Chemistry 361
Problem Set 10 part II
Due:Friday 11 December, 2009

Problem 6 (10 points)

For the following autocatalytic enzymatic reaction, find the rate of the reaction associated with the mechanism.

$$S \;+\; E \xrightarrow{k^{obs}} P \;+\; E \tag{1}$$

Mechanism

$$S + E \xrightarrow{k_1^+} SE \tag{2}$$
$$SE \xrightarrow{k_1^-} S + E \tag{3}$$
$$SE \xrightarrow{k_2} P + E \tag{4}$$

but the product activates an inactive isomer of the enzyme

$$P + \bar{E} \xrightarrow{k_a^+} E \tag{5}$$
$$E \xrightarrow{k_a^-} P + \bar{E} \tag{6}$$

Problem 7 (10 points)

For the following enzymatic reaction, find the rate of the reaction associated with the mechanism.

$$S \;+\; E \xrightarrow{k^{obs}} P \;+\; E \tag{7}$$

Mechanism

$$S + E \xrightarrow{k_1^+} SE \tag{8}$$

$$SE \xrightarrow{k_1^-} S + E \tag{9}$$

$$SE \xrightarrow{k_2} P + E \tag{10}$$

but the product inhibits the active isomer of the enzyme

$$P + E \xrightarrow{k_i^+} \bar{E} \tag{11}$$

$$\bar{E} \xrightarrow{k_i^-} P + E \tag{12}$$

Problem 8 (10 points)

For the following overall reaction, find the rate of the reaction associated with the mechanism.

$$RX + Y^- \xrightarrow{k^{obs}} RY + X^- \tag{13}$$

Mechanism

$$RX \xrightarrow{k_1^+} R^+ + X^- \tag{14}$$

$$R^+ + X^- \xrightarrow{k_1^-} RX \tag{15}$$

$$R^+ + Y^- \xrightarrow{k_2} RY \tag{16}$$

a) Assume that Eq.(14) and Eq.(15) achieve equilibrium and find the rate of the reaction in Eq. (13).

b) Now use the Steady State Approximation for the intermediates and find the rate of the reaction in Eq.(13).

c) Under which conditions rates in a) and b) are equal.

Problem 9 (10 points)

The following mechanism first suggested by Se'lkov (1962), used by Gierer and Meinhardt in development, Schankenberg in chemical systems and Grey and Scott in contimous stir tank reactors (CSTR), is now widely know as the Autocatalator

$$Ao \xrightarrow{k_o} A \tag{17}$$
$$A + 2B \xrightarrow{k} 3\ B \tag{18}$$
$$B \xrightarrow{k_d} \phi \tag{19}$$

Using the mass action laws we get the following ODEs:

$$\frac{d[A]}{d\ t} = r_\circ - k\ [A]\ [B]^2 \tag{20}$$
$$\frac{d[B]}{d\ t} = k\ [A]\ [B]^2 - k_d\ [B] \tag{21}$$

where $r_\circ = k_\circ\ A_\circ$. For Eqs. (25, 26):
b) Find the steady states $(\bar{A}, \bar{B})$ and any constraints in the parameter values
c) Calculate the relaxation matrix (Jacobian) as a function of the steady states $(\bar{A}, \bar{B})$.
d) Calculate the relaxation matrix as a function of the parameters.
e) Find an analytical expression for the bifurcation relation that separates homogeneous stable steady state and oscillatory solutions.

Problem 10 (10 points)

The following mechanism, first suggested by Higgins (1962), considers the following elementary reations

$$Ao \xrightarrow{k_o} A \tag{22}$$
$$A + B \xrightarrow{k} 2\ B \tag{23}$$
$$B \xrightarrow{E} \phi \tag{24}$$

Using the mass action laws we get the following ODEs:

$$\frac{d[A]}{d\,t} = r_\circ - k\,[A]\,[B] \tag{25}$$
$$\frac{d[B]}{d\,t} = k\,[A]\,[B] - \frac{V\ [B]}{K + [B]} \tag{26}$$

where $r_\circ = k_\circ\ A_\circ$. For Eqs. (25, 26):
b) Find the steady states $(\bar{A}, \bar{B})$ and any constraints in the parameter values
c) Calculate the relaxation matrix (Jacobian) as a function of the steady states $(\bar{A}, \bar{B})$.
d) Calculate the relaxation matrix as a function of the parameters.
e) Find an analytical expression for the bifurcation relation that separates homogeneous stable steady state and oscillatory solutions.