CBE 40445
Fall 2020
Homework #4
Due 9/11/20

1. N_2O_5 decomposes as follows:

$$2N_2O_5 \Rightarrow 4NO_2 + O_2$$

Experimentally, the rate of reaction was found to be:

$$r = \frac{d[O_2]}{dt} = k[N_2O_5]$$

Show that the following sequence can lead to a reaction rate expression that would be consistent with the experimental observations:

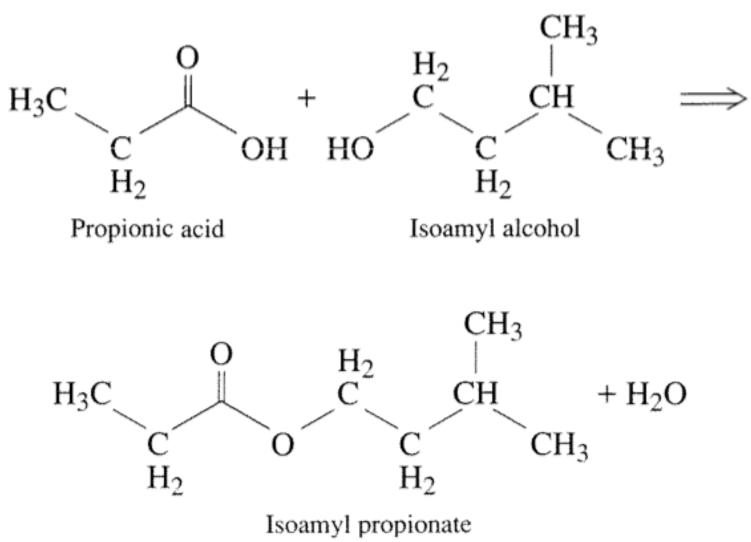
$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO$$

$$NO + NO_3 \xrightarrow{k_3} 2NO_2$$

2.

Mensah et al. studied the esterification of propionic acid (P) and isoamyl alcohol (A) to isoamyl propionate and water in the presence of the lipase enzyme [P. Mensah, J. L. Gainer, and G. Carta, *Biotechnol. Bioeng.*, **60** (1998) 434.] The product ester has a pleasant fruity aroma and is used in perfumery and cosmetics. This enzyme-catalyzed reaction is shown below:



This reaction appears to proceed through a "ping pong bi bi" mechanism with substrate inhibition. The rate expression for the forward rate of reaction is given by:

$$r = \frac{r_{max} C_P C_A}{C_P C_A + K_1 C_P\left(1 + \frac{C_P}{K_{Pi}}\right) + K_2 C_A}$$

Use nonlinear regression with the following initial rate data to find values of r_{max}, K_1, K_2, and K_{Pi}. Make sure to use several different starting values of the parameters in your analysis. Show appropriate plots that compare the model to the experimental data.

Initial rate data for esterification of propionic acid and isoamyl alcohol in hexane with Lipozyme-IM (immobilized lipase) at 24°C.

C_P (mol L^{-1})	C_A (mol L^{-1})	Rate (mmol h^{-1} g^{-1})
0.15	0.10	1.19
0.15	0.20	1.74
0.15	0.41	1.92
0.15	0.60	1.97
0.15	0.82	2.06
0.15	1.04	2.09
0.33	0.10	0.90
0.33	0.11	1.00
0.33	0.20	1.29
0.33	0.41	1.63
0.33	0.60	1.88
0.33	0.81	1.94
0.33	1.01	1.97
0.60	0.13	0.80
0.60	0.13	0.79
0.60	0.20	1.03
0.60	0.42	1.45
0.60	0.62	1.61
0.60	0.83	1.74
0.60	1.04	1.89
0.72	0.14	0.73
0.72	0.20	0.90
0.72	0.41	1.27
0.72	0.61	1.51
0.72	0.82	1.56
0.72	0.85	1.69
0.72	1.06	1.75
0.93	0.21	0.70
0.93	0.42	1.16
0.93	0.65	1.37
0.93	0.93	1.51
0.93	1.13	1.70

From P. Mensah, J. L. Gainer and G. Carta, *Biotechnol. Bioeng.*, **60** (1998) 434.

the explosion limit.

4. Molecules present in the feed inhibit some reactions catalyzed by enzymes. In this problem, the kinetics of inhibition are investigated (from M. L. Shuler and F. Kargi, *Bioprocess Engineering, Basic Concepts,* Prentice Hall, Englewood Cliffs, NJ, 1992).

   (a) Competitive inhibitors are often similar to the substrate and thus compete for the enzyme active site. Assuming that the binding of substrate S and inhibitor I are equilibrated, the following equations summarize the relevant reactions:

$$Ez + S \underset{}{\overset{K_m}{\rightleftarrows}} EzS \xrightarrow{k_2} Ez + P$$

$$Ez + I \overset{K_i}{\rightleftarrows} EzI$$

   Show how the rate of product formation can be expressed as:

$$r = \frac{r_{max} C_S}{K_m\left[1 + \frac{C_I}{K_i}\right] + C_S}$$

   (b) Uncompetitive inhibitors do not bind to the free enzyme itself, but instead they react with the enzyme-substrate complex. Consider the reaction scheme for uncompetitive inhibition:

$$Ez + S \overset{K_m}{\rightleftarrows} EzS \xrightarrow{k_2} Ez + P$$

$$EzS + I \overset{K_i}{\rightleftarrows} EzSI$$

   Show how the rate of product formation can be expressed as:

$$r = \frac{\dfrac{r_{max}}{\left(1 + \dfrac{C_I}{K_i}\right)} C_S}{\dfrac{K_m}{\left(1 + \dfrac{C_I}{K_i}\right)} + C_S}$$