

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 $\frac{d[B]}{dt} \approx 0$:

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

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

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

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

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

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

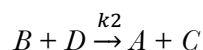
Problem 2

(Pre-equilibrium problem)

a) Step 1:



b) Step 2:



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 $[ES]$:

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

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

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

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 figure.)

(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



(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 $v = 0$.