

CE 561, Exam 1, October 22, 2001

This exam consists of 3 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 40 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. 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.

In matrix form, these can be written as:

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

(b) 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.

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

$$\frac{d}{dt} \begin{bmatrix} [A] \\ [B] \\ [C] \end{bmatrix} = \begin{bmatrix} -(k_1 + k_3) & 0 & 0 \\ 2k_1 & -k_2 & 0 \\ 2k_3 & k_2 & 0 \end{bmatrix} \begin{bmatrix} [A] \\ [B] \\ [C] \end{bmatrix}$$

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

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

Taking the Laplace transform of the rate equations, and denoting the Laplace transform of the concentration of the species by c_A , c_B , and c_C , converts the differential equations to the following algebraic equations:

$$s c_A - C_{A0} = -(k_1 + k_3) c_A$$

$$s c_B = 2k_1 c_A - k_2 c_B$$

$$s c_C = 2k_3 c_A + k_2 c_B$$

These three equations can 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.

- (e) 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.

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.

- (f) 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 $C_A = C_{A0}$, $C_B = C_C = 0$.

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 $C_A(t=0) = C_{A0}$. The solution to this is

$$C_A = C_{A0} \exp(-(k_1 + k_3)t)$$

For C_B we have

$$\frac{dC_B}{dt} = 2k_1C_A - k_2C_B = 2k_1C_{A0} \exp(-(k_1 + k_3)t) - k_2C_B$$

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

$$\frac{dC_B}{dt} = \frac{df}{dt} \exp(-k_2t) - k_2f \exp(-k_2t) = 2k_1C_{A0} \exp(-(k_1 + k_3)t) - f \exp(-k_2t)$$

$$\frac{df}{dt} = 2k_1C_{A0} \exp((k_2 - k_1 - k_3)t)$$

$$f = \frac{2k_1C_{A0}}{k_2 - k_1 - k_3} \exp((k_2 - k_1 - k_3)t) + A$$

where A is a constant of integration, so

$$C_B = \frac{2k_1C_{A0}}{k_2 - k_1 - k_3} \exp(-(k_1 + k_3)t) + A \exp(-k_2t)$$

at $t = 0$,

$$C_B = \frac{2k_1C_{A0}}{k_2 - k_1 - k_3} + A = 0$$

so

$$A = -\frac{2k_1C_{A0}}{k_2 - k_1 - k_3}$$

and

$$C_B = \frac{2k_1C_{A0}}{k_2 - k_1 - k_3} (\exp(-(k_1 + k_3)t) - \exp(-k_2t))$$

Finally, for C_C we have

$$\frac{dC_C}{dt} = 2k_3C_A + k_2C_B = -2 \frac{dC_A}{dt} - \frac{dC_B}{dt}$$

Integrating this once shows that

$$C_C - C_{C0} = -2(C_A - C_{A0}) - (C_B - C_{B0})$$

Substituting in the solutions for C_A and C_B gives

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

(g) Derive an equation for the *scaled sensitivity* of the concentration of species A to the rate constant for the reaction $A \rightarrow 2B$.

By definition, this scaled sensitivity coefficient is

$$\sigma_{11} = \frac{k_1}{C_A} \frac{\partial C_A}{\partial k_1}$$

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

$$\sigma_{11} = \frac{k_1}{C_{A0} \exp(-(k_1 + k_3)t)} \frac{\partial}{\partial k_1} (C_{A0} \exp(-(k_1 + k_3)t))$$

$$\sigma_{11} = \frac{k_1}{C_{A0} \exp(-(k_1 + k_3)t)} (-t C_{A0} \exp(-(k_1 + k_3)t))$$

$$\sigma_{11} = -k_1 t$$

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

	Al	HCl	AlCl	H	Transition State
M (amu)	26.98	36.46	62.43	1.01	63.44
I (amu Å²)		1.6	69.8		1.2; 89.4; 90.5
$\Delta H_f(0 \text{ K})$ (kJ/mol)	337.7	-94.6	-54.0	213.4	256.1
ν (cm⁻¹)		2845	473		-2836; 285; 470
g_{elec}	2	1	1	2	2
Hard Sphere Collision Diameter (Å)	3.0	3.8	4.2	2.0	

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

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

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

AlCl is a diatomic molecule (and therefore linear). It has 3 translational, 2 rotational, and 1 vibrational degree 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 triatomic structure and is non-linear. 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 2 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 Al and HCl at 1000 K?

The hard sphere collisional rate constant is given by

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

where the collision cross-section σ is given by

$$\sigma = \pi \left(\frac{d_{Al} + d_{HCl}}{2} \right)^2 = \pi \left(\frac{3.0 + 3.8}{2} \times 10^{-10} \text{ m} \right)^2 = 3.63 \times 10^{-19} \text{ m}^2$$

and the reduced mass for the colliding particles is

$$\mu = \frac{m_{Al} + m_{HCl}}{m_{Al} m_{HCl}} = \frac{26.98 + 36.46}{26.98 \cdot 36.46} \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 2.58 \times 10^{-26} \text{ kg}$$

so

$$k_{coll} = 3.63 \times 10^{-19} \text{ m}^2 \left(\frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{\pi(2.58 \times 10^{-26} \text{ kg})} \right)^{1/2} = 4.24 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 2.55 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

(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.

The enthalpy of formation of the reactants at 0 K is $337.7 - 94.6 = 243.1 \text{ kJ/mol}$.

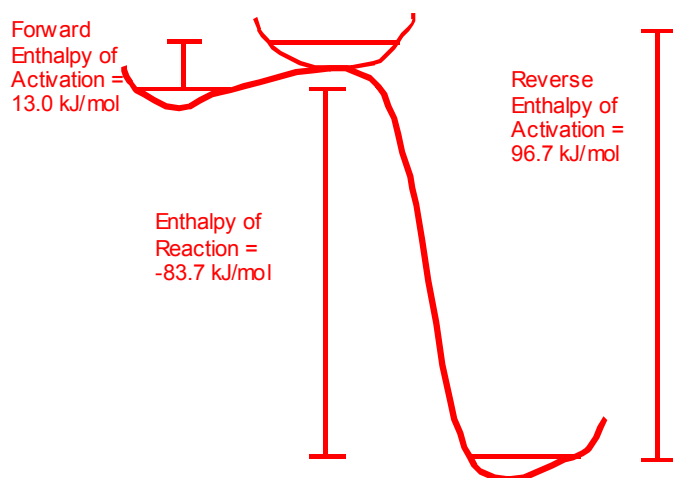
The enthalpy of formation of the transition state at 0 K is 256.1 kJ/mol .

The enthalpy of formation of the products at 0 K is $213.4 - 54.0 = 159.4 \text{ kJ/mol}$.

So, the forward enthalpy of activation is $256.1 - 243.1 = 13.0 \text{ kJ/mol}$,

and the reverse enthalpy of activation is $256.1 - 159.4 = 96.7 \text{ kJ/mol}$,

and the enthalpy of reaction is $159.4 - 243.1 = -83.7 \text{ kJ/mol}$



(c) Using transition state theory, calculate the forward rate constant, the reverse rate constant, and the equilibrium constant for this reaction at 1000 K.

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

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

Likewise, the reverse rate constant is given by

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

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

The Partition Functions are as follows:

For Al, an atom,

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \left(\frac{2\pi(26.98/6.022 \times 10^{26}) \text{kg} (1.381 \times 10^{-23}) \text{J K}^{-1} (1000) \text{K}}{(6.626 \times 10^{-34} \text{J s})^2}\right)^{3/2} = 8.33 \times 10^{32} \text{m}^{-3}$$

and

$$Q_{elec} = 2$$

$$\text{so } Q_{Al}/V = 1.67 \times 10^{33}$$

For HCl, a diatomic molecule,

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

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

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-2845}{694.4}\right)\right)} = 1.02$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\pi^2 (1.6/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{J K}^{-1} (1000) \text{K}}{1 (6.626 \times 10^{-34} \text{J s})^2} = 66.0$$

$$Q_{elec} = 1$$

$$\text{so } Q_{HCl}/V = 1.309 \times 10^{33} * 1.02 * 66.0 = 8.81 \times 10^{34} \text{m}^{-3}$$

AlCl is another diatomic molecule, and its partition function is computed in the same way as for HCl.

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

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-473}{694.4}\right)\right)} = 2.02$$

$$Q_{rot} = \frac{8\pi^2 I k T}{\sigma h^2} = \frac{8\pi^2 (69.8/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{1 (6.626 \times 10^{-34} \text{ J s})^2} = 2880$$

$$Q_{elec} = 1$$

$$\text{so } Q_{AICI}/V = 2.93 \times 10^{33} * 2.02 * 2880 = 1.70 \times 10^{37} \text{ m}^{-3}$$

For H, another atom,

$$Q_{trans}/V = \left(\frac{2\pi m k T}{h^2} \right)^{3/2} = \left(\frac{2\pi (1.01/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 6.03 \times 10^{30} \text{ m}^{-3}$$

and

$$Q_{elec} = 2$$

$$\text{so } Q_{Al}/V = 1.21 \times 10^{31}$$

Finally, the transition state is a non-linear structure, so its partition functions are slightly different. We exclude the reaction coordinate (the motion with the imaginary vibrational frequency) from the computation:

$$Q_{trans}/V = \left(\frac{2\pi (63.44/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 3.00 \times 10^{33} \text{ m}^{-3}$$

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-285}{694.4}\right) \right) \left(1 - \exp\left(\frac{-470}{694.4}\right) \right)} = 6.04$$

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

$$Q_{rot} = \sqrt{\pi I_A I_B I_C} \left(\frac{8\pi^2 (1.381 \times 10^{-23}) \text{ J K}^{-1} (2000) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2}$$

$$Q_{rot} = \sqrt{\pi (1.2/6.022 \times 10^{46}) \text{ kg m}^2 (89.4/6.022 \times 10^{46}) \text{ kg m}^2 (90.5/6.022 \times 10^{46}) \text{ kg m}^2} \left(\frac{8\pi^2 (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2}$$

$$Q_{rot} = 265 \sqrt{\pi (1.2)(89.4)(90.5)} = 46260$$

and

$$Q_{elec} = 2$$

$$\text{so } Q_{TS}/V = 3.00 \times 10^{33} * 6.04 * 46260 * 2 = 1.67 \times 10^{39} \text{ m}^{-3}$$

So, the forward rate constant is:

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

$$k_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{1.67 \times 10^{39} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3} \cdot 8.81 \times 10^{34} \text{ m}^{-3}} \exp\left(\frac{-13000 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (1000) \text{ K}}\right)$$

$$k_f = 2.08 \times 10^{13} \text{ s}^{-1} \cdot 1.14 \times 10^{-29} \text{ m}^3 \cdot 0.209 = 4.96 \times 10^{-16} \text{ m}^3 \text{ s}^{-1} = 4.96 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} = 3.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

and the reverse rate constant is

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

$$k_r = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{1.68 \times 10^{39} \text{ m}^{-3}}{1.70 \times 10^{37} \text{ m}^{-3} \cdot 1.21 \times 10^{31} \text{ m}^{-3}} \exp\left(\frac{-96700 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (1000) \text{ K}}\right)$$

$$k_r = 2.08 \times 10^{13} \text{ s}^{-1} \cdot 8.14 \times 10^{-30} \text{ m}^3 \cdot 8.89 \times 10^{-6} = 1.50 \times 10^{-21} \text{ m}^3 \text{ s}^{-1} = 1.50 \times 10^{-21} \text{ cm}^3 \text{ s}^{-1} = 9.0 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

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

$$K_{eq} = 3.0 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} / 9.0 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 3.3 \times 10^4.$$

- (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?

The pre-exponential factor is

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

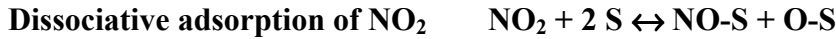
$$A_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{1.67 \times 10^{39} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3} \cdot 8.81 \times 10^{34} \text{ m}^{-3}}$$

$$A_f = 2.08 \times 10^{13} \text{ s}^{-1} \cdot 1.04 \times 10^{-29} \text{ m}^3 = 2.4 \times 10^{-16} \text{ m}^3 \text{ s}^{-1} = 2.4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} = 1.4 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The collision rate computed in part (b) was $2.55 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} = 2.55 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

So, the pre-exponential factor from transition state theory is a factor of $2.55/1.4 = 1.8$ smaller than the computed hard-sphere collision rate. If we were to use a steric factor, it would be $1.4/2.55 = 0.56$.

3. Consider the surface catalyzed decomposition of NO₂, with the following reversible adsorption, desorption steps and irreversible reaction step:



Where S is a surface site and NO-S, O-S, and N-S are surface bound species.

- (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 (NO decomposition) is rate limiting and irreversible, derive an expression for the overall reaction rate in terms of the adsorption equilibrium constants and the rate constants for the NO decomposition surface reaction.

If the surface decomposition of NO is rate-limiting, then the overall rate is equal to the rate of that surface reaction:

$$r = r_4 = k_4 \theta_{NO} \theta_S$$

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

$$\theta_{NO} \theta_O = K_{NO_2} [NO_2] \theta_S^2$$

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

$$\theta_N^2 = K_{N_2} [N_2] \theta_S^2$$

and we also have the overall site balance

$$\theta_{NO} + \theta_O + \theta_N + \theta_S = 1$$

Solving the equilibrium relationships for the NO, O, and N fractional coverage in terms of the vacant site fractional coverage gives:

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

$$\theta_N = (K_{N_2} [N_2])^{1/2} \theta_S$$

$$\theta_{NO} = (K_{NO_2} [NO_2] \theta_S^2) / \theta_O = (K_{NO_2} [NO_2] \theta_S^2) / (K_{O_2} [O_2])^{1/2} \theta_S = (K_{NO_2} [NO_2]) / (K_{O_2} [O_2])^{1/2} \theta_S$$

Substituting the equilibrium relationships into the site balance gives

$$(1 + (K_{O_2} [O_2])^{1/2} + (K_{N_2} [N_2])^{1/2} + (K_{NO_2} [NO_2]) / (K_{O_2} [O_2])^{1/2}) \theta_S = 1$$

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

$$\theta_S = \frac{1}{1 + \sqrt{K_{O_2} [O_2]} + \sqrt{K_{N_2} [N_2]} + K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]}}, \quad \theta_O = \frac{K_{C_2H_4} [C_2H_4]}{1 + \sqrt{K_{O_2} [O_2]} + \sqrt{K_{N_2} [N_2]} + K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]}}$$

$$\theta_N = \frac{\sqrt{K_{N_2} [N_2]}}{1 + \sqrt{K_{O_2} [O_2]} + \sqrt{K_{N_2} [N_2]} + K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]}}, \quad \theta_{NO} = \frac{K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]}}{1 + \sqrt{K_{O_2} [O_2]} + \sqrt{K_{N_2} [N_2]} + K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]}}$$

Substituting these expressions for θ_{NO} and θ_S into the rate expression gives

$$r = \frac{k_4 K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]}}{(1 + \sqrt{K_{O_2} [O_2]} + \sqrt{K_{N_2} [N_2]} + K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]})^2}$$

- (b) Show that if the gas phase O_2 and N_2 concentrations are much greater than the gas phase NO_2 concentration, 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 NO_2 concentration and independent of the other species concentrations. That is, show that if $[O_2] \gg [NO_2]$, $[N_2] \gg [NO_2]$, $K_{O_2}[O_2] \ll 1$, $K_{N_2}[N_2] \ll 1$, and $K_{NO_2}[NO_2] \ll 1$, then the reaction rate can approximately be written as $r = k_{eff}[CO]$ and find k_{eff} in terms of $[O_2]$, $[N_2]$, the surface reaction rate constants, and the adsorption equilibrium constants.

If the N_2 and O_2 concentrations are much greater than the NO_2 concentration, then they 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

$$r \cong k_4 K_{NO_2} [NO_2] / \sqrt{K_{O_2} [O_2]} = k_{eff} [NO_2]$$

where the effective rate constant is given by

$$k_{eff} = k_4 K_{NO_2} / \sqrt{K_{O_2} [O_2]}$$

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 0.001 cm/s. The catalyst porosity (fraction of the catalyst volume made up of pores) is $\epsilon_s = 0.4$. The catalyst density is $\rho_c = 2.0 \text{ g/cm}^3$. The catalyst specific surface area is $50 \text{ m}^2 \text{ g}^{-1}$. The effective diffusion coefficient for NO_2 in the gas mixture in the catalyst pores is $D_e = 0.2 \text{ cm}^2 \text{ s}^{-1}$.

- (c) Make a sketch of how the reaction rate *per mass of catalyst* will depend on the thickness of the monolith walls. Since there is gas on both sides of each wall, the thickness is equivalent to $2l$ in our analysis of an infinite porous slab of catalyst.

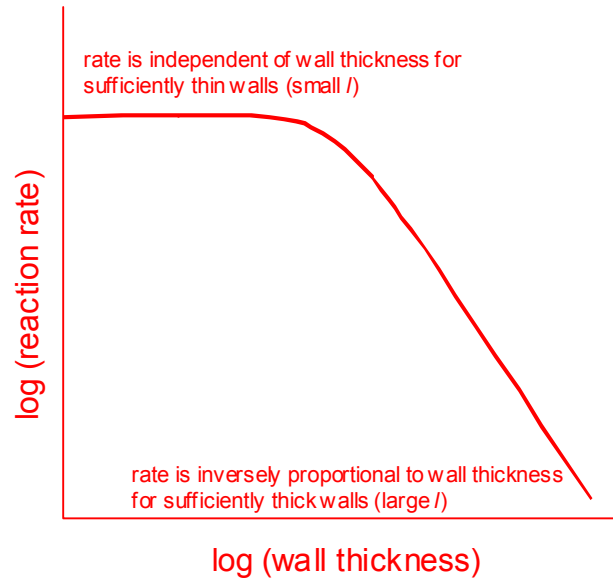
For an infinite slab of catalyst with thickness = $2l$, we know that the effectiveness factor is given by

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

where the Thiele modulus is defined by

$$\phi = l \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \epsilon_s^2}}$$

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



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

We first need to compute the value of the Thiele modulus for which the effectiveness factor is 0.5 (the rate is equal to $\frac{1}{2}$ of what it would be with no diffusional limitations). This should be for a value of the Thiele modulus a bit greater than 1, since this is mild diffusional limitations. A little trial and error using the expression for the Thiele modulus from part (c) shows that $\eta = 0.5$ for $\phi = 1.915$. Using the corresponding definition of the Thiele modulus given in part (c), we have

$$\phi = l \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \varepsilon_s^2}} = 1.915 = l \text{ (cm)} \sqrt{\frac{500000 \text{ (cm}^2/\text{g)} 2.0 \text{ (g/cm}^3\text{)} 0.001 \text{ (cm/s)}}{0.2 \text{ (cm}^2/\text{s)} 0.4}}$$

from which $l = 0.017 \text{ cm}$.

As a practical matter, these walls would not be thick enough to have the mechanical strength required for use in a catalytic converter monolith. So, the catalyst would either have to be supported on some thicker material, or most of the catalyst will go unused.