

## CE 561, Exam 1, October 22, 2001

This exam consists of 3 questions, each 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 40 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.

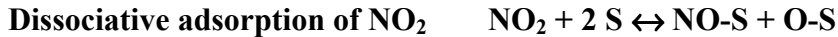
1. (35 points total) Consider the following irreversible, first-order reactions of gas phase molecules A, B, and C, occurring in a constant-volume isothermal batch reactor that initially contains only species A at an initial concentration  $C_{A0}$ .
  - (1)  $A \rightarrow 2 B$  with  $r_1 = k_1 C_A$
  - (2)  $B \rightarrow C$  with  $r_2 = k_2 C_B$
  - (3)  $A \rightarrow 2 C$  with  $r_3 = k_3 C_A$
- (a) Write these reactions in matrix form (4 points).
- (b) Write the rate equations for the concentrations of the three 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*) (5 points).
- (d) Describe briefly how you would solve these equations using Laplace transform methods. (*you do not have to actually solve them*) (5 points).
- (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 points).
- (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  $C_A = C_{A0}$ ,  $C_B = C_C = 0$  (6 points).
- (g) Derive an equation for the *scaled sensitivity* of the concentration of species A to the rate constant for the reaction  $A \rightarrow 2 B$  (6 points).

2. (35 points total) Consider the elementary gas phase reaction  $\text{Al} + \text{HCl} \leftrightarrow \text{AlCl} + \text{H}$ . 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  $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

	Al	HCl	AlCl	H	Transition State
<b>M (amu)</b>	26.98	36.46	62.43	1.01	63.44
<b>I (amu Å<sup>2</sup>)</b>		1.6	69.8		1.2; 89.4; 90.5
<b><math>\Delta H_f(0 \text{ K})</math> (kJ/mol)</b>	337.7	-94.6	-54.0	213.4	256.1
<b><math>\nu</math> (cm<sup>-1</sup>)</b>		2845	473		-2836; 285; 470
<b><math>g_{\text{elec}}</math></b>	2	1	1	2	2
<b>Hard Sphere Collision Diameter (Å)</b>	3.0	3.8	4.2	2.0	

- (a) How many translational, rotational, and vibrational degrees of freedom do each of the reactants, transition state, and products have? (5 points).
- (b) What is the hard-sphere collisional rate constant for collisions between Al and HCl at 1000 K? (5 points).
- (c) 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.
- (c) Using transition state theory, calculate the forward rate constant, the reverse rate constant, and the equilibrium constant for this reaction at 1000 K (15 points).
- (d) Compare the pre-exponential factor for the forward reaction to the hard-sphere collision rate constant from part (a). If we were describing the reaction in terms of the collision rate constant, what would be the steric factor for the reaction? (5 points).

3. Consider the surface catalyzed oxidation of  $\text{NO}_2$ , with the following reversible adsorption, desorption steps and irreversible reaction step:



Where  $\text{S}$  is a surface site and  $\text{NO-S}$ ,  $\text{O-S}$ , and  $\text{N-S}$  are surface bound species.

- (a) Assuming that all of the adsorption steps obey the Langmuir isotherm (for competitive adsorption on the same surface sites), and that the surface reaction ( $\text{NO}$  decomposition) is rate limiting and irreversible, derive an expression for the overall reaction rate in terms of the adsorption equilibrium constants and the rate constants for the  $\text{NO}$  decomposition surface reaction (10 points).
- (b) Show that if the gas phase  $\text{O}_2$  and  $\text{N}_2$  concentrations are much greater than the gas phase  $\text{NO}_2$  concentration, and the adsorption equilibrium constants are sufficiently small that the total fractional surface coverage is small (much less than 1), then the reaction will be first order in the  $\text{NO}_2$  concentration and independent of the other species concentrations. That is, show that if  $[\text{O}_2] \gg [\text{NO}_2]$ ,  $[\text{N}_2] \gg [\text{NO}_2]$ ,  $K_{\text{O}_2}[\text{O}_2] \ll 1$ ,  $K_{\text{N}_2}[\text{N}_2] \ll 1$ , and  $K_{\text{NO}_2}[\text{NO}_2] \ll 1$ , then the reaction rate can approximately be written as  $r = k_{\text{eff}}[\text{CO}]$  and find  $k_{\text{eff}}$  in terms of  $[\text{O}_2]$ ,  $[\text{N}_2]$ , the surface reaction rate constants, and the adsorption equilibrium constants (5 points).

Suppose that this reaction is occurring in the catalytic converter of an automobile, under the pseudo-first-order conditions described in part (b). The active catalyst is supported on a porous alumina monolith (which can be approximated as an infinite slab of porous material). The effective surface rate constant, as defined in part (b) ( $k_{\text{eff}}$  in  $r = k_{\text{eff}}[\text{CO}]$ ) for the conditions in the catalytic converter is  $0.001 \text{ cm/s}$ . The catalyst porosity (fraction of the catalyst volume made up of pores) is  $\epsilon_s = 0.4$ . The catalyst density is  $\rho_c = 2.0 \text{ g/cm}^3$ . The catalyst specific surface area is  $50 \text{ m}^2 \text{ g}^{-1}$ . The effective diffusion coefficient for  $\text{NO}_2$  in the gas mixture in the catalyst pores is  $D_e = 0.2 \text{ cm}^2 \text{ s}^{-1}$ .

- (c) Make a sketch of how the reaction rate *per mass of catalyst* will depend on the thickness of the monolith walls. Since there is gas on both sides of each wall, the thickness is equivalent to  $2l$  in our analysis of an infinite porous slab of catalyst (5 points).
- (d) Calculate the thickness of the monolith walls for which the reaction rate per mass of catalyst will be equal to  $\frac{1}{2}$  of what it would be in the absence of any diffusional limitations (10 points).