

CE 561, Exam 1, October 26, 2007

This exam consists of 4 questions, each with multiple parts. You should be careful not to get stuck on one part. If you do not know how to do a problem, move on and return to it if you have time at the end.

You may use a calculator and a single letter-size sheet (2-sided) of notes to aid you on this exam. You may not exchange notes with or otherwise consult your fellow students. If you talk to your fellow students during the exam, I will assume that you are cheating, you will be asked to leave, and you will fail the exam.

You will have 2 hours and 50 minutes to complete the exam. Please use a separate blue book for each exam problem. Carefully explain any assumptions you make, label what part of what problem you are working on, and define the symbols that you use. The point value of each part is indicated – budget your effort accordingly. There are 100 points total.

1. (35 points total) Consider the following first-order reactions among molecules A, B, and C, occurring in a constant-volume isothermal batch reactor that initially contains only species A at an initial concentration C_{A0} .

- (1) $A \rightarrow B + C$ with $r_1 = k_1 C_A$
- (2) $C \leftrightarrow D$ with $r_2 = k_2 C_C - k_{-2} C_D$
- (3) $A \rightarrow B + D$ with $r_3 = k_3 C_A$

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

In matrix form, these can be written as:

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

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

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

If the second reaction is treated as a single reaction

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

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

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

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

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

- (d) Describe a numerical method that could be used to integrate the rate equations. Outline the algorithm used in this method and state the advantages and disadvantages of the method (4 points).

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

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

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

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

Applying this repeatedly, with sufficiently small values of 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 $C_A = C_{A0}$, $C_B = C_C = C_D = 0$ (15 points).

Examination of the equations shows that both C_A and C_B only depend on C_A . Thus, these two equations can be solved separately. For C_A , we have

$$\frac{dC_A}{dt} = -(k_1 + k_3)C_A \text{ with } C_A(t = 0) = C_{A0}$$

This is our favorite ODE, with solution

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

Adding the equations for C_A and C_B (or analyzing the reaction stoichiometry in some other way) shows that

$$\begin{aligned} \frac{dC_A}{dt} + \frac{dC_B}{dt} &= -(k_1 + k_3)C_A + (k_1 + k_3)C_A = 0 \\ \frac{d(C_A + C_B)}{dt} &= 0 \end{aligned}$$

Integrating this gives $C_A + C_B = \text{a constant} = C_{A0}$. Thus,

$$C_B = C_{A0} - C_A = C_{A0}(1 - \exp(-(k_1 + k_3)t))$$

Similarly, adding the ODEs for C_C and C_D gives

$$\begin{aligned} \frac{dC_C}{dt} + \frac{dC_D}{dt} &= k_1C_A - k_2C_C + k_{-2}C_D + k_3C_A + k_2C_C - k_{-2}C_D \\ \frac{d(C_C + C_D)}{dt} &= (k_1 + k_3)C_A = (k_1 + k_3)C_{A0} \exp(-(k_1 + k_3)t) \end{aligned}$$

Integrating this gives

$$C_C + C_D = A - C_{A0} \exp(-(k_1 + k_3)t)$$

Where A is a constant of integration. Using the initial condition at $t = 0$, shows that $A = C_{A0}$, so we have

$$C_C + C_D = C_{A0} (1 - \exp(-(k_1 + k_3)t))$$

This can be used to obtain a single equation for either C_C or C_D . Solving for C_D , we have

$$C_D = C_{A0} (1 - \exp(-(k_1 + k_3)t)) - C_C$$

And substituting this into the ODE for C_C gives

$$\begin{aligned} \frac{dC_C}{dt} &= k_1C_A - k_2C_C + k_{-2} (C_{A0} (1 - \exp(-(k_1 + k_3)t)) - C_C) \\ \frac{dC_C}{dt} &= k_1C_{A0} \exp(-(k_1 + k_3)t) - (k_2 + k_{-2})C_C + k_{-2}C_{A0} (1 - \exp(-(k_1 + k_3)t)) \\ \frac{dC_C}{dt} + (k_2 + k_{-2})C_C &= C_{A0} (k_{-2} + (k_1 - k_{-2}) \exp(-(k_1 + k_3)t)) \end{aligned}$$

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

$$C_C = f(t) \exp(-(k_2 + k_{-2})t)$$

For which

$$\frac{dC_C}{dt} = -(k_2 + k_{-2})f(t) \exp(-(k_2 + k_{-2})t) + \frac{df}{dt} \exp(-(k_2 + k_{-2})t)$$

Substituting this into the ODE for C_C :

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

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

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

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

Integrating this once gives

$$f = \frac{C_{A_0} k_{-2}}{k_2 + k_{-2}} \exp((k_2 + k_{-2})t) + \frac{C_{A_0} (k_1 - k_{-2})}{(k_2 + k_{-2} - k_1 - k_3)} \exp((k_2 + k_{-2} - k_1 - k_3)t) + K$$

Where K is a constant of integration that can be evaluated using the initial condition that $f = 0$ at $t = 0$, from which

$$K = -\frac{C_{A_0} k_{-2}}{k_2 + k_{-2}} - \frac{C_{A_0} (k_1 - k_{-2})}{(k_2 + k_{-2} - k_1 - k_3)}$$

And thus

$$f = \frac{C_{A_0} k_{-2}}{k_2 + k_{-2}} (\exp((k_2 + k_{-2})t) - 1) + \frac{C_{A_0} (k_1 - k_{-2})}{(k_2 + k_{-2} - k_1 - k_3)} (\exp((k_2 + k_{-2} - k_1 - k_3)t) - 1)$$

And

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

Finally,

$$C_D = C_{A_0} (1 - \exp(-(k_1 + k_3)t)) - \frac{C_{A_0} k_{-2}}{k_2 + k_{-2}} (1 - \exp(-(k_2 + k_{-2})t)) - \frac{C_{A_0} (k_1 - k_{-2})}{(k_2 + k_{-2} - k_1 - k_3)} (\exp(-(k_1 + k_3)t) - \exp(-(k_2 + k_{-2})t))$$

- (f) If there are i A molecules, j C molecules, and k D molecules in the system at time t , what is the probability that at some very short time later ($t + \Delta t$) there are $j + 1$ C molecules? Write your answer in terms of the rate constants. Assume that the time interval is short enough that, at most, one reaction event can occur during it (4 points).

If the time interval is sufficiently short that, at most, one reaction occurs, then there are two possible ways to have $j + 1$ C molecules: by reaction 1, with rate $k_1 i$ or by the reverse of reaction 2, with rate $k_{-2} k$. So, the total probability of having $j + 1$ C molecules at time $t + \Delta t$ is

$$P_{j+1}(t + \Delta t) = W_{j,j+1}(\Delta t) = k_1 i \Delta t + k_{-2} k \Delta t = (k_1 i + k_{-2} k) \Delta t$$

2. (25 points total) Consider the elementary gas phase reaction $\text{OH} + \text{H}_2 \leftrightarrow \text{H}_2\text{O} + \text{H}$. 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 $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$.

	OH	H ₂	H ₂ O	H	Transition State
M (amu)	17.01	2.02	18.02	1.01	19.03
I (amu Å²)	0.89	0.28	0.60, 1.16, 1.81		0.93, 5.99, 6.90
ΔH_f(0 K) (kJ/mol)	37.0	0	-238.9	216.0	60.6
ν (cm⁻¹)	3738	4401	1595, 3657, 3756		1210i, 573, 690, 1191, 2439, 3675
g_{elec}	2	1	1	2	2
σ (rotational symmetry number)	1	2	2		1
Hard Sphere Collision Diameter (Å)	2.8	2.9	2.6	2.0	3.0

- (a) What is the hard-sphere collisional rate constant for collisions between OH and H₂ at 300 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

$$\sigma = \pi \left(\frac{d_{OH} + d_{H_2}}{2} \right)^2 = \pi \left(\frac{2.8 + 2.9}{2} \times 10^{-10} \text{ m} \right)^2 = 2.55 \times 10^{-19} \text{ m}^2$$

and the reduced mass for the colliding molecules is

$$\mu = \frac{m_{OH} m_{H_2}}{m_{OH} + m_{H_2}} = \frac{17.01 \cdot 2.02}{17.01 + 2.02} \times \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 3.00 \times 10^{-27} \text{ kg}$$

so

$$k_{coll} = 2.55 \times 10^{-19} \text{ m}^2 \left(\frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}{\pi(3.00 \times 10^{-27} \text{ kg})} \right)^{1/2} = 4.78 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 2.87 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

- (b) Sketch the profile of enthalpy vs. reaction coordinate (at 0 K) for this reaction, clearly labeling the enthalpy of reaction and the forward and reverse enthalpy of activation (4 points).

The enthalpy of formation of the reactants at 0 K is $0 + 37.0 = 37.0 \text{ kJ/mol}$.

The enthalpy of formation of the transition state at 0 K is 60.6 kJ/mol .

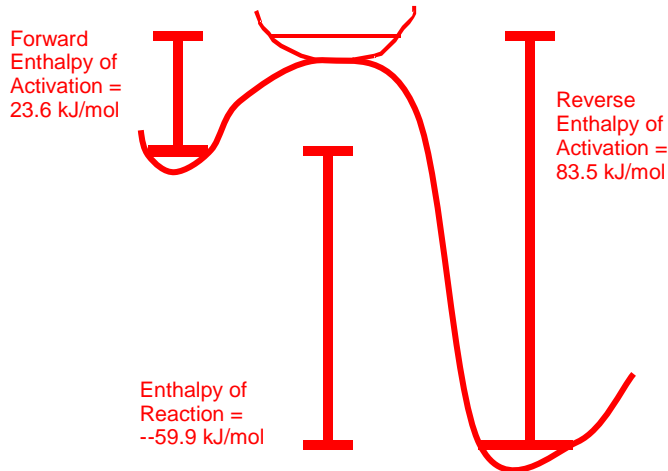
The enthalpy of formation of the products at 0 K is $-238.9 + 216.0 = -22.9 \text{ kJ/mol}$.

Thus, the forward enthalpy of activation is $60.6 - 37.0 = 23.6 \text{ kJ/mol}$,

and the reverse enthalpy of activation is $60.6 - (-22.9) = 83.5 \text{ kJ/mol}$,

and the enthalpy of reaction is $-22.9 - 37.0 = -59.9 \text{ kJ/mol}$

A sketch of the reaction energetics therefore looks like this:



(c) Using transition state theory, calculate the forward rate constant for this reaction at 300 K (12 points).

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

$$k_f = \frac{kT}{h} \frac{(Q^\ddagger/V)}{(Q_{\text{HCl}}/V)(Q_{\text{Cl}}/V)} \exp\left(\frac{-E_o}{kT}\right)$$

The partition functions are as follows:

For OH, a diatomic molecule,

$$Q_{\text{trans}}/V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \left(\frac{2\pi(17.01/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (300) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2}\right)^{3/2} = 6.85 \times 10^{31} \text{ m}^{-3}$$

$$Q_{\text{vib}} = \frac{1}{1 - \exp\left(\frac{-h\nu}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-1.44 \text{ (cm K)} \nu}{300 \text{ K}}\right)}$$

$$Q_{\text{vib}} = \frac{1}{\left(1 - \exp\left(\frac{-1.44 * 3738}{300}\right)\right)} = 1.00$$

$$Q_{\text{rot}} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\pi^2 (0.89/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (300) \text{ K}}{1(6.626 \times 10^{-34} \text{ J s})^2} = 11.0$$

$$Q_{\text{elec}} = 2$$

$$\text{so } Q_{\text{OH}}/V = 6.85 \times 10^{31} * 1 * 11.0 * 2 = 1.51 \times 10^{33} \text{ m}^{-3}$$

For H₂, also a diatomic molecule,

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \left(\frac{2\pi (2.02/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (300) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 2.80 \times 10^{30} \text{ m}^{-3}$$

$Q_{vib} = 1$ (we know this because it was 1 for the OH vibration, and the H_2 vibration is even higher in frequency – no need to calculate it)

$$Q_{rot} = \frac{8\pi^2 I kT}{\sigma h^2} = \frac{8\pi^2 (0.28/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (300) \text{ K}}{2(6.626 \times 10^{-34} \text{ J s})^2} = 1.73$$

$$Q_{elec} = 1$$

$$\text{so } Q_{\text{H}_2}/V = 2.80 \times 10^{30} * 1.0 * 1.73 * 1 = 4.85 \times 10^{30} \text{ m}^{-3}$$

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

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} = \left(\frac{2\pi (19.03/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (300) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} = 8.11 \times 10^{31} \text{ m}^{-3}$$

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

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-573}{208.3}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-690}{208.3}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-1191}{208.3}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-2439}{208.3}\right)\right)} \frac{1}{\left(1 - \exp\left(\frac{-3675}{208.3}\right)\right)}$$

$$Q_{vib} = 1.068 * 1.038 * 1.003 * 1 * 1 = 1.11$$

(None of the vibrations contribute much at this temperature, because kT is much less than the energy of a vibrational quantum, even for the lowest frequency in the structure.)

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

$$Q_{rot} = \frac{\sqrt{\pi}}{1} \left(\frac{8\pi^2 (1/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (300) \text{ K}}{1(6.626 \times 10^{-34} \text{ J s})^2} \right)^{3/2} (I_A I_B I_C)^{1/2}$$

$$Q_{rot} = 77.1(0.93 * 5.99 * 6.90)^{1/2} = 18370$$

$$Q_{elec} = 2$$

$$\text{so } Q_{TS}/V = 8.11 \times 10^{31} * 1.11 * 18370 * 2 = 1.65 \times 10^{36} \text{ m}^{-3}$$

So, the forward rate constant is:

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

$$k_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (300) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{1.65 \times 10^{36} \text{ m}^{-3}}{1.51 \times 10^{33} \text{ m}^{-3} \cdot 4.85 \times 10^{30} \text{ m}^{-3}} \exp\left(\frac{-23600 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (300) \text{ K}}\right)$$

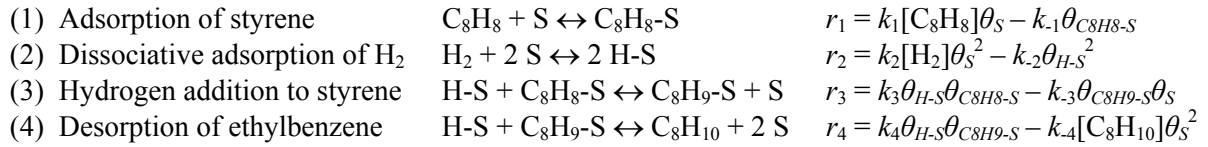
$$k_f = 6.25 \times 10^{12} \text{ s}^{-1} \cdot 2.25 \times 10^{-28} \text{ m}^3 \cdot 7.78 \times 10^{-5} = 1.09 \times 10^{-19} \text{ m}^3 \text{ s}^{-1} = 6.75 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1} = 6.59 \times 10^{10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

(d) Describe an approximation used in transition state theory that is likely to be a poor approximation for this particular reaction (4 points).

For this particular reaction, the worst approximation is probably the assumption of classical behavior – ignoring the possibility of tunneling. Because the H atom is very light, and the reaction involves transfer of an H atom, it turns out that transition state theory would underestimate the reaction rate. Various semi-empirical tunneling corrections are available that might be used to correct for this.

Another less obvious problem is with the use of the classical rotational partition function for the H₂ atom. This classical partition function is based on the assumption that there is a continuum of rotational energy levels. However, because the moment of inertia of H₂ is so small, the energy spacing of rotational levels is unusually large, and rotation is quantized at room temperature.

3. (25 points total) Consider the catalytic hydrogenation of styrene to ethylbenzene via the following sequence of reactions:



Where H-S, C_8H_8-S , and C_8H_9-S are surface species, and S is an empty surface site. The overall reaction is $H_2 + C_8H_8 \rightarrow C_8H_{10}$. Adsorption and reaction steps obey mass action kinetics.

(a) Derive a rate expression for the overall reaction in terms of the forward and reverse rate constants of the four reactions, assuming that hydrogen addition to styrene (step 3) is rate-limiting (15 points).

If step (3) is rate-limiting, then steps 1, 2, and 4 can assumed to be in quasi-equilibrium. From equilibrium of step (1), we get

$$\theta_{C_8H_8-S} = (k_1/k_{-1}) [C_8H_8]\theta_S$$

From equilibrium of step (2), we have

$$\theta_{H-S} = (k_2[H_2]/k_{-2})^{0.5} \theta_S$$

From equilibrium of step (4), we have

$$\theta_{C_8H_9-S} = k_{-4}[C_8H_{10}]\theta_S^2/k_4\theta_{H-S} = (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5} \theta_S$$

Substituting these into the overall site balance gives

$$\theta_S + \theta_{C_8H_8-S} + \theta_{H-S} + \theta_{C_8H_9-S} = 1$$

$$(1 + (k_1/k_{-1}) [C_8H_8] + (k_2[H_2]/k_{-2})^{0.5} + (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5}) \theta_S = 1$$

$$\theta_S = 1/(1 + (k_1/k_{-1}) [C_8H_8] + (k_2[H_2]/k_{-2})^{0.5} + (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5})$$

Thus,

$$\theta_{C_8H_8-S} = (k_1/k_{-1}) [C_8H_8]/(1 + (k_1/k_{-1}) [C_8H_8] + (k_2[H_2]/k_{-2})^{0.5} + (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5})$$

$$\theta_{H-S} = (k_2[H_2]/k_{-2})^{0.5}/(1 + (k_1/k_{-1}) [C_8H_8] + (k_2[H_2]/k_{-2})^{0.5} + (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5})$$

$$\theta_{C_8H_9-S} = (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5}/(1 + (k_1/k_{-1}) [C_8H_8] + (k_2[H_2]/k_{-2})^{0.5} + (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5})$$

and finally, the overall rate of reaction is equal to the rate of step (3), which is

$$r = r_3 = k_3\theta_{H-S}\theta_{C_8H_8-S} - k_{-3}\theta_{C_8H_9-S}\theta_S$$

$$r = (k_3 (k_2[H_2]/k_{-2})^{0.5} (k_1/k_{-1}) [C_8H_8] - k_{-3}(k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5}) / (1 + (k_1/k_{-1}) [C_8H_8] + (k_2[H_2]/k_{-2})^{0.5} + (k_{-4}[C_8H_{10}]/k_4) (k_2[H_2]/k_{-2})^{-0.5})^2$$

Or, with nicer formatting:

$$r = \frac{k_3 \sqrt{k_2[H_2]/k_{-2}} \left(\frac{k_1[C_8H_8]}{k_{-1}} \right) - k_{-3} \left(\frac{k_{-4}[C_8H_{10}]}{k_4} \right) \sqrt{k_{-2}/k_2[H_2]}}{\left(1 + \frac{k_1[C_8H_8]}{k_{-1}} + \sqrt{k_2[H_2]/k_{-2}} + \left(\frac{k_{-4}[C_8H_{10}]}{k_4} \right) \sqrt{k_{-2}/k_2[H_2]} \right)^2}$$

(b) If H_2 is present in large excess, if step (3) is effectively irreversible, and if the surface coverage of all adsorbed species is low, then the reaction becomes pseudo-first-order in

$[C_8H_8]$, with effective rate constant $k_{eff} = \frac{k_1 k_3}{k_{-1}} \sqrt{k_2[H_2]/k_{-2}}$ (if your answer to part (a) is

correct, you should be able to simplify it to this using these assumptions, but you are not required to do so). Suppose the reaction takes place in a 2 mm cubic pellet of porous catalyst. The catalyst has a specific surface area of 50 m²/g, a pore volume fraction of 0.35 and a pellet density of 3.5 g/cm³. The diffusion coefficient of styrene in H₂ within the catalyst pores is 0.1 cm²/s, and the tortuosity of the pores is estimated to be 3.0. For what value of k_{eff} will pore diffusion limitations reduce the reaction rate by a factor of 2, compared to the rate in the absence of pore diffusion limitations? (10 points)

The reaction rate will be reduced by a factor of 2 when the effectiveness factor is 0.5. Using the generic (slab) form for the effectiveness factor vs. Thiele modulus, we want to solve

$$\tanh(\phi)/\phi = 0.5$$

Rearranging this to $\phi = \tanh(\phi)/0.5$ and iterating, starting from $\phi = 2$ leads to

$$\phi = 1.92$$

For an arbitrary pellet shape, the Thiele modulus is defined by $\phi = \frac{V}{S} \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \epsilon_s}}$, which makes

the effectiveness factor vs. Thiele modulus curve approximately the same as the slab solution that we just used. For a cube of diameter 2 mm, we have $V = 8 \text{ mm}^3$ and $S = 6 * 4 \text{ mm}^2 = 24 \text{ mm}^2$, so $V/S = 0.3333 \text{ mm} = 0.03333 \text{ cm}$. The Thiele modulus is then

$$\phi = 0.03333 \text{ cm} \sqrt{\frac{500000 \text{ cm}^2 \text{ g}^{-1} * 3.5 \text{ g cm}^{-3} * k_r * 3}{0.1 \text{ cm}^2 \text{ s}^{-1} * 0.35}} = 408 \sqrt{k_r}$$

where k_r has units of cm/s. Setting the Thiele modulus equal to 1.92 gives $k_r = 2.2 \times 10^{-5} \text{ cm/s}$.

4. (15 points total) Consider the homogeneous gas-phase dehydrogenation of ethylbenzene to styrene ($C_8H_{10} \rightarrow C_8H_8 + H_2$). 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 (6 points).

Let ethylbenzene be denoted by 'A', let styrene be denoted by 'B', and let hydrogen be denoted by 'C' so we have our favorite reaction $A \rightarrow B + C$. 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 – a reversible energy transfer step followed by an irreversible reaction step:



Where A^* denotes an ethylbenzene 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 (5 points).

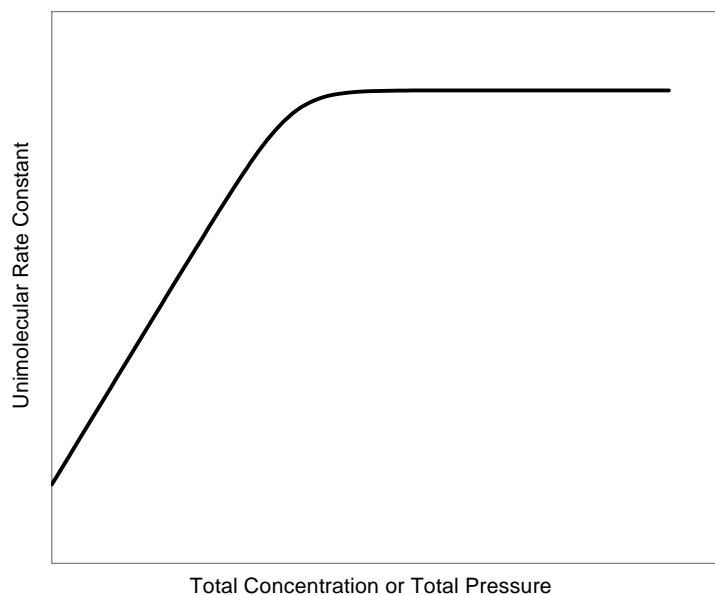
For very high pressures, $k_{-1}[M] \gg k_2$, so k_2 can be neglected in the denominator of k_{uni} leaving the high-pressure limiting rate constant, which we usually call k_∞ .

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

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 (4 points).

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 .