

Solutions to the Practice Problems on the Relationship between Kinetics and Equilibrium

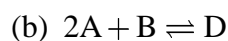
1. The rate of production of C (for instance) is

$$\frac{d[C]}{dt} = k_1[A][B] - k_{-1}[C].$$

At equilibrium, $d[C]/dt = 0$ so

$$\begin{aligned} k_1[A][B] &= k_{-1}[C]. \\ \therefore \frac{[C]}{[A][B]} &= \frac{k_1}{k_{-1}} = K. \\ \therefore k_{-1} &= \frac{k_1}{K} = \frac{1.4 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}}{1.2 \times 10^{15} \text{ L/mol}} = 1.2 \times 10^{-18} \text{ s}^{-1}. \end{aligned}$$

2. (a) A and B are reactants. C is an intermediate. D is a product.



(c)

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1[A][B] + k_{-1}[C] - k_2[A][C] + k_{-2}[D] \\ \frac{d[B]}{dt} &= -k_1[A][B] + k_{-1}[C] \\ \frac{d[C]}{dt} &= k_1[A][B] - k_{-1}[C] - k_2[A][C] + k_{-2}[D] \\ \frac{d[D]}{dt} &= k_2[A][C] - k_{-2}[D] \end{aligned}$$

- (d) At equilibrium, all of the rates vanish. In particular, $\frac{d[B]}{dt} = \frac{d[D]}{dt} = 0$. From $\frac{d[B]}{dt} = 0$, we get

$$k_1[A][B] = k_{-1}[C]$$

from which it follows that

$$\frac{[C]}{[A][B]} = \frac{k_1}{k_{-1}}. \quad (1)$$

From $\frac{d[D]}{dt} = 0$, we get the additional condition

$$\begin{aligned} k_2[A][C] &= k_{-2}[D] \\ \text{or } \frac{[D]}{[A][C]} &= \frac{k_2}{k_{-2}}. \end{aligned} \quad (2)$$

The equilibrium constant for the overall reaction is

$$K = \frac{[\text{D}]}{[\text{A}]^2[\text{B}]}.$$

If we multiply equations 1 and 2 together, we get

$$\begin{aligned} \frac{[\text{C}]}{[\text{A}][\text{B}]} \frac{[\text{D}]}{[\text{A}][\text{C}]} &= \frac{[\text{D}]}{[\text{A}]^2[\text{B}]} = \frac{k_1}{k_{-1}} \frac{k_2}{k_{-2}}. \\ \therefore K &= \frac{k_1 k_2}{k_{-1} k_{-2}}. \end{aligned}$$