

## CE 561, Exam 1, November 1, 2006

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.

1. (33 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  $C_{A0}$ .

- (1)  $A \rightarrow B + C$  with  $r_1 = k_1 C_A$
- (2)  $B \leftrightarrow C$  with  $r_2 = k_2 C_B - k_3 C_C$

(a) Write these reactions in matrix form (4 points).

In matrix form, these can be written as:

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

If the forward and reverse directions of the second reaction are treated as separate reactions, or as

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

If the second reaction is treated as a single reaction

(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 (4 points).

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

$$\frac{d}{dt} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & k_3 \\ k_1 & k_2 & -k_3 \end{bmatrix} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

(c) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*) (4 points).

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

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

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

(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 (4 points).

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

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

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

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

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.

(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  $C_A = C_{A0}$ ,  $C_B = C_C = 0$  (13 points).

Since the first reaction is irreversible, the concentration of A is not dependent on the concentration of B or C. So, we can solve for the concentration of A separately. The rate equation for A is our favorite ODE,

$$\frac{dC_A}{dt} = -k_1 C_A \text{ with } C_A(t = 0) = C_{A0}$$

for which we have the familiar solution

$$C_A = C_{A0} \exp(-k_1 t)$$

The rate equations for B and C are then

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B + k_3 C_C$$

$$\frac{dC_C}{dt} = k_1 C_A + k_2 C_B - k_3 C_C$$

Adding these, we have

$$\frac{d(C_B + C_C)}{dt} = 2k_1 C_A$$

Substituting the solution for  $C_A$  into this

$$\frac{d(C_B + C_C)}{dt} = 2k_1 C_{A0} \exp(-k_1 t)$$

Integrating this with respect to  $t$  gives

$$C_B + C_C = K - 2C_{A0} \exp(-k_1 t)$$

Where  $K$  is a constant of integration. Applying the initial condition that  $C_B + C_C = 0$  at  $t = 0$  shows that  $K = 2C_{A0}$ . Thus,

$$C_B + C_C = 2C_{A0} (1 - \exp(-k_1 t))$$

Solving this for  $C_C$  in terms of  $C_B$ :

$$C_C = 2C_{A0} (1 - \exp(-k_1 t)) - C_B$$

Substituting this into the rate equation for B gives a single ODE for  $C_B$ :

$$\frac{dC_B}{dt} = k_1 C_{A0} \exp(-k_1 t) - k_2 C_B + k_3 (2C_{A0} (1 - \exp(-k_1 t)) - C_B)$$

$$\frac{dC_B}{dt} + (k_2 + k_3) C_B = C_{A0} (2k_3 + (k_1 - 2k_3) \exp(-k_1 t))$$

Now, we can guess that the solution will be of the form

$$C_B = f(t) \exp(-(k_2 + k_3)t)$$

For which

$$\frac{dC_B}{dt} = -(k_2 + k_3) f(t) \exp(-(k_2 + k_3)t) + \frac{df}{dt} \exp(-(k_2 + k_3)t)$$

Substituting this into the ODE for  $C_B$ :

$$-(k_2 + k_3) f(t) \exp(-(k_2 + k_3)t) + \frac{df}{dt} \exp(-(k_2 + k_3)t) + (k_2 + k_3) f(t) \exp(-(k_2 + k_3)t) = C_{A0} (2k_3 + (k_1 - 2k_3) \exp(-k_1 t))$$

The first and third terms on the LHS cancel as expected, and we are left with

$$\frac{df}{dt} = C_{A0} (2k_3 + (k_1 - 2k_3) \exp(-k_1 t)) \exp((k_2 + k_3)t)$$

$$\frac{df}{dt} = C_{A0} (2k_3 \exp((k_2 + k_3)t) + (k_1 - 2k_3) \exp((k_2 + k_3 - k_1)t))$$

Integrating with respect to  $t$  gives

$$f = K + C_{A0} \left( \frac{2k_3}{k_2 + k_3} \exp((k_2 + k_3)t) + \frac{k_1 - 2k_3}{k_2 + k_3 - k_1} \exp((k_2 + k_3 - k_1)t) \right)$$

Where  $K$  is a constant of integration. Applying the initial condition that  $C_B(t=0) = 0$ , and therefore  $f(t=0) = 0$ , we have

$$K = -C_{A0} \left( \frac{2k_3}{k_2 + k_3} + \frac{k_1 - 2k_3}{k_2 + k_3 - k_1} \right)$$

And therefore

$$f = C_{A0} \left( \frac{2k_3}{k_2 + k_3} (\exp((k_2 + k_3)t) - 1) + \frac{k_1 - 2k_3}{k_2 + k_3 - k_1} (\exp((k_2 + k_3 - k_1)t) - 1) \right)$$

And

$$C_B = C_{A_0} \left( \frac{2k_3}{k_2 + k_3} (1 - \exp(-(k_2 + k_3)t)) + \frac{k_1 - 2k_3}{k_2 + k_3 - k_1} (\exp(-k_1t) - \exp(-(k_2 + k_3)t)) \right)$$

And finally

$$C_C = C_{A_0} \left( 2(1 - \exp(-k_1t)) - \frac{2k_3}{k_2 + k_3} (1 - \exp(-(k_2 + k_3)t)) - \frac{k_1 - 2k_3}{k_2 + k_3 - k_1} (\exp(-k_1t) - \exp(-(k_2 + k_3)t)) \right)$$

- (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 (4 pts).

If the time interval is sufficiently short that, at most, one reaction occurs, then there are two possible ways to have  $j+1$  B molecules: by reaction 1, with rate  $k_1i$  or by the reverse of reaction 2, with rate  $k_3k$ . So, the total probability of having  $j+1$  molecules at time  $t+\Delta t$  is

$$P_{j+1}(t+\Delta t) = W_{j+1}(\Delta t) = k_1i\Delta t + k_3k\Delta t = (k_1i + k_3k) \Delta t$$

2. (22 points total) Consider the elementary gas phase reaction  $\text{AlCl} + \text{HCl} \leftrightarrow \text{AlCl}_2 + \text{H}$ . 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  $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .

	AlCl	HCl	AlCl <sub>2</sub>	H	Transition State
<b>M (amu)</b>	62.43	36.46	97.88	1.01	98.89
<b>I (amu Å<sup>2</sup>)</b>	69.8	1.62	22.6, 235, 258		29.0, 245, 274
<b>ΔH<sub>f</sub>(0 K) (kJ/mol)</b>	-64.2	-92.4	-238.4	216.0	-17.9
<b>ν (cm<sup>-1</sup>)</b>	473	2845	148, 451, 567		1275 <sub>i</sub> , 113, 285, 309, 429, 524
<b>g<sub>elec</sub></b>	1	1	2	2	1
<b>σ (rotational symmetry number)</b>	1	1	2		1
<b>Hard Sphere Collision Diameter (Å)</b>	3.8	3.5	4.8	2.0	5.0

- (a) What is the hard-sphere collisional rate constant for collisions between AlCl and HCl at 1000 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

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

and the reduced mass for the colliding particles is

$$\mu = \frac{m_{\text{AlCl}} m_{\text{HCl}}}{m_{\text{AlCl}} + m_{\text{HCl}}} = \frac{62.43 \cdot 36.46}{62.43 + 36.46} \times \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 3.82 \times 10^{-26} \text{ kg}$$

so

$$k_{coll} = 4.19 \times 10^{-19} \text{ m}^2 \left( \frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{\pi(3.82 \times 10^{-26} \text{ kg})} \right)^{1/2} = 4.02 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 2.42 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

- (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 (4 points).

The enthalpy of formation of the reactants at 0 K is  $-64.2 - 92.4 = -156.6 \text{ kJ/mol}$ .

The enthalpy of formation of the transition state at 0 K is  $-17.9 \text{ kJ/mol}$ .

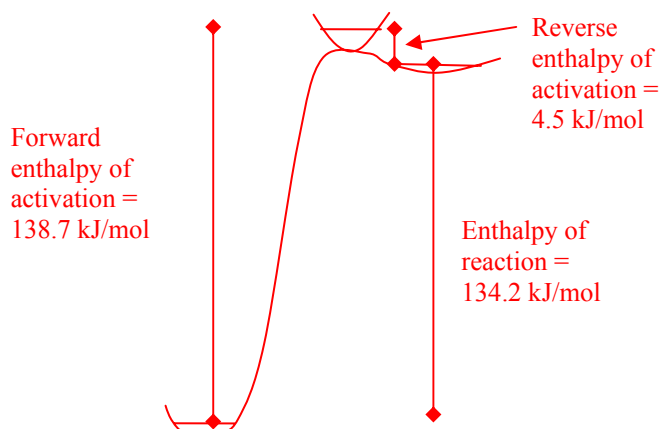
The enthalpy of formation of the products at 0 K is  $-238.4 + 216.0 = -22.4 \text{ kJ/mol}$ .

So, the forward enthalpy of activation is  $-17.9 - (-156.6) = 138.7 \text{ kJ/mol}$ ,

and the reverse enthalpy of activation is  $-17.9 - (-22.4) = 4.5 \text{ kJ/mol}$ ,

and the enthalpy of reaction is  $-22.4 - (-156.6) = 134.2 \text{ kJ/mol}$

A sketch of the reaction energetics thus looks like this:



(c) Using transition state theory, calculate the forward rate constant for this reaction at 1000 K (13 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 AlCl, a diatomic molecule,

$$Q_{\text{trans}}/V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \left(\frac{2\pi(62.43/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2}\right)^{3/2} = 2.93 \times 10^{33} \text{ m}^{-3}$$

$$Q_{\text{vib}} = \frac{1}{1 - \exp\left(\frac{-h\nu}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-1.44 \text{ (cm K)} \nu}{1000 \text{ K}}\right)}$$

$$Q_{\text{vib}} = \frac{1}{\left(1 - \exp\left(\frac{-1.44 * 473}{1000}\right)\right)} = 2.024$$

$$Q_{\text{rot}} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\pi^2 (69.8/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2} = 2879$$

$$Q_{\text{elec}} = 1$$

$$\text{so } Q_{\text{AlCl}}/V = 2.93 \times 10^{33} * 2.024 * 2879 = 1.71 \times 10^{37} \text{ m}^{-3}$$

For HCl, also a diatomic molecule,

$$Q_{trans}/V = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} = \left( \frac{2\pi (36.46/6.022 \times 10^{26}) \text{kg} (1.381 \times 10^{-23}) \text{J K}^{-1} (1000) \text{K}}{(6.626 \times 10^{-34} \text{J s})^2} \right)^{3/2} = 1.309 \times 10^{33} \text{m}^{-3}$$

$$Q_{vib} = \frac{1}{1 - \exp\left(\frac{-hv}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-1.44 \text{ (cm K)} \bar{\nu}}{1000 \text{ K}}\right)}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-1.44 * 2984}{1000}\right)\right)} = 1.014$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\pi^2 (1.62/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{J K}^{-1} (1000) \text{K}}{1 (6.626 \times 10^{-34} \text{J s})^2} = 66.8$$

$$Q_{elec} = 1$$

$$\text{so } Q_{HCl}/V = 1.309 \times 10^{33} * 1.014 * 66.8 = 8.86 \times 10^{34} \text{m}^{-3}$$

Finally, the transition state is a nonlinear polyatomic molecule (with 3 distinct moments of inertia and  $3N - 6 = 6$  vibrational frequencies (including the imaginary vibrational frequency that corresponds to the reaction coordinate and that is excluded from the partition function calculation). For it, we have:

$$Q_{trans}/V = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} = \left( \frac{2\pi (98.89/6.022 \times 10^{26}) \text{kg} (1.381 \times 10^{-23}) \text{J K}^{-1} (1000) \text{K}}{(6.626 \times 10^{-34} \text{J s})^2} \right)^{3/2} = 5.847 \times 10^{33} \text{m}^{-3}$$

$$Q_{vib} = \frac{1}{\prod_i 1 - \exp\left(\frac{-hv_i}{kT}\right)} = \frac{1}{\prod_i 1 - \exp\left(\frac{-1.44 \text{ (cm K)} \bar{\nu}_i}{1000 \text{ K}}\right)}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-113}{694.4}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-285}{694.4}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-309}{694.4}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-429}{694.4}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-524}{694.4}\right)\right)}$$

$$Q_{vib} = 6.659 * 2.971 * 2.784 * 2.170 * 1.887 = 225.5$$

$$Q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{8\pi^2 I_A kT}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_B kT}{h^2} \right)^{1/2} \left( \frac{8\pi^2 I_C kT}{h^2} \right)^{1/2}$$

$$Q_{rot} = \frac{\sqrt{\pi}}{1} \left( \frac{8\pi^2 (1/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{J K}^{-1} (1000) \text{K}}{1 (6.626 \times 10^{-34} \text{J s})^2} \right)^{3/2} (I_A I_B I_C)^{1/2}$$

$$Q_{rot} = 469.4 (29.0 * 245 * 274)^{1/2} = 6.55 \times 10^5$$

$$Q_{elec} = 1$$

$$\text{so } Q_{TS}/V = 5.847 \times 10^{33} * 225.5 * 6.55 \times 10^5 = 8.64 \times 10^{41} \text{m}^{-3}$$

So, the forward rate constant is:

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

$$k_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{8.636 \times 10^{41} \text{ m}^{-3}}{1.71 \times 10^{37} \text{ m}^{-3} \cdot 8.86 \times 10^{34} \text{ m}^{-3}} \exp\left(\frac{-138700 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (1000) \text{ K}}\right)$$

$$k_f = 2.084 \times 10^{13} \text{ s}^{-1} \cdot 5.700 \times 10^{-31} \text{ m}^3 \cdot 5.686 \times 10^{-8} = 6.75 \times 10^{-25} \text{ m}^3 \text{ s}^{-1} = 6.75 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} = 407000 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

3. (36 points total) Consider the catalytic combustion of hydrogen ( $H_2$ ) by the reaction mechanism shown below:



Where O-S, H-S, and OH-S are surface species, and S is an empty surface site. The overall reaction is  $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ . Adsorption and reaction steps obey mass action kinetics.

- (a) Derive a rate expression for the overall reaction in terms of the forward and reverse rate constants of the four reactions, assuming that desorption of water is rate-limiting (13 points).

If the final step,  $H_2O$  desorption, is rate limiting, then the overall reaction rate will be equal to the rate of this step. The rate of production of  $H_2O$  is equal to the rate of this step, and the rate of production of  $H_2O$  is also the overall reaction rate. If  $H_2O$  desorption is rate limiting, then we can assume that the other three reactions are approximately in equilibrium:

$$r_1 = k_{1f} [H_2] \theta_s^2 - k_{1r} \theta_H^2 \approx 0$$

$$\theta_H = \sqrt{\frac{k_{1f} [H_2]}{k_{1r}}} \theta_s = \sqrt{K_1 [H_2]} \theta_s$$

$$r_2 = k_{2f} [O_2] \theta_s^2 - k_{2r} \theta_O^2 \approx 0$$

$$\theta_O = \sqrt{\frac{k_{2f} [O_2]}{k_{2r}}} \theta_s = \sqrt{K_2 [O_2]} \theta_s$$

$$r_3 = k_{3f} \theta_H \theta_O - k_{3r} \theta_{OH} \theta_s \approx 0$$

$$\theta_{OH} = \frac{k_{3f} \theta_H \theta_O}{k_{3r} \theta_s} = \frac{K_3 \theta_H \theta_O}{\theta_s} = \frac{K_3 \sqrt{K_1 [H_2]} \theta_s \sqrt{K_2 [O_2]} \theta_s}{\theta_s}$$

$$\theta_{OH} = K_3 \sqrt{K_1 [H_2] K_2 [O_2]} \theta_s$$

As shown above, the equilibrium relationships for the three reactions allow us to write each of the other surface coverages in terms of the coverage of empty sites,  $\theta_s$ . We can then solve for  $\theta_s$  using the overall site balance and substitute the result into the above expressions to get all of the surface site fractions:

$$\theta_s + \theta_H + \theta_O + \theta_{OH} = 1$$

$$\theta_s \left( 1 + \sqrt{K_1 [H_2]} + \sqrt{K_2 [O_2]} + K_3 \sqrt{K_1 [H_2] K_2 [O_2]} \right) = 1$$

$$\theta_s = \frac{1}{1 + \sqrt{K_1 [H_2]} + \sqrt{K_2 [O_2]} + K_3 \sqrt{K_1 [H_2] K_2 [O_2]}}$$

$$\theta_H = \frac{\sqrt{K_1 [H_2]}}{1 + \sqrt{K_1 [H_2]} + \sqrt{K_2 [O_2]} + K_3 \sqrt{K_1 [H_2] K_2 [O_2]}}$$

$$\theta_O = \frac{\sqrt{K_2 [O_2]}}{1 + \sqrt{K_1 [H_2]} + \sqrt{K_2 [O_2]} + K_3 \sqrt{K_1 [H_2] K_2 [O_2]}}$$

$$\theta_{OH} = \frac{K_3 \sqrt{K_1 [H_2] K_2 [O_2]}}{1 + \sqrt{K_1 [H_2]} + \sqrt{K_2 [O_2]} + K_3 \sqrt{K_1 [H_2] K_2 [O_2]}}$$

Finally, we can substitute these into the expression for the rate of the 4<sup>th</sup> (rate-limiting) step to get the overall reaction rate:

$$r = r_4 = k_{4f} \theta_H \theta_{OH} - k_{4r} [H_2O] \theta_S^2$$

$$r = \frac{k_{4f} K_3 K_1 [H_2] \sqrt{K_2 [O_2]} - k_{4r} [H_2O]}{\left(1 + \sqrt{K_1 [H_2]} + \sqrt{K_2 [O_2]} + K_3 \sqrt{K_1 [H_2] K_2 [O_2]}\right)^2}$$

Suppose that this reaction occurs at 400K and a pressure of 1 bar. Near the reactor inlet, the product (H<sub>2</sub>O) concentration is negligibly small, and the reactant concentrations are [O<sub>2</sub>] = 1.72 × 10<sup>19</sup> molecules/cm<sup>3</sup> and [H<sub>2</sub>] = 9.05 × 10<sup>17</sup> molecules/cm<sup>3</sup>. At this temperature, the adsorption equilibrium constants for H<sub>2</sub> (reaction 1) and O<sub>2</sub> (reaction 2) are 1 × 10<sup>-22</sup> cm<sup>3</sup>/molecule and 6 × 10<sup>-23</sup> cm<sup>3</sup>/molecule, respectively. The equilibrium constant for the surface hydroxyl formation (reaction 3) is 5.0 (dimensionless). The rate constant for H<sub>2</sub>O desorption (reaction 4 in the forward direction) is 3 × 10<sup>15</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>.

(b) Under these conditions, what are the approximate surface coverages (site fractions) of H, O, and OH? (4 points)

For this, we basically plug in the numbers to the expressions from part (a). We have:

$$\sqrt{K_1 [H_2]} = \sqrt{1 \times 10^{-22} \cdot 9.05 \times 10^{17}} = 0.0095$$

$$\sqrt{K_2 [O_2]} = \sqrt{6 \times 10^{-23} \cdot 1.72 \times 10^{19}} = 0.032$$

$$K_3 \sqrt{K_1 [H_2] K_2 [O_2]} = 5 \cdot 0.0095 \cdot 0.032 = 0.0015$$

Thus, the denominator in the site fraction expressions is

$$1 + \sqrt{K_1 [H_2]} + \sqrt{K_2 [O_2]} + K_3 \sqrt{K_1 [H_2] K_2 [O_2]} = 1.043$$

The site fractions are then

$$\theta_H = \frac{0.0095}{1.043} = 0.0091$$

$$\theta_O = \frac{0.0321}{1.043} = 0.031$$

$$\theta_{OH} = \frac{0.0015}{1.043} = 0.0015$$

$$\theta_S = \frac{1}{1.043} = 0.959$$

(c) Under these conditions, the reaction is approximately first order in hydrogen. That is, the overall rate is approximately  $r = k_{eff}[\text{H}_2]$ . What is the value of  $k_{eff}$ ? (4 points).

Since there is a negligible amount of water present, we can neglect the reverse of the fourth reaction (good, since we don't have a rate constant for it). Since oxygen is present in large excess, its concentration will remain approximately constant. Since oxygen is the most abundant surface species (other than vacant sites) the denominator of the rate expression will also remain approximately constant. With these assumptions, and plugging in the numbers, we get:

$$r = \frac{k_{4f}K_3K_1[\text{H}_2]\sqrt{K_2[\text{O}_2]} - k_{4r}[\text{H}_2\text{O}]}{\left(1 + \sqrt{K_1[\text{H}_2]} + \sqrt{K_2[\text{O}_2]} + K_3\sqrt{K_1[\text{H}_2]K_2[\text{O}_2]}\right)^2}$$

$$r = \frac{k_{4f}K_3K_1[\text{H}_2]\sqrt{K_2[\text{O}_2]}}{(1.043)^2}$$

$$r = \frac{3 \times 10^{15} \times 5 \times 1 \times 10^{-22} [\text{H}_2] 0.0321}{(1.043)^2} = 4.43 \times 10^{-8} [\text{H}_2]$$

From the above rate expression, paying careful attention to get the units right, we see that the effective first-order rate constant is  $4.43 \times 10^{-8}$  cm/s. The units come from the fact that the rate is in molecules  $\text{cm}^{-2} \text{s}^{-1}$  (from the surface rate constant for reaction 4) and the  $[\text{H}_2]$  concentration is being measured in molecules per  $\text{cm}^3$ .

Suppose this reaction occurs, under these conditions, on a porous monolith catalyst that can be treated as an infinite slab of thickness  $2l$ . The catalyst density is  $\rho_c = 1.2 \text{ g/cm}^3$ . Its specific surface area is  $S_g = 120 \text{ m}^2/\text{g}$ , and the effective diffusion coefficient for  $\text{H}_2$  within the catalyst is  $D_{e,\text{H}_2} = 0.08 \text{ cm}^2/\text{s}$ .

(d) What is the reaction rate *per volume of catalyst* (in molecules per second per  $\text{cm}^3$  of catalyst) under the conditions given above, if the catalyst pellets are small enough that there are no diffusional limitations? (4 points)

The reaction rate per volume of catalyst is simply the reaction rate per unit surface area multiplied by the specific surface area (area/mass) and the catalyst density (mass/volume). So, the rate per catalyst volume is:

$$r_v = 4.43 \times 10^{-8} \text{ cm/s} * 120 \text{ m}^2/\text{g} * 10^4 \text{ cm}^2/\text{m}^2 * 1.2 \text{ g/cm}^3 * [\text{H}_2] = 0.064 \text{ s}^{-1} [\text{H}_2]$$

For the initial  $\text{H}_2$  concentration of  $9.05 \times 10^{17}$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ , the initial reaction rate is

$$r_v = 5.8 \times 10^{16} \text{ molecules per second per cm}^3 \text{ of catalyst}$$

(e) Calculate the slab thickness (monolith wall thickness,  $2l$ ) for which the observed reaction rate will be half of the rate that would be obtained in the absence of any diffusion limitations. (10 points)

For this slab geometry, the effectiveness factor is given by

$$\eta = \frac{\tanh(\phi)}{\phi}$$

Where the Thiele modulus is given by

$$\phi = l \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \epsilon_s}} = l \sqrt{\frac{k_v}{D_e}} = l \sqrt{\frac{0.064 \text{ s}^{-1}}{0.08 \text{ cm}^2 \text{ s}^{-1}}} = 0.89l$$

with  $l$  in cm.

So, we want to find the value of Thiele modulus for which the effectiveness factor is 0.5. Although we cannot solve for the Thiele modulus explicitly in terms of the effectiveness factor, we can do so iteratively:

$$\eta = \frac{\tanh(\phi)}{\phi} = 0.5$$

$$\phi = \frac{\tanh(\phi)}{0.5} = 2 \tanh(\phi)$$

Starting from an initial guess of 2, this converges to give a Thiele modulus of 1.915. Thus,  $l = 1.915/0.89 = 2.15$  cm. We expect the effectiveness factor to be 0.5 for a wall thickness of  $2l = 4.3$  cm (thicker than we would ever want to make the wall).

4. Suppose benzoyl peroxide is decomposed by photolysis in water to produce benzoate free radicals at a concentration of  $10^{13}$  molecules per  $\text{cm}^3$ . Recombination of these free radicals is expected to be a diffusion-limited reaction. The diffusion coefficient of benzoate radicals in water at  $25^\circ\text{C}$  is estimated to be equal to that of benzoic acid in water:  $1.0 \times 10^{-5} \text{ cm}^2/\text{s}$ . The radicals are expected to recombine at a (center-to-center) reaction distance of about  $3.0 \text{ \AA}$ . Estimate the diffusion-limited rate constant for the benzoate radicals and the initial recombination rate. Approximately what time will be required for the radical concentration to drop to  $10^{12}$  molecules per  $\text{cm}^3$ ? (10 points).

The diffusion limited rate constant for reaction of dilute species in solution is given by

$$k_D = 4\pi Dd$$

where  $D$  is the diffusion coefficient of the reagents relative to one another, and  $d$  is the distance at which they react. For reaction of identical species, we should divide this by 2, just like we did for the collision rate in the gas phase. However, the relative diffusion coefficient will be twice the ordinary diffusion coefficient. So, we have

$$k_D = 4\pi * 10^{-5} \text{ cm}^2/\text{s} * 3 \times 10^{-8} \text{ cm} = 3.8 \times 10^{-12} \text{ cm}^3/\text{s} = 2.3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The recombination rate will be

$$r = k_D [\text{R}\cdot]^2, \text{ where } [\text{R}\cdot] \text{ is the concentration of benzoate radicals.}$$

So, initially,

$$r = 3.8 \times 10^{-12} \text{ cm}^3/\text{s} * (10^{13} \text{ cm}^{-3})^2 = 3.8 \times 10^{14} \text{ molecules cm}^{-3} \text{ s}^{-1} = 6.26 \times 10^{-10} \text{ mol cm}^{-3} \text{ s}^{-1}$$

The rate of change of radical concentration will be given by

$$\frac{dC}{dt} = -2k_D C^2$$

The initial condition for this ODE is that at  $t = 0$ ,  $C = 10^{13}$ . To solve it, we can write:

$$-\frac{dC}{C^2} = 2k_D dt$$

Integrating

$$\frac{1}{C} - \frac{1}{C_0} = 2k_D t$$

We want to find the  $t$  for which  $C$  is  $10^{12}$ . So

$$\frac{1}{10^{12}} - \frac{1}{10^{13}} = 9 \times 10^{-13} = 2k_D t = 7.6 \times 10^{-12} t$$

And finally,  $t = 0.12 \text{ s}$