

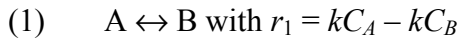
## CE 561, Exam 1, October 23, 2003

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).



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

In matrix form, these can be written as:

$$\begin{bmatrix} -1 & 1 & 0 \\ -1 & 0 & 1 \\ 0 & -1 & 1 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \end{bmatrix} = \underline{0}$$

(b) Write the rate equations for the concentrations of the 3 species in matrix form. Use a  $3 \times 3$  matrix of rate coefficients and a three element vector of concentrations (5 points).

The rate equations can be written terms of the vector of concentrations and a matrix of rate constants as:

$$\frac{d}{dt} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -2k & k & 0 \\ k & -2k & 0 \\ k & k & 0 \end{bmatrix} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

(b) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*) (5 points).

If  $\underline{\underline{M}}$  is the matrix of rate constants from part (b), and  $\underline{\underline{C}}_0$  is the vector of concentrations at  $t = 0$ , then we know that the solution can be written as

$$\underline{\underline{C}}(t) = \exp(\underline{\underline{M}}t) \underline{\underline{C}}_0 \text{ or } \underline{\underline{C}}(t) = (\underline{\underline{T}} \exp(\underline{\underline{\Lambda}}t) \underline{\underline{T}}^{-1}) \underline{\underline{C}}_0$$

where  $\underline{\Lambda}$  is the diagonal matrix of the eigenvalues of  $\underline{M}$ , and  $\underline{T}$  is the matrix whose columns contain the corresponding eigenvectors of  $\underline{M}$ . To write the solution in this form, we find the eigenvalues of  $\underline{M}$  by solving  $\det(\underline{M} - \lambda \underline{I}) = 0$  for  $\lambda$ . For each solution,  $\lambda_i$ , we find the corresponding eigenvector  $x_i$  by solving  $\underline{M}x_i = \lambda_i x_i$ . The eigenvectors and eigenvalues are then placed in the matrices  $\underline{T}$  and  $\underline{\Lambda}$ , respectively. We then take the inverse of  $\underline{T}$ , then multiply the matrices to get  $C(t)$  according to the equation given above.

- (c) 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).

The simplest method is the explicit Euler method. In this method, if we denote the equations as

$$\frac{d\underline{C}}{dt} = f(\underline{C})$$

then this method gives the values of  $\underline{C}$  at time  $t + \Delta t$  as

$$\underline{C}(t + \Delta t) = \underline{C}(t) + f(\underline{C}(t))\Delta t$$

Applying this repeatedly, with sufficiently small values of  $\Delta t$  gives us the concentrations vs. time. The principal advantage of this method is its simplicity and ease of implementation. Disadvantages are its relatively low accuracy (of order  $\Delta t$ ) and its poor stability characteristics. For stiff ODE's, we may have to take very small time steps to retain numerical stability of the solution process.

- (d) 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).

Since reaction 1 is reversible, the equations for  $C_A$  and  $C_B$  are coupled and we have to solve them simultaneously, but we see that neither  $C_A$  nor  $C_B$  depends on  $C_C$  (because C is formed irreversibly). So, we can obtain  $C_C$  from the stoichiometric relationship  $C_C = C_{A0} - C_A - C_B$  after solving for  $C_A$  and  $C_B$ . To solve for  $C_A$  and  $C_B$  we can use the matrix method as described in part (b), but with just a  $2 \times 2$  matrix (leaving C out):

$$\frac{d}{dt} \begin{bmatrix} C_A \\ C_B \end{bmatrix} = \begin{bmatrix} -2k & k \\ k & -2k \end{bmatrix} \begin{bmatrix} C_A \\ C_B \end{bmatrix}$$

The matrix of rate constants is

$$\underline{M} = \begin{bmatrix} -2k & k \\ k & -2k \end{bmatrix}$$

To find the eigenvalues, we solve

$$\det(\underline{\underline{M}} - \lambda \underline{\underline{I}}) = \det \begin{bmatrix} -(2k + \lambda) & k \\ k & -(2k + \lambda) \end{bmatrix} = 0$$

$$4k^2 + 4k\lambda + \lambda^2 - k^2 = 0$$

$$\lambda^2 + 4k\lambda + 3k^2 = (\lambda + k)(\lambda + 3k) = 0$$

So the eigenvalues are  $\lambda_1 = -k$ , and  $\lambda_2 = -3k$  (the numbering 1 or 2 is arbitrary). We find the corresponding eigenvectors by solving  $\underline{\underline{M}}\underline{x}_i = \lambda_i \underline{x}_i$ , or  $(\underline{\underline{M}} - \lambda_i \underline{\underline{I}})\underline{x}_i = 0$  for each eigenvalue. For  $\lambda_1 = -k$  this gives

$$\begin{bmatrix} -(2k - k) & k \\ k & -(2k - k) \end{bmatrix} \underline{x}_i = \begin{bmatrix} -k & k \\ k & -k \end{bmatrix} \begin{bmatrix} x_{1,1} \\ x_{1,2} \end{bmatrix} = 0$$

so  $x_{1,1} = x_{1,2}$ . So, the first eigenvector is any constant multiple of  $[1, 1]^T$ . If we want it to be normalized (have length 1), we can pick

$$\underline{x}_1 = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$$

Likewise for  $\lambda_2 = -3k$  we have

$$\begin{bmatrix} -(2k - 3k) & k \\ k & -(2k - 3k) \end{bmatrix} \underline{x}_i = \begin{bmatrix} k & k \\ k & k \end{bmatrix} \begin{bmatrix} x_{2,1} \\ x_{2,2} \end{bmatrix} = 0$$

so  $x_{2,1} = -x_{2,2}$ . So, the second eigenvector is any constant multiple of  $[1, -1]^T$ . If we want it to be normalized (have length 1), we can pick

$$\underline{x}_2 = \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix}$$

So, the matrix of eigenvectors is

$$\underline{\underline{T}} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

For a 2 by 2 matrix, we can find the inverse directly, by solving:

$$\begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} a & b \\ c & d \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

where I have used  $a, b, c$ , and  $d$  to represent the elements of the inverse. From this, we get

$$\frac{a+c}{\sqrt{2}} = 1 \quad \frac{b+d}{\sqrt{2}} = 0$$

$$\frac{a-c}{\sqrt{2}} = 0 \quad \frac{b-d}{\sqrt{2}} = 1$$

and solving these gives

$$a = c = \frac{\sqrt{2}}{2} = \frac{1}{\sqrt{2}}$$

$$b = -d = \frac{\sqrt{2}}{2} = \frac{1}{\sqrt{2}}$$

and therefore

$$\underline{T}^{-1} = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix}$$

If we were lucky, we might have remembered that if we start with a symmetric matrix and normalize the eigenvalues, the inverse of the matrix of eigenvalues is equal to the transpose of the matrix of eigenvalues (which in this case is the same as the matrix of eigenvalues because the matrix of eigenvalues is also symmetric).

So, we can write the solution as:

$$\underline{C}(t) = (\underline{T} \exp(\underline{\Lambda}t) \underline{T}^{-1}) \underline{C}_o$$

$$\underline{C}(t) = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} e^{-kt} & 0 \\ 0 & e^{-3kt} \end{bmatrix} \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} C_{A_o} \\ 0 \end{bmatrix}$$

Multiplying this out gives

$$\underline{C}(t) = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} e^{-kt} & 0 \\ 0 & e^{-3kt} \end{bmatrix} \begin{bmatrix} \frac{C_{A_o}}{\sqrt{2}} \\ \frac{C_{A_o}}{\sqrt{2}} \end{bmatrix}$$

$$\underline{C}(t) = \begin{bmatrix} \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} & -\frac{1}{\sqrt{2}} \end{bmatrix} \begin{bmatrix} \frac{C_{A_o}}{\sqrt{2}} e^{-kt} \\ \frac{C_{A_o}}{\sqrt{2}} e^{-3kt} \end{bmatrix} = \begin{bmatrix} \frac{C_{A_o}}{2} (e^{-kt} + e^{-3kt}) \\ \frac{C_{A_o}}{2} (e^{-kt} - e^{-3kt}) \end{bmatrix}$$

So, our final answer is

$$C_A = \frac{1}{2} C_{A_o} (e^{-kt} + e^{-3kt})$$

$$C_B = \frac{1}{2} C_{A_o} (e^{-kt} - e^{-3kt})$$

$$C_C = C_{A_o} - (C_A + C_B) = C_{A_o} (1 - e^{-kt})$$

- (e) 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).

We will have  $j-1$  B molecules if 1 B molecule reacts, which could happen either via the reverse of reaction 1 (with rate  $kj$ ) or by reaction 3 (also with rate  $kj$ ) so the conditional probability that if

we have  $j$  B molecules at time  $t$  that we will have  $j-1$  B molecules at time  $t + \Delta t$  is given by  $W_{j,j-1}(\Delta t) = 2kj\Delta t$ .

2. 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	Cl <sub>2</sub>	H	Transition State
<b>M (amu)</b>	35.45	36.46	70.90	1.01	71.91
<b>I (amu Å<sup>2</sup>)</b>		1.62	72.8		76.2
<b>ΔH<sub>f</sub>(0 K) (kJ/mol)</b>	119.7	-92.3	0	216.0	228.2
<b>ν (cm<sup>-1</sup>)</b>		2980	530		512i, 240, 358, 1470
<b>g<sub>elec</sub></b>	2	1	1	2	2
<b>σ (rotational symmetry number)</b>		1	2		1
<b>Hard Sphere Collision Diameter (Å)</b>	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).

The hard sphere collisional rate constant is given by

$$k_{coll} = \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2}$$

where the collision cross-section  $\sigma$  is given by

$$\sigma = \pi \left( \frac{d_{Cl} + d_{HCl}}{2} \right)^2 = \pi \left( \frac{3.5 + 3.8}{2} \times 10^{-10} \text{ m} \right)^2 = 4.19 \times 10^{-19} \text{ m}^2$$

and the reduced mass for the colliding particles is

$$\mu = \frac{m_{Cl} m_{HCl}}{m_{Cl} + m_{HCl}} = \frac{35.45 \cdot 36.46}{35.45 + 36.46} \times \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 2.98 \times 10^{-26} \text{ kg}$$

so

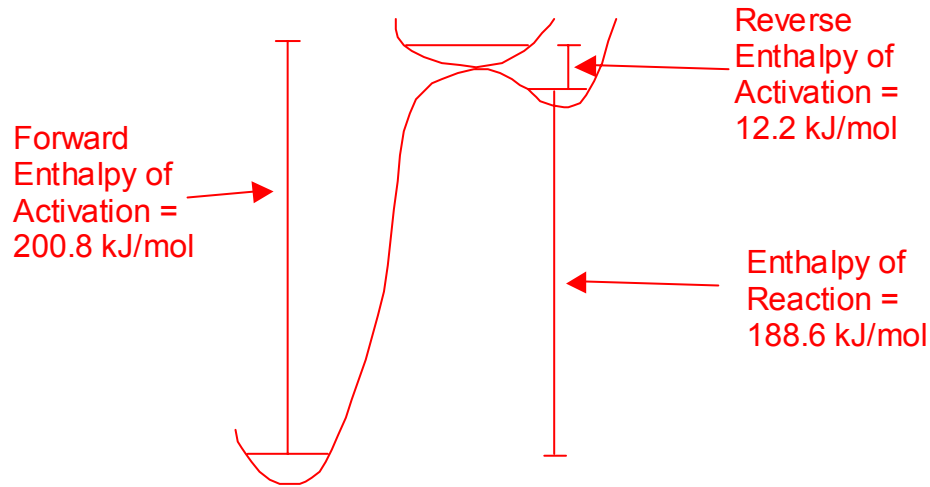
$$k_{coll} = 4.19 \times 10^{-19} \text{ m}^2 \left( \frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(800 \text{ K})}{\pi(2.98 \times 10^{-26} \text{ kg})} \right)^{1/2} = 4.07 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 2.45 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

- (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).

The enthalpy of formation of the reactants at 0 K is  $119.7 - 92.3 = 27.4 \text{ kJ/mol}$ .

The enthalpy of formation of the transition state at 0 K is  $228.2 \text{ kJ/mol}$ .

The enthalpy of formation of the products at 0 K is  $0 + 216.0 = 216.0$  kJ/mol.  
 So, the forward enthalpy of activation is  $228.2 - 27.4 = 200.8$  kJ/mol,  
 and the reverse enthalpy of activation is  $228.2 - 216.0 = 12.2$  kJ/mol,  
 and the enthalpy of reaction is  $216.0 - 27.4 = 188.6$  kJ/mol



(c) Using transition state theory, calculate the forward rate constant for this reaction at 800 K (10 points).

According to transition state theory, the forward rate constant is given by:

$$k_f = \frac{kT}{h} \frac{(Q^\ddagger / V)}{(Q_{\text{HCl}} / V)(Q_{\text{Cl}} / V)} \exp\left(\frac{-E_o}{kT}\right)$$

The Partition Functions are as follows:

For HCl, a diatomic molecule,

$$Q_{\text{trans}} / V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \left(\frac{2\pi(36.46 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (600) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2}\right)^{3/2} = 6.083 \times 10^{32} \text{ m}^{-3}$$

$$Q_{\text{vib}} = \frac{1}{1 - \exp\left(\frac{-h\nu}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-1.44 \text{ (cm K)} \bar{\nu}}{600 \text{ K}}\right)}$$

$$Q_{\text{vib}} = \frac{1}{\left(1 - \exp\left(\frac{-2984}{416.7}\right)\right)} = 1.0008$$

$$Q_{rot} = \frac{8\pi^2 I k T}{\sigma h^2} = \frac{8\pi^2 (1.62 / 6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (600) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2} = 40.1$$

$$Q_{elec} = 1$$

$$\text{so } Q_{HC}/V = 6.083 \times 10^{32} * 40.1 = 2.44 \times 10^{34} \text{ m}^{-3}$$

For Cl, an atom,

$$Q_{trans} / V = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} = \left( \frac{2\pi (35.45 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (600) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 5.832 \times 10^{32} \text{ m}^{-3}$$

and

$$Q_{elec} = 2$$

$$\text{so } Q_{Cl}/V = 1.166 \times 10^{33}$$

Finally, we see from the fact that it has a single moment of inertia and 3N-5 vibrational frequencies (including the imaginary frequency) that the transition state is another linear molecule, so:

$$Q_{trans} / V = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} = \left( \frac{2\pi (71.91 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (600) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 1.685 \times 10^{33} \text{ m}^{-3}$$

$$Q_{vib} = \frac{1}{\prod_i 1 - \exp\left(\frac{-h\nu_i}{kT}\right)} = \frac{1}{\prod_i 1 - \exp\left(\frac{-1.44 \text{ (cm K)} \nu_i}{600 \text{ K}}\right)}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-240}{416.7}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-358}{416.7}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-1470}{416.7}\right)\right)} = 4.082$$

$$Q_{rot} = \frac{8\pi^2 I k T}{\sigma h^2} = \frac{8\pi^2 (76.2 / 6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (600) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2} = 1885.6$$

$$Q_{elec} = 2$$

$$\text{so } Q_{TS}/V = 1.685 \times 10^{33} * 4.082 * 1885.6 * 2 = 2.594 \times 10^{37} \text{ m}^{-3}$$

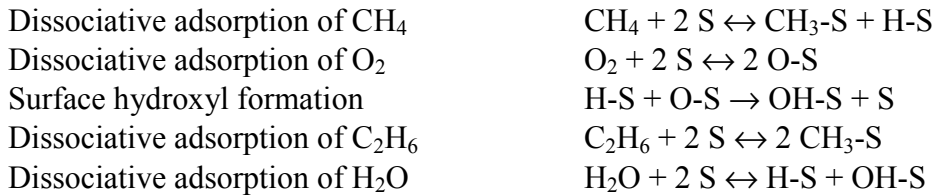
So, the forward rate constant is:

$$k_f = \frac{kT}{h} \frac{(Q_{TS}^\ddagger/V)}{(Q_{SiCl}/V)(Q_{HCl}/V)} \exp\left(\frac{-E_{o,f}}{kT}\right)$$

$$k_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (600) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{2.594 \times 10^{37} \text{ m}^{-3}}{2.44 \times 10^{34} \text{ m}^{-3} \cdot 1.166 \times 10^{33} \text{ m}^{-3}} \exp\left(\frac{-200800 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (600) \text{ K}}\right)$$

$$k_f = 1.251 \times 10^{13} \text{ s}^{-1} \cdot 9.118 \times 10^{-31} \text{ m}^3 \cdot 3.297 \times 10^{-18} = 3.76 \times 10^{-35} \text{ m}^3 \text{ s}^{-1} = 3.76 \times 10^{-29} \text{ cm}^3 \text{ s}^{-1} = 2.26 \times 10^{-5} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

3. (30 points total) Consider the surface catalyzed oxidative coupling of methane (CH<sub>4</sub>) to ethane (C<sub>2</sub>H<sub>6</sub>) by the reaction mechanism shown below:



Where S is a surface site and O-S, H-S, CH<sub>3</sub>-S and OH-S are surface bound species, and S is an empty surface site. The overall reaction is 2 CH<sub>4</sub> + ½O<sub>2</sub> → C<sub>2</sub>H<sub>6</sub> + H<sub>2</sub>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).

If the surface reaction is rate limiting, then the overall rate is proportional to the rate of the irreversible surface reaction. From the overall stoichiometry, we see that each OH formed leads to production of one H<sub>2</sub>O molecule, which corresponds to consumption of 2 CH<sub>4</sub> molecules and production of 1 C<sub>2</sub>H<sub>6</sub> molecule. So, if by 'rate' we mean the rate of the reaction as written above, then

$$r = r_3 = k_3 \theta_H \theta_O$$

The adsorption/desorption steps are then very close to equilibrium and we can use the adsorption equilibrium expressions to relate the fractional coverages:

$$\theta_H \theta_{CH_3} = K_{CH_4} [CH_4] \theta_S^2$$

$$\theta_O^2 = K_{O_2} [O_2] \theta_S^2$$

$$\theta_{CH_3}^2 = K_{C_2H_6} [C_2H_6] \theta_S^2$$

$$\theta_H \theta_{OH} = K_{H_2O} [H_2O] \theta_S^2$$

and we also have the overall site balance

$$\theta_H + \theta_{CH_3} + \theta_O + \theta_{OH} + \theta_S = 1$$

This works out well – we have five equations in five unknowns

Solving the equilibrium relationships for the H, O, and OH fractional coverages in terms of the vacant site fractional coverage gives:

$$\theta_H = K_{CH_4} [CH_4] \theta_S^2 / \theta_{CH_3} = K_{CH_4} [CH_4] / (K_{C_2H_6} [C_2H_6])^{1/2} * \theta_S$$

$$\begin{aligned}\theta_O &= (K_{O_2}[O_2])^{1/2} \theta_S \\ \theta_{CH_3} &= (K_{C_2H_6}[C_2H_6])^{1/2} \theta_S \\ \theta_{OH} &= K_{H_2O}[H_2O] \theta_S^2 / \theta_H = K_{H_2O}[H_2O] (K_{C_2H_6}[C_2H_6])^{1/2} / (K_{CH_4}[CH_4]) * \theta_S\end{aligned}$$

Substituting the equilibrium relationships into the site balance gives

$$(K_{CH_4}[CH_4]/(K_{CH_3}[CH_3])^{1/2} + (K_{O_2}[O_2])^{1/2} + (K_{CH_3}[CH_3])^{1/2} + K_{H_2O}[H_2O](K_{CH_3}[CH_3])^{1/2}/(K_{CH_4}[CH_4]) + 1) \theta_S = 1$$

From which

$$\theta_S = \frac{1}{1 + \frac{\sqrt{K_{C_2H_6}[C_2H_6]} + \sqrt{K_{O_2}[O_2]} + K_{CH_4}[CH_4]/\sqrt{K_{C_2H_6}[C_2H_6]} + K_{H_2O}[H_2O]\sqrt{K_{C_2H_6}[C_2H_6]}/K_{CH_4}[CH_4]}$$

$$\theta_O = \frac{\sqrt{K_{O_2}[O_2]}}{1 + \frac{\sqrt{K_{C_2H_6}[C_2H_6]} + \sqrt{K_{O_2}[O_2]} + K_{CH_4}[CH_4]/\sqrt{K_{C_2H_6}[C_2H_6]} + K_{H_2O}[H_2O]\sqrt{K_{C_2H_6}[C_2H_6]}/K_{CH_4}[CH_4]}$$

$$\theta_H = \frac{\frac{K_{CH_4}[CH_4]}{\sqrt{K_{C_2H_6}[C_2H_6]}}}{1 + \frac{\sqrt{K_{C_2H_6}[C_2H_6]} + \sqrt{K_{O_2}[O_2]} + K_{CH_4}[CH_4]/\sqrt{K_{C_2H_6}[C_2H_6]} + K_{H_2O}[H_2O]\sqrt{K_{C_2H_6}[C_2H_6]}/K_{CH_4}[CH_4]}$$

$$\theta_{OH} = \frac{\frac{K_{H_2O}[H_2O]\sqrt{K_{C_2H_6}[C_2H_6]}}{K_{CH_4}[CH_4]}}{1 + \frac{\sqrt{K_{C_2H_6}[C_2H_6]} + \sqrt{K_{O_2}[O_2]} + K_{CH_4}[CH_4]/\sqrt{K_{C_2H_6}[C_2H_6]} + K_{H_2O}[H_2O]\sqrt{K_{C_2H_6}[C_2H_6]}/K_{CH_4}[CH_4]}$$

$$\theta_{CH_3} = \frac{\sqrt{K_{C_2H_6}[C_2H_6]}}{1 + \frac{\sqrt{K_{C_2H_6}[C_2H_6]} + \sqrt{K_{O_2}[O_2]} + K_{CH_4}[CH_4]/\sqrt{K_{C_2H_6}[C_2H_6]} + K_{H_2O}[H_2O]\sqrt{K_{C_2H_6}[C_2H_6]}/K_{CH_4}[CH_4]}$$

Substituting these expressions for  $\theta_H$  and  $\theta_O$  into  $r = r_3 = k_3 \theta_H \theta_O$  gives

$$r = k_3 \theta_H \theta_O = \frac{\sqrt{K_{O_2}[O_2]} K_{CH_4}[CH_4] / \sqrt{K_{C_2H_6}[C_2H_6]}}{\left(1 + \frac{\sqrt{K_{C_2H_6}[C_2H_6]} + \sqrt{K_{O_2}[O_2]} + K_{CH_4}[CH_4]/\sqrt{K_{C_2H_6}[C_2H_6]} + K_{H_2O}[H_2O]\sqrt{K_{C_2H_6}[C_2H_6]}/K_{CH_4}[CH_4]}{\right)^2}$$

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  $r = k_{eff}[CH_4]$ . The active catalyst is supported on porous alumina spheres. The effective surface rate constant, ( $k_{eff}$  in  $r = k_{eff}[CH_4]$ ) for the conditions in the reactor is  $2 \times 10^{-7}$  cm/s. The catalyst density is  $\rho_c = 1.8$  g/cm<sup>3</sup>. The catalyst specific surface area is  $40$  m<sup>2</sup> g<sup>-1</sup>. The effective diffusion coefficient for H<sub>2</sub> in the gas mixture in the catalyst pores is  $D_e = 0.02$  cm<sup>2</sup> s<sup>-1</sup>.

- (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)

The rate per catalyst mass will be the rate per surface area times the surface area per catalyst mass. The rate per surface area is  $r_s = 2 \times 10^{-7} \text{ cm/s} * 2 \times 10^{-6} \text{ mol cm}^{-3} = 4 \times 10^{-13} \text{ mol cm}^{-3} \text{ s}^{-1}$ . Multiplying this by the specific surface area of  $40 \text{ m}^2 \text{ g}^{-1} = 4 \times 10^5 \text{ cm}^2 \text{ g}^{-1}$  gives  $r_m = 4 \times 10^{-13} \text{ mol cm}^{-3} \text{ s}^{-1} * 4 \times 10^5 \text{ cm}^2 (\text{g cat})^{-1} = 1.6 \times 10^{-7} \text{ mol (g cat)}^{-1} \text{ s}^{-1}$ .

- (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)

For a spherical catalyst pellet, we know that the effectiveness factor for this first-order reaction will be given by

$$\eta = \frac{3 \phi \coth(\phi) - 1}{\phi}$$

where the Thiele modulus is defined by

$$\phi = R \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \epsilon_s^2}} \quad \text{or} \quad \eta = \frac{1}{\phi} \frac{3 \phi \coth(3\phi) - 1}{3\phi} \quad \text{with} \quad \phi = \frac{R}{3} \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \epsilon_s^2}}$$

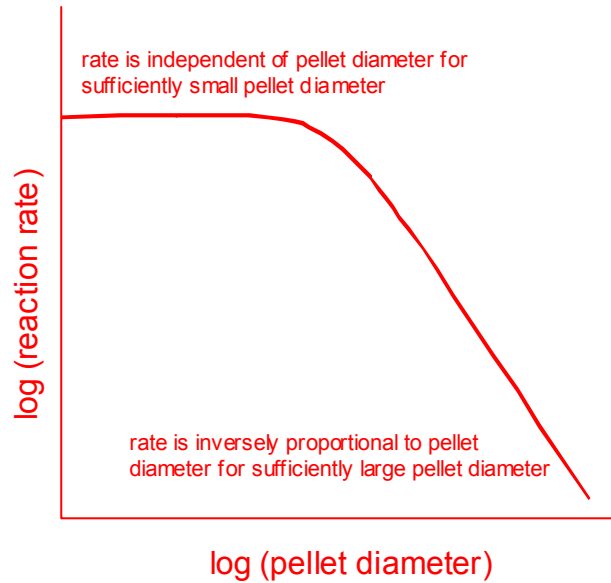
We first need to compute the value of the Thiele modulus for which the effectiveness factor is 0.2 (so the rate is equal to 20% of what it would be with no diffusional limitations). This should be for a value of the Thiele modulus (with the first definition) of around 15, since this effectiveness factor corresponds to fairly large diffusion limitations, where the effectiveness factor goes to  $3/\phi$ . A little trial and error using the expression for the Thiele modulus from above shows that  $\eta = 0.2$  for  $\phi = 13.9$  (with the first definition of  $\phi$ , or 4.63 with the second definition). Using the corresponding definition of the Thiele modulus given in part (c), we have

$$\phi = R \sqrt{\frac{S_g \rho_c k_r \tau}{D_{Ae}}} = 13.9 = \frac{d(\text{cm})}{2} \sqrt{\frac{400000 (\text{cm}^2/\text{g}) 1.8 (\text{g}/\text{cm}^3) 0.0000007 (\text{cm}/\text{s})}{0.02 (\text{cm}^2/\text{s})}} = 1.34d(\text{cm})$$

from which  $d = 13.9/1.34 = 10.4 \text{ cm}$ .

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

The reaction rate is proportional to the effectiveness factor, and the Thiele modulus is proportional to the pellet diameter, so a plot of the reaction rate vs. pellet diameter will have the same shape as a plot of effectiveness factor vs. Thiele modulus. This familiar plot looks like:



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)

We can write such a reaction as the generic unimolecular decomposition  $A \rightarrow B + C$ , where in this case A is chloroethane, B is ethylene, and C is HCl.

The simplest model of this process that gives a qualitatively correct picture of the pressure dependence is the Lindemann-Hinshelwood model, in which we assume that the reaction occurs in 2 steps - an energy transfer step followed by a reaction step:



Where  $A^*$  denotes a chloroethane molecule that has enough energy to react, and  $[M]$  is the total concentration of all species in the gas mixture ( $p/(RT)$  in terms of the pressure). Since  $A^*$  is a short-lived reactive entity, we can apply the steady-state approximation to it to get

$$\frac{d[A^*]}{dt} = 0 = r_1 - r_2 = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*]$$

from which  $r_1 = r_2$ , and

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

The overall reaction rate is then given by  $r = r_1 = r_2 = k_2[A^*]$ , or

$$r = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2} [A]$$

And the effective unimolecular rate constant is

$$k_{uni} = \frac{r}{[A]} = \frac{k_1 k_2 [M]}{k_{-1} [M] + k_2}$$

- (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)

For very high pressures,  $k_{-1}[M] \gg k_2$ , so  $k_2$  can be neglected in the denominator of  $k_{uni}$  leaving the high-pressure limiting rate constant, which we usually call  $k_\infty$ .

$$k_\infty = \frac{k_1 k_2 [M]}{k_{-1} [M]} = \frac{k_1 k_2}{k_{-1}}$$

Conversely, for very low pressures  $k_{-1}[M] \ll k_2$ , so  $k_{-1}[M]$  can be neglected in the denominator of  $k_{uni}$  leaving the low-pressure limiting rate constant, which we usually call  $k_0[M]$

$$k_0[M] = \frac{k_1 k_2 [M]}{k_2} = k_1 [M]$$

In the high-pressure limit, the unimolecular rate constant is independent of pressure, while in the low-pressure limit, it is directly proportional to pressure. Therefore, a log-log plot of the unimolecular rate constant vs. pressure over a wide range of pressures will look like:

