

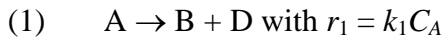
CE 561, Exam 1, October 15, 2002

This exam consists of 3 questions, each with multiple parts, plus a short bonus question at the end. 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 irreversible, first-order reactions of gas phase 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} .



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

In matrix form, these can be written as:

$$\begin{bmatrix} -1 & 1 & 0 & 1 \\ 0 & 1 & -1 & 0 \\ -1 & 0 & 2 & 0 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \end{bmatrix} = \underline{0}$$

(b) Write the rate equations for the concentrations of the four species in matrix form. Use a 4×4 matrix of rate coefficients and a four-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:

$$\frac{d}{dt} \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix} = \begin{bmatrix} -(k_1 + k_3) & 0 & 0 & 0 \\ k_1 & 0 & k_2 & 0 \\ 2k_3 & 0 & -k_2 & 0 \\ k_1 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} C_A \\ C_B \\ C_C \\ C_D \end{bmatrix}$$

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

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

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

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 λ . For each solution, λ_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.

- (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).

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 Δt 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 Δt) 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 $C_A = C_{Ao}$, $C_B = C_C = 0$ (8 points).

Since the reactions are irreversible, we can just integrate the rate equations sequentially (one at a time). The concentration of A is independent of the other concentrations. For it, we just have our favorite ODE

$$\frac{dC_A}{dt} = -(k_1 + k_3)C_A$$

with $C_A(t = 0) = C_{Ao}$. The solution to this is

$$C_A = C_{Ao} \exp(-(k_1 + k_3)t)$$

For C_B we have

$$\frac{dC_B}{dt} = k_1 C_A + k_2 C_C = k_1 C_{Ao} \exp(-(k_1 + k_3)t) + k_2 C_C$$

This one has C_C in it, so we don't want to solve it until after we've solved for C_C .

For C_C we have

$$\frac{dC_C}{dt} = 2k_3C_A - k_2C_C = 2k_3C_{A_0} \exp(-(k_1 + k_3)t) - k_2C_C$$

If C_C is of the form $C_C(t) = f(t) \exp(-k_2t)$, and we substitute it into the above equation, then

$$\frac{dC_C}{dt} = \frac{df}{dt} \exp(-k_2t) - k_2f \exp(-k_2t) = 2k_3C_{A_0} \exp(-(k_1 + k_3)t) - k_2f \exp(-k_2t)$$

$$\frac{df}{dt} = 2k_3C_{A_0} \exp((k_2 - k_1 - k_3)t)$$

$$f = \frac{2k_3C_{A_0}}{k_2 - k_1 - k_3} \exp((k_2 - k_1 - k_3)t) + A$$

where A is a constant of integration, so

$$C_C = \frac{2k_3C_{A_0}}{k_2 - k_1 - k_3} \exp(-(k_1 + k_3)t) + A \exp(-k_2t)$$

at $t = 0$,

$$C_C = \frac{2k_3C_{A_0}}{k_2 - k_1 - k_3} + A = 0$$

so

$$A = -\frac{2k_3C_{A_0}}{k_2 - k_1 - k_3}$$

and

$$C_C = \frac{2k_3C_{A_0}}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t))$$

For C_D we have

$$\frac{dC_D}{dt} = k_1C_A = k_1C_{A_0} \exp(-(k_1 + k_3)t)$$

We can integrate this directly to give

$$C_D = A - \frac{k_1C_{A_0}}{k_1 + k_3} \exp(-(k_1 + k_3)t)$$

where A is a constant of integration again

At $t = 0$,

$$C_D = A - \frac{k_1C_{A_0}}{k_1 + k_3} = 0$$

so this time

$$A = \frac{k_1C_{A_0}}{k_1 + k_3}$$

and

$$C_D = \frac{k_1C_{A_0}}{k_1 + k_3} (1 - \exp(-(k_1 + k_3)t))$$

Finally, we can go back and solve for C_B , since we now know everything else. One way to do this would be to substitute our solution for C_C into the equation for C_B given above and then solve for C_B like we solved for C_C . Alternatively, we can add up 2 times the first rate equation plus all the others to get:

$$\frac{d}{dt}(2C_A + C_B + C_C + C_D) = -2(k_1 + k_3)C_A + k_1C_A + k_2C_C + 2k_3C_A - k_2C_C + k_1C_A$$

$$\frac{d}{dt}(2C_A + C_B + C_C + C_D) = 0$$

$$2C_A + C_B + C_C + C_D = \text{a constant} = 2C_{A0}$$

So, we have the stoichiometric constraint that we would expect:

$$C_B = 2C_{A0} - 2C_A - C_C - C_D$$

$$C_B = C_{A0} \left(2 - 2\exp(-(k_1 + k_3)t) - \frac{2k_3}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t)) - \frac{k_1}{k_1 + k_3} (1 - \exp(-k_1t)) \right)$$

- (f) Derive an equation for the *scaled sensitivity* of the concentration of species C to the rate constant for the reaction $A \rightarrow B + D$ (7 points).

By definition, this scaled sensitivity coefficient is

$$\sigma_{31} = \frac{k_1}{C_C} \frac{\partial C_C}{\partial k_1}$$

So, all we have to do is take the partial derivative of the expression from (e) for C_C with respect to k_1 :

$$\sigma_{31} = \frac{k_1}{\frac{2k_3C_{A0}}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t))} \frac{\partial}{\partial k_1} \left(\frac{2k_3C_{A0}}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t)) \right)$$

$$\sigma_{31} = \frac{k_1}{\frac{2k_3C_{A0}}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t))} \left(\frac{2k_3C_{A0}}{k_2 - k_1 - k_3} \left(-t \exp(-(k_1 + k_3)t) + \frac{1}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t)) \right) \right)$$

$$\sigma_{31} = \frac{k_1 \left(-t \exp(-(k_1 + k_3)t) + \frac{1}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t)) \right)}{(\exp(-(k_1 + k_3)t) - \exp(-k_2t))}$$

We see that even though the rate equation for C_C does not depend explicitly on k_1 (species C isn't involved in reaction 1), changing k_1 still has an effect on C_C .

2. (40 points total) Consider the elementary gas phase reaction $\text{SiCl} + \text{HCl} \leftrightarrow \text{SiCl}_2 + \text{H}$. 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 $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

	SiCl	HCl	SiCl₂	H	Transition State
M (amu)	63.54	36.46	98.99	1.01	100
I (amu Å²)	67.3	1.62	34.6; 182.1; 216.6		41.5; 197.0; 236.0
ΔH_f(0 K) (kJ/mol)	145.2	-92.3	-174.4	216.0	103.4
ν (cm⁻¹)	539	2984	207; 534; 534		2410i; 161; 302; 322; 483; 528
g_{elec}	2	1	1	2	2
σ (rotational symmetry number)	1	1	2		1
Hard Sphere Collision Diameter (Å)	4.3	3.8	4.8	2.0	5.0

- (a) How many translational, rotational, and vibrational degrees of freedom do each of the reactants, transition state, and products have? (5 points).

SiCl is a diatomic molecule (and therefore linear). It has 3 translational, 2 rotational, and 1 vibrational degree of freedom.

HCl is a diatomic molecule (and therefore linear). It has 3 translational, 2 rotational, and 1 vibrational degree of freedom.

SiCl₂ is a non-linear triatomic molecule. We can tell that it is non-linear because it has 3 distinct moments of inertia, as given in the table. It has 3 translational, 3 rotational, and 3 vibrational degrees of freedom.

H is an atom. It has 3 translational degrees of freedom and no rotational or vibrational degrees of freedom.

The transition state is a tetraatomic structure and is non-linear. Again, we can tell that it is non-linear because it has 3 distinct moments of inertia, as given in the table. It therefore has 3 translational degrees of freedom, 3 rotational degrees of freedom, and 5 vibrational degrees of freedom. Its final degree of freedom is the reaction coordinate (treated as a translational degree of freedom in transition state theory, but listed as a vibrational degree of freedom with an imaginary vibrational frequency in the table).

- (b) What is the hard-sphere collisional rate constant for collisions between SiCl 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 σ is given by

$$\sigma = \pi \left(\frac{d_{SiCl} + d_{HCl}}{2} \right)^2 = \pi \left(\frac{4.3 + 3.8}{2} \times 10^{-10} \text{ m} \right)^2 = 5.15 \times 10^{-19} \text{ m}^2$$

and the reduced mass for the colliding particles is

$$\mu = \frac{m_{SiCl} m_{HCl}}{m_{SiCl} + m_{HCl}} = \frac{63.54 \cdot 36.46}{63.54 + 36.46} \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 3.85 \times 10^{-26} \text{ kg}$$

so

$$k_{coll} = 5.15 \times 10^{-19} \text{ m}^2 \left(\frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(800\text{K})}{\pi(3.85 \times 10^{-26} \text{ kg})} \right)^{1/2} = 4.40 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 2.65 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

(c) 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 $145.2 - 92.3 = 52.9 \text{ kJ/mol}$.

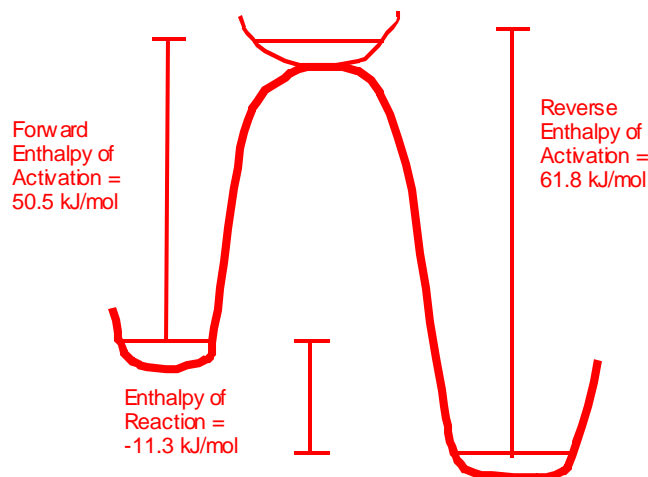
The enthalpy of formation of the transition state at 0 K is 103.4 kJ/mol .

The enthalpy of formation of the products at 0 K is $-174.4 + 216.0 = 41.6 \text{ kJ/mol}$.

So, the forward enthalpy of activation is $103.4 - 52.9 = 50.5 \text{ kJ/mol}$,

and the reverse enthalpy of activation is $103.4 - 41.6 = 61.8 \text{ kJ/mol}$,

and the enthalpy of reaction is $41.6 - 52.9 = -11.3 \text{ kJ/mol}$



(d) Using transition state theory, calculate the forward rate constant, the reverse rate constant, and the equilibrium constant for this reaction at 800 K (20 points).

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

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

Likewise, the reverse rate constant is given by

$$k_r = \frac{kT}{h} \frac{(Q_{TS}^\ddagger / V)}{(Q_{SiCl_2} / V)(Q_H / V)} \exp\left(\frac{-E_{o,r}}{kT}\right)$$

and the equilibrium constant is just the ratio of the forward to reverse rate constants

The Partition Functions are as follows:

For SiCl, a diatomic molecule,

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \left(\frac{2\pi (63.54 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 2.155 \times 10^{33} \text{ m}^{-3}$$

$$Q_{vib} = \frac{1}{1 - \exp\left(\frac{-h\nu}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-1.44 \text{ (cm K)} \bar{\nu}}{800 \text{ K}}\right)}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-539}{555.6}\right)\right)} = 1.610$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\pi^2 (67.3 / 6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2} = 2220$$

$$Q_{elec} = 2$$

$$\text{so } Q_{SiCl}/V = 2.155 \times 10^{33} * 1.61 * 2220 * 2 = 1.540 \times 10^{37} \text{ m}^{-3}$$

For HCl, a diatomic molecule,

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \left(\frac{2\pi (36.46 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 9.366 \times 10^{32} \text{ m}^{-3}$$

$$Q_{vib} = \frac{1}{1 - \exp\left(\frac{-h\nu}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-1.44 \text{ (cm K)} \bar{\nu}}{800 \text{ K}}\right)}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-2984}{555.6}\right)\right)} = 1.005$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\pi^2 (1.62 / 6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2} = 53.4$$

$$Q_{elec} = 1$$

$$\text{so } Q_{HCl}/V = 9.366 \times 10^{32} * 1.005 * 53.4 = 5.029 \times 10^{34} \text{ m}^{-3}$$

For SiCl₂, a nonlinear triatomic molecule,

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \left(\frac{2\pi (98.99 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 4.190 \times 10^{33} \text{ m}^{-3}$$

$$Q_{vib} = \prod_i \frac{1}{1 - \exp\left(\frac{-h\nu_i}{kT}\right)} = \prod_i \frac{1}{1 - \exp\left(\frac{-1.44 (\text{cm K}) \bar{\nu}_i}{800 \text{ K}}\right)}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-207}{555.6}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-539}{555.6}\right)\right)^2} = 8.338$$

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

$$Q_{rot} = \frac{\sqrt{\pi}}{2} \left(\frac{8\pi^2 (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2 6.022 \times 10^{46}} \right)^{3/2} (34.6 * 182.1 * 216.6)^{1/2} = 1.962 \times 10^5$$

$$Q_{elec} = 1$$

$$\text{so } Q_{SiCl_2}/V = 4.190 \times 10^{33} * 8.338 * 1.962 \times 10^5 = 6.854 \times 10^{39} \text{ m}^{-3}$$

For H, an atom,

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \left(\frac{2\pi (1.01 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 4.305 \times 10^{30} \text{ m}^{-3}$$

and

$$Q_{elec} = 2$$

$$\text{so } Q_H/V = 8.611 \times 10^{30}$$

Finally, the transition state is another non-linear structure, so its partition functions are like those of SiCl₂. We exclude the reaction coordinate (the motion with the imaginary vibrational frequency) from the computation:

$$Q_{trans}/V = \left(\frac{2\pi (100.0 / 6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 4.254 \times 10^{33} \text{ m}^{-3}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-161}{555.6}\right)\right) \left(1 - \exp\left(\frac{-302}{555.6}\right)\right) \left(1 - \exp\left(\frac{-322}{555.6}\right)\right) \left(1 - \exp\left(\frac{-483}{555.6}\right)\right) \left(1 - \exp\left(\frac{-528}{555.6}\right)\right)} = 60.50$$

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

$$Q_{rot} = \sqrt{\pi} \left(\frac{8\pi^2 (1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2 6.022 \times 10^{46}} \right)^{3/2} (41.5 * 197 * 236)^{1/2} = 4.666 \times 10^5$$

and

$$Q_{elec} = 2$$

$$\text{so } Q_{TS}/V = 4.254 \times 10^{33} * 60.50 * 4.666 \times 10^5 * 2 = 2.402 \times 10^{41} \text{ m}^{-3}$$

So, the forward rate constant is:

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

$$k_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{2.402 \times 10^{41} \text{ m}^{-3}}{1.540 \times 10^{37} \text{ m}^{-3} 5.029 \times 10^{34} \text{ m}^{-3}} \exp\left(\frac{-50500 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (800) \text{ K}}\right)$$

$$k_f = 2.08 \times 10^{13} \text{ s}^{-1} \bullet 3.10 \times 10^{-31} \text{ m}^3 \bullet 5.042 \times 10^{-4} = 1.63 \times 10^{-21} \text{ m}^3 \text{ s}^{-1} = 3.26 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} = 1.96 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and the reverse rate constant is

$$k_r = \frac{kT}{h} \frac{(Q_{TS}^\ddagger / V)}{(Q_{SiCl_2} / V)(Q_H / V)} \exp\left(\frac{-E_{o,r}}{kT}\right)$$

$$k_r = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{2.402 \times 10^{41} \text{ m}^{-3}}{6.854 \times 10^{39} \text{ m}^{-3} 8.611 \times 10^{30} \text{ m}^{-3}} \exp\left(\frac{-61800 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (800) \text{ K}}\right)$$

$$k_r = 2.08 \times 10^{13} \text{ s}^{-1} \bullet 4.07 \times 10^{-30} \text{ m}^3 \bullet 9.220 \times 10^{-5} = 3.902 \times 10^{-21} \text{ m}^3 \text{ s}^{-1} = 7.80 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} = 4.70 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The equilibrium constant is just the ratio of the forward to reverse rate constant,

$$K_{eq} = 1.96 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} / 4.70 \times 10^9 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 0.417.$$

- (e) 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? (5 points).

The pre-exponential factor is approximately

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

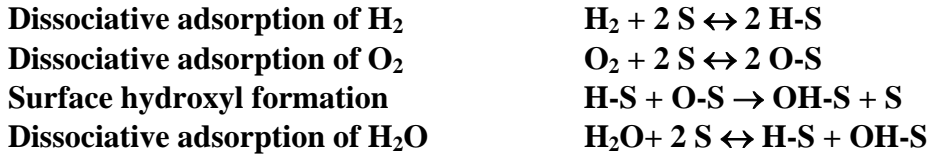
$$A_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (800) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{2.402 \times 10^{41} \text{ m}^{-3}}{1.540 \times 10^{37} \text{ m}^{-3} 5.029 \times 10^{34} \text{ m}^{-3}}$$

$$A_f = 2.08 \times 10^{13} \text{ s}^{-1} \bullet 3.10 \times 10^{-31} \text{ m}^3 = 6.44 \times 10^{-18} \text{ m}^3 \text{ s}^{-1} = 6.44 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} = 3.88 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The collision rate computed in part (b) was $2.65 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 2.65 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

So, the pre-exponential factor from transition state theory is a factor of 68 smaller than the computed hard-sphere collision rate. If we were to use a steric factor, it would be $3.88 \times 10^{12} / 2.65 \times 10^{14} = 0.015$.

3. (25 points total) Consider the surface catalyzed oxidation of hydrogen (catalytic combustion), with the following reversible adsorption and desorption steps and irreversible reaction step:



Where S is a surface site and O-S, H-S, and OH-S are surface bound species, and S is an empty surface site. The 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 equal to the rate of the irreversible surface reaction:

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

We can use the adsorption equilibrium expressions to relate the fractional coverages:

$$\theta_H^2 = K_{H_2} [\text{H}_2] \theta_S^2$$

$$\theta_O^2 = K_{O_2} [\text{O}_2] \theta_S^2$$

$$\theta_H \theta_{OH} = K_{H_2O} [\text{H}_2\text{O}] \theta_S^2$$

and we also have the overall site balance

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

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

$$\theta_H = (K_{H_2} [\text{H}_2])^{1/2} \theta_S$$

$$\theta_O = (K_{O_2} [\text{O}_2])^{1/2} \theta_S$$

$$\theta_{OH} = (K_{H_2O} [\text{H}_2\text{O}] \theta_S^2) / \theta_H = (K_{H_2O} [\text{H}_2\text{O}] \theta_S^2) / ((K_{H_2} [\text{H}_2])^{1/2} \theta_S) = K_{H_2O} [\text{H}_2\text{O}] / (K_{H_2} [\text{H}_2])^{1/2} \theta_S$$

Substituting the equilibrium relationships into the site balance gives

$$((K_{H_2} [\text{H}_2])^{1/2} + (K_{O_2} [\text{O}_2])^{1/2} + K_{H_2O} [\text{H}_2\text{O}] / (K_{H_2} [\text{H}_2])^{1/2} + 1) \theta_S = 1$$

From which

$$\theta_S = \frac{1}{1 + \sqrt{K_{H_2} [\text{H}_2]} + \sqrt{K_{O_2} [\text{O}_2]} + \frac{K_{H_2O} [\text{H}_2\text{O}]}{\sqrt{K_{H_2} [\text{H}_2}}}, \quad \theta_O = \frac{\sqrt{K_{O_2} [\text{O}_2]}}{1 + \sqrt{K_{H_2} [\text{H}_2]} + \sqrt{K_{O_2} [\text{O}_2]} + \frac{K_{H_2O} [\text{H}_2\text{O}]}{\sqrt{K_{H_2} [\text{H}_2}}}$$

$$\theta_H = \frac{\sqrt{K_{H_2} [\text{H}_2]}}{1 + \sqrt{K_{H_2} [\text{H}_2]} + \sqrt{K_{O_2} [\text{O}_2]} + \frac{K_{H_2O} [\text{H}_2\text{O}]}{\sqrt{K_{H_2} [\text{H}_2}}}, \quad \theta_{OH} = \frac{\frac{K_{H_2O} [\text{H}_2\text{O}]}{\sqrt{K_{H_2} [\text{H}_2]}}}{1 + \sqrt{K_{H_2} [\text{H}_2]} + \sqrt{K_{O_2} [\text{O}_2]} + \frac{K_{H_2O} [\text{H}_2\text{O}]}{\sqrt{K_{H_2} [\text{H}_2}}}$$

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

$$r = k_3 \theta_H \theta_O = \frac{k_3 \sqrt{K_{O_2} [O_2]} \sqrt{K_{H_2} [H_2]}}{\left(1 + \sqrt{K_{H_2} [H_2]} + \sqrt{K_{O_2} [O_2]} + \frac{K_{H_2 O} [H_2 O]}{\sqrt{K_{H_2} [H_2]}} \right)^2}$$

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 $r = k_{eff}[H_2]$. The active catalyst is supported on porous silica spheres. The effective surface rate constant, (k_{eff} in $r = k_{eff}[H_2]$) for the conditions in the reactor is 0.00005 cm/s . The catalyst porosity (fraction of the catalyst volume made up of pores) is $\varepsilon_s = 0.4$. The catalyst density is $\rho_c = 2.5 \text{ g/cm}^3$. The catalyst specific surface area is $80 \text{ m}^2 \text{ g}^{-1}$. The effective diffusion coefficient for H_2 in the gas mixture in the catalyst pores is $D_e = 0.3 \text{ cm}^2 \text{ s}^{-1}$.

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

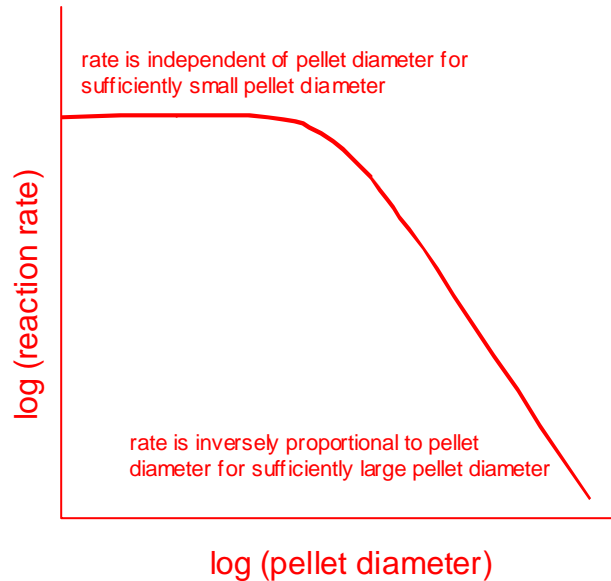
For a spherical catalyst pellet, we know that the effectiveness factor for this first-order reaction will be given by

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

where the Thiele modulus is defined by

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

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:



- (c) Calculate the pellet diameter 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 points).

We first need to compute the value of the Thiele modulus for which the effectiveness factor is 0.5 (the rate is equal to 50% of what it would be with no diffusional limitations). This should be for a value of the Thiele modulus of order of magnitude 1, since this is mild diffusional limitations. A little trial and error using the expression for the Thiele modulus from part (b) shows that $\eta = 0.5$ for $\phi = 4.73$ (with the first definition of ϕ , or 1.56 with the second definition). Using the corresponding definition of the Thiele modulus given in part (c), we have

$$\phi = R \sqrt{\frac{S_g \rho_c k_r}{D_{Ae} \epsilon_s}} = 4.73 = \frac{d(\text{cm})}{2} \sqrt{\frac{800000 (\text{cm}^2/\text{g}) 2.5 (\text{g}/\text{cm}^3) 0.00005 (\text{cm}/\text{s})}{0.3 (\text{cm}^2/\text{s}) 0.4}} = 14.4d (\text{cm})$$

from which $d = 4.73/14.4 = 0.33 \text{ cm}$

BONUS QUESTION:

Identify up to three *substantially different major topics* from the course so far that were not addressed on this exam (3 points each).

Some good answers are

Stochastic descriptions of reacting systems (Kinetic Monte Carlo simulations)

Normal mode analysis

Unimolecular reactions (pressure dependent rate constants)

Reactions in liquids

Data fitting/Nonlinear regression