Detailed Balance

The relationship between the overall forward and reverse reaction rates must be independent of the molecularity of intervening mechanistic steps.

$$A + B \rightleftarrows C + D \qquad K_{eq} = \left(\frac{[C][D]}{[A][B]}\right)_{eq}$$

$$2\,A + M \underset{k_{MA}}{\overset{k_{AM}}{\rightleftarrows}} A_2 + M \qquad \text{Step 1.}$$

$$A_2 + B \underset{k_{XA}}{\overset{k_{AB}}{\rightleftarrows}} A + X \qquad \text{Step 2.}$$

$$X \underset{k_{DC}}{\overset{k_{x}}{\rightleftarrows}} C + D \qquad \text{Step 3.}$$

$$\frac{1}{V}\frac{d\xi_1}{dt} = 2\,k_{AM}\,[A]^2[M] - k_{MA}\,[A_2][M] = 0 \qquad K_{eq,1} = \left(\frac{[A_2][M]}{[A]^2[M]}\right)_{eq} \equiv \frac{2\,k_{AM}}{k_{MA}}$$

$$\frac{1}{V}\frac{d\xi_2}{dt} = k_{AB}\,[A_2][B] - k_{XA}\,[A][X] = 0 \qquad K_{eq,2} = \left(\frac{[A][X]}{[A_2][B]}\right)_{eq} \equiv \frac{k_{AB}}{k_{XA}}$$

$$\frac{1}{V}\frac{d\xi_3}{dt} = k_X\,[X] - k_{CD}\,[C][D] = 0 \qquad K_{eq,3} = \left(\frac{[C][D]}{[X]}\right)_{eq} \equiv \frac{k_X}{k_{DC}}$$

The mechanistic steps for the forward processes add to give the overall reaction stoichiometry. The product of the equilibrium constants for the individual mechanistic steps always gives the overall equilibrium constant:

$$K_{eq,1}\,K_{eq,2}\,K_{eq,3} = \left(\frac{[A_2][M]}{[A]^2[M]}\right)_{eq}\left(\frac{[A][X]}{[A_2][B]}\right)_{eq}\left(\frac{[C][D]}{[X]}\right)_{eq} = \left(\frac{[C][D]}{[A][B]}\right)_{eq} = K_{eq}$$

$$K_{eq} = \frac{2\,k_{AM}}{k_{MA}}\,\frac{k_{AB}}{k_{XA}}\,\frac{k_X}{k_{DC}}$$

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C + D \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} E + F \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} G + H \;....$$

$$K_{eq} = \frac{k_1\,k_2\,k_3\,....}{k_{-1}\,k_{-2}\,k_{-3}....}$$