

CE 561, Exam 1, October 23, 2003

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, not counting the bonus question.

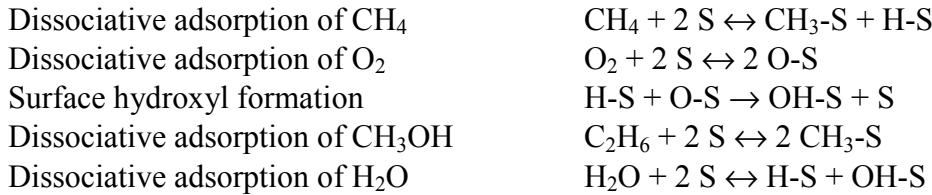
1. (35 points total) Consider the following first-order reactions among molecules A, B, and C, occurring in a constant-volume isothermal batch reactor that initially contains only species A at an initial concentration C_{A0} . Note that to make the problem simpler, all of the rate constants have been set equal (all of the k 's are the same).
 - (1) $A \leftrightarrow B$ with $r_1 = kC_A - kC_B$
 - (2) $A \rightarrow C$ with $r_2 = kC_A$
 - (3) $B \rightarrow C$ with $r_3 = kC_B$
- (a) Write these reactions in matrix form (5 points).
- (b) Write the rate equations for the concentrations of the 3 species in matrix form. Use a 3×3 matrix of rate coefficients and a three 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 $C_A = C_{A0}$, $C_B = C_C = 0$ (10 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 (5 pts).

2. (20 points total) Consider the elementary gas phase reaction $\text{Cl} + \text{HCl} \leftrightarrow \text{Cl}_2 + \text{H}$. 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 $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

	Cl	HCl	Cl₂	H	Transition State
M (amu)	35.45	36.46	70.90	1.01	71.91
I (amu Å²)		1.62	72.8		76.2
ΔH_r(0 K) (kJ/mol)	119.7	-92.3	0	216.0	228.2
ν (cm⁻¹)		2980	530		512i, 240, 358, 1470
g_{elec}	2	1	1	2	2
σ (rotational symmetry number)		1	2		1
Hard Sphere Collision Diameter (Å)	3.5	3.8	4.8	2.0	5.0

- (a) What is the hard-sphere collisional rate constant for collisions between Cl and HCl at 800 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 (5 points).
- (c) Using transition state theory, calculate the forward rate constant for this reaction at 600 K (10 points).

3. (30 points total) Consider the surface catalyzed oxidative coupling of methane (CH_4) to ethane (C_2H_6) by the reaction mechanism shown below:



Where S is a surface site and O-S, H-S, $\text{CH}_3\text{-S}$ and OH-S are surface bound species, and S is an empty surface site. The overall reaction is $2 \text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O}$. 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 $r = k_{\text{eff}}[\text{CH}_4]$. The active catalyst is supported on porous alumina spheres. The effective surface rate constant, (k_{eff} in $r = k_{\text{eff}}[\text{CH}_4]$) for the conditions in the reactor is 2×10^{-7} cm/s. The catalyst density is $\rho_c = 1.8$ g/cm³. The catalyst specific surface area is $40 \text{ m}^2 \text{ g}^{-1}$. The *effective* diffusion coefficient for H_2 in the gas mixture in the catalyst pores is $D_e = 0.02 \text{ cm}^2 \text{ s}^{-1}$.

- (b) What is the reaction rate *per mass of catalyst* (in moles per second per gram of catalyst) at a reactant concentration of $[\text{CH}_4] = 2 \times 10^{-6} \text{ mol cm}^{-3}$ if the catalyst pellets are small enough that there are no diffusional limitations? (5 points)
- (c) Calculate the pellet diameter for which the reaction rate per mass of catalyst will be equal to 20% of what it would be in the absence of any diffusional limitations. (10 points)
- (d) Make a sketch of how the reaction rate *per mass of catalyst* will depend on the diameter of the spherical catalyst pellet. (5 points)

4. (15 pts) Consider the decomposition of chloroethane ($\text{CH}_3\text{CH}_2\text{Cl}$) to ethylene plus HCl in the gas phase. 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. (10 pts)
- (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 pts)