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:

$$\frac{d[\mathrm{Br}]}{dt} = 2k_1[\mathrm{Br_2}] - 2k_{-1}[\mathrm{Br}]^2 - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_{-2}[\mathrm{HBr}][\mathrm{H}] = 0, \tag{2}$$

$$\frac{d[\mathrm{H}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{HBr}][\mathrm{H}] - k_3[\mathrm{H}][\mathrm{Br_2}] = 0. \tag{3}$$

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

$$[\mathrm{H}] = \frac{k_2[\mathrm{Br}][\mathrm{H_2}]}{k_{-2}[\mathrm{HBr}] + k_3[\mathrm{Br_2}]}, \tag{4}$$

while summing up (2) and (3)* we can get $2k_1[\mathrm{Br_2}] - 2k_{-1}[\mathrm{Br}]^2 = 0$ from which we obtain the explicit expression for [Br] as**

$$[\mathrm{Br}] = \sqrt{\frac{k_1}{k_{-1}}[\mathrm{Br_2}]} \tag{5}$$

(b) We are looking for the overall rate expression

$$v := -\frac{d[\mathrm{Br_2}]}{dt} = k_1[\mathrm{Br_2}] - k_{-1}[\mathrm{Br}]^2 + k_3[\mathrm{H}][\mathrm{Br_2}], \tag{6}$$

in terms of $[\mathrm{H_2}]$, $[\mathrm{Br_2}]$ and [HBr], which we get if we substitute (4) and (5) into (6), which finally gives

$$v := -\frac{d[\mathrm{Br_2}]}{dt} = \frac{k_2\sqrt{\frac{k_1}{k_{-1}}}[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}]}{1 + \frac{k_{-2}}{k_3}\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}} = \frac{k[\mathrm{Br_2}]^{1/2}[\mathrm{H_2}]}{1 + m\frac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}},$$

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

$$[\mathrm{H}] = \frac{k_2\,(k_1/k_{-1})^{1/2}\,[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{k_3[\mathrm{Br_2}] + k_{-2}[\mathrm{HBr}]}. \tag{7}$$

Rate of reaction is also equal to rate of consumption of $[\mathrm{H_2}]$, therefore

$$v = -\frac{d[\mathrm{H_2}]}{dt} = k_2[\mathrm{Br}][\mathrm{H_2}] - k_{-2}[\mathrm{H}][\mathrm{HBr}]. \tag{8}$$

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

* Note: A little trick to simplify algebra.

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

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

Problem 2

$$\begin{array}{lcl} E & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & ES \overset{k_2}{\rightarrow} E + P \\ \updownarrow K_{EI} & & \\ EI & & \end{array}$$

In steady state:

$$\frac{d\,[ES]}{dt} = k_1\,[E]\,[S] - (k\;_1 + k_2)\,[ES] = 0,$$
$$\frac{d\,[EI]}{dt} = k_i\,[E]\,[I] - k\;_i\,[EI] = 0.$$

This implies

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

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

$$v = k_2\,[ES] \approx \frac{k_2}{K_M}\,[E]\,[S]_0 \propto [E]\,. \tag{9}$$

Without inhibitor:

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

With inhibitor:

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

Degree of inhibition is

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

Two simple checks:

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

Problem 3

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

$$\mathrm{CH_3CHO} \xrightarrow{k_1} \mathrm{CH_3} + \mathrm{CHO} \tag{1}$$

$$\mathrm{CH_3} + \mathrm{CH_3CHO} \xrightarrow{k_2} \mathrm{CH_4} + \mathrm{CH_3CO} \tag{2}$$

$$\mathrm{CH_3CO} \xrightarrow{k_3} \mathrm{CH_3} + \mathrm{CO} \tag{3}$$

$$2\,\mathrm{CH_3} \xrightarrow{k_4} \mathrm{C_2H_6} \tag{4}$$

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 $\mathrm{CH_4}$ that contains only the concentration of the reactant $[\mathrm{CH_3CHO}]$. Assume that all radical species are present only in low concentrations in order to make suitable approximations.

$$\frac{d[\mathrm{CH_4}]}{dt} = k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}]$$

We make the steady-state approximation for $\mathrm{CH_3}$ and for $\mathrm{CH_3CO}$.

$$0 = \frac{d[\mathrm{CH_3CO}]}{dt} = k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}] - k_3[\mathrm{CH_3CO}]$$

$$[\mathrm{CH_3CO}] = \frac{k_2}{k_3}[\mathrm{CH_3}][\mathrm{CH_3CHO}]$$

$$0 = \frac{d[\mathrm{CH_3}]}{dt} = k_1[\mathrm{CH_3CHO}] - k_2[\mathrm{CH_3}][\mathrm{CH_3CHO}] + k_3[\mathrm{CH_3CO}] - 2k_4[\mathrm{CH_3}]^2$$

We replace $[\mathrm{CH_3CO}]$ and isolate $[\mathrm{CH_3}]$

$$[\mathrm{CH_3}] = \left(\frac{k_1}{2k_4}[\mathrm{CH_3CHO}]\right)^{\frac{1}{2}}$$

and obtain

$$\frac{d[\mathrm{CH_4}]}{dt} = k_2\left(\frac{k_1}{2k_4}\right)^{\frac{1}{2}}[\mathrm{CH_3CHO}]^{\frac{3}{2}}$$