

## CE 561, Exam 1, November 1, 2006

This exam consists of 4 questions, most with multiple parts. You should be careful not to get stuck on one part. If you do not know how to do a problem, move on and return to it if you have time at the end.

You may use a calculator and a single letter-size sheet (2-sided) of notes to aid you on this exam. You may not exchange notes with or otherwise consult your fellow students. If you talk to your fellow students during the exam, I will assume that you are cheating, you will be asked to leave, and you will fail the exam.

You will have 2 hours and 50 minutes to complete the exam. Please use a separate blue book for each exam problem. Carefully explain any assumptions you make, label what part of what problem you are working on, and define the symbols that you use. The point value of each part is indicated – budget your effort accordingly. There are 100 points total.

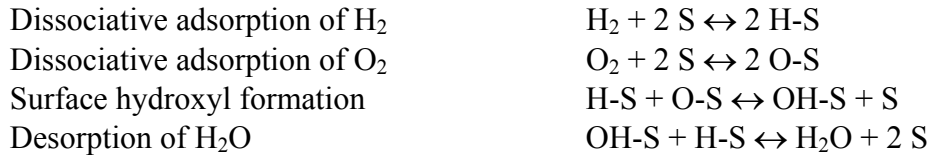
1. (33 points total) Consider the following first-order reactions among molecules A, B, and C, occurring in a constant-volume isothermal batch reactor that initially contains only species A at an initial concentration  $C_{A0}$ .
  - (1)  $A \rightarrow B + C$  with  $r_1 = k_1 C_A$
  - (2)  $B \leftrightarrow C$  with  $r_2 = k_2 C_B - k_3 C_C$
- (a) Write these reactions in matrix form (4 points).
- (b) Write the rate equations for the concentrations of the 3 species in matrix form. Use a  $3 \times 3$  matrix of rate coefficients and a three element vector of concentrations (4 points).
- (c) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*) (4 points).
- (d) 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 (4 points).
- (e) 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  $C_A = C_{A0}$ ,  $C_B = C_C = 0$  (13 points).
- (f) If there are  $i$  A molecules,  $j$  B molecules, and  $k$  C molecules in the system at time  $t$ , what is the probability that at some very short time later ( $t + \Delta t$ ) there are  $j + 1$  B molecules? Write your answer in terms of the rate constants. Assume that the time interval is short enough that, at most, one reaction event can occur during it (4 pts).

2. (22 points total) Consider the elementary gas phase reaction  $\text{AlCl} + \text{HCl} \leftrightarrow \text{AlCl}_2 + \text{H}$ . Calculated properties of the reactants, transition state, and products are given in the following table. Boltzmann's constant is  $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$ , Planck's constant is  $h = 6.63 \times 10^{-34} \text{ J s}$ , and the ideal gas constant is  $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

	<b>AlCl</b>	<b>HCl</b>	<b>AlCl<sub>2</sub></b>	<b>H</b>	<b>Transition State</b>
<b>M (amu)</b>	62.43	36.46	97.88	1.01	98.89
<b>I (amu Å<sup>2</sup>)</b>	69.8	1.62	22.6, 235, 258		29.0, 245, 274
<b>ΔH<sub>f</sub>(0 K) (kJ/mol)</b>	-64.2	-92.4	-238.4	216.0	-17.9
<b>ν (cm<sup>-1</sup>)</b>	473	2845	148, 451, 567		1275 <sub>i</sub> , 113, 285, 309, 429, 524
<b>g<sub>elec</sub></b>	1	1	2	2	1
<b>σ (rotational symmetry number)</b>	1	1	2		1
<b>Hard Sphere Collision Diameter (Å)</b>	3.8	3.5	4.8	2.0	5.0

- (a) What is the hard-sphere collisional rate constant for collisions between AlCl and HCl at 1000 K? (5 points).
- (b) Sketch the profile of enthalpy vs. reaction coordinate (at 0 K) for this reaction, clearly labeling the enthalpy of reaction and the forward and reverse enthalpy of activation (4 points).
- (c) Using transition state theory, calculate the forward rate constant for this reaction at 1000 K (13 points).

3. (36 points total) Consider the catalytic combustion of hydrogen ( $H_2$ ) by the reaction mechanism shown below:



Where O-S, H-S, and OH-S are surface species, and S is an empty surface site. The overall reaction is  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ . Adsorption and reaction steps obey mass action kinetics.

- (a) Derive a rate expression for the overall reaction in terms of the forward and reverse rate constants of the four reactions, assuming that desorption of water is rate-limiting (13 points).

Suppose that this reaction occurs at 400K and a pressure of 1 bar. Near the reactor inlet, the product ( $H_2O$ ) concentration is negligibly small, and the reactant concentrations are  $[O_2] = 1.72 \times 10^{19}$  molecules/cm<sup>3</sup> and  $[H_2] = 9.05 \times 10^{17}$  molecules/cm<sup>3</sup>. At this temperature, the adsorption equilibrium constants for  $H_2$  (reaction 1) and  $O_2$  (reaction 2) are  $1 \times 10^{-22}$  cm<sup>3</sup>/molecule and  $6 \times 10^{-23}$  cm<sup>3</sup>/molecule, respectively. The equilibrium constant for the surface hydroxyl formation (reaction 3) is 5.0 (dimensionless). The rate constant for  $H_2O$  desorption (reaction 4 in the forward direction) is  $3 \times 10^{15}$  molecules cm<sup>-2</sup> s<sup>-1</sup>.

- (b) Under these conditions, what are the approximate surface coverages (site fractions) of H, O, and OH? (4 points)
- (c) Under these conditions, the reaction is approximately first order in hydrogen. That is, the overall rate is approximately  $r = k_{eff}[H_2]$ . What is the value of  $k_{eff}$ ? (4 points).

Suppose this reaction occurs, under these conditions, on a porous monolith catalyst that can be treated as an infinite slab of thickness  $2l$ . The catalyst density is  $\rho_c = 1.2$  g/cm<sup>3</sup>. Its specific surface area is  $S_g = 120$  m<sup>2</sup>/g, and the effective diffusion coefficient for  $H_2$  within the catalyst is  $D_{e,H_2} = 0.08$  cm<sup>2</sup>/s.

- (d) What is the reaction rate *per volume of catalyst* (in molecules per second per cm<sup>3</sup> of catalyst) under the conditions given above, if the catalyst pellets are small enough that there are no diffusional limitations? (4 points)
- (e) Calculate the slab thickness (monolith wall thickness,  $2l$ ) for which the observed reaction rate will be half of the rate that would be obtained in the absence of any diffusion limitations. (10 points)

4. Suppose benzoyl peroxide is decomposed by photolysis in water to produce benzoate free radicals at a concentration of  $10^{13}$  molecules per  $\text{cm}^3$ . Recombination of these free radicals is expected to be a diffusion-limited reaction. The diffusion coefficient of benzoate radicals in water at 25 °C is estimated to be equal to that of benzoic acid in water:  $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$ . The radicals are expected to recombine at a (center-to-center) reaction distance of about 3.0 Å. Estimate the diffusion-limited rate constant for the benzoate radicals and the initial recombination rate. Approximately what time will be required for the radical concentration to drop to  $10^{12}$  molecules per  $\text{cm}^3$ ? (10 points).