Dynamics and Kinetics. Exercises 4: Solutions

Problem 1

(1) $\frac{d[A]}{dt} = -k_1[A] + k_{-1}[B]$

(2) $\frac{d[B]}{dt} = k_1[A] - k_{-1}[B] - k_3[B][C]$

(3) $\frac{d[D]}{dt} = -\frac{d[C]}{dt} = k_3[B][C]$

Invoking the steady-state approximation, we set $\frac{d[B]}{dt} \approx 0$:

$$[B]_{\mathrm{ss}} = \frac{k_1[A]}{k_{-1} + k_3[C]}$$

$$v = \frac{d[D]}{dt} = \frac{k_3 k_1[A][C]}{k_{-1} + k_3[C]}$$

At high pressure, $k_3[C] \gg k_{-1}$ and so:

$$v \approx k_1[A] \qquad \text{(first order).}$$

At low pressure, $k_3[C] \ll k_{-1}$ and so

$$v \cong \frac{k_3 k_1}{k_{-1}}[A][C] \qquad \text{(second order).}$$

Problem 2

(Pre-equilibrium problem)

a) Step 1:

$$2A \rightleftharpoons D, \qquad K_1 = \frac{[D]}{[A]^2}.$$

b) Step 2:

$$B + D \xrightarrow{k2} A + C$$

Assuming equilibrium in the first reaction is much faster than the rate in the second reaction:

$$\frac{d[C]}{dt} = k_2[B][D] \approx k_2[B]K_1[A]^2 = K_1 k_2[A]^2[B]$$

Problem 3

Rate equations for $[E]$ and $[ES]$:

$$\frac{d[E]}{dt} = -\frac{d[ES]}{dt} = (k_{\ 1} + k_2)\,[ES] - k_1[E][S] \tag{1}$$

(a) At $t = 0$; $[E]_0 = [E]_0$, $[ES]_0 = 0$.

For $t \to \infty$, $[E]_\infty = [E]_0$; $[ES]_\infty = 0$.

For $0 < t < \infty$: $[ES]_t > 0$, $[E]_t < [E]_0$ since $[E]_0 = [E]_t + [ES]_t$.

Since $[E]_t$, $[ES]_t$ are continuous functions, $[E]_t$ has a minimum and $[ES]_t$ has a maximum. (It helps if you draw a gure.)

(b) At the extremum (occurring at time t_*), we must have $d[E] \,/\, dt = 0$ in Eq. (1):

$$(k_{-1} + k_2)\ [ES]_{t^*} = k_1\ [E]_{t^*}\, [S]_{t^*}.$$

(Note that this condition turns out to be equivalent to the steady-state condition.)

Problem 4

$$E + S \rightleftharpoons ES \rightarrow P$$

(a) Assume E is in steady state: $0 = \frac{d[E]}{dt} = -\frac{d[ES]}{dt} \Rightarrow$ OK: the same equation as before.

$$[ES] = \frac{k_1}{k_{\ 1} + k_2}\,[E]\,[S]$$

We obtain again the Michaelis-Menten equation. (The only problem with this s.s. approximation is that $[E]$ is not small.)

(b) Assume S is in steady state: $0 = \frac{d[S]}{dt} = -k_1\,[E]\,[S] + k_{\ 1}\,[ES]$

$$[ES] = \frac{k_1}{k_{-1}}\,[E]\,[S]\,,$$

$$v = k_2\,[ES] = \frac{k_2 k_1}{k_{\ 1}}\,[E]\,[S]$$

The result is the same as for the special case of Michaelis-Menten for pre-equilibrium, i.e., for $k_2 \ll k_{-1}$.
(But the s.s. assumption is only correct if $[S]_0 \ll [E]_0$.)

Assume P is in steady state: $0 = \frac{d[P]}{dt} = k_2\,[ES] \Rightarrow [ES] = 0$. Clearly, this is a contradictory result since then $v = 0$.