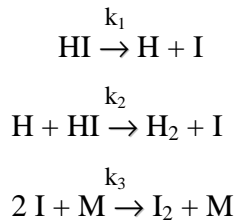


Handin 4: Kinetics Mechanisms

1. The decomposition of HI is given by the reaction $2 \text{HI} \rightarrow \text{H}_2 + \text{I}_2$. One proposed mechanism is:



Use the steady-state approximation to find the rate law for this mechanism. Show that this mechanism does not agree with the experimentally determined rate law:

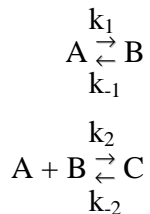
$$\frac{d[\text{H}_2]}{dt} = k [\text{HI}]^2$$

2. Using the Principle of Detailed Balance, show that the mechanism in Problem 1 generates the expected overall equilibrium ratio when the reaction is at equilibrium:

$$K_{\text{eq}} = \left(\frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} \right)$$

Assume that the reverse rate constants are given as k_{-1} , k_{-2} , k_{-3} . Give the relationship between the rate constants and the equilibrium constant.

3. The reaction $2 \text{A} \rightleftharpoons \text{C}$ is proposed to have the following mechanism:



(a). Show that at equilibrium:

$$-\frac{1}{2} \frac{d[\text{A}]}{dt} = \frac{d[\text{C}]}{dt} = k_1[\text{A}] - \left(\frac{k_1 k_{-1}[\text{A}] + k_{-1} k_2 [\text{C}]}{k_{-1} + k_2[\text{A}]} \right)$$

(b). In terms of the overall process, $2\text{A} \rightarrow \text{C}$, at equilibrium we would write the overall rate law in terms of the initial reactant and the final product:

$$v = -\frac{1}{2} \frac{d[\text{A}]}{dt} = k_f [\text{A}]^2 - k_r [\text{C}]$$

Show that the equation in part (a) reduces to this last overall equation and find the relationship between the overall equilibrium constant and the four rate constants for the mechanistic steps.