Dynamics and Kinetics. Exercise 6

Problem 1

The reaction between hydrogen and bromine $H_2 + Br_2 \rightarrow 2HBr$ is an example of a chain reaction. It has a composite mechanism:

Initiation: $Br_2 \xrightarrow{k_1} 2Br$

Chain propagation: $Br + H_2 \xrightarrow{k_2} HBr + H$; $H + Br_2 \xrightarrow{k_3} HBr + Br$

Inhibition: $H + HBr \xrightarrow{k_{-2}} H_2 + Br$

Termination: $2Br \xrightarrow{k_{-1}} Br_2$

Use the steady-state approximation for intermediates Br and H to derive the overall rate expression:

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

How are k and m related to the rate constants $k_1, k_{-1}, \ldots, k_3$?

Problem 2

Consider the *competitive* mechanism of inhibition of an enzymatic reaction discussed in lecture:

$$\begin{array}{ccccc} E & +S+I & \overset{K_{ES}}{\rightleftharpoons} & ES & \overset{k_3}{\rightarrow} & E+P \\ \updownarrow K_{EI} & & & & & \\ EI & & & & & \end{array}$$

- Assume that the substrate and inhibitor are present in great excess of the enzyme, apply the steady-state treatment, and obtain the rate equation.
- Obtain an expression for the degree of inhibition ϵ, defined as:

$$\epsilon = \frac{v_0 - v}{v_0}$$

where v is the rate in the presence of inhibitor and v_0 is the rate in its absence.

Problem 3

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

$$CH_3CHO \xrightarrow{k_1} CH_3 + CHO \quad (1)$$

$$CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO \quad (2)$$

$$CH_3CO \xrightarrow{k_3} CH_3 + CO \quad (3)$$

$$2\,CH_3 \xrightarrow{k_4} C_2H_6 \quad (4)$$

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

b) Derive a rate law for the formation of CH_4 that contains only the concentration of the reactant $[CH_3CHO]$. Assume that all radical species are present only in low concentrations in order to make suitable approximations.