

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)

In matrix form, these can be written as:

$$\begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ -1 & 0 & 1 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = \underline{0}$$

(b) Determine, using the stoichiometric matrix, the number of linearly independent reactions in this set. (3 pts)

The number of independent reactions is equal to the rank of the stoichiometric matrix. Formally, we can perform Gaussian elimination on the stoichiometric matrix from part (a) to find the rank of the matrix. Subtracting the first row from the third row, then subtracting the second row from the third row gives

$$\begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \end{bmatrix} = \underline{0}$$

The rank of the stoichiometric matrix is 2. The third reaction is simply the sum of the first two.

(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)

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

$$\frac{d}{dt} \begin{bmatrix} [A_1] \\ [A_2] \\ [A_3] \end{bmatrix} = \begin{bmatrix} -k_1 - k_3 & 0 & 0 \\ k_1 & -k_2 & 0 \\ k_3 & k_2 & 0 \end{bmatrix} \begin{bmatrix} [A_1] \\ [A_2] \\ [A_3] \end{bmatrix}$$

(d) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*). (3 pts)

If \underline{M} is the stoichiometric matrix from part (c), and \underline{C}_o 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.

- (e) Describe briefly how you would solve these equations using Laplace transform methods. (you do not have to actually solve them). (3 pts)

Taking the Laplace transform of the rate equations, and denoting the Laplace transform of the concentration of species A_i by c_i , converts the differential equations to the following algebraic equations:

$$sc_1 - [A_1]_o = -(k_1 + k_3)c_1$$

$$sc_2 - [A_2]_o = k_1c_1 - k_2c_2$$

$$sc_3 - [A_3]_o = k_3c_1 + k_2c_2$$

These three equations can easily be solved for c_1 , c_2 , and c_3 . These solutions can then be expanded in partial fractions so that each solution is a sum of terms that each contain only a single factor of the form $(s + a)$ in the denominator. The inverse Laplace transform can then be taken, converting each $(s + a)^{-1}$ factor to $\exp(-at)$, giving the concentrations as functions of time.

- (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)

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.

- (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 $[A_1] = [A_1]_o$, $[A_2] = [A_3] = 0$ (5 pts)

Either of the matrix or Laplace transform methods would give the solution. However, the simplest thing to do is probably to first solve for $[A_1]$, which is independent of the other

concentrations, then use that solution to solve for $[A_2]$, and finally find $[A_3]$ from the reaction stoichiometry ($[A_3] = [A_1]_o - [A_2] - [A_1]$). For $[A_1]$, we have

$$\frac{d[A_1]}{dt} = -(k_1 + k_3)[A_1], \text{ with } [A_1](t=0) = [A_1]_o$$

This is the rate equation for a single, first-order reaction (with total rate constant $k_1 + k_3$), which we can solve 'by inspection' to get

$$[A_1](t) = [A_1]_o \exp(-(k_1 + k_3)t)$$

Substituting this into the rate equation for $[A_2]$ gives

$$\frac{d[A_2]}{dt} = k_1[A_1]_o \exp(-(k_1 + k_3)t) - k_2[A_2], \text{ with } [A_2](t=0) = 0$$

We guess that the solution is of the form $[A_2](t) = f(t)\exp(-k_2t)$. Substituting this into the rate equation, gives

$$\frac{d[A_2]}{dt} = -k_2 \exp(-k_2t)f(t) + \exp(-k_2t)\frac{df(t)}{dt} = k_1[A_1]_o \exp(-(k_1 + k_3)t) - k_2 \exp(-k_2t)f(t)$$

or
$$\frac{df(t)}{dt} = k_1[A_1]_o \exp((k_2 - k_1 - k_3)t)$$

Integrating this gives

$$f(t) = \frac{k_1[A_1]_o}{(k_2 - k_1 - k_3)} \exp((k_2 - k_1 - k_3)t) + C_{\text{int}}$$

where C_{int} is a constant of integration. This gives

$$[A_2](t) = \frac{k_1[A_1]_o}{(k_2 - k_1 - k_3)} \exp(-(k_1 + k_3)t) + C_{\text{int}} \exp(-k_2t)$$

Applying the initial condition gives

$$[A_2](t=0) = \frac{k_1[A_1]_o}{(k_2 - k_1 - k_3)} + C_{\text{int}} = 0, \text{ or } C_{\text{int}} = \frac{-k_1[A_1]_o}{(k_2 - k_1 - k_3)}$$

So, finally, we have

$$[A_2](t) = \frac{k_1[A_1]_o}{(k_2 - k_1 - k_3)} \left(\exp(-(k_1 + k_3)t) - \exp(-k_2t) \right)$$

and

$$[A_3](t) = [A_1]_o \left(1 - \frac{k_1}{(k_2 - k_1 - k_3)} \left(\exp(-(k_1 + k_3)t) - \exp(-k_2t) \right) - \exp(-(k_1 + k_3)t) \right)$$

(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)

By definition, the scaled sensitivity coefficient of $[A_2]$ to k_3 is

$$\sigma_{23} = \frac{k_3}{[A_2]} \frac{\partial [A_2]}{\partial k_3}$$

Applying this to the expression for $[A_2]$ found in part (g) gives

$$\sigma_{23} = \frac{k_3}{\frac{k_1[A_1]_o}{(k_2 - k_1 - k_3)} \left(\exp(-(k_1 + k_3)t) - \exp(-k_2t) \right)} \frac{\partial}{\partial k_3} \left(\frac{k_1[A_1]_o}{(k_2 - k_1 - k_3)} \left(\exp(-(k_1 + k_3)t) - \exp(-k_2t) \right) \right)$$

$$\sigma_{23} = \frac{k_3}{\left(\exp(-(k_1 + k_3)t) - \exp(-k_2t)\right)} \left(\frac{1}{(k_2 - k_1 - k_3)} \left(\exp(-(k_1 + k_3)t) - \exp(-k_2t) \right) - t \exp(-(k_1 + k_3)t) \right)$$

$$\sigma_{23} = \frac{k_3}{k_2 - k_1 - k_3} - \frac{k_3 t \exp(-(k_1 + k_3)t)}{\exp(-(k_1 + k_3)t) - \exp(-k_2t)}$$

- (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)

To have $j+2$ A_2 molecules, reaction 1 must occur. The probability that it will occur in some very short time Δt is simply the rate at which it occurs multiplied by the time interval:

$$P(j+1) = k_2 j (\Delta t)$$

(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, 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)

The hard sphere collisional rate constant is given by

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

where the collision cross-section σ is given by

$$\sigma = \pi \left(\frac{d_H + d_{HCl}}{2} \right)^2 = \pi \left(\frac{2.0 + 3.8}{2} \times 10^{-10} \text{ m} \right)^2 = 2.64 \times 10^{-19} \text{ m}^2$$

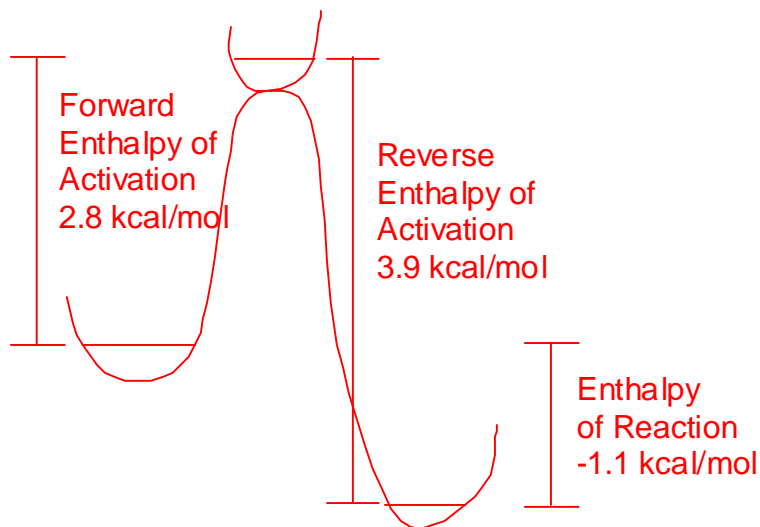
and the reduced mass for the colliding particles is

$$\mu = \frac{m_H + m_{HCl}}{m_H m_{HCl}} = \frac{1 \cdot 36.5}{1 + 36.5} \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 1.62 \times 10^{-27} \text{ kg}$$

so

$$k_{coll} = 2.64 \times 10^{-19} \text{ m}^2 \left(\frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(298\text{K})}{\pi(1.62 \times 10^{-27} \text{ kg})} \right)^{1/2} = 6.71 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 4.04 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

- (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.

According to the thermodynamic formulation of transition state theory

$$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^{act}}{R}\right) \exp\left(\frac{-\Delta H^{act}}{RT}\right)$$

This evaluates to

$$k = 6.21 \times 10^{12} \exp(-10.87) \exp(-4.73) = 1.04 \times 10^6 \text{ atm}^{-1} \text{ s}^{-1}$$

From the ideal gas law, 1 atm corresponds to $101325/8.314/298 = 40.9 \text{ mol m}^{-3}$.
Dividing by this factor gives $k = 2.5 \times 10^4 \text{ m}^3 \text{ mol}^{-1} \text{ s}$

The equilibrium constant is given by $K = \exp(-\Delta G_{rxn}/RT)$ or

$$K = \exp\left(\frac{\Delta S_{rxn}}{R}\right) \exp\left(\frac{-\Delta H_{rxn}}{RT}\right) = \exp(-1.41) \exp(1.86) = 1.57$$

The reverse rate constant is $k_r = k_f/K = 1.6 \times 10^4 \text{ m}^3 \text{ mol}^{-1} \text{ s}$

- (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)

The pre-exponential factor from the thermodynamic formulation of transition state theory (as in part (c)) is

$$k = 6.21 \times 10^{12} \exp(-10.87) = 1.18 \times 10^8 \text{ atm}^{-1} \text{ s}^{-1} = 2.9 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The steric factor is the ratio of this pre-exponential factor to the collision rate,
 $2.9 \times 10^6 / 4.04 \times 10^8 = 0.0072$

- (d) How many translational, rotational, and vibrational degrees of freedom do each of the reactants, transition state, and products have? (3 pts)

The H atom has 3 translational, 0 rotational, and 0 vibrational degrees of freedom

HCl has 3 translational, 2 rotational, and 1 vibrational degrees of freedom

The *linear* transition state has 3 translational, 2 rotational, and 3 vibrational degrees of freedom, plus the degree of freedom corresponding to the reaction coordinate

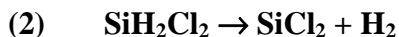
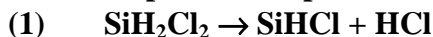
H₂ has 3 translational, 2 rotational, and 1 vibrational degrees of freedom, and

Cl has 3 translational, 0 rotational, and 0 vibrational degrees of freedom.

- (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)

Neglecting the temperature dependence of the vibrational partition function, the partition function for the atoms goes as $T^{3/2}$ and the partition function for the linear molecules goes as $T^{5/2}$. The universal frequency factor ($k_B T/h$) contributes an additional factor of T . So, both the forward and reverse pre-exponential factors go as $(T T^{5/2}) / (T^{3/2} T^{5/2}) = T^{-1/2}$.

2. (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)

As in the Lindemann theory for a single channel unimolecular decomposition, we apply the pseudo-steady-state approximation to the activated dichlorosilane molecules

$$\frac{d[\text{SiH}_2\text{Cl}_2^*]}{dt} = k_1[\text{SiH}_2\text{Cl}_2][\text{M}] - k_{-1}[\text{SiH}_2\text{Cl}_2^*][\text{M}] - k_2[\text{SiH}_2\text{Cl}_2^*] - k_3[\text{SiH}_2\text{Cl}_2^*] = 0$$

$$[\text{SiH}_2\text{Cl}_2^*] = \frac{k_1[\text{SiH}_2\text{Cl}_2][\text{M}]}{k_{-1}[\text{M}] + k_2 + k_3}$$

The rate of channel (1) is $k_2[\text{SiH}_2\text{Cl}_2^*]$, and the rate of channel (2) is $k_3[\text{SiH}_2\text{Cl}_2^*]$, or

$$r_{\text{uni}(1)} = \frac{k_1 k_2 [\text{SiH}_2\text{Cl}_2][\text{M}]}{k_{-1}[\text{M}] + k_2 + k_3}$$

$$r_{\text{uni}(2)} = \frac{k_1 k_3 [\text{SiH}_2\text{Cl}_2][\text{M}]}{k_{-1}[\text{M}] + k_2 + k_3}$$

The effective rate constants for the two reaction channels are

$$k_{\text{uni}(1)} = \frac{k_1 k_2 [\text{M}]}{k_{-1}[\text{M}] + k_2 + k_3}$$

$$k_{\text{uni}(2)} = \frac{k_1 k_3 [\text{M}]}{k_{-1}[\text{M}] + k_2 + k_3}$$

In the high pressure limit ($k_{-1}[\text{M}] \gg k_2 + k_3$) both channels become independent of pressure, and we have

$$k_{\infty(1)} = \frac{k_1 k_2}{k_{-1}}$$

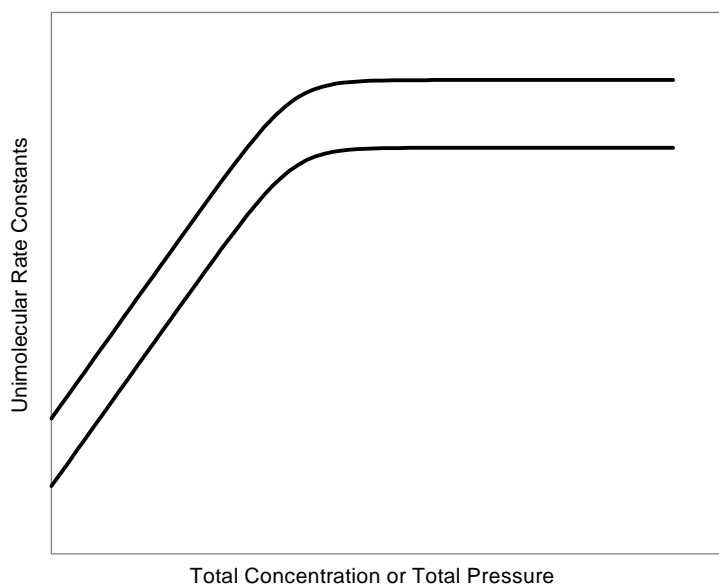
$$k_{\infty(2)} = \frac{k_1 k_3}{k_{-1}}$$

In the low pressure limit ($k_{-1}[\text{M}] \ll k_2 + k_3$) both unimolecular rate constants are proportional to the total concentration (pressure)

$$k_{o(1)} = \frac{k_1 k_2 [\text{M}]}{k_2 + k_3}$$

$$k_{o(2)} = \frac{k_1 k_3 [\text{M}]}{k_2 + k_3}$$

The pressure dependence of both channels, at this simple level of theory, is exactly the same. A sketch of the unimolecular rate constants looks like:



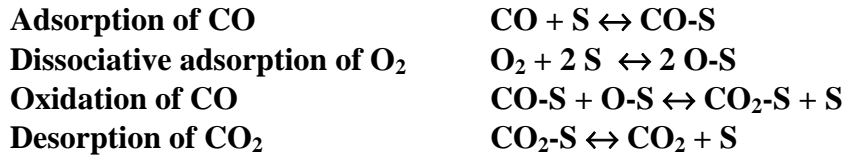
- (b) If the activation energy for the second channel ($\text{SiH}_2\text{Cl}_2 \rightarrow \text{SiCl}_2 + \text{H}_2$) is greater than that for the first channel ($\text{SiH}_2\text{Cl}_2 \rightarrow \text{SiHCl} + \text{HCl}$) which channel will exhibit pressure dependence at higher pressures? Why? (3 pts)

The channel with the higher activation energy (channel (2)) will exhibit pressure dependence at higher pressures than the other channel. Pressure dependence arises when collisions cannot maintain the equilibrium distribution of reactant energies above the threshold for reaction. The distribution will be most depleted at the highest energies. The reaction that requires the higher energy will therefore be more affected.

- (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)

We could consider activated reactant molecules with a range of energies and use energy dependent rate constants for k_1 , k_2 , and k_3 .

3. (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 CO₂-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)

If the surface reaction is rate-limiting, then the overall rate is equal to the rate of the surface reaction:

$$r = r_3 = k_3 \theta_{\text{CO}} \theta_{\text{O}}$$

If the adsorption steps are in equilibrium, then we can write

$$\theta_{\text{CO}} = K_{\text{CO}}[\text{CO}] \theta_{\text{S}}$$

$$\theta_{\text{O}}^2 = K_{\text{O}_2}[\text{O}_2] \theta_{\text{S}}^2$$

$$\theta_{\text{CO}_2} = K_{\text{CO}_2}[\text{CO}_2] \theta_{\text{S}}$$

and we also have the overall site balance

$$\theta_{\text{CO}} + \theta_{\text{O}} + \theta_{\text{CO}_2} + \theta_{\text{S}} = 1$$

Substituting the equilibrium relationships into the site balance gives

$$(1 + K_{\text{CO}}[\text{CO}] + (K_{\text{O}_2}[\text{O}_2])^{1/2} + K_{\text{CO}_2}[\text{CO}_2]) \theta_{\text{S}} = 1$$

Solving this and using the equilibrium relationships gives the site fractions:

$$\theta_{\text{S}} = \frac{1}{1 + K_{\text{CO}}[\text{CO}] + \sqrt{K_{\text{O}_2}[\text{O}_2]} + K_{\text{CO}_2}[\text{CO}_2]}, \quad \theta_{\text{CO}} = \frac{K_{\text{CO}}[\text{CO}]}{1 + K_{\text{CO}}[\text{CO}] + \sqrt{K_{\text{O}_2}[\text{O}_2]} + K_{\text{CO}_2}[\text{CO}_2]}$$

$$\theta_{\text{O}} = \frac{\sqrt{K_{\text{O}_2}[\text{O}_2]}}{1 + K_{\text{CO}}[\text{CO}] + \sqrt{K_{\text{O}_2}[\text{O}_2]} + K_{\text{CO}_2}[\text{CO}_2]}, \quad \theta_{\text{CO}_2} = \frac{K_{\text{CO}_2}[\text{CO}_2]}{1 + K_{\text{CO}}[\text{CO}] + \sqrt{K_{\text{O}_2}[\text{O}_2]} + K_{\text{CO}_2}[\text{CO}_2]}$$

Substituting these expressions for θ_{O} and θ_{CO} into the rate expression gives

$$r = \frac{k_3 K_{\text{CO}}[\text{CO}] \sqrt{K_{\text{O}_2}[\text{O}_2]}}{(1 + K_{\text{CO}}[\text{CO}] + \sqrt{K_{\text{O}_2}[\text{O}_2]} + K_{\text{CO}_2}[\text{CO}_2])^2}$$

- (b) Show that if the gas phase O₂ concentration is much greater than the gas phase CO and CO₂ 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 [O₂] >> [CO], [O₂] >> [CO₂], $K_{\text{CO}}[\text{CO}] \ll 1$, $K_{\text{O}_2}[\text{O}_2] \ll 1$, 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 [O₂], the surface reaction rate constants, and the adsorption equilibrium constants. (5 pts)

If the O_2 concentration is much greater than the CO concentration, then it can be taken to be approximately constant. If the surface coverages are all much less than 1, then the denominator of the rate expression is approximately equal to one, so the rate expression becomes

$$r \approx k_3 K_{CO} [CO] \sqrt{K_{O_2} [O_2]} = k_{eff} [CO]$$

where the effective rate constant is given by $k_{eff} = k_3 K_{CO} (K_{O_2} [O_2])^{1/2}$

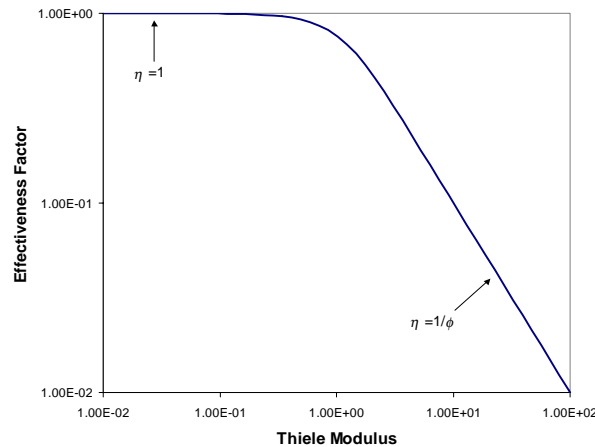
Suppose that this reaction is occurring in the catalytic converter of an automobile, under the pseudo-first-order conditions described in part (b). The active catalyst is supported on a porous alumina monolith (which can be approximated as an infinite slab of porous material). The effective surface rate constant, as defined in part (b) (k_{eff} in $r = k_{eff}[CO]$) for the conditions in the catalytic converter 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 150 m² g⁻¹. The *effective* diffusion coefficient for CO in the gas mixture in the catalyst pores is 0.1 cm² 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)

The reaction rate (per catalyst volume) is proportional to the effectiveness factor, and the Thiele modulus is proportional to the thickness of the catalyst slab. Therefore, a plot of reaction rate per catalyst volume vs. the wall thickness will have the same shape as a plot of the effectiveness factor vs. Thiele modulus, which is given by

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

On a log-log scale, this looks like:



- (d) Calculate the thickness of the monolith walls for which the reaction rate per mass of catalyst will be equal to $1/2$ of what it would be in the absence of any diffusional limitations. (10 pts)

By the definition of the effectiveness factor, the rate per mass of catalyst will be half of what it would be without diffusional limitations when the effectiveness factor is 0.5. So, we solve $\tanh(\phi) = 0.5\phi$ by trial and error to get $\phi = 1.92$

Setting the definition of the Thiele modulus equal to 1.92 gives

$$\phi = l \sqrt{\frac{S_g \rho_c k_r}{D_{eA} \epsilon_s}} = l \sqrt{\frac{150 \text{ m}^2 \text{ g}^{-1} 2.5 \text{ g cm}^{-3} 1 \times 10^{-5} \text{ cm s}^{-1} 10^4 \text{ cm}^2}{0.1 \text{ cm}^2 \text{ s}^{-1} 0.4}} = l(30.62 \text{ cm}^{-1}) = 1.92$$

This gives $l = 0.063 \text{ cm} = 0.63 \text{ mm}$. The monolith walls can be $2l = 1.25 \text{ mm}$ thick.