

CE 561, Exam 1, October 16, 2000

This exam consists of four questions, each with multiple parts. It is intended to provide fairly comprehensive coverage of the first half of our course, and is therefore rather long. You should therefore 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. 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. Good luck.

1. (33 pts) Consider the following two reactions:



- (a) Write these reactions in matrix form. (3 pts)
- (b) Write the rate equations for the concentrations of the three species in matrix form. (3 pts)
- (c) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*). (4 pts)
- (d) Describe briefly how you would solve these equations using Laplace transform methods. (*you do not have to actually solve them*). (4 pts)
- (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. (4 pts)
- (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 pts)
- (g) Find an analytical expression for the *scaled sensitivity coefficient* of the concentration of A to the rate constant for the second reaction (k_3). (6 pts)
- (h) 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. (3 pts)

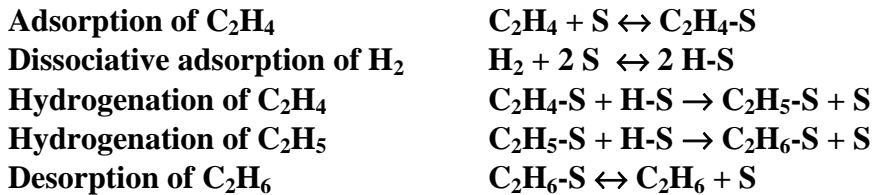
2. (25 pts) Consider the elementary gas phase reaction $\text{CH}_3 + \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}$. For this reaction (at 298 K and 1 atm) the enthalpy of reaction is $\Delta H_{rxn} = -0.5 \text{ kcal mol}^{-1}$. The entropy of reaction is $\Delta S_{rxn} = -6.7 \text{ cal mol}^{-1} \text{ K}^{-1}$. The enthalpy of activation is $\Delta H^\ddagger = 12.6 \text{ kcal mol}^{-1}$, and the entropy of activation is $\Delta S^\ddagger = -26.5 \text{ cal mol}^{-1} \text{ K}^{-1}$. The atomic mass of H is 1.0 amu. The atomic mass of C is 12.0 amu. The hard-sphere collision diameters for CH_3 , H_2 , CH_4 , and H are 3.8, 2.9, and 3.7, and 2.1 angstroms, respectively. Boltzmann's constant, k_B , is $1.38 \times 10^{-23} \text{ J K}^{-1}$, Planck's constant is $h = 6.63 \times 10^{-34} \text{ J s}$, and the ideal gas constant is $1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

- (a) How many translational, rotational, and vibrational degrees of freedom do each of the reactants, transition state, and products have? (4 pts)
- (b) What is the hard-sphere collisional rate constant for collisions between CH_3 and H_2 at 298 K and 1 atmosphere? (4 pts)
- (c) Sketch the profile of enthalpy vs. reaction coordinate for this reaction, clearly labeling the enthalpy of reaction and the forward and reverse enthalpy of activation. (4 pts)
- (d) Using the thermodynamic formulation of transition state theory, calculate the forward rate constant, the equilibrium constant, and the reverse rate constant for the reaction at 298 K. (9 pts)
- Note that the enthalpy and entropy changes given are for standard conditions of 1 atm and 298 K. The rate constant from the thermodynamic formulation of transition state theory will therefore be expressed in terms of partial pressure (in atmospheres) of reactants rather than in terms of concentrations of reactants.
- (e) Compare the pre-exponential factor for the forward reaction found in part (d) to the hard-sphere collision rate constant from part (b). If we were describing the reaction in terms of the collision rate constant, what would be the steric factor for the reaction? (4 pts)

3. (12 pts) Consider the isomerization of 1,2-butadiene to 1,3-butadiene 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. (5 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. (4 pts)
- (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. (3 pts)

4. (30 pts) Consider the surface catalyzed hydrogenation of ethylene, with the following adsorption, reaction, and diffusion steps:



Where S is an empty surface site and C₂H₄-S, H-S, C₂H₅-S, and C₂H₆-S are adsorbed surface species. Note that this mechanism assumes that C₂H₅ does not desorb (only C₂H₅-S is included).

- (a) Assuming that the adsorption and desorption steps obey the Langmuir isotherm (for competitive adsorption on the same surface sites), and that the hydrogenation of C₂H₄ is irreversible and rate limiting, derive an expression for the overall reaction rate in terms of the adsorption equilibrium constants and the rate constant for the surface reactions. (10 pts)
- (b) Show that if the gas phase H₂ concentration is much greater than the gas phase C₂H₄ and C₂H₆ concentrations 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 C₂H₄ concentration and independent of the other species concentrations. That is, show that if $[H_2] \gg [C_2H_4]$, $[H_2] \gg [C_2H_6]$, $K_{C_2H_4}[C_2H_4] \ll 1$, $K_{H_2}[H_2] \ll 1$, and $K_{C_2H_6}[C_2H_6] \ll 1$, then the reaction rate can approximately be written as $r = k_{eff}[C_2H_4]$ and find k_{eff} in terms of $[H_2]$, the surface reaction rate constants, and the adsorption equilibrium constants. (5 pts)

Suppose that this reaction is occurring in a spherical porous alumina catalyst pellet under the pseudo-first-order conditions described in part (b). The active catalyst is present inside the pores of the alumina, and reaction occurs on the pore surfaces. The effective surface rate constant, as defined in part (b) (k_{eff} in $r = k_{eff}[C_2H_4]$) for the conditions of interest is 1×10^{-5} cm/s. The catalyst porosity (fraction of the catalyst volume made up of pores) is $\epsilon_s = 0.4$. The catalyst density is $\rho_c = 2.5$ g/cm³. The catalyst specific surface area is 100 m² g⁻¹. The effective diffusion coefficient for C₂H₄ in the gas mixture in the catalyst pores is $D_e = 0.2$ cm² s⁻¹.

- (c) Make a sketch of how the reaction rate *per mass of catalyst* will depend on the diameter of the spherical catalyst pellets. (5 pts)
- (d) Calculate the sphere diameter for which the reaction rate per mass of catalyst will be equal to 80% of what it would be in the absence of any diffusional limitations. (10 pts)