CHEM1612 Worksheet 5 – Answers to Critical Thinking Questions

The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

Model 1: Elementary Steps
1. (a) It will double.
   (b) It will double.
   (c) \( \text{rate } \propto [\text{Br}_2(g)] \) or \( \text{rate } = k[\text{Br}_2(g)] \)

2. (a) The number of collisions will double.
   (b) The number of collisions will double.
   (c) \( \text{rate } \propto [\text{Br}_2(g)][\text{H}(g)] \) or \( \text{rate } = k[\text{Br}_2(g)][\text{H}(g)] \)

3. (a) The number of collisions will increase by a factor of 4: it will quadruple.
   (b) \( \text{rate } \propto [\text{Br}_2(g)][\text{H}(g)] \) or \( \text{rate } = k[\text{NO}(g)]^2 \)

Model 2: A Multi-Step Mechanism
1. (a) The first step is the rate determining step.
   (b) \( \text{rate } \propto [\text{NO}_2][\text{O}_3] \) or \( \text{rate } = k_1[\text{NO}_2][\text{O}_3] \)

2. (a) The second step is the rate determining step.
   (b) \( \text{rate } \propto [O][\text{O}_3] \) or \( \text{rate } = k_2[O][\text{O}_3] \)
   (c) equilibrium constant \( K = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \)
   (d) \( [O] = \frac{K[\text{O}_3]}{[\text{O}_2]} \)
   (e) \( \text{rate } = k_2[O][\text{O}_3] = k_2 \times \frac{K[\text{O}_3]}{[\text{O}_2]} \times [\text{O}_3] = k_2 K \frac{[\text{O}_3]^2}{[\text{O}_2]} = \frac{k'[\text{O}_3]^2}{[\text{O}_2]} \) where \( k' = k_2K \)
   (f) The rates of the forward and backward reactions are the same.
   (g) rate of forward reaction = \( k_1[\text{O}_3] \)
   rate of backward reaction = \( k_{-1}[\text{O}_2][\text{O}] \)

As these rates are equal at equilibrium:

\[
\frac{k_1[\text{O}_3]}{k_{-1}} = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} = K \quad \text{so} \quad K = k_1 / k_{-1} \text{ or } k' = k_2k_1/k_{-1}
\]

3. For the rate determining step,
   \( \text{rate } = k_2[\text{NO}_2][\text{O}_2] \)
   This involves \([\text{N}_2\text{O}_2]\) which is an intermediate and cannot be controlled experimentally. However, if the first step is at equilibrium:

\[
K_{\text{eq}} = \frac{[\text{N}_2\text{O}_2]}{[\text{NO}]^2} \quad \text{or} \quad [\text{N}_2\text{O}_2] = K_{\text{eq}}[\text{NO}]^2
\]

Substituting this into the rate equation gives:

\[
\text{rate } = k_2[\text{N}_2\text{O}_2][\text{O}_2] = k_2 \times K_{\text{eq}}[\text{NO}]^2 \times [\text{O}_2] = k_2 K_{\text{eq}}[\text{NO}]^2[\text{O}_2] = k[\text{NO}]^2[\text{O}_2] \quad \text{where} \quad k = k_2K_{\text{eq}}
\]

The proposed mechanism is consistent with the experimental rate law, and warrants further investigation.