1. (4 points) SHOW ALL WORK. In the reaction $2A \rightarrow 3B$, $[A]$ drops from 0.5684 M to 0.5522 M in 2.50 min. What is the average rate of formation of B in this time interval, in M/s?

Answer: \[ \text{avg rate} = \frac{(0.5684 - 0.5522)}{(2.50 \text{ min})} \times \frac{1 \text{ min}}{60 \text{ sec}} = 1.08 \times 10^{-4} \text{ mol/L s} \]

Multiple by 3 mol B/2 mol A to get $1.62 \times 10^{-4} \text{ M/s}$

2. (10 points) SHOW ALL WORK. For the following reaction,

\[ 2 \text{HgCl}_2(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightarrow 2 \text{Cl}^-_\text{aq} + 2 \text{CO}_2(\text{g}) + \text{Hg}_2\text{Cl}_2(\text{s}) \]

<table>
<thead>
<tr>
<th>Expt</th>
<th>[HgCl$_2$]</th>
<th>[C$_2$O$_4^{2-}$]</th>
<th>Initial rate, M/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.105</td>
<td>0.15</td>
<td>1.8 x 10$^{-5}$</td>
</tr>
<tr>
<td>2</td>
<td>0.105</td>
<td>0.30</td>
<td>7.1 x 10$^{-5}$</td>
</tr>
<tr>
<td>3</td>
<td>0.052</td>
<td>0.30</td>
<td>3.5 x 10$^{-5}$</td>
</tr>
<tr>
<td>4</td>
<td>0.0025</td>
<td>0.045</td>
<td>?</td>
</tr>
</tbody>
</table>

a) Determine the rate law.

b) Calculate the value of the rate constant $k$.

c) Consider a hypothetical experiment 4 as shown above. Predict its initial rate.

Answer: a) \[ \text{rate} = k [\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^y \]

To get $x$, use expts 2 and 3

\[(0.105/0.052)^x = (7.1/3.5) = 2, \text{ so } x = 1 \]

To get $y$, use expts 1 and 2

\[(0.30/0.15)^y = (7.1/1.8) = 4, \text{ so } y = 2 \]

\[ \text{Rate} = k [\text{HgCl}_2] [\text{C}_2\text{O}_4^{2-}]^2 \]

b) \[ (1.8 \times 10^{-5} \text{ M/s}) = k (0.105 \text{ M})(0.15 \text{ M})^2 \]

\[ k = 7.6 \times 10^{-3} \text{ M}^2 \text{ s}^{-1} \]

c) \[ \text{rate} = (7.6 \times 10^{-3})(0.0025)(0.045)^2 = 3.8 \times 10^{-8} \text{ M/s} \]

3. (3 points) The reaction

\[ 2 \text{HI}_\text{(g)} \rightarrow \text{H}_2\text{(g)} + \text{I}_2\text{(g)} \]

has rate \[ k[\text{HI}]^2 \text{, with } k = 0.079 \text{ L/mol s at 508 °C} \]. What is $t_{1/2}$ if $[\text{HI}]_0 = 0.050 \text{ M}$?

2$^{nd}$ order reaction

\[ t_{1/2} = \frac{1}{k[\text{A}]_0} = \frac{1}{(0.079 \text{ M}^{-1} \text{ s}^{-1})(0.050 \text{ M})} = 2.5 \times 10^2 \text{ s} \]
4. (5 points) **SHOW ALL WORK.** $N_2O_5$ is not very stable. It decomposes by the first order reaction

$$2 \text{N}_2\text{O}_5(g) \rightarrow 2 \text{N}_2\text{O}_4(g) + \text{O}_2(g)$$

At 45 °C, the rate constant is $6.22 \times 10^{-4} \text{ s}^{-1}$. If $[\text{N}_2\text{O}_5]_0 = 0.100 \text{ M}$, how long will it take for the concentration to drop to 0.0100 M?

**Answer:**

$$\ln \left( \frac{[A]_0}{[A]_t} \right) = kt = \ln \left( \frac{0.100}{0.0100} \right)$$

$$t = 3.70 \times 10^3 \text{ s}$$

5. (3 points)

a) Ozone reacts with NO in the atmosphere to form NO$_2$, part of smog.

$$\text{NO}(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)$$

If this reaction occurs in a single elementary step, what is the predicted rate law?

**Answer:** a) $rate = k[\text{NO}][\text{O}_3]$ 

b) If the decomposition of NO$_2$Cl has the following mechanism, what is the predicted rate law?

Slow $\text{NO}_2\text{Cl}(g) \rightarrow \text{NO}_2(g) + \text{Cl}(g)$

Fast $\text{NO}_2\text{Cl}(g) + \text{Cl}(g) \rightarrow \text{NO}_2(g) + \text{Cl}_2(g)$

**Answer:** b) $rate = k[\text{NO}_2\text{Cl}]$

6. (2 points) The reaction $\text{CH}_3\text{I}(g) + \text{HI}(g) \rightarrow \text{CH}_4(g) + \text{I}_2(g)$ has $k = 4.3 \text{ M}^{-1} \text{ s}^{-1}$ at 375 °C and $k = 29 \text{ M}^{-1} \text{ s}^{-1}$ at 425 °C. What equation would you use to find the $E_a$, in kJ/mol? [do not do the calculation!!]

**Answer:**

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

7. (3 points) Draw a reaction coordinate diagram for a simple *exothermic* reaction, label your axes, and on your figure *clearly label*

a. the activation energy $E_a$

b. the energy of the transition state

c. $\Delta H^\circ$

**Answer:**

![Reaction coordinate diagram](image-url)
1. (4 points) **SHOW ALL WORK.** In the reaction $3A \rightarrow 2B$, $[A]$ drops from 0.3578 M to 0.3466 M in 3.50 min. What is the average rate of formation of $B$ in this time interval, in M/s?

**Answer:**

Average rate = \(rac{(0.3578 - 0.3466)}{3.50 \text{ min}} \times \frac{1 \text{ min}}{60 \text{ sec}}\) = \(5.33 \times 10^{-5}\) mol/L s for $A$

Multiple by 2 mol B/3 mol A to get \(3.56 \times 10^{-5}\) M/s

2. (10 points) **SHOW ALL WORK.** For the following reaction,

\[ \text{NH}_4^+ (aq) + \text{NO}_2^- (aq) \rightarrow 2 \text{H}_2\text{O(l)} + \text{N}_2(g) \]

<table>
<thead>
<tr>
<th>Expt</th>
<th>$[\text{NH}_4^+]$</th>
<th>$[\text{NO}_2^-]$</th>
<th>Initial rate, M/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.24</td>
<td>0.10</td>
<td>7.2 \times 10^{-6}</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.10</td>
<td>3.6 \times 10^{-6}</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>0.15</td>
<td>5.4 \times 10^{-6}</td>
</tr>
<tr>
<td>4</td>
<td>0.39</td>
<td>0.052</td>
<td>?</td>
</tr>
</tbody>
</table>

a) Determine the rate law.

b) Calculate the value of the rate constant $k$.

c) Consider a hypothetical experiment 4 as shown above. Predict its initial rate.

**Answer:**

a) \(\text{rate} = k[\text{NH}_4^+]^x[\text{NO}_2^-]^y\)

To get $x$, use expts 1 and 2

\[(0.24/0.12)^x = (7.2/3.6) = 2, \text{ so } x = 1\]

To get $y$, use expts 2 and 3

\[(0.15/0.10)^y = (5.4/3.6) = 1.5, \text{ so } y = 1\]

\[\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-]\]

b) \(7.2 \times 10^{-6} = k(0.24)(0.10)\)

\[k = 3.0 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}\]

c) \(\text{rate} = (3.0 \times 10^{-4})(0.39)(0.052) = 6.1 \times 10^{-6} \text{ M/s}\)

3. (3 points) The reaction

\[2 \text{HI(g)} \rightarrow \text{H}_2(g) + \text{I}_2(g)\]

has rate $= k[\text{HI}]^2$, with $k = 0.125 \text{ L/mol} \cdot \text{s}$ at 550 °C. What is $t_{1/2}$ if $[\text{HI}]_0 = 0.075 \text{ M}$?

**Answer:**

It is second order, so $t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(0.125)(0.075)} = 1.1 \times 10^2 \text{ s}$
4. (5 points) **SHOW ALL WORK.** N₂O₅ is not very stable. It decomposes by the first order reaction

\[ 2 \text{N}_2\text{O}_5(g) \rightarrow 2 \text{N}_2\text{O}_4(g) + \text{O}_2(g) \]

At 55 °C, the rate constant is \(1.22 \times 10^{-3}\) s\(^{-1}\). If \([\text{N}_2\text{O}_5]_0 = 0.200\) M, how long will it take for the concentration to drop to 0.0300 M?

\[ \text{rate} = (1.22 \times 10^{-3} \text{ s}^{-1})[\text{N}_2\text{O}_5] \]

\[ \ln([A]_0/[A]_t) = kt = \ln(0.200/0.0300) = (1.22 \times 10^{-3})t \]

\[ t = 1.56 \times 10^3 \text{ s} \]

5. (3 points) Nitrous oxide decomposes in the gas phase according to the equation:

\[ 2 \text{N}_2\text{O}(g) \rightarrow 2 \text{N}_2(g) + \text{O}_2(g) \]

a) If this reaction occurs in a single elementary step, what is the predicted rate law?

b) If the reaction mechanism is two steps, as follows, what is the predicted rate law?

Slow  \( \text{N}_2\text{O}(g) \rightarrow \text{N}_2(g) + \text{O}(g) \)

Fast  \( \text{N}_2\text{O}(g) + \text{O}(g) \rightarrow \text{N}_2(g) + \text{O}_2(g) \)

**Answer:**

a) \( \text{rate} = k[\text{N}_2\text{O}]^2 \)

b) \( \text{rate} = k[\text{N}_2\text{O}] \)

6. (2 points) The reaction \( \text{H}_2\text{O}_2(aq) + 3 \text{I}^-(aq) + 2 \text{H}^+(aq) \rightarrow \text{I}_3^-(aq) + 2 \text{H}_2\text{O}(l) \) has \( k = 2.9 \text{ M}^{-1} \text{ s}^{-1} \) at 475 °C and \( k = 32 \text{ M}^{-1} \text{ s}^{-1} \) at 525 °C. What equation would you use to find the \( E_a \), in kJ/mol? [do not do the calculation!!]

**Answer:** \( \ln(k_2/k_1) = (-E_a/R)(1/T_2 - 1/T_1) \)

7. (3 points) Draw a reaction coordinate diagram for a simple *endothermic* reaction, label your axes, and on your figure *clearly label*

a. \( \Delta H^\circ \)

b. the energy of the activated complex

c. the activation energy \( E_a \)

**Answer:**

[Diagram with labeled axes and reaction coordinate]