

CE 561, Exam 1, October 27, 1998

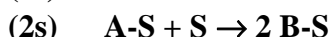
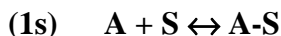
The exam consists of one long problem, with 21 parts (labelled (a) through (u)). Some, but not all of the parts depend on previous parts. Carefully explain any assumptions you make, label what part of the problem you are working on, and define the symbols that you use. The point value of each part is indicated – budget your effort accordingly. Good luck.

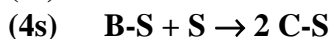
Consider the consecutive, effectively irreversible, first-order reactions of gas phase molecules A, B, and C, occurring in a system where they are highly diluted in an inert gas:



- (a) Write these reactions in matrix form. (3 pts.)
- (b) Write the rate equations for the concentrations of the three species in matrix form. Use a 3×3 matrix of rate coefficients and a three-element vector of concentrations. (4 pts.)
- (c) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*). (5 pts.)
- (d) Describe briefly how you would solve these equations using Laplace transform methods. (*you do not have to actually solve them*). (5 pts.)
- (e) Describe a numerical method that could be used to integrate the rate equations. Outline the algorithm used in this method and state the advantages and disadvantages of the method. (5 pts.)
- (f) Proceed to solve the rate equations by any method you choose. You should obtain expressions for the concentrations of A, B, and C as functions of time. The initial concentrations (at $t = 0$) are $C_A = C_{A0}$, $C_B = C_C = 0$. (5 pts.)
- (g) What reaction time maximizes the yield of B (moles of B produced per mole of A initially present)? Give your solution in terms of the initial concentration of A and the rate constants for the two reactions. (5 pts.)
- (h) What is the maximum attainable yield of B? Again, give your result in terms of the rate constant and initial concentration of A. (3 pts.)
- (i) Derive an equation for the *scaled sensitivity* of the concentration of species A to the rate constant for the reaction $A \rightarrow 2 B$. (5 pts.)

For parts (j) through (m), assume that the reactions that we have been working with are catalyzed by a solid surface. The sequence of elementary steps by which they occur are:





Where **S** represents a vacant surface site.

- (j) Assuming that steps (2s) and (4s) are irreversible and rate-limiting, so that the other three steps are in quasi-equilibrium (obeying a Langmuir adsorption isotherm), derive expressions for the rates of the overall reactions ($\text{A} \rightarrow 2 \text{B}$ and $\text{B} \rightarrow 2 \text{C}$), in terms of rate constants and equilibrium constants for the 5 elementary steps ((1s) through (5s)) and the gas phase concentrations. (10 pts.)

In experiments on a single-crystal, flat catalyst surface at 298 K, the reaction rates were found to be

$$\text{Rate of } \text{A} \rightarrow 2 \text{B} = r_1 \text{ (moles cm}^{-2} \text{ s}^{-1}\text{)} = 3.0 \times 10^{-4} \text{ (cm/s)} \times C_A \text{ (moles/cm}^3\text{)}$$

$$\text{Rate of } \text{B} \rightarrow 2 \text{C} = r_2 \text{ (moles cm}^{-2} \text{ s}^{-1}\text{)} = 1.5 \times 10^{-4} \text{ (cm/s)} \times C_B \text{ (moles/cm}^3\text{)}$$

- (k) What does the fact that the reactions are both apparently first order tell us about the surface coverages of the reactants and products? (3 pts.)
- (l) If the diffusion coefficients of A, B, and C in the inert gas are all about $0.3 \text{ cm}^2/\text{s}$ and we plan to use the catalyst in a very thin film on an alumina support with a porosity of 0.4, a pellet density of 2.4 g/cm^3 , and a surface area of $120 \text{ m}^2/\text{g}$, about how large can we make the catalyst pellets before pore diffusion will begin to affect the reaction rate? Show how you have made your estimate (no credit for just guessing). (5 pts.)
- (m) How would pore diffusion limitations effect the yield of B? (3 pts.)

At sufficiently high temperatures, these same reactions will occur in the gas phase without a catalyst.

For parts (n) through (s), let A, B, and C, be cyclooctane (C_8H_{16}), cyclobutane (C_4H_8), and ethylene (C_2H_4), respectively. For these problems, the reactions $\text{A} \rightarrow 2 \text{B}$ and $\text{B} \rightarrow 2 \text{C}$ are assumed to be elementary gas phase reactions, occurring in a nitrogen (N_2) bath gas. The mole fractions of A, B, and C are very small.

- (n) How many vibrational, rotational, and translational degrees of freedom do each of the three molecules have? (3 pts.)
- (o) Will the entropy of reaction for each of the two reactions be positive, negative, or nearly zero? Why? (3 pts.)
- (p) Write the simplest rate expressions that you can that qualitatively describe the pressure dependence of the two reactions. Sketch a log-log plot of the unimolecular rate constant vs. total pressure. What are the limiting values of the unimolecular rate constant at high and low pressures? (10 pts.)

- (q) If the two reactions have the same activation energy, which one will exhibit pressure dependence at higher pressures and why? How might this effect the yield of B? (4 pts.)
- (r) At 298 K and 1 atmosphere total pressure, about how many collisions per second will a particular A molecule have with the nitrogen bath gas molecules? Assume that the effective hard-sphere collision diameters for C_8H_{16} and N_2 are 7.0 Å and 3.6 Å, respectively. (5 pts.)
- (s) Based on transition state theory, and neglecting contributions from the vibrational partition functions, what is the expected temperature dependence of the pre-exponential factor for each of the reactions? (4 pts.)

For the rest of the problem (parts (t) and (u)), assume that the reactions are occurring in an organic solvent rather than in the gas phase (still with no catalyst).

- (t) As the temperature is increased, the solution reaction changes its apparent activation energy from about 30 kcal/mol at 298 K to only 3 kcal/mol above 370 K. Explain this temperature dependence of the reaction rate. (5 pts.)
- (u) In the regime where the apparent activation energy is 3 kcal/mol, the reaction is carried out in a series of solvents. They are all mixtures of linear alkanes, but they have different average molecular weights, and therefore different viscosities, ranging from 10 cP to 1000 cP. How do you expect the reaction rate to depend on the solvent viscosity? (5 pts.)