CE 561, Exam 1, November 7, 2008

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 three letter-size sheets (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 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. Consider the following two reactions:
   (1) A → B with rate $r_1 = k_1C_A$
   (2) B ↔ C with rate $r_2 = k_2C_B - k_3C_C$

   (a) Write these reactions in matrix form. (5 points)

   (b) Write the rate equations for the concentrations of the three species in matrix form. (5 points)

   (c) Explain how you would solve these equations to obtain expressions for the concentrations of A, B, and C as functions of time, for initial conditions of $C_A(t = 0) = C_{Ao}$, $C_B(t = 0) = C_C(t = 0) = 0$. Take your solution as far as you can in the time available. (10 points)

   (d) Show how you would find an analytical expression for the *scaled sensitivity coefficient* of the concentration of *B* to the forward rate constant for the second reaction (k_2). Set up the equations and provide a clear description of an appropriate method of solving the problem. Take your solution as far as you can in the time available. (10 points)

   (e) 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. (5 points)

2. Consider the elementary gas phase reaction Al + H_2 ↔ AlH_2. Properties of the reactants, transition state, and products are given below. Boltzmann's constant is $k_B = 1.38\times10^{-23}$ J K^{-1}, and Planck's constant is $h = 6.63\times10^{-34}$ J s.

	Al	**H_2**	**AlH_2**	**Transition State**
***M* (amu)**	26.98	2.02	29.00	29.00
***I* (amu Å^2)**		0.28	1.3; 3.9; 5.1	1.5; 4.5; 6.0
ΔH_f(0 K) (kJ/mol)	337.7	0.0	280.0	451.9
ν (cm^{-1})		4140	729; 1750; 1790	4003*i*; 758; 1346
g_{elec}	2	1	2	2
Hard Sphere Collision Diameter (Å)	3.0	2.9	3.5	

(a) How many translational, rotational, and vibrational degrees of freedom do each of the reactants, transition state, and product have? (5 points).

(b) What is the hard-sphere collisional rate constant for collisions between Al and H_2 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. (5 points)

(c) Use transition state theory to calculate the forward rate constant for this reaction at 1000 K, for pressures sufficiently high that it is independent of pressure. (15 points)

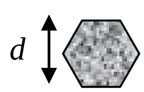
(d) Sketch and qualitatively describe the expected pressure dependence of the forward rate constant for this reaction. (5 points)

3. Consider the surface-catalyzed cracking of ethane to ethylene and hydrogen, by the following mechanism:

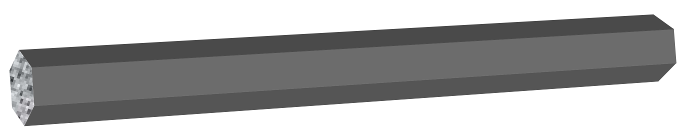
(1) Ethane adsorption	$C_2H_6 + 2S \leftrightarrow C_2H_5\text{-}S + H\text{-}S$	$r_1 = k_1[C_2H_6]\theta_S^2 - k_{-1}\theta_{C2H5}\theta_H$
(2) Hydrogen loss from ethyl	$C_2H_5\text{-}S + S \leftrightarrow C_2H_4\text{-}S + H\text{-}S$	$r_2 = k_2\theta_{C2H5}\theta_S - k_{-2}\theta_{C2H4}\theta_H$
(3) H_2 desorption	$2\ H\text{-}S \leftrightarrow H_2 + 2\ S$	$r_3 = k_3\theta_H^2 - k_{-3}[H_2]\theta_S^2$
(4) Ethylene desorption	$C_2H_4\text{-}S \leftrightarrow C_2H_4 + S$	$r_4 = k_4\theta_{C2H4} - k_{-4}[C_2H_4]\theta_S$

Derive a rate expression for the overall reaction in terms of the forward and reverse rate constants of the four reactions, assuming that hydrogen desorption (step 3) is rate-limiting (15 points).

4. Suppose a surface reaction with first-order kinetics occurs on the pore walls within a porous catalyst pellet that has been formed into long rods with a hexagonal cross-section, as illustrated below:



End view


Oblique view of catalyst rods.

If the effective diffusion coefficient of the reactant within the catalyst is 0.1 cm^2/s, the catalyst specific surface area is 30 m^2/g, the catalyst pellet density is 0.8 g/cm^3, and the rate constant for the first order surface reaction is 10 cm/s, estimate the rod width d for which diffusion limitations will reduce the overall reaction rate by a factor of 2 from the rate that would be observed in the absence of diffusion limitations. (15 points)