

**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.



**Mechanism**



but the product activates an inactive isomer of the enzyme



### Problem 7 (10 points)

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



#### Mechanism



but the product inhibits the active isomer of the enzyme



### Problem 8 (10 points)

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



#### Mechanism



- Assume that Eq.(14) and Eq.(15) achieve equilibrium and find the rate of the reaction in Eq. (13).
- Now use the Steady State Approximation for the intermediates and find the rate of the reaction in Eq.(13).
- 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 continuous stir tank reactors (CSTR), is now widely know as the Autocatalator



Using the mass action laws we get the following ODEs:

$$\frac{d[A]}{d t} = r_o - k [A] [B]^2 \quad (20)$$

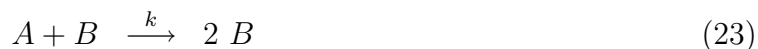
$$\frac{d[B]}{d t} = k [A] [B]^2 - k_d [B] \quad (21)$$

where  $r_o = k_o A_o$ . 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 reactions



Using the mass action laws we get the following ODEs:

$$\frac{d[A]}{dt} = r_0 - k [A] [B] \quad (25)$$

$$\frac{d[B]}{dt} = k [A] [B] - \frac{V [B]}{K + [B]} \quad (26)$$

where  $r_0 = k_0 A_0$ . 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.