CE 561, Exam 1, October 15, 2002

This exam consists of 3 questions, each with multiple parts, plus a short bonus question at the end. 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, not counting the bonus question.

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_{Ao}.
   (1) A $\rightarrow$ B + D with $r_1 = k_1 C_A$
   (2) C $\rightarrow$ B with $r_2 = k_2 C_C$
   (3) A $\rightarrow$ 2 C with $r_3 = k_3 C_A$

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

(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 $C_A = C_{Ao}$, $C_B = C_C = 0$ (8 points).

(f) Derive an equation for the *scaled sensitivity* of the concentration of species C to the rate constant for the reaction A $\rightarrow$ B + D (7 points).

2. (40 points total) Consider the elementary gas phase reaction SiCl + HCl ↔ $SiCl_2$ + 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}.

	SiCl	HCl	$SiCl_2$	H	Transition State
M (amu)	63.54	36.46	98.99	1.01	100
I (amu Å^2)	67.3	1.62	34.6; 182.1; 216.6		41.5; 197.0; 236.0
ΔH_f(0 K) (kJ/mol)	145.2	-92.3	-174.4	216.0	103.4
ν (cm^{-1})	539	2984	207; 534; 534		2410*i*; 161; 302; 322; 483; 528
g_{elec}	2	1	1	2	2
σ (rotational symmetry number)	1	1	2		1
Hard Sphere Collision Diameter (Å)	4.3	3.8	4.8	2.0	5.0

(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 SiCl and HCl at 800 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).

(d) Using transition state theory, calculate the forward rate constant, the reverse rate constant, and the equilibrium constant for this reaction at 800 K (20 points).

(e) 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. (25 points total) Consider the surface catalyzed oxidation of hydrogen (catalytic combustion), with the following reversible adsorption and desorption steps and irreversible reaction step:

Dissociative adsorption of H_2	**$H_2 + 2\ S \leftrightarrow 2\ H\text{-}S$**
Dissociative adsorption of O_2	**$O_2 + 2\ S \leftrightarrow 2\ O\text{-}S$**
Surface hydroxyl formation	**$H\text{-}S + O\text{-}S \rightarrow OH\text{-}S + S$**
Dissociative adsorption of H_2O	**$H_2O + 2\ S \leftrightarrow H\text{-}S + OH\text{-}S$**

Where S is a surface site and O-S, H-S, and OH-S are surface bound species, and S is an empty surface site. The adsorption and reaction steps obey mass action kinetics.

(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 (surface hydroxyl formation) is rate limiting and irreversible, derive an expression for the overall reaction rate in terms of the adsorption equilibrium constants and the rate constant for the hydroxyl formation surface reaction (10 points).

Suppose that this reaction is occurring in a bed of spherical catalyst pellets, under pseudo-first-order conditions where the reaction rate can be described approximately as $r = k_{eff}[H_2]$. The active catalyst is supported on porous silica spheres. The effective surface rate constant, (k_{eff} in $r = k_{eff}[H_2]$) for the conditions in the reactor is 0.00005 cm/s. The catalyst porosity (fraction of the catalyst volume made up of pores) is $\varepsilon_s = 0.4$. The catalyst density is $\rho_c = 2.5$ g/cm^3. The catalyst specific surface area is 80 m^2 g^{-1}. The *effective* diffusion coefficient for H_2 in the gas mixture in the catalyst pores is $D_e = 0.3$ cm^2 s^{-1}.

(b) Make a sketch of how the reaction rate *per mass of catalyst* will depend on the diameter of the spherical catalyst pellet. (5 points).

(c) Calculate the pellet diameter for which the reaction rate per mass of catalyst will be equal to ½ of what it would be in the absence of any diffusional limitations (10 points).

BONUS QUESTION:

Identify up to three *substantially different major topics* from the course so far that were not addressed on this exam (3 points each).