

CE 561, Exam 1, October 18, 1999

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.

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. (30 pts.) Consider the following three effectively irreversible, first-order reactions of gas phase molecules A_1 , A_2 , and A_3 ,

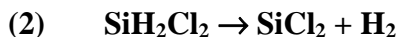
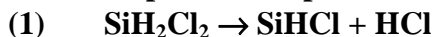


- (a) Write these reactions in matrix form. (3 pts)
- (b) Determine, using the stoichiometric matrix, the number of linearly independent reactions in this set. (3 pts)
- (c) Write the rate equations for the concentrations of the three species in matrix form. Use a 3×3 matrix of rate coefficients and a three-element vector of concentrations. (3 pts)
- (d) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*). (3 pts)
- (e) Describe briefly how you would solve these equations using Laplace transform methods. (*you do not have to actually solve them*). (3 pts)
- (f) 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. (3 pts)
- (g) Proceed to solve the rate equations by any method you choose. You should obtain expressions for the concentrations of A_1 , A_2 , and A_3 as functions of time. The initial concentrations (at $t = 0$) are $[A_1] = [A_1]_0$, $[A_2] = [A_3] = 0$ (5 pts)
- (h) Find an analytical expression for the *scaled sensitivity coefficient* of the concentration of A_2 to the rate constant for reaction number 3. (4 pts)
- (i) If there are i A_1 molecules, j A_2 molecules, and k A_3 molecules in the system at time t , what is the probability that at some very short time later ($t + \Delta t$) there are $j + 1$ A_2 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. (24 pts) Consider the elementary gas phase reaction $\text{H} + \text{HCl} \leftrightarrow \text{H}_2 + \text{Cl}$. For this reaction (at 298.15 K and 1 atm) the enthalpy of reaction is $\Delta H_{rxn} = -1.1 \text{ kcal mol}^{-1}$. The entropy of reaction is $\Delta S_{rxn} = -2.8 \text{ cal mol}^{-1} \text{ K}^{-1}$. The enthalpy of activation is $\Delta H^\ddagger = 2.8 \text{ kcal mol}^{-1}$, and the entropy of activation is $\Delta S^\ddagger = -21.6 \text{ cal mol}^{-1} \text{ K}^{-1}$. The reaction proceeds through a linear transition state. The atomic mass of H is 1.0 amu. The atomic mass of Cl is 35.5 amu. The hard-sphere collision diameters for H, Cl, and HCl are 2.0, 3.4, and 3.8 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) What is the hard-sphere collisional rate constant for collisions between H and HCl at 298.15 K and 1 atmosphere? (3 pts)
- (b) 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. (3 pts)
- (c) 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 298.15 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.
- (d) 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? (3 pts)
- (e) How many translational, rotational, and vibrational degrees of freedom do each of the reactants, transition state, and products have? (3 pts)
- (f) Based on part (d) and transition state theory, how do you expect the pre-exponential factor for the forward and reverse reactions to depend on temperature? (3 pts)

3. (16 pts) Dichlorosilane (SiH_2Cl_2) can decompose by two competing elementary reactions that are both pressure dependent.

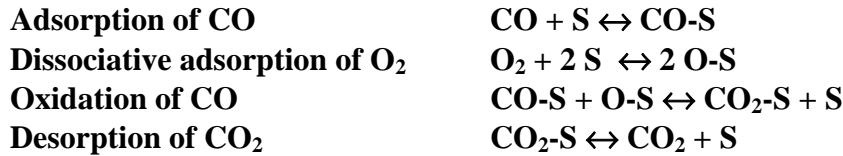


As in the simple Lindemann mechanism for a single channel reaction, we can write this process as:



- (a) Derive an expression for the pressure dependent unimolecular rate constant for each reaction path in terms of the rate constants k_1 , k_{-1} , k_2 , and k_3 . Remember that the total concentration $[\text{M}]$ is proportional to pressure. Sketch the effective unimolecular rate constant for each channel vs. pressure on a log-log scale. What are the high pressure and low pressure limits for the effective rate constant for each channel? (10 pts)
- (b) If the activation energy for the second channel ($\text{SiH}_2\text{Cl}_2 \rightarrow \text{SiCl}_2 + \text{H}_2$) is greater than that for the first channel ($\text{SiH}_2\text{Cl}_2 \rightarrow \text{SiHCl} + \text{HCl}$), which channel will exhibit pressure dependence at higher pressures? Why? (3 pts)
- (c) Describe an 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 oxidation of CO, with the following adsorption, reaction, and diffusion steps:



Where S is a surface site and CO-S, O-S, and $\text{CO}_2\text{-S}$ are surface bound species.

- (a) Assuming that the adsorption and desorption steps obey the Langmuir isotherm (for competitive adsorption on the same surface sites), and that the surface reaction (oxidation of CO) 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 reaction. (10 pts)
- (b) Show that if the gas phase O_2 concentration is much greater than the gas phase CO and CO_2 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 CO concentration and independent of the other species concentrations. That is, show that if $[\text{O}_2] \gg [\text{CO}]$, $[\text{O}_2] \gg [\text{CO}_2]$, $K_{\text{CO}}[\text{CO}] \ll 1$, $K_{\text{O}_2}[\text{O}_2] \ll 1$, and $K_{\text{CO}_2}[\text{CO}_2] \ll 1$, then the reaction rate can approximately be written as $r = k_{\text{eff}}[\text{CO}]$ and find k_{eff} in terms of $[\text{O}_2]$, the surface reaction rate constants, and the adsorption equilibrium constants. (5 pts)

Suppose that this reaction is occurring in the catalytic converter of an automobile, under the pseudo-first-order conditions described in part (b). The active catalyst is supported on a porous alumina monolith (which can be approximated as an infinite slab of porous material). The effective surface rate constant, as defined in part (b) (k_{eff} in $r = k_{\text{eff}}[\text{CO}]$) for the conditions in the catalytic converter is $1 \times 10^5 \text{ cm/s}$. The catalyst porosity (fraction of the catalyst volume made up of pores) is $\epsilon_s = 0.4$. The catalyst density is $\rho_c = 2.5 \text{ g/cm}^3$. The catalyst specific surface area is $150 \text{ m}^2 \text{ g}^{-1}$. The effective diffusion coefficient for CO in the gas mixture in the catalyst pores is $D_{\text{eCO}} = 0.1 \text{ cm}^2 \text{ s}^{-1}$.

- (c) Make a sketch of how the reaction rate *per mass of catalyst* will depend on the thickness of the monolith walls. Since there is gas on both sides of each wall, the thickness is equivalent to $2l$ in our analysis of an infinite porous slab of catalyst. (5 pts)
- (d) Calculate the thickness of the monolith walls for which the reaction rate per mass of catalyst will be equal to $\frac{1}{2}$ of what it would be in the absence of any diffusional limitations. (10 pts)