CE 561, Exam 1, October 26, 2007

This exam consists of 4 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 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. (35 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_{Ao}.

   (1) $\mathrm{A} \rightarrow \mathrm{B} + \mathrm{C}$ with $r_1 = k_1 C_\mathrm{A}$
   (2) $\mathrm{C} \leftrightarrow \mathrm{D}$ with $r_2 = k_2 C_\mathrm{C} - k_{-2} C_D$
   (3) $\mathrm{A} \rightarrow \mathrm{B} + \mathrm{D}$ with $r_3 = k_3 C_\mathrm{A}$

(a) Write these reactions in matrix form (4 points).

(b) Write the rate equations for the concentrations of the 4 species in matrix form. Use a 4×4 matrix of rate coefficients and a four element vector of concentrations (4 points).

(c) Describe briefly how you would solve these equations using matrix methods *(you do <u>not</u> 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 $C_A = C_{Ao}$, $C_B = C_C = C_D = 0$ (15 points).

(f) If there are i A molecules, j C molecules, and k D molecules in the system at time t, what is the probability that at some very short time later ($t+\Delta t$) there are $j+1$ C 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 points).

2. (25 points total) Consider the elementary gas phase reaction $OH + H_2 \leftrightarrow H_2O + H$. Calculated properties of the reactants, transition state, and products are given in the following table. Boltzmann's constant is $k_B = 1.38\times10^{-23}$ J K^{-1}, Planck's constant is $h = 6.63\times10^{-34}$ J s, and the ideal gas constant is $R = 1.987$ cal mol^{-1} K^{-1} = 8.314 J mol^{-1} K^{-1}.

	OH	**H_2**	**H_2O**	**H**	**Transition State**
M (amu)	17.01	2.02	18.02	1.01	19.03
I (amu Å^2)	0.89	0.28	0.60, 1.16, 1.81		0.93, 5.99, 6.90
ΔH_f(0 K) (kJ/mol)	37.0	0	-238.9	216.0	60.6
ν (cm^{-1})	3738	4401	1595, 3657, 3756		1210*i*, 573, 690, 1191, 2439, 3675
g_{elec}	2	1	1	2	2
σ (rotational symmetry number)	1	2	2		1
Hard Sphere Collision Diameter (Å)	2.8	2.9	2.6	2.0	3.0

(a) What is the hard-sphere collisional rate constant for collisions between OH and H_2 at 300 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 300 K (12 points).

(d) Describe an approximation used in transition state theory that is likely to be a poor approximation for this particular reaction (4 points).

3. (25 points total) Consider the catalytic hydrogenation of styrene to ethylbenzene via the following sequence of reactions:

(1) Adsorption of styrene	$C_8H_8 + S \leftrightarrow C_8H_8\text{-}S$	$r_1 = k_1[C_8H_8]\theta_S - k_{-1}\theta_{C8H8\text{-}S}$
(2) Dissociative adsorption of H_2	$H_2 + 2\,S \leftrightarrow 2\,H\text{-}S$	$r_2 = k_2[H_2]\theta_S^2 - k_{-2}\theta_{H\text{-}S}^2$
(3) Hydrogen addition to styrene	$H\text{-}S + C_8H_8\text{-}S \leftrightarrow C_8H_9\text{-}S + S$	$r_3 = k_3\theta_{H\text{-}S}\theta_{C8H8\text{-}S} - k_{-3}\theta_{C8H9\text{-}S}\theta_S$
(4) Desorption of ethylbenzene	$H\text{-}S + C_8H_9\text{-}S \leftrightarrow C_8H_{10} + 2\,S$	$r_4 = k_4\theta_{H\text{-}S}\theta_{C8H9\text{-}S} - k_{-4}[C_8H_{10}]\theta_S^2$

Where H-S, C_8H_8-S, and C_8H_9-S are surface species, and S is an empty surface site. The overall reaction is $H_2 + C_8H_8 \rightarrow C_8H_{10}$. 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 hydrogen addition to styrene (step 3) is rate-limiting (15 points).

(b) If H_2 is present in large excess, if step (3) is effectively irreversible, and if the surface coverage of all adsorbed species is low, then the reaction becomes pseudo-first-order in $[C_8H_8]$, with effective rate constant $k_{eff} = \frac{k_1 k_3}{k_{-1}}\sqrt{k_2[H_2] \big/ k_{-2}}$ *(if your answer to part (a) is correct, you should be able to simplify it to this using these assumptions, but you are not required to do so)*. Suppose the reaction takes place in a 2 mm cubic pellet of porous catalyst. The catalyst has a specific surface area of 50 m^2/g, a pore volume fraction of 0.35 and a pellet density of 3.5 g/cm^3. The diffusion coefficient of styrene in H_2 within the catalyst pores is 0.1 cm^2/s, and the tortuosity of the pores is estimated to be 3.0. For what value of k_{eff} will pore diffusion limitations reduce the reaction rate by a factor of 2, compared to the rate in the absence of pore diffusion limitations? (10 points)

4. (15 points total) Consider the homogeneous gas-phase dehydrogenation of ethylbenzene to styrene ($C_8H_{10} \rightarrow C_8H_8 + H_2$). This is an elementary reaction with a substantial energetic barrier.

(a) Derive the simplest rate expression that you can that gives a qualitatively correct description of the pressure dependence of this reaction (6 points).

(b) Sketch a log-log plot of the unimolecular rate constant vs. pressure for this reaction. Show how the expression derived in part (a) for the unimolecular rate constant can be simplified for very high pressures and for very low pressures, and illustrate these limiting cases on your sketch (5 points).

(c) Describe one improvement you could make to the treatment of the pressure dependence that you used in part (a) that would lead to more quantitative description of the pressure dependence of the reactions (4 points).