

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 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 O_2 per C-mole of biomass) when it is assumed that CO_2 , H_2O 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 NO₃ species as an intermediate. Under what conditions would you expect r_{NO} 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⁻¹, $K_{eq,1}=1$ 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.*