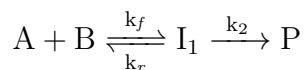


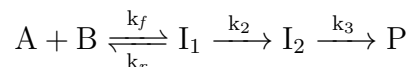
CHEM 361A - Lecture 18 Activity  
Consecutive Chemical Reactions

## In Class

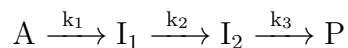
1. Consider the following reaction



- (a) Write a rate law expression for  $[A]$ ,  $[I_1]$ , and  $[P]$ .
- (b) Open the MATLAB program Activity18Q1.m. Verify that your rate law expressions from 1a match those written in line 13? Vary  $k_f$  and  $k_r$  OR  $k_2$  and graphically determine the rate constants that
- i. the pre-equilibrium approximation is valid. When the pre-equilibrium approximation is valid, why don't  $[A]$  and  $[I_1]$  match (note:  $[A]_0 = [B]_0 = 1$  and  $[I_1]_0 = 0$ )?
  - ii. the steady state approximation is valid. How do you know when it's valid?
2. Consider the following reaction



- (a) If  $k_2, k_3 \gg k_f, k_r$ , write an expression for  $[I_1]$  and  $[I_2]$  in terms of rate constants,  $[A]$ , and  $[B]$ .
- (b) If  $k_2, k_3 \ll k_f, k_r$ , write an expression for  $[I_1]$  in terms of rate constants,  $[A]$  and  $[B]$ .
3. Consider the following reaction mechanism



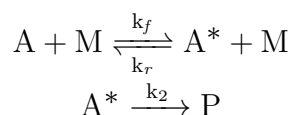
where  $k_1 = 2.0 \times 10^{-4} \text{ s}^{-1}$ ,  $k_2 = 0.5 \text{ s}^{-1}$ ,  $k_3 = 0.7 \text{ s}^{-1}$ , and  $[A]_0 = 0.5 \text{ M}$ , while  $[I_1]_0 = [I_2]_0 = [P]_0 = 0$ .

- (a) Write the rate law expressions for  $A$ ,  $I_1$ ,  $I_2$ , and  $P$ .
- (b) Open the MATLAB code Activity18Q3.m and set the rate constants. Verify that your rate law expressions match what is on line 13. Run the code. Do the results match what you expect?
- (c) What is the  $[A]$  as a function of time.

- (d) What is the  $[I_1]$  as a function of time.
- (e) What is the  $[I_2]$  as a function of time.
- (f) What is the  $[P]$  at  $t = 2500$  s.
- (g) Can we determine a maximum time for  $[I_1]$  and  $[I_2]$  with these expressions? Explain your answer.

## Homework

4. The Lindemann Mechanism was developed to describe the observed concentration dependence in unimolecular dissociation reactions. It can be generalised as:



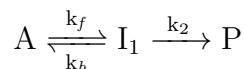
This reaction occurs when species A collides with another molecule in the system (M) and becomes activated ( $A^*$ ). This activated molecule can either become deactivated (through collision), or decompose into the product, P. Assume that all the reactions in the Lindemann Mechanism are elementary.

- (a) Write a rate law expression that describes the rate of change of the formation of products as a function of time. ( $\frac{d[P]}{dt} = k_2[A^*]$ )
- (b) Assume that  $k_2 \gg k_f, k_r$ . Write an expression for the  $[A^*]$  as a function of  $[A]$  and  $[M]$ . ( $[A^*] = \frac{k_f[A][M]}{k_r[M] + k_2}$ )
- (c) Using your expressions from 4a and 4b, show that

$$\frac{dP}{dt} = \frac{k_2 k_f [A][M]}{k_r [M] + k_2}$$

- (d) For the production of P, what is the order of M at very high  $[M]$ ? Does this make sense? Explain. (Order of M is zero)
- (e) For the production of P, what is the order of M at very low  $[M]$ ? Does this make sense? Explain. (Order of M is one)

5. Consider the following reaction mechanism



- (a) If  $k_f = 4.0 \times 10^{-3} \text{ s}^{-1}$ ,  $k_b = 7 \times 10^{-3} \text{ s}^{-1}$ ,  $k_2 = 10.5 \text{ s}^{-1}$ , and  $[A]_0 = 0.25 \text{ M}$ , while  $[I_1]_0 = [P]_0 = 0$ , determine  $[P]$  at  $t = 250$  s. ( $[P] = 0.158 \text{ M}$ )
- (b) If  $k_f = 70 \text{ s}^{-1}$ ,  $k_b = 40 \text{ s}^{-1}$ ,  $k_2 = 1.05 \times 10^{-2} \text{ s}^{-1}$ , and  $[A]_0 = 0.25 \text{ M}$ , while  $[I_1]_0 = [P]_0 = 0$ , determine  $[P]$  at  $t = 250$  s. ( $[P] = 0.203 \text{ M}$ )