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) rate $\propto [Br_2(g)]$ or rate = $k[Br_2(g)]$
2. (a) The number of collisions will double.
   (b) The number of collisions will double.
   (c) rate $\propto [Br_2(g)][H(g)]$ or rate = $k[Br_2(g)][H(g)]$
3. (a) The number of collisions will increase by a factor of 4: it will quadruple.
   (b) rate $\propto [NO(g)]^2$ or rate = $k[NO(g)]^2$

Model 2: A Multi-Step Mechanism

1. (a) The first step is the rate determining step.
   (b) rate $\propto [NO_2][O_3]$ or rate = $k_1[NO_2][O_3]$
2. (a) The second step is the rate determining step.
   (b) rate $\propto [O][O_3]$ or rate = $k_2[O][O_3]$
   (c) equilibrium constant = $K = \frac{[O_2][O]}{[O_3]}$
   (d) $[O] = \frac{K[O_3]}{[O_2]}$
   (e) rate = $k_2[O][O_3] = k_2 \times \frac{K[O_3]}{[O_2]} \times [O_3] = \frac{k_2K[O_3]^2}{[O_2]} = \frac{k'[O_3]^2}{[O_2]}$ where $k' = k_2K$
   (f) The rates of the forward and backward reactions are the same.
   (g) rate of forward reaction = $k_1[O_3]$

   rate of backward reaction = $k_{-1}[O_2][O]$

   As these rates are equal at equilibrium:

   $$k_1[O_3] = k_{-1}[O_2][O] \quad \text{or} \quad \frac{k_1}{k_{-1}} = \frac{[O_2][O]}{[O_3]} = K \quad \text{so} \quad K = k_1 / k_{-1} \text{ or } k' = k_2k_1/k_{-1}$$
3. For the rate determining step,

   rate = $k_2[N_2O_2][O_2]$

   This involves $[N_2O_2]$ which is an intermediate and cannot be controlled experimentally. However, if the first step is at equilibrium:

   $$K_{eq} = \frac{[N_2O_2]}{[NO]^2} \quad \text{or } [N_2O_2] = K_{eq}[NO]^2$$

   Substituting this into the rate equation gives:

   $$\text{rate} = k_2[N_2O_2][O_2] = k_2 \times K_{eq}[NO]^2 \times [O_2] = k_2K_{eq}[NO]^2[O_2] = k[NO]^2[O_2] \quad \text{where } k = k_2K_{eq}$$

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