Determining reaction mechanism based on initial rate data

1. A reaction has the experimental rate law, rate = k[A]^2.
   a. How will the rate change if the concentration of A is tripled?

   If rate_1 = k[A]^2, then rate_2 = k[3A]^2 = 3^2 * k[A]^2 = 9 * k[A]^2 = 9 * rate_1.
   So the rate would be 9 times faster.

   b. How will the rate change if the concentration of A is halved?

   If rate_1 = k[A]^2, then rate_2 = k[\frac{1}{2}A]^2 = \left(\frac{1}{2}\right)^2 * k[A]^2 = \frac{1}{4} * k[A]^2 = \frac{1}{4} * rate_1.
   So the rate would decrease. It would be a fourth of the original rate.

2. A reaction has the experimental rate law, rate = k[A].
   a. How will the rate change if the concentration of A is tripled?

   If rate_1 = k[A], then rate_2 = k[3A] = 3 * k[A] = 3 * rate_1.
   So the rate would be 3 times faster.

   b. How will the rate change if the concentration of A is halved?

   If rate_1 = k[A], then rate_2 = k[\frac{1}{2}A] = \left(\frac{1}{2}\right) * k[A] = \frac{1}{2} * rate_1.
   So the rate would decrease. It would be one half of the original rate.
3. Three mechanisms for the reaction \( \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \) have been proposed:

a. Mechanism A
   Step 1: \( \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{NO}(g) \)

b. Mechanism B
   Step 1: \( \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}(g) + \text{NO}_3(g) \) (slow)
   Step 2: \( \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{NO}_2(g) \) (fast)

c. Mechanism C
   Step 1: \( \text{NO}_2(g) + \text{NO}_2(g) \rightarrow \text{NO}(g) + \text{NO}_3(g) \) (fast, equilibrium)
   Step 2: \( \text{NO}_3(g) + \text{CO}(g) \rightarrow \text{CO}_2(g) + \text{NO}_2(g) \) (slow)

Which mechanism agrees with the following initial rate data:

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Initial ([\text{NO}_2]) (mol/L)</th>
<th>Initial ([\text{CO}]) (mol/L)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.133</td>
<td>0.074</td>
<td>0.144</td>
</tr>
<tr>
<td>2</td>
<td>0.399</td>
<td>0.074</td>
<td>1.296</td>
</tr>
<tr>
<td>3</td>
<td>0.133</td>
<td>0.370</td>
<td>0.144</td>
</tr>
</tbody>
</table>

These types of problems can be tackled in a three steps

- **Step 1:** What is the rate law that matches up with the initial rate data given?
  
  We see that when we triple the \( \text{NO}_2 \) concentration, the rate is 9 times greater. This means the reaction is second order with respect to \( \text{NO}_2 \). We see that when we increase the concentration of \( \text{CO} \) by 5 times, the rate does not change. This means the reaction is zero order with respect to \( \text{CO} \). Thus, the experimental rate law is rate=k[\( \text{NO}_2 \)]^2

- **Step 2:** What are the rate laws of the proposed mechanisms?
  
  Mechanism A: rate=k_a[\( \text{NO}_2 \)][\( \text{CO} \)]
  Mechanism B: rate = k_b[\( \text{NO}_2 \)]^2
  Mechanism C: rate=k_c[\( \text{NO}_3 \)][\( \text{CO} \)] (We do not need to solve this further to eliminate the intermediates because we know that [\( \text{CO} \)] is not in the experimental rate law. Thus, this mechanism does not agree with the experimental data.)

- **Step 3:** Which mechanism matches up with the experimental rate law?
  
  The rate law for mechanism B and the experimental rate law match up. So, mechanism B agrees with the initial rate data.
4. Three mechanisms for the reaction $O_2(g) + 2 \text{NO}(g) \rightarrow 2 \text{NO}_2(g)$ have been proposed:

   a. Mechanism A
      Step 1: $O_2(g) + \text{NO}(g) \rightarrow \text{NO}_3(g)$  \hspace{1cm} \text{(fast, equilibrium)}
      Step 2: $\text{NO}_3(g) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{NO}_2(g)$ \hspace{1cm} \text{(slow)}

   b. Mechanism B
      Step 1: $\text{NO}(g) + \text{NO}(g) \rightarrow \text{N}_2\text{O}_2(g)$ \hspace{1cm} \text{(slow)}
      Step 2: $O_2(g) + \text{N}_2\text{O}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$ \hspace{1cm} \text{(fast)}
      Step 3: $\text{N}_2\text{O}_4(g) \rightarrow \text{NO}_2(g) + \text{NO}_2(g)$ \hspace{1cm} \text{(fast)}

Which mechanism agrees with the following initial rate data:

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>Initial $[O_2]$ (mol/L)</th>
<th>Initial $[\text{NO}]$ (mol/L)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.210</td>
<td>0.122</td>
<td>0.136</td>
</tr>
<tr>
<td>2</td>
<td>0.420</td>
<td>0.122</td>
<td>0.272</td>
</tr>
<tr>
<td>3</td>
<td>0.210</td>
<td>0.244</td>
<td>0.544</td>
</tr>
</tbody>
</table>

- **Step 1:** What is the rate law that matches up with the initial rate data given?
  
  $\text{rate}=k[O_2][\text{NO}]^2$

- **Step 2:** What are the rate laws of the proposed mechanisms?
  
  Mechanism A: $\text{rate}_a=k_a[O_2][\text{NO}_2]^2$ because
  
  $\text{rate}_{\text{slow}}=k_{\text{slow}}[\text{NO}][\text{NO}_3]$ and $K_{\text{step}1}=\frac{[\text{NO}_3]}{[O_2][\text{NO}]}$
  
  so $[\text{NO}_3]=K_{\text{step}1}[O_2][\text{NO}]$
  
  so $\text{rate}_a=k_a[O_2][\text{NO}]^2$ where $k_a=k_{\text{slow}} \cdot K_{\text{step}1}$

  Mechanism B: $\text{rate}_b=k_b[\text{NO}]^2$

- **Step 3:** Which mechanism matches up with the experimental rate law?
  
  The rate law for mechanism A and the experimental rate law match up. So, mechanism A agrees with the initial rate data.
Going from rate laws to the integrated rate equations

5. The rate law for the reaction $\text{C}_4\text{H}_9\text{Cl} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{HCl}$ is rate = $k[\text{C}_4\text{H}_9\text{Cl}]$.
   a. What would the integrated rate equation look like for this reaction?

   $$[\text{C}_4\text{H}_9\text{Cl}](t) = [\text{C}_4\text{H}_9\text{Cl}]_0 \times e^{-kt}$$

   b. How would a plot of this equation look?

   It would be an exponential decay graph similar to

   ![Exponential Decay Graph]

   c. How could you find $k$ from the plot?

   To find $k$, you would need to plot $\ln([\text{C}_4\text{H}_9\text{Cl}](t))$ vs. $t$ (time).
   This will a straight line with the equation, $\ln([\text{C}_4\text{H}_9\text{Cl}](t)) = \ln([\text{C}_4\text{H}_9\text{Cl}]_0) - kt$.
   Thus, the slope = $-k$, so $k = -$slope.

6. The rate law for the reaction $2\text{NO}_2 \rightarrow 2\text{NO} + \text{O}_2$ is rate = $k[\text{NO}_2]^2$.
   a. What would the integrated rate equation look like for this reaction?

   $$\frac{1}{[\text{NO}_2](t)} = \frac{1}{[\text{NO}_2]_0} + kt$$

   b. How would a plot of this equation look?

   A plot of $\frac{1}{[\text{NO}_2](t)}$ vs. $t$ (time), would be a straight line with the equation, $\frac{1}{[\text{NO}_2](t)} = \frac{1}{[\text{NO}_2]_0} + kt$

   c. How could you find $k$ from the plot?

   With the above plot, slope = $k$, so $k = $slope.
Activation Energy

7. Given the data below for the reaction of the decomposition of iodoethane into ethane and hydrogen iodide,

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>660</td>
<td>7.2 * 10⁻⁴</td>
</tr>
<tr>
<td>680</td>
<td>2.2 * 10⁻³</td>
</tr>
<tr>
<td>720</td>
<td>1.7 * 10⁻²</td>
</tr>
<tr>
<td>760</td>
<td>0.11</td>
</tr>
</tbody>
</table>

a. Calculate the activation energy for the reaction.

These types of problems can be tackled in a two steps

- **Step 1:** Make an Arrhenius plot, lnk vs. 1/T
  To make an Arrhenius plot, you need to enter this data into an excel spreadsheet, have excel calculate lnk and 1/T, make a scatterplot of lnk vs. 1/T and finally have excel display the trendline and its equation.

- **Step 2:** Calculate Eₐ using the slope of the line
  You need the Arrhenius plot because it gives you the line which has the generic equation lnk=lnA−\( \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right) \).
  So, the slope of the line in your plot is equal to \(-\frac{E_a}{R}\). So, Eₐ = slope*(-R). Thus, Eₐ = slope*(-R) = (-25207 K)(-8.314 J K⁻¹ mol⁻¹) = 2.1 * 10⁵ J/mol = 2.1 * 10² kJ/mol.

b. What is the value of the rate constant at 400 °C?

400 °C = 673 K
So, lnk=lnA−\( \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right) \)= 30.95 -25207\( \left( \frac{1}{673} \right) \)= -6.5047
So, k = e⁻⁶⁵⁰⁴⁷= 0.0015 = 1.5 * 10⁻³ s⁻¹
8. Given the data below for the reaction of the conversion of cyclopropane into propene,

<table>
<thead>
<tr>
<th>T (K)</th>
<th>k (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>750</td>
<td>1.8 * 10⁻⁴</td>
</tr>
<tr>
<td>800</td>
<td>2.7 * 10⁻³</td>
</tr>
<tr>
<td>850</td>
<td>3.0 * 10⁻²</td>
</tr>
<tr>
<td>900</td>
<td>0.26</td>
</tr>
</tbody>
</table>

a. Calculate the activation energy for the reaction.

- **Step 1:** Make an Arrhenius plot, ln(k) vs. 1/T

  ![Question 8: Ink vs. 1/T](image)

  

  - **Step 2:** Calculate $E_a$ using the slope of the line

  

  \[ E_a = \text{slope} \times (-R) = (-32734 \text{ K})(-8.314 \text{ J K}^{-1} \text{ mol}^{-1}) = 2.7 \times 10^5 \text{ J/mol} = 2.7 \times 10^2 \text{ kJ/mol}. \]

b. What is the value of the rate constant at 600 °C?

  

  600 °C = 873 K

  So, $\ln(k) = \ln(A) - \left( \frac{E_a}{R} \right) \left( \frac{1}{T} \right) = 35.01 - 32734 \left( \frac{1}{873} \right) = -2.4860$

  So, $k = e^{-2.4860} = 0.083 = 8.3 \times 10^{-2} \text{ s}^{-1}$