

### 10.37 Spring 2007

#### Problem Set 2 due Wednesday, Feb. 21.

**Problem 1.** The microorganism *Mycobacterium vaccae* is able to grow with ethane as the sole source of carbon and energy and  $\text{NH}_3$  as the nitrogen source. The limiting substrate is ethane, and  $Y_{sx} = 22.8$  gram dry weight per mole of ethane. ( $Y_{sx}$  = Yield of biomass (x) from ethane (s = substrate)).

- a. Except for small amounts of S and P, an analysis of dry cell mass is C, 47.60 wt%; N, 7.30 wt%; H, 7.33 wt%; ash, 3.00 wt%. The remainder is taken to be oxygen, which can not be detected in the analysis. Determine the elemental composition for the ash-free biomass,  $\text{CH}_a\text{O}_b\text{N}_c$ , and the formula weight per C-atom. Also determine  $Y_{sx}$ , in the units of C-moles of biomass per C-mole of ethane.
- b. Calculate the oxygen consumption  $Y_{xo}$  (moles of  $\text{O}_2$  per C-mole of biomass) when it is assumed that  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_a\text{O}_b\text{N}_c$  are the only metabolic products. Write the full stoichiometric equation for the growth process, and determine the heat evolved per kilogram dry weight. Assume  $\Delta H_{\text{ethane}} = 1560$  kJ/mol,  $\Delta H_{\text{NH}_3} = 383$  kJ/mol,  $\Delta H_{\text{biomass}} = 19$  kJ/gram dry weight.

**Problem 2.** The gas phase homogeneous oxidation reaction



is known to have a third-order rate law:

$$r_{\text{NO}} = -2k[\text{NO}]^2[\text{O}_2]$$

at least under atmospheric conditions. However, the rate constant decreases as T increases, contrary to what happens in all direct elementary step termolecular reactions. So this reaction must actually go through more than one elementary step. Provide a mechanism that explains this strange behavior, that includes an NO<sub>3</sub> species as an intermediate. Under what conditions would you expect r<sub>NO</sub> to deviate significantly from the normal third-order expression above? What is the PSSH rate law for the reverse reaction?

**Problem 3.** The Michaelis-Menton reaction mechanism usually assumed for enzymatic reactions is:



- Consider a well-mixed batch reactor with initial enzyme concentration  $[E]_0$  and initial substrate concentration  $[S]_0$ . Write expressions for the rate of change of concentration of  $[S]$ ,  $[ES]$ ,  $[E]$ , and  $[P]$  in terms of  $k_1$ ,  $k_2$ , and  $K_{eq,1}$ , and concentration variables.
- Write a Matlab function that solves this set of differential equations for the concentration of all species in time given inputs  $k_1$ ,  $k_2$ ,  $K_{eq,1}$ ,  $[E]_0$ ,  $[S]_0$ .
- The pseudo-steady approximation may be applied on the reactive intermediate species  $[ES]$ . This approximation is:  $\frac{d[ES]}{dt} \approx 0$ . Using this pseudo-steady approximation, verify that the rate of change of  $[S]$  is given by the expression:
 
$$\frac{d[S]}{dt} = -\frac{v_{max}[S]}{K_M + [S]}$$
 What are  $v_{max}$  and  $K_M$  in terms of the other constants in this problem:  $k_1$ ,  $k_2$ ,  $K_{eq,1}$ ,  $[E]_0$ ,  $[S]_0$ ?
- What does the rate  $\frac{d[S]}{dt}$  simplify to in the limit  $[S] \gg K_M$ ? What about the limit  $K_M \gg [S]$ ?
- Consider the following conditions:  $k_1=10^9$  liter/mole-s,  $k_2=1$  s<sup>-1</sup>,  $K_{eq,1}=1$  liter/mole,  $[E]_0=10^{-6}$  M,  $[S]_0=0.01$  M. Find analytical solutions for  $[S](t)$ ,  $[ES](t)$ ,

and  $[P](t)$ . *Hint: determine what  $\frac{d[S]}{dt}$  regime these conditions lie within.*

Compare the analytical solution with the full numerical solution by plotting them together: plot  $[S](t)$ ,  $[ES](t)$  and  $[P](t)$  for both the numerical and analytical solutions (three plots). Use a solid line for the analytical solutions and open symbols for the numerical solutions. Run the simulation at least until the conversion  $X_P = [P]/[S]_0 \geq 99\%$ . After approximately how much time does the pseudo-steady approximation become valid? *Hint: look at the short-time behavior of  $[ES](t)$  in your numerical solution to find the answer.*