k' \frac{[\text{CO}][\text{NO}_2]}{[\text{NO}]} \)

This matches our experimentally determined rate law so it is a possible mechanism.

C) \( r = k [\text{O}_2][\text{CO}] \)

The only reason to use the equilibrium is to get rid of something that is not in the overall reaction. Since the rate law does not contain anything that is not already in the overall reaction (no intermediates) there is no reason to continue. This does not match.

6a) \( r = k [\text{NO}_2]^2 [\text{H}_2] \)

6b) \( 2.4 \times 10^{-5} = k [1 \times 10^{-2} \text{ M}]^2 [0.2 \times 10^{-2} \text{ M}] \) so, \( K = 120 \text{ 1/M}^2\text{s} \)

6c) \( r = (120 \text{ 1/M}^2\text{s}) \times (3 \times 10^{-2})^2 (1.2 \times 10^{-2}) = 1.296 \times 10^{-3} \text{ M/s} \)

6d) Both i & ii are consistent but i) is a single step 3\textsuperscript{rd} order reaction so ii is the answer.

6e) \( k_{cat} [\text{Pt}] + 1 \)

6f) Heterogeneous catalyst. Platinum is a solid.

6g) Assume \( k_1 @ 298 \text{ K} \) and \( 1.65 k_1 @ 304.8 \text{ K} \)

\[
\ln \frac{1.65k_1}{k_1} = \frac{E_a}{8.314} \left( \frac{304.8 - 298}{304.8 \times 298} \right) \]

\( E_a = 55,6130 \text{ J/mol} \)

7) \( r = k [\text{NO}_2]^2 [\text{H}_2] \)
A & B are consistent but A is a single step third order process so it doesn't occur. Therefore the answer is B.

8) Only C matches the experimentally determined rate law.

9a) \[ \text{rate} = k \ [I] \ [\text{OCl}^-] \]

9b) \[ 6.1 \times 10^{-4} = k \ [0.20 \text{ M}] \ [0.05 \text{ M}] \text{ so, } k = 0.061 \text{ 1/Ms @ 25}^\circ \text{C} \]
\[ 14.4 \times 10^{-4} = k \ [0.20 \text{ M}] \ [0.05 \text{ M}] \text{ so, } k = 0.144 \text{ 1/Ms @ 33}^\circ \text{C} \]

9c) \[
\ln \frac{0.144}{0.061} = \frac{E_a}{8.314} \left( \frac{306 - 298}{306 \times 298} \right) \text{ Ea} = 81,399 \text{ J/mol}
\]

9d) \[
\ln \frac{K_{45^\circ}}{0.061} = \frac{81,399}{8.314} \left( \frac{318 - 298}{318 \times 298} \right) \text{ K}_{45^\circ} = 0.4816
\]

\[ t_{1/2} = 1/[A]K \text{ for } 2^{\text{nd}} \text{ order reaction so, } t_{1/2} = 1/[0.25](0.4816) = 8.305 \text{ seconds} \]

10a) \[ \text{rate} = k \ [\text{S}_2\text{O}_3^{2-}] \ [\text{I}_3^-] \]

10b) \[ 2.56 \times 10^{-4} \text{ M/s} = k \ [0.04 \text{ M}] \ [0.12 \text{ M}] \text{ so, } k = 5.33 \times 10^{-2} \text{ 1/Ms} \]

10c) The reaction is 2\text{nd} order so it will take a minimum of 1 step.

10d) \[ 2.56 \times 10^{-4} \text{ M/s} = k \ [0.04 \text{ M}] \ [0.12 \text{ M}] \text{ so, } k_1 = 5.33 \times 10^{-2} \text{ 1/Ms @ 25 C} \]
\[ 4.80 \times 10^{-4} \text{ M/s} = k \ [0.04 \text{ M}] \ [0.12 \text{ M}] \text{ so, } k_2 = 0.10 \text{ 1/Ms @ 35 C} \]

\[
\ln \frac{0.10}{5.33 \times 10^{-2}} = \frac{E_a}{8.314} \left( \frac{308 - 298}{308 \times 298} \right) \text{ Ea} = 47,969 \text{ J/mol}
\]

10e) \[
\ln \frac{2k_1}{k_1} = \frac{47,969}{8.314} \left( \frac{1}{298} - \frac{1}{T_2} \right) \text{ T}_2 = 309.6 \text{ K}
\]

11) \[ t_1 = 30 \text{ min } @ \ 100^\circ \text{C } \text{ and } t_2 = 12 \text{ min } @ \ 110^\circ \text{C} \]

\[
\ln \frac{30\text{ min}}{12\text{ min}} = \frac{E_a}{8.314} \left( \frac{383 - 373}{383 \times 373} \right) \text{ Ea} = 108,830 \text{ J/mol}
\]

12) \[
\ln \frac{10}{X} = \frac{0.693}{1386 \text{ sec}} (1500 \text{ sec}) \text{ X} = 4.72 \text{ grams}
\]

13) \[
\ln \frac{15.3 \text{ dpm}}{9.1 \text{ dpm}} = \frac{0.693}{5730 \text{ yrs}} \Delta t \text{ \Delta t = 4296 yrs}
\]
14) moles U + moles Pb = moles U initially in the sample (Parent)

\[
\frac{3.2 \times 10^{-3} \text{ g U}}{238 \text{ g/mol}} = 1.3445 \times 10^{-5} \text{ mol U} \quad \text{(Parent)} \quad \text{and} \quad \frac{2.2 \times 10^{-5} \text{ g Pb}}{207.2 \text{ g/mol}} = 1.062 \times 10^{-5} \text{ mol Pb} \quad \text{(daughter)}
\]

Total Parent = \(1.3445 \times 10^{-5} \text{ mol U} + 1.062 \times 10^{-7} \text{ mol Pb} = 1.355 \times 10^{-5} \text{ mol U}\)

\[
\ln \left( \frac{1.355 \times 10^{-5} \text{ mol U}}{1.3445 \times 10^{-5} \text{ mol U}} \right) = \frac{0.693}{4.41 \times 10^9 \text{ yrs}} \Delta t \quad \Delta t = 5.01 \times 10^7 \text{ yrs}
\]

15) \(\frac{100}{10} = \frac{0.693}{35 \text{ days}} \Delta t \quad \Delta t = 116.3 \text{ days} = \text{summer vacation!}\)

16a) 54.5 min @ 27°C and 13.7 min @ 37°C

\[
\ln \left( \frac{54.5 \text{ min}}{13.7 \text{ min}} \right) = \frac{\text{Ea}}{8.314} \left( \frac{310 - 300}{310 \times 300} \right) \quad \text{Ea} = 106,764 \text{ J/mol}
\]

16b) No, it makes no difference.

For 1\(^{st}\) order reaction \(t_{1/2} = \frac{0.693}{k}\)

For both of these \(t_{1/2} \propto 1/k\)

For 2\(^{nd}\) order reaction \(t_{1/2} = \frac{1}{[A]k}\)

As long as \([A]\) is the same for all runs, you can directly substitute \(t_{1/2}\) for \(1/k\)

17) \(\ln \left( \frac{10}{X} \right) = \frac{0.693}{8.07 \text{ days}} \quad X = 8.42 \text{ grams}\)
18) 22.35 min @ 50°C and 0.35 min @ 60°C

\[
\ln \frac{22.35 \text{ min}}{0.35 \text{ min}} = \frac{E_a}{8.314} \left( \frac{333 - 323}{333 \times 323} \right)
\]

\[E_a = 371,706 \text{ J/mol}\]
CLOSED BOOK EXAM - No books or notes allowed. ALL work must be shown for full credit. You may use a calculator.

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<tr>
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</table>

Important Equations -

\[
\ln \left( \frac{A_f}{A_i} \right) = kt \quad t_{1/2} = \frac{0.693}{k} \quad \frac{1}{A_f} - \frac{1}{A_i} = kt \quad t_{1/2} = \frac{1}{[A]k}
\]

\[
\ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad R = 8.314 \text{ J/mol-K}
\]

1) As you know, ozone (O$_3$) protects us from ultraviolet light in our upper atmosphere. Ozone can break up to form oxygen by the following reaction,

\[
2 \text{O}_3 \rightarrow 3 \text{O}_2
\]

The rate law for this reaction is known to be \( \text{rate} = k \ [\text{O}_3]^2 / [\text{O}_2] \). Which of the following is a possible mechanism for this reaction? Show your work.

a) \( 2 \text{O}_3 \rightarrow 3 \text{O}_2 \) slow

b) \( \text{O}_3 \leftrightarrow \text{O}_2 + \text{O} \) fast eq.
   \( \text{O}_3 + \text{O} \rightarrow 2 \text{O}_2 \) slow

c) \( \text{O}_2 \leftrightarrow 2 \text{O} \) fast eq.
   \( \text{O}_3 + \text{O} \rightarrow 2 \text{O}_2 \) slow
2) The following experimental data was obtained for the bromination of acetone at 30°C.

\[ 2 \text{I}^- + 2 \text{H}^+ + \text{H}_2\text{O}_2 \rightarrow \text{I}_2 + 2 \text{H}_2\text{O} \]

<table>
<thead>
<tr>
<th>Rate/M/sec</th>
<th>[I]/M</th>
<th>[H]/M</th>
<th>[H]/M</th>
<th>[H]O/M</th>
</tr>
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<tr>
<td>1.64x10^{-5}</td>
<td>0.15</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>3.28x10^{-5}</td>
<td>0.30</td>
<td>0.10</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>7.38x10^{-5}</td>
<td>0.45</td>
<td>0.15</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>1.64x10^{-4}</td>
<td>0.20</td>
<td>0.25</td>
<td>0.30</td>
<td></td>
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2a) Write a rate law consistent with this data.

Rate =

2b) What is the value and units of the rate constant?

2c) Copper ions (Cu^{2+}) are known to be a catalyst for this reaction. Please write down the catalyzed rate law for this reaction.

3) Cryosurgical procedures involve lowering the body temperature of the patient prior to surgery. The activation energy for the beating of the heart muscle is about 30 kJ/mol (30,000 J/mol) A persons normal body temperature is 98.6°F (or 37°C) and most people have a pulse rate of about 75 beats/min. Using this information estimate a persons pulse if their body temperature is dropped to 72°F (22°C).
4) Technetium is a relatively light element that has never been found on earth. As a consequence, the only technetium we have is man-made and radioactive. If a sample of Tc has a decay rate of 983 dpm and exactly 25 minutes later it has a decay rate of 937 dpm, what is half-life of Technetium?

5a) A reaction was set up using concentrations of 1.2 M and 0.30 M. When the half life was measured one took 3.1 minutes and the other took 3.6 minutes respectively. Was the reaction first or second order? Please explain your choice.

5b) Can a 5\textsuperscript{th} order reaction occur? Please explain.

5c) Please give two reasons why a reaction might be zero order.

5d) Why do reactions tend to speed up when you heat them?
**CLOSED BOOK EXAM** - No books or notes allowed. ALL work must be shown for full credit. You may use a calculator.

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\[
\ln(A_f/A_i) = kt \quad t_{1/2} = 0.693/k \\
ln(k_1/k_2) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \\
R = 8.314 \text{ J/mol-K}
\]

1) As you know, ozone (O\(_3\)) protects us from ultraviolet light in our upper atmosphere. Ozone can break up to form oxygen by the following reaction,

\[
2 \text{O}_3 \rightarrow 3 \text{O}_2
\]

The rate law for this reaction is known to be \( \text{rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} \). Which of the following is a possible mechanism for this reaction? Show your work

a) \( 2 \text{O}_3 \rightarrow 3 \text{O}_2 \) slow

\[
\text{rate} = k \ [\text{O}_3]^2 
\]

does not match

b) \( \text{O}_3 \leftrightarrow \text{O}_2 + \text{O} \) fast eq.

\[
\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2 \text{ slow}
\]

\[
\text{rate} = k \ [\text{O}_3] [\text{O}]
\]

Keq = \( \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \) \( \Rightarrow \) \( [\text{O}] = \text{Keq} \frac{[\text{O}_2]}{[\text{O}_3]} \)

\[
\text{Rate} = k \text{Keq} \frac{[\text{O}_2]^2}{[\text{O}_3]} = k' \frac{[\text{O}_3]^2}{[\text{O}_2]} \text{ matches}
\]

c) \( \text{O}_2 \leftrightarrow 2 \text{O} \) fast eq.

\[
\text{O}_3 + \text{O} \rightarrow 2 \text{O}_2 \text{ slow}
\]

\[
\text{rate} = k \ [\text{O}_3] [\text{O}]
\]

Keq = \( \frac{[\text{O}^2]}{[\text{O}_3]} \) \( \Rightarrow \) \( [\text{O}] = \sqrt{\text{Keq}[O]^2} \)

\[
\text{Rate} = k \text{Keq} \frac{[\text{O}_3]^2 [\text{O}_2]^{1/2}}{[\text{O}_2]} = k' \frac{[\text{O}_3]}{[\text{O}_2]^{1/2}} \text{ does not match}
\]
2) The following experimental data was obtained for the bromination of acetone at 30°C.

\[ 2 \Gamma + 2 H^+ + H_2O_2 \rightarrow I_2 + 2 H_2O \]

<table>
<thead>
<tr>
<th>Rate/M/sec</th>
<th>[\Gamma]/M</th>
<th>[H^+]/M</th>
<th>[H_2O_2]/M</th>
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<tr>
<td>1.64x10^{-5}</td>
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<td>0.10</td>
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<td>1.64x10^{-4}</td>
<td>0.20</td>
<td>0.25</td>
<td>0.30</td>
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2a) Write a rate law consistent with this data.

Rate = \( k [\Gamma] [H^+] [H_2O_2] \)

2b) What is the value and units of the rate constant?

\[ 1.64 \times 10^{-5} \text{ M/s} = k [0.15 \text{ M}] [0.10 \text{ M}] [0.10 \text{ M}] \quad k = 0.01093 \text{ 1/M}^2\text{s} \]

2c) Copper ions (\( Cu^{2+} \)) are known to be a catalyst for this reaction. Please write down the catalyzed rate law for this reaction.

Rate = \( (k_{\text{cat}}[Cu^{2+}] + 1) k [\Gamma] [H^+] [H_2O_2] \)

3) Cryosurgical procedures involve lowering the body temperature of the patient prior to surgery. The activation energy for the beating of the heart muscle is about 30 kJ/mol (30,000 J/mol). A person’s normal body temperature is 98.6°F (or 37°C) and most people have a pulse rate of about 75 beats/min. Using this information estimate a person’s pulse if their body temperature is dropped to 72°F (22°C).

\[ \ln \left( \frac{75 \text{ bpm}}{X \text{ bpm}} \right) = \frac{30,000}{8.314} \left( \frac{310 - 295}{310 \times 295} \right) \]

\[ X \text{ bpm} = 41.50 \text{ bpm} \]
4) Technetium is a relatively light element that has never been found on earth. As a consequence, the only technetium we have is man-made and radioactive. If a sample of Tc has a decay rate of 983 dpm and exactly 25 minutes later it has a decay rate of 937 dpm, what is half-life of Technetium?

\[
\ln \frac{983 \text{ dpm}}{937 \text{ dpm}} = \frac{0.693}{t_{\frac{1}{2}}} \quad 25 \text{ min}
\]

\[t_{\frac{1}{2}} = 361.5 \text{ min}\]

5a) A reaction was set up using concentrations of 1.2 M and 0.30 M. When the half life was measured one took 3.1 minutes and the other took 3.6 minutes respectively. Was the reaction first or second order? Please explain your choice.

_The reaction is first order._ First order reactions have half-lives that are independent of concentration. Although the concentration changed by a factor of four, the time stayed essentially constant. The small difference in time is experimental error. With a four-fold change in concentration, a 2\textsuperscript{nd} order reaction would have changed by a factor four.

5b) Can a 5\textsuperscript{th} order reaction occur? Please explain.

_Yes, but it would take at least four steps for a 5\textsuperscript{th} order reaction to occur._

5c) Please give two reasons why a reaction might be zero order.

1. _Though required for the reaction to occur, the compound may not be involved in the slow step of the reaction._
2. _The component may be a spectator ion and not involved with the reaction at all._
3. _Adding more reactant to a saturated catalyst will not cause the reaction to speed up and will appear to be zero order._

5d) Why do reactions tend to speed up when you heat them?

_Reactions speed up because they are hitting each other more often so more of the molecules have enough energy to exceed the activation energy._
1a) A sample of $^{131}$I was purified and then analyzed for iodine content. It was found that the sample was 99.8% pure. 25 hours later the sample was tested again and it was found that the sample was now just 78.2% pure. What is the half-life of $^{131}$I?

1b) How long would it take for 90% of a sample of $^{131}$I to decay?
2) The following experimental data were obtained for the reaction at 295 K,

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \]

<table>
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<td>0.10</td>
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<td>1.2x10$^{-3}$</td>
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<td>0.010</td>
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<tr>
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<td>2.4x10$^{-3}$</td>
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2a) Write a rate law consistent with this data.

Rate =

2b) What is the value and units of the rate constant?

2c) What is the rate of the reaction when [H$_2$] = 0.30 M and [Br$_2$] = 0.025 M?

2d) Which of the following are a possible mechanism for the above reaction? Show your work.

a) \[ \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \quad \text{slow} \]

b) \[ \text{Br}_2 \leftrightarrow 2 \text{Br} \]
   \[ \text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \quad \text{slow} \]
   \[ \text{H} + \text{Br} \rightarrow \text{HBr} \quad \text{fast} \]

c) \[ \text{H}_2 + \frac{1}{2} \text{Br}_2 \rightarrow \text{HBr} + \text{H} \quad \text{slow} \]
   \[ \text{H} + \frac{1}{2} \text{Br}_2 \rightarrow \text{HBr} \quad \text{fast} \]
3) If a reaction has an activation energy of 112.4 kJ, how hot must you get the reaction to increase the rate of the reaction 1.5 times? Assume an initial temperature of 25ºC.

4a) Why do reactions tend to speed up when you heat them?

4b) What term must be added to a reaction to account for the presence of a catalyst?

5) Assume that the cooking of an egg is a first order process. Assume further that it takes 3 minutes to half-cook (soft boil) an egg at 100ºC. If the activation energy of the cooking of an egg is 75 kJ/mole, how long would it take to soft boil an egg at the top of Mt. Everest where water boils at 80ºC?
Chemistry 121                                      Name_________________________________
First Exam                                          February 21, 2008

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Important Equations -

\[
\ln\left(\frac{A_i}{A_f}\right) = k\Delta t \quad t_{1/2} = \frac{0.693}{k}
\]

\[
\frac{1}{A_f} - \frac{1}{A_i} = k\Delta t \quad t_{1/2} = \frac{1}{[A]k}
\]

\[
\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)
\]

\[
R = 8.314 \text{ J/mol-K}
\]

1a) A sample of \(^{131}\)I was purified and then analyzed for iodine content. It was found that the sample was 99.8\% pure. 25 hours later the sample was tested again and it was found that the sample was now just 78.2\% pure. What is the half-life of \(^{131}\)I?

\[
\ln\left(\frac{99.8\%}{78.2\%}\right) = \frac{0.693}{t_{1/2}}
\]

\[
t_{1/2} = 71.03 \text{ hours (2.96 days)}
\]

1b) How long would it take for 90\% of a sample of \(^{131}\)I to decay?

\[
\ln\left(\frac{100\%}{10\%}\right) = \frac{0.693}{\Delta t}
\]

\[
\Delta t = 236 \text{ hours}
\]
2) The following experimental data were obtained for the reaction at 295 K, 

\[ \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \]

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<th>[Br\textsubscript{2}]/M</th>
<th>Rate/(M/sec)</th>
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<tr>
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<td>0.010</td>
<td>4.8x10\textsuperscript{-3}</td>
</tr>
<tr>
<td>0.10</td>
<td>0.040</td>
<td>2.4x10\textsuperscript{-3}</td>
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2a) Write a rate law consistent with this data.

Rate = k [H\textsubscript{2}] [Br\textsubscript{2}]\textsuperscript{\frac{1}{2}}

2b) What is the value and units of the rate constant?

1.2x10\textsuperscript{-3} M/s = k (0.10 M) (0.010 M) \[\Psi\] k = 1.2 1/Ms

2c) What is the rate of the reaction when [H\textsubscript{2}] = 0.30 M and [Br\textsubscript{2}] = 0.025 M?

rate = 1.2 1/Ms (0.30 M) (0.025 M) = 9x10\textsuperscript{-3} M/s

2d) Which of the following are a possible mechanism for the above reaction? Show your work.

a) \text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr} \quad \text{slow} \\
rate = k [H\textsubscript{2}] [Br\textsubscript{2}] \quad \text{doesn’t match}

b) \text{Br}_2 \leftrightarrow 2 \text{Br} \\
\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H} \quad \text{slow} \\
\text{H} + \text{Br} \rightarrow \text{HBr} \quad \text{fast} \\
\text{rate} = k [\text{Br}] [\text{H}_2] \\
\text{Keq} = \frac{[\text{Br}]^2}{[\text{Br}_2]} \Rightarrow [\text{Br}] = \sqrt{\text{Keq} [\text{Br}_2]} \\
\text{rate} = k \text{Keq}^{\frac{1}{2}} [\text{H}_2] [\text{Br}_2]^{\frac{1}{2}} \\
\text{possible right answer}

c) \text{H}_2 + \frac{1}{2} \text{Br}_2 \rightarrow \text{HBr} + \text{H} \quad \text{slow} \\
\text{H} + \frac{1}{2} \text{Br}_2 \rightarrow \text{HBr} \quad \text{fast} \\
\text{rate} = k [\text{H}_2] [\text{Br}_2]^{\frac{1}{2}} \\
\text{possible right answer}
3) If a reaction has an activation energy of 112.4 kJ, how hot must you get the reaction to increase the rate of the reaction 1.5 times? Assume an initial temperature of 25°C.

\[ \ln \frac{1.5 k_2}{k_2} = \frac{112,400}{8.314} \left( \frac{1}{298K} - \frac{1}{T_2} \right) \]

\[ T_2 = 300.68 \text{ K} \]

4a) What do catalysts do to speed up a reaction?

*They provide an alternate route for the reaction to occur.*

4b) What term must be added to a reaction to account for the presence of a catalyst?

\[ [\text{kc} \text{at } [\text{Cat}] + 1] \]

5) Assume that the cooking of an egg is a first order process. Assume further that it takes 3 minutes to half-cook (soft boil) an egg at 100°C. If the activation energy of the cooking of an egg is 75 kJ/mole, how long would it take to soft boil an egg at the top of Mt. Everest where water boils at 80°C?

\[ t_1 = 3 \text{ min } @ 100°C \text{ and } t_2 @ 80°C \]

\[ \ln \frac{t_2}{3 \text{ min}} = \frac{75,000}{8.314} \left( \frac{373 - 353}{373 \times 353} \right) \]

\[ t_2 = 11.81 \text{ min} \]