EVALUATE REACTION MECHANISMS & RATE DATA

Directions: Complete the following assignment using any resources you have EXCEPT other people. This assignment will be graded as a take-home quiz.

1) Ozone (O₃) reacts with nitrogen dioxide (NO₂) in the atmosphere, as shown in the reaction equation below.

\[ O_3(g) + 2 \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_5(g) + \text{O}_2(g) \]

Four proposed reaction mechanisms (RMs) are listed below.

**RM 1:**
Step 1: \( O_3(g) + 2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_5(g) + \text{O}_2(g) \)

**RM 2:**
Step 1: \( O_3(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) + \text{O}_2(g) \quad (\text{slow}) \)
Step 2: \( \text{NO}_3(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_5(g) \quad (\text{fast}) \)

**RM 3:**
Step 1: \( O_3(g) \rightarrow \text{O}(g) + \text{O}_2(g) \quad (\text{slow}) \)
Step 2: \( \text{O}(g) + \text{NO}_2(g) \rightarrow \text{NO}_3(g) \quad (\text{fast}) \)
Step 3: \( \text{NO}_3(g) + \text{NO}_2(g) \rightarrow \text{N}_2\text{O}_5(g) \quad (\text{fast}) \)

**RM 4:**
Step 1: \( \text{NO}_2(g) + \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \quad (\text{fast, reversible}) \)
Step 2: \( \text{N}_2\text{O}_4(g) + \text{O}_3(g) \rightarrow \text{N}_2\text{O}_5(g) + \text{O}_2(g) \quad (\text{slow}) \)

(a) A student proposes RM 1 as a possible reaction mechanism. The proposed reaction mechanism in RM 1 would support a rate law that is first order for \( O_3 \) and second order for \( \text{NO}_2 \) (rate = \( k_1[O_3][\text{NO}_2]^2 \)).

(i) A mixture of \( O_3 \) and \( \text{NO}_2 \) gases is placed in a container, and the pressure is doubled by halving the volume. How will the initial rate of reaction be affected, according to the rate law for RM 1? Justify your response.

(ii) If experimental data support this rate law, how likely is RM 1 to be correct? Explain your reasoning.

(iii) If two different plausible reaction mechanisms, RM X and RM Y, predict the same rate law, what additional experimental evidence would be helpful in deciding which is more plausible? Explain your reasoning.
(b) Write the rate laws predicted by the proposed reaction mechanisms RM 2, RM 3, and RM 4. For each, briefly explain or justify how you determined the rate law.

(i) RM 2 rate =  
Explanation:  

(ii) RM 3 rate =  
Explanation:  

(iii) RM 4 rate =  
Explanation:  

The table to the right shows some initial rate data for this reaction, based on experimental results.

(c) Which of the four proposed reaction mechanisms is best supported by the initial rate data shown in the table? Justify your reasoning using values from the table.

<table>
<thead>
<tr>
<th>Trial</th>
<th>[O₂] (M)</th>
<th>[NO₂] (M)</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.016</td>
<td>0.005</td>
<td>7.6×10⁻³</td>
</tr>
<tr>
<td>2</td>
<td>0.016</td>
<td>0.010</td>
<td>15.2×10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>0.008</td>
<td>0.005</td>
<td>3.8×10⁻³</td>
</tr>
<tr>
<td>4</td>
<td>0.015</td>
<td>0.008</td>
<td>11.4×10⁻³</td>
</tr>
</tbody>
</table>

(d) Based on the initial rate data, how certain could a chemist be about the correctness of a rate law and the feasibility of a reaction mechanism? Explain your reasoning.

2) Oxygen and nitrogen monoxide (NO) gases can react to form nitrogen dioxide (NO₂). The balanced overall reaction and the experimentally determined rate law for this reaction are shown below.

\[
\text{O}_2(g) + 2 \text{NO}(g) \rightarrow 2 \text{NO}_2(g)
\]

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

Two proposed reaction mechanisms (RMs) are shown on the next page. The two reaction mechanisms have identical steps but different predicted speeds for those steps.

RM 1:

Step 1: 2NO (g) → N₂O₂ (g)  (slow)
Step 2: N₂O₂ (g) + O₂ (g) → 2NO₂ (g)  (fast)

RM 2:

Step 1: 2NO (g) ⇌ N₂O₂ (g)  (fast equilibrium)
Step 2: N₂O₂ (g) + O₂ (g) → 2NO₂ (g)  (slow)

(a) Explain, in terms of molecular collisions, why the balanced overall reaction would not likely be considered a plausible reaction mechanism.
(b) What are the rate laws for the two proposed mechanisms? Justify your answers based on the steps shown in the proposed reaction mechanisms.

(i) RM 1:

(ii) RM 2:

(c) Must one of these two reaction mechanisms be considered the correct reaction mechanism? Explain your reasoning.

3) The chemical industry uses a method called the Contact Process to produce sulfuric acid (H₂SO₄). In the first step of this process, a 1:1 ratio of sulfur dioxide (SO₂) and oxygen gases is forced into a reaction chamber at a temperature of 400-450°C and a pressure of 1-2 atm to produce sulfur trioxide (SO₃). During this process, the gas mixture flows over vanadium(V) oxide (V₂O₅) pellets, which act as a catalyst. The equation for this reaction and the most likely reaction mechanism are shown below:

\[ \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \xrightarrow{\text{V}_2\text{O}_5} \text{SO}_3(g) \quad \Delta H^\circ = -98.9 \text{ kJ/mol}_{\text{rxn}} \]

- Step 1: \( \text{SO}_2(g) + \text{V}_2\text{O}_5(s) \rightarrow \text{SO}_3(g) + \text{V}_2\text{O}_4(s) \)
- Step 2: \( \frac{1}{2}\text{O}_2(g) + \text{V}_2\text{O}_4(s) \rightarrow \text{V}_2\text{O}_5(s) \)

(a) List **two** ways in which an enthalpy vs. reaction path diagram for the catalyzed reaction would be the same or would be different compared to the same diagram for the uncatalyzed reaction.

(b) Assume that the catalyst is sold at a fixed cost per metric ton. Describe a way to alter the catalyst that would speed up the reaction rate without significantly increasing the cost. Justify your response.
(c) Knowing that substances burn rapidly in pure oxygen, a student suggests increasing the concentration of O₂ from the 1:1 ratio to a 1:100 ratio to increase the reaction rate.

(i) Explain, in terms of molecules, why this change would most likely decrease the rate of reaction.

(ii) Describe one change involving the reaction conditions, other than increasing the temperature, that would increase the rate of reaction, and explain why that change would increase the rate of reaction.

4) An equation for a moderately slow reaction is shown below.

\[ A(aq) + B(aq) \leftrightarrow C(aq) + D(aq) \]

The information to the right relates to the reaction represented in the equation above.

(a) Explain, at a molecular level, why increasing the temperature of a system such as the one shown will increase the rate of reaction in both the forward direction and the reverse direction?

(b) Compare the values of the rate constants, \( k_f \) and \( k_r \). Justify your response by using the rate laws and the relative concentrations of the reactants and products at equilibrium.

(c) Temperature and the activation energy for a reaction both help to determine the value of the rate constant for the reaction’s rate law. Explain the relationship of each factor to the rate constant, using kinetic molecular theory (KMT).

(i) Temperature:

(ii) Activation energy: