Dynamics and Kinetics. Exercise 4

Problem 1

Set up the rate expressions for all species in the following mechanism:

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_{-1}} A$$

$$B + C \xrightarrow{k_3} D$$

If the concentration of B is small compared with the concentrations of A, C, and D, the steady-state approximation may be used to derive the rate law. Show that this reaction may follow first-order kinetics at high pressures and second-order kinetics at low pressures.

Problem 2

The reaction A + B → C takes place in two steps by the mechanism $2A \rightleftharpoons D$ followed by $B + D \xrightarrow{k_2} A + C$. The first step comes to a rapid equilibrium (constant K_1). Derive an expression for the rate of formation of C in terms of K_1, k_2, [A] and [B].

Problem 3

Given the Michaelis-Menten mechanism:

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

use the rate equations to prove mathematically that [E](t) has a minimum and [ES](t) has a maximum. Determine the relation between [E](t), [S](t) and [ES](t) at the extrema.

Problem 4

Given the Michaelis-Menten mechanism shown in Problem 3, examine what would happen if you assumed that S or E or P reaches a steady-state. Would you obtain conflicting results?