

Dynamics and Kinetics. Exercises 6: Solutions

Problem 1

Direct solution [but involving substantial algebra after Eq. (6)]:

(a) Using the steady-state approximation for intermediates Br and H we get the following two equations:

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - 2k_{-1}[\text{Br}]^2 - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_{-2}[\text{HBr}][\text{H}] = 0, \quad (2)$$

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{HBr}][\text{H}] - k_3[\text{H}][\text{Br}_2] = 0. \quad (3)$$

From (3) we can explicitly express [H] as

$$[\text{H}] = \frac{k_2[\text{Br}][\text{H}_2]}{k_{-2}[\text{HBr}] + k_3[\text{Br}_2]}, \quad (4)$$

while summing up (2) and (3)* we can get $2k_1[\text{Br}_2] - 2k_{-1}[\text{Br}]^2 = 0$ from which we obtain the explicit expression for [Br] as**

$$[\text{Br}] = \sqrt{\frac{k_1}{k_{-1}}}[\text{Br}_2] \quad (5)$$

(b) We are looking for the overall rate expression

$$v := -\frac{d[\text{Br}_2]}{dt} = k_1[\text{Br}_2] - k_{-1}[\text{Br}]^2 + k_3[\text{H}][\text{Br}_2], \quad (6)$$

in terms of $[\text{H}_2]$, $[\text{Br}_2]$ and $[\text{HBr}]$, which we get if we substitute (4) and (5) into (6), which finally gives

$$v := -\frac{d[\text{Br}_2]}{dt} = \frac{k_2\sqrt{\frac{k_1}{k_{-1}}}[\text{Br}_2]^{1/2}[\text{H}_2]}{1 + \frac{k_{-2}}{k_3}\frac{[\text{HBr}]}{[\text{Br}_2]}} = \frac{k[\text{Br}_2]^{1/2}[\text{H}_2]}{1 + m\frac{[\text{HBr}]}{[\text{Br}_2]}},$$

where $k \equiv k_2\sqrt{\frac{k_1}{k_{-1}}}$ and $m \equiv \frac{k_{-2}}{k_3}$.

Alternative solution [with very little algebra but requiring more thinking]:

(a) Steady-state approximation and calculation of [H] and [Br]: same procedure as before.

(b) We substitute (5) into (4) to obtain

$$[\text{H}] = \frac{k_2(k_1/k_{-1})^{1/2}[\text{H}_2][\text{Br}_2]^{1/2}}{k_3[\text{Br}_2] + k_{-2}[\text{HBr}]}. \quad (7)$$

Rate of reaction is also equal to rate of consumption of $[\text{H}_2]$, therefore

$$v = -\frac{d[\text{H}_2]}{dt} = k_2[\text{Br}][\text{H}_2] - k_{-2}[\text{H}][\text{HBr}]. \quad (8)$$

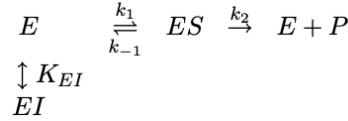
Subtracting* (3) from (8) and using expression (7) for [H], we get

* Note: A little trick to simplify algebra.

$$v = k_3 [\text{H}][\text{Br}_2] = \frac{k_2 k_3 (k_1/k_{-1})^{1/2} [\text{H}_2][\text{Br}_2]^{3/2}}{k_3 [\text{Br}_2] + k_{-2} [\text{HBr}]} = \frac{k_2 (k_1/k_{-1})^{1/2} [\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{k_{-2}}{k_3} \frac{[\text{HBr}]}{[\text{Br}_2]}} = \frac{k [\text{H}_2][\text{Br}_2]^{1/2}}{1 + m [\text{HBr}]/[\text{Br}_2]}.$$

** Note: as if equilibrium $\text{Br}_2 \rightleftharpoons 2\text{Br}$, which is not true at all in general.

Problem 2



In steady state:

$$\begin{aligned} \frac{d[ES]}{dt} &= k_1 [E][S] - (k_{-1} + k_2) [ES] = 0, \\ \frac{d[EI]}{dt} &= k_i [E][I] - k_{-i} [EI] = 0. \end{aligned}$$

This implies

$$\begin{aligned} [ES] &= \frac{k_1}{k_{-1} + k_2} [E][S] = \frac{1}{K_M} [E][S] \approx \frac{1}{K_M} [E][S]_0, \\ [EI] &= \frac{k_i}{k_{-i}} [E][I] = \frac{1}{K_{EI}} [E][I] \approx \frac{1}{K_{EI}} [E][I]_0, \end{aligned}$$

where in the last equations we assumed $[E]_0 \ll [S]_0$ and $[E]_0 \ll [I]_0$ (in other words, we used the pseudo-first order approximation).

Rate of reaction

$$v = k_2 [ES] \approx \frac{k_2}{K_M} [E][S]_0 \propto [E]. \quad (9)$$

Without inhibitor:

$$[E]_0 = [E]' + [ES]' = [E]' \underbrace{\left(1 + \frac{1}{K_M} [S]_0\right)}_{x'}. \quad (10)$$

With inhibitor:

$$[E]_0 = [E]'' + [ES]'' + [EI]'' = [E]'' \underbrace{\left(1 + \frac{1}{K_M} [S]_0 + \frac{1}{K_{EI}} [I]_0\right)}_{x''}. \quad (11)$$

Degree of inhibition is

$$\epsilon := \frac{v' - v''}{v'} \stackrel{(9)}{=} \frac{[E]' - [E]''}{[E]'} \stackrel{(10)-(11)}{=} \frac{\frac{1}{x'} - \frac{1}{x''}}{\frac{1}{x'}} = \frac{x'' - x'}{x''} = \frac{\frac{[I]_0}{K_{EI}}}{1 + \frac{[S]_0}{K_M} + \frac{[I]_0}{K_{EI}}}.$$

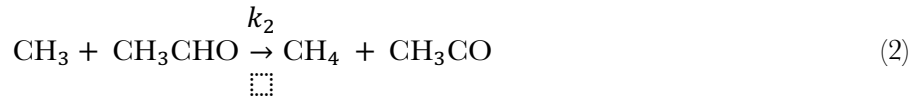
Two simple checks:

$$[I]_0 = 0 \Rightarrow \epsilon = 0 \Rightarrow v'' = v': \quad \text{OK,}$$

$$[I]_0 \rightarrow \infty \Rightarrow \epsilon \rightarrow 1 \Rightarrow v'' = 0: \quad \text{OK.}$$

Problem 3

Acetaldehyde has been proposed to decompose according to the following mechanism.



a) In this radical chain reaction, identify the initiation, propagation, and termination steps.

(1) initiation , (2+3) propagation , (4) termination

b) Derive a rate law for the formation of CH_4 that contains only the concentration of the reactant $[\text{CH}_3\text{CHO}]$. Assume that all radical species are present only in low concentrations in order to make suitable approximations.

$$\frac{d[\text{CH}_4]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}]$$

We make the steady-state approximation for CH_3 and for CH_3CO .

$$0 = \frac{d[\text{CH}_3\text{CO}]}{dt} = k_2[\text{CH}_3][\text{CH}_3\text{CHO}] - k_3[\text{CH}_3\text{CO}]$$

$$[\text{CH}_3\text{CO}] = \frac{k_2}{k_3} [\text{CH}_3][\text{CH}_3\text{CHO}]$$

$$0 = \frac{d[\text{CH}_3]}{dt} = k_1[\text{CH}_3\text{CHO}] - k_2[\text{CH}_3][\text{CH}_3\text{CHO}] + k_3[\text{CH}_3\text{CO}] - 2k_4[\text{CH}_3]^2$$

We replace $[\text{CH}_3\text{CO}]$ and isolate $[\text{CH}_3]$

$$[\text{CH}_3] = \left(\frac{k_1}{2k_4} [\text{CH}_3\text{CHO}] \right)^{\frac{1}{2}}$$

and obtain

$$\frac{d[\text{CH}_4]}{dt} = k_2 \left(\frac{k_1}{2k_4} \right)^{\frac{1}{2}} [\text{CH}_3\text{CHO}]^{\frac{3}{2}}$$