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

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

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

At equilibrium, $d[\mathrm{C}]/dt = 0$ so

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

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

   (b) $2\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{D}$

   (c)

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

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

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

   from which it follows that

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

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

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

The equilibrium constant for the overall reaction is

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

If we multiply equations 1 and 2 together, we get

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