

## CE 561, Exam 1, October 16, 2000

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.

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. 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. Good luck.

1. (33 pts) Consider the following two reactions:

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

(a) Write these reactions in matrix form. (3 pts)

In matrix form, these can be written as:

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

(b) Write the rate equations for the concentrations of the three species in matrix form. (3 pts)

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

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

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

If  $\underline{M}$  is the matrix of rate constants from part (b), 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  $\underline{\underline{M}}$  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  $C(t)$  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). (4 pts)

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:

$$\begin{aligned} s c_A - [A]_o &= -k_1 c_A + k_2 c_B \\ s c_B - [B]_o &= k_1 c_A - (k_2 + k_3) c_B \\ s c_C - [C]_o &= k_3 c_B \end{aligned}$$

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. (4 pts)

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.

- (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  $C_A = C_{A0}$ ,  $C_B = C_C = 0$ . (6 pts)

Either the matrix or Laplace transform methods would work. We cannot simply integrate the equations sequentially, because they are coupled. I'll use the Laplace transform method here. Putting the above initial conditions into the transformed equations gives

$$s c_A - C_{Ao} = -k_1 c_A + k_2 c_B$$

$$s c_B = k_1 c_A - (k_2 + k_3) c_B$$

$$s c_C = k_3 c_B$$

from which

$$c_A = \frac{C_{Ao} + k_2 c_B}{s + k_1}$$

$$\left( s + k_2 + k_3 - \frac{k_1 k_2}{s + k_1} \right) c_B = \frac{k_1 C_{Ao}}{s + k_1}$$

$$c_B = \frac{k_1 C_{Ao}}{s + k_1} \frac{s + k_1}{(s + k_2 + k_3)(s + k_1) - k_1 k_2} = \frac{k_1 C_{Ao}}{s^2 + (k_1 + k_2 + k_3)s + k_1 k_3}$$

$$c_A = \frac{C_{Ao}}{s + k_1} + \frac{k_1 k_2 C_{Ao}}{(s^2 + (k_1 + k_2 + k_3)s + k_1 k_3)(s + k_1)}$$

$$c_C = \frac{k_3 c_B}{s} = \frac{k_1 k_3 C_{Ao}}{s(s^2 + (k_1 + k_2 + k_3)s + k_1 k_3)}$$

now, we must factor the denominator and expand these in partial fractions

$$s^2 + (k_1 + k_2 + k_3)s + k_1 k_3 = \left( s + \frac{1}{2} \left( k_1 + k_2 + k_3 + \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right) \right) \left( s + \frac{1}{2} \left( k_1 + k_2 + k_3 - \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right) \right)$$

To make this more compact, let's define:

$$\alpha = \frac{1}{2} \left( k_1 + k_2 + k_3 + \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right)$$

$$\beta = \frac{1}{2} \left( k_1 + k_2 + k_3 - \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} \right)$$

Expanding the solution for  $c_B$  in partial fractions gives:

$$c_B = \frac{A}{s + \alpha} + \frac{B}{s + \beta}$$

$$A(s + \beta) + B(s + \alpha) = k_1 C_{Ao}$$

$$A + B = 0, \quad \text{so } B = -A$$

$$\beta A + \alpha B = (\beta - \alpha) A = k_1 C_{Ao}$$

$$-A \sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3} = k_1 C_{Ao}$$

$$A = \frac{k_1 C_{Ao}}{\beta - \alpha}, \quad B = \frac{-k_1 C_{Ao}}{\beta - \alpha}$$

So

$$c_B = \frac{k_1 C_{Ao}}{\beta - \alpha} \left( \frac{1}{s + \alpha} - \frac{1}{s + \beta} \right)$$

The solution for  $c_A$  can be expanded in partial fractions in a similar way:

$$c_A = \frac{C_{Ao}}{s + k_1} + \frac{A}{s + \alpha} + \frac{B}{s + \beta} + \frac{C}{s + k_1}$$

$$A(s + \beta)(s + k_1) + B(s + \alpha)(s + k_1) + C(s + \alpha)(s + \beta) = k_1 k_2 C_{Ao}$$

$$A + B + C = 0$$

$$(k_1 + \beta)A + (k_1 + \alpha)B + (\alpha + \beta)C = 0$$

$$(k_1 \beta)A + (k_1 \alpha)B + (\alpha \beta)C = k_1 k_2 C_{Ao}$$

$$(k_1 + \beta)A + (k_1 + \alpha)B + (\alpha + \beta)(-A - B) = 0$$

$$(k_1 - \alpha)A + (k_1 - \beta)B = 0$$

$$B = \frac{-(k_1 - \alpha)}{(k_1 - \beta)} A$$

$$(k_1 \beta)A + (k_1 \alpha) \frac{-(k_1 - \alpha)}{(k_1 - \beta)} A - (\alpha \beta) \left( 1 - \frac{(k_1 - \alpha)}{(k_1 - \beta)} \right) A = k_1 k_2 C_{Ao}$$

$$\left( \frac{k_1^2 \beta + k_1 \beta^2 - k_1^2 \alpha - k_1 \alpha^2 + \alpha \beta^2 + \alpha^2 \beta}{k_1 - \beta} \right) A = k_1 k_2 C_{Ao}$$

$$A = \frac{k_1 k_2 C_{Ao} (k_1 - \beta)}{(k_1 + \alpha)(k_1 + \beta)(\beta - \alpha)}$$

$$B = \frac{-k_1 k_2 C_{Ao} (k_1 - \alpha)}{(k_1 + \alpha)(k_1 + \beta)(\beta - \alpha)}$$

$$C = \frac{k_1 k_2 C_{Ao}}{(k_1 + \alpha)(k_1 + \beta)}$$

$$c_A = C_{Ao} \left( \frac{1}{s + k_1} + \left( \frac{k_1 k_2 C_{Ao}}{(k_1 + \alpha)(k_1 + \beta)} \right) \left( \frac{1}{s + k_1} + \frac{k_1 - \beta}{(\beta - \alpha)(s + \alpha)} - \frac{k_1 - \alpha}{(\beta - \alpha)(s + \beta)} \right) \right)$$

Inverting the Laplace transforms to get the concentrations  $C_A$  and  $C_B$  gives

$$C_A = C_{Ao} \left( \exp(-k_1 t) + \frac{k_1 k_2}{(k_1 + \alpha)(k_1 + \beta)} \left( \exp(-k_1 t) + \frac{k_1 - \beta}{\beta - \alpha} \exp(-\alpha t) - \frac{k_1 - \alpha}{\beta - \alpha} \exp(-\beta t) \right) \right)$$

$$C_B = \frac{k_1 C_{Ao}}{\beta - \alpha} (\exp(-\alpha t) - \exp(-\beta t))$$

Finally, we could solve expand the expression for  $c_C$  in partial fractions and invert the transform. However, we can also get  $C_C$  from stoichiometry as  $C_C = C_{Ao} - C_A - C_B$

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

- (g) Find an analytical expression for the *scaled sensitivity coefficient* of the concentration of A to the rate constant for the second reaction ( $k_3$ ). (6 pts)

By definition, this scaled sensitivity coefficient is

$$\sigma_{13} = \frac{k_3}{C_A} \frac{\partial C_A}{\partial k_3}$$

So, we just need to take this partial derivative of the expression for  $C_A$  found in part (f). It's only dependence on  $k_3$  is through the groups we called  $\alpha$  and  $\beta$ .

$$\sigma_{13} = \frac{k_3}{C_A} \frac{\partial}{\partial k_3} \left( \exp(-k_1 t) + \frac{k_1 k_2}{(k_1 + \alpha)(k_1 + \beta)} \left( \exp(-k_1 t) + \frac{k_1 - \beta}{\beta - \alpha} \exp(-\alpha t) - \frac{k_1 - \alpha}{\beta - \alpha} \exp(-\beta t) \right) \right)$$

$$\sigma_{13} = \frac{k_3 \left( \frac{k_1 k_2}{(k_1 + \alpha)(k_1 + \beta)} \left( -\alpha \left( \frac{k_1 - \beta}{\beta - \alpha} \right) \exp(-\alpha t) \frac{\partial \alpha}{\partial k_3} + \beta \left( \frac{k_1 - \alpha}{\beta - \alpha} \right) \exp(-\beta t) \frac{\partial \beta}{\partial k_3} - \frac{1}{\beta - \alpha} \exp(-\alpha t) \frac{\partial \beta}{\partial k_3} + \frac{1}{\beta - \alpha} \exp(-\beta t) \frac{\partial \alpha}{\partial k_3} + \left( \frac{k_1 - \alpha}{(\beta - \alpha)^2} \exp(-\beta t) - \frac{k_1 - \beta}{(\beta - \alpha)^2} \exp(-\alpha t) \right) \frac{\partial (\beta - \alpha)}{\partial k_3} \right) \right)}{\exp(-k_1 t) + \frac{k_1 k_2}{(k_1 + \alpha)(k_1 + \beta)} \left( \exp(-k_1 t) + \frac{k_1 - \beta}{\beta - \alpha} \exp(-\alpha t) - \frac{k_1 - \alpha}{\beta - \alpha} \exp(-\beta t) \right)}$$

This could be simplified further, but I won't do so here.

In this, we need to substitute

$$\frac{\partial \alpha}{\partial k_3} = \frac{1}{2} \left( 1 + \frac{(k_1 + k_2 + k_3) - 2k_1}{\sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}} \right)$$

$$\frac{\partial \beta}{\partial k_3} = \frac{1}{2} \left( 1 - \frac{(k_1 + k_2 + k_3) - 2k_1}{\sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}} \right)$$

$$\frac{\partial (\beta - \alpha)}{\partial k_3} = - \frac{(k_1 + k_2 + k_3) - 2k_1}{\sqrt{(k_1 + k_2 + k_3)^2 - 4k_1 k_3}}$$

After substituting this in, we could probably simplify the whole thing further, but if you got this far, you are more than deserving of full credit!

- (h) 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. (3 pts)

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

$$P(j+1) = k_1 i (\Delta t)$$

2. (25 pts) Consider the elementary gas phase reaction  $\text{CH}_3 + \text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}$ . For this reaction (at 298 K and 1 atm) the enthalpy of reaction is  $\Delta H_{rxn} = -0.5 \text{ kcal mol}^{-1}$ . The entropy of reaction is  $\Delta S_{rxn} = -6.7 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The enthalpy of activation is  $\Delta H^\ddagger = 12.6 \text{ kcal mol}^{-1}$ , and the entropy of activation is  $\Delta S^\ddagger = -26.5 \text{ cal mol}^{-1} \text{ K}^{-1}$ . The atomic mass of H is 1.0 amu. The atomic mass of C is 12.0 amu. The hard-sphere collision diameters for  $\text{CH}_3$ ,  $\text{H}_2$ ,  $\text{CH}_4$ , and H are 3.8, 2.9, and 3.7, and 2.1 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) How many translational, rotational, and vibrational degrees of freedom do each of the reactants, transition state, and products have? (4 pts)

$\text{CH}_3$  is a non-linear molecule made up of 4 atoms, and it therefore has  $3 \cdot 4 - 6 = 6$  vibrational degrees of freedom, 3 translational degrees of freedom, and 3 rotational degrees of freedom.

$\text{H}_2$  is a linear molecule made up of 2 atoms, and it has  $3 \cdot 2 - 5 = 1$  vibrational degree of freedom, 3 translational degrees of freedom, and 2 rotational degrees of freedom.

$\text{CH}_4$  is a non-linear molecule made up of 5 atoms, so it has  $3 \cdot 5 - 6 = 9$  vibrational degrees of freedom, 3 translational degrees of freedom, and 3 rotational degrees of freedom.

H is an atom, so it has no vibrational degrees of freedom, 3 translational degrees of freedom, and no rotational degrees of freedom.

(b) What is the hard-sphere collisional rate constant for collisions between  $\text{CH}_3$  and  $\text{H}_2$  at 298 K and 1 atmosphere? (4 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  $\sigma$  is given by

$$\sigma = \pi \left( \frac{d_{\text{CH}_3} + d_{\text{H}_2}}{2} \right)^2 = \pi \left( \frac{3.8 + 2.9}{2} \times 10^{-10} \text{ m} \right)^2 = 3.53 \times 10^{-19} \text{ m}^2$$

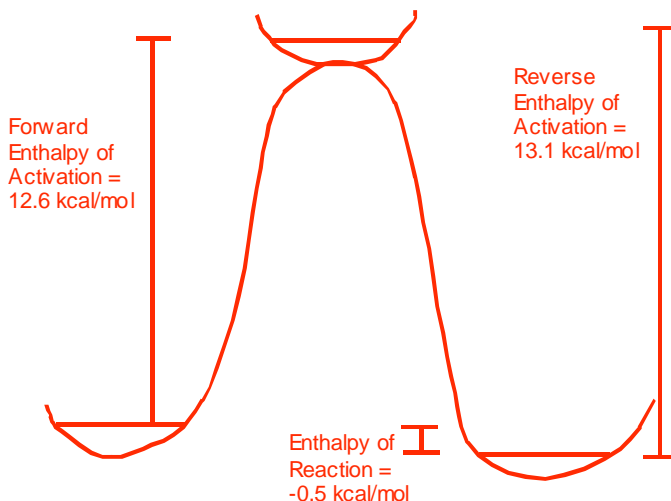
and the reduced mass for the colliding particles is

$$\mu = \frac{m_{\text{CH}_3} m_{\text{H}_2}}{m_{\text{CH}_3} + m_{\text{H}_2}} = \frac{15 \cdot 2}{15 + 2} \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 2.93 \times 10^{-27} \text{ kg}$$

so

$$k_{coll} = 3.53 \times 10^{-19} \text{ m}^2 \left( \frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{\pi(2.93 \times 10^{-27} \text{ kg})} \right)^{1/2} = 6.67 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 4.02 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

(c) 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. (4 pts)



- (d) 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 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

$$k_f = 6.2 \times 10^{12} \exp(-13.34) \exp(-21.28) = 5.7 \times 10^{-3} \text{ atm}^{-1} \text{ s}^{-1}$$

From the ideal gas law, 1 atm corresponds to  $101325/8.314/298 = 40.9 \text{ mol m}^{-3}$ .  
Dividing by this factor gives  $k = 1.4 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ s}$

The equilibrium constant is given by

$$K = \exp\left(\frac{\Delta G_{rxn}}{R}\right) = \exp\left(\frac{\Delta S_{rxn}}{R}\right) \exp\left(\frac{-\Delta H_{rxn}}{RT}\right) = \exp\left(\frac{-6.7}{1.987}\right) \exp\left(\frac{500}{1.987 * 298}\right) = 0.0799$$

The reverse rate constant is simply  $k_r = K/k_f = 1.4 \times 10^{-4} \text{ m}^3 \text{ mol}^{-1} \text{ s} / 0.0799 = 1.8 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \text{ s}$

- (e) Compare the pre-exponential factor for the forward reaction found in part (d) to the hard-sphere collision rate constant from part (b). If we were describing the reaction in terms of the collision rate constant, what would be the steric factor for the reaction? (4 pts)

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

$$k = 6.2 \times 10^{12} \exp(-13.34) = 9.97 \times 10^6 \text{ atm}^{-1} \text{ s}^{-1} = 2.4 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

The steric factor is the ratio of this pre-exponential factor to the collision rate,  
 $2.4 \times 10^5 / 4.02 \times 10^8 = 0.00061$

3. (12 pts) Consider the isomerization of 1,2-butadiene to 1,3-butadiene in the gas phase. This is an elementary reaction with a substantial energetic barrier.

- (a) Derive the simplest rate expression that you can that gives a qualitatively correct description of the pressure dependence of this reaction. (5 pts)

Let 1,2-butadiene be denoted by 'A' and 1,3-butadiene be denoted by 'B', so we have our favorite reaction  $A \rightarrow B$ . The simplest model of this process that gives a qualitatively correct picture of the pressure dependence is the Lindemann-Hinshelwood model, in which we assume that the reaction occurs in 2 steps - an energy transfer step followed by a reaction step:



Where  $A^*$  denotes an 1,2-butadiene molecule that has enough energy to react, and  $[M]$  is the total concentration of all species in the gas mixture ( $p/(RT)$  in terms of the pressure). Since  $A^*$  is a short-lived reactive entity, we can apply the steady-state approximation to it to get

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

from which  $r_1 = r_2$ , and

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

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

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

And the effective unimolecular rate constant is

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

- (b) Sketch a log-log plot of the unimolecular rate constant vs. pressure for this reaction. Show how the expression derived in part (a) for the unimolecular rate constant can be simplified for very high pressures and for very low pressures, and illustrate these limiting cases on your sketch. (4 pts)

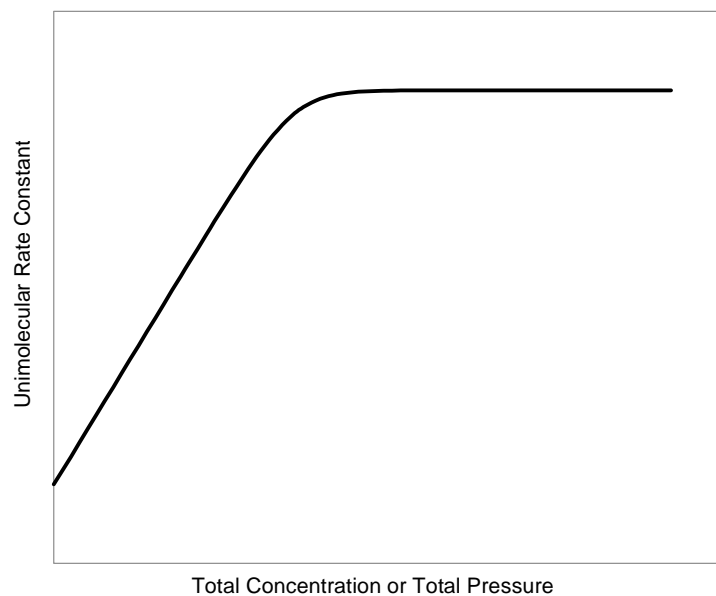
For very high pressures,  $k_{-1}[M] \gg k_2$ , so  $k_2$  can be neglected in the denominator of  $k_{uni}$  leaving the high-pressure limiting rate constant, which we usually call  $k_\infty$ .

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

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

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

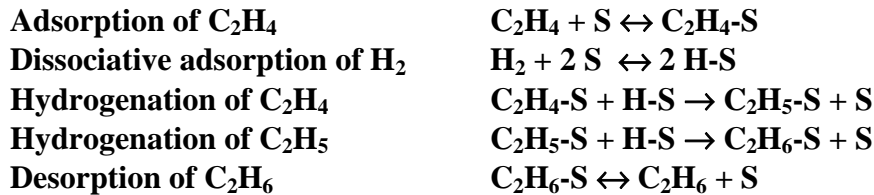
In the high-pressure limit, the unimolecular rate constant is independent of pressure, while in the low-pressure limit, it is directly proportional to pressure. Therefore, a log-log plot of the unimolecular rate constant vs. pressure over a wide range of pressures will look like:



- (c) Describe one 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)

One possibility would be to consider activated reactant molecules with a range of energies and use energy dependent rate constants for  $k_1$ , and  $k_2$ .

4. (30 pts) Consider the surface catalyzed hydrogenation of ethylene, with the following adsorption, reaction, and diffusion steps:



Where S is an empty surface site and  $C_2H_4-S$ , H-S,  $C_2H_5-S$ , and  $C_2H_6-S$  are adsorbed surface species. Note that this mechanism assumes that  $C_2H_5$  does not desorb (only  $C_2H_5-S$  is included).

- (a) Assuming that the adsorption and desorption steps obey the Langmuir isotherm (for competitive adsorption on the same surface sites), and that the hydrogenation of  $C_2H_4$  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 reactions. (10 pts)

**If the 1st surface reaction is rate-limiting, then the overall rate is equal to the rate of the 1st surface reaction:**

$$r = r_3 = k_3 \theta_{C_2H_4} \theta_H$$

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

$$\theta_{C_2H_4} = K_{C_2H_4} [C_2H_4] \theta_S$$

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

$$\theta_{C_2H_6} = K_{C_2H_6} [C_2H_6] \theta_S$$

**and we also have the overall site balance**

$$\theta_{C_2H_4} + \theta_H + \theta_{C_2H_6} + \theta_S = 1$$

**Substituting the equilibrium relationships into the site balance gives**

$$(1 + K_{C_2H_4} [C_2H_4] + (K_{H_2} [H_2])^{1/2} + K_{C_2H_6} [C_2H_6]) \theta_S = 1$$

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

$$\theta_S = \frac{1}{1 + K_{C_2H_4} [C_2H_4] + \sqrt{K_{H_2} [H_2]} + K_{C_2H_6} [C_2H_6]}, \quad \theta_{C_2H_4} = \frac{K_{C_2H_4} [C_2H_4]}{1 + K_{C_2H_4} [C_2H_4] + \sqrt{K_{H_2} [H_2]} + K_{C_2H_6} [C_2H_6]}$$

$$\theta_H = \frac{\sqrt{K_{H_2} [H_2]}}{1 + K_{C_2H_4} [C_2H_4] + \sqrt{K_{H_2} [H_2]} + K_{C_2H_6} [C_2H_6]}, \quad \theta_{C_2H_6} = \frac{K_{C_2H_6} [C_2H_6]}{1 + K_{C_2H_4} [C_2H_4] + \sqrt{K_{H_2} [H_2]} + K_{C_2H_6} [C_2H_6]}$$

**Substituting these expressions for  $\theta_H$  and  $\theta_{C_2H_4}$  into the rate expression gives**

$$r = \frac{k_3 K_{C_2H_4} [C_2H_4] \sqrt{K_{H_2} [H_2]}}{(1 + K_{C_2H_4} [C_2H_4] + \sqrt{K_{H_2} [H_2]} + K_{C_2H_6} [C_2H_6])^2}$$

- (b) Show that if the gas phase  $H_2$  concentration is much greater than the gas phase  $C_2H_4$  and  $C_2H_6$  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  $C_2H_4$  concentration and independent of the other species concentrations.

That is, show that if  $[H_2] \gg [C_2H_4]$ ,  $[H_2] \gg [C_2H_6]$ ,  $K_{C_2H_4}[C_2H_4] \ll 1$ ,  $K_{H_2}[H_2] \ll 1$ , and  $K_{C_2H_6}[C_2H_6] \ll 1$ , then the reaction rate can approximately be written as  $r = k_{eff}[C_2H_4]$  and find  $k_{eff}$  in terms of  $[H_2]$ , the surface reaction rate constants, and the adsorption equilibrium constants. (5 pts)

**If the  $H_2$  concentration is much greater than the  $C_2H_4$  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**

$$r \approx k_3 K_{C_2H_4} [C_2H_4] \sqrt{K_{H_2} [H_2]} = k_{eff} [C_2H_4]$$

**where the effective rate constant is given by  $k_{eff} = k_3 K_{C_2H_4} (K_{H_2} [H_2])^{1/2}$**

Suppose that this reaction is occurring in a spherical porous alumina catalyst pellet under the pseudo-first-order conditions described in part (b). The active catalyst is present inside the pores of the alumina, and reaction occurs on the pore surfaces. The effective surface rate constant, as defined in part (b) ( $k_{eff}$  in  $r = k_{eff}[C_2H_4]$ ) for the conditions of interest is  $1 \times 10^{-5}$  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/cm<sup>3</sup>. The catalyst specific surface area is  $100$  m<sup>2</sup> g<sup>-1</sup>. The effective diffusion coefficient for  $C_2H_4$  in the gas mixture in the catalyst pores is  $D_e = 0.2$  cm<sup>2</sup> s<sup>-1</sup>.

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

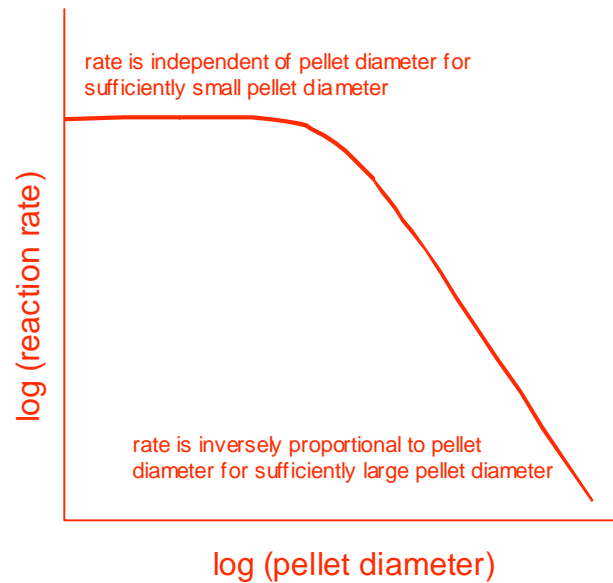
For a spherical catalyst pellet, we know that the effectiveness factor for this first-order reaction will be given by

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

where the Thiele modulus is defined by

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

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:



- (d) Calculate the sphere diameter for which the reaction rate per mass of catalyst will be equal to 80% of what it would be in the absence of any diffusional limitations. (10 pts)

We first need to compute the value of the Thiele modulus for which the effectiveness factor is 0.8 (the rate is equal to 80% 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 (c) shows that  $\eta = 0.8$  for  $\phi = 2.04$ . Using the corresponding definition of the Thiele modulus given in part (c), we have

$$\phi = R \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \epsilon_s^2}} = 2.04 = \frac{d(\text{cm})}{2} \sqrt{\frac{1000000 (\text{cm}^2/\text{g}) 2.5 (\text{g}/\text{cm}^3) 0.00001 (\text{cm}/\text{s})}{0.2 (\text{cm}^2/\text{s}) 0.4}}$$

from which  $d = 0.23 \text{ cm}$ .