

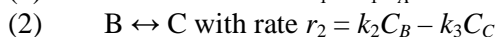
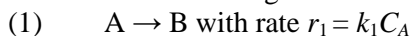
CE 561, Exam 1, November 7, 2008

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 three letter-size sheets (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 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 two reactions:



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

In matrix form, these can be written as:

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

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

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

If the second reaction is treated as a single reaction

(b) Write the rate equations for the concentrations of the three species in matrix form. (5 points)

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

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

(c) Explain how you would solve these equations to obtain expressions for the concentrations of A, B, and C as functions of time, for initial conditions of $C_A(t=0) = C_{A_0}$, $C_B(t=0) = C_C(t=0) = 0$. Take your solution as far as you can in the time available. (10 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 $C(t)$ according to the equation given above.

$$\det(\underline{\underline{M}} - \lambda \underline{\underline{I}}) = \det \begin{bmatrix} -k_1 - \lambda & 0 & 0 \\ k_1 & -k_2 - \lambda & k_3 \\ 0 & k_2 & -k_3 - \lambda \end{bmatrix} = (-k_1 - \lambda)((-k_2 - \lambda)(-k_3 - \lambda) - k_2 k_3) = 0$$

$$(-k_1 - \lambda)(k_2 k_3 + (k_2 + k_3)\lambda + \lambda^2 - k_2 k_3) = (-k_1 - \lambda)(\lambda + k_2 + k_3)\lambda = 0$$

So, the three eigenvalues are $\lambda_1 = -k_1$, $\lambda_2 = -(k_2 + k_3)$, and $\lambda_3 = 0$. Corresponding eigenvectors are obtained by substituting the eigenvalues into $\underline{\underline{M}}x_i = \lambda_i x_i$. For $\lambda_1 = -k_1$ this gives

$$\begin{bmatrix} 0 & 0 & 0 \\ k_1 & -k_2 + k_1 & k_3 \\ 0 & k_2 & -k_3 + k_1 \end{bmatrix} \begin{bmatrix} x_{1,1} \\ x_{1,2} \\ x_{1,3} \end{bmatrix} = 0$$

$$k_1 x_{1,1} + (k_1 - k_2)x_{1,2} + k_3 x_{1,3} = 0$$

$$k_2 x_{1,2} + (k_1 - k_3)x_{1,3} = 0$$

$$x_{1,3} = \frac{k_2}{k_3 - k_1} x_{1,2}$$

$$x_{1,1} = \frac{(k_2 - k_1)x_{1,2} - k_3 x_{1,3}}{k_1} = \frac{(k_2 - k_1) - k_3 \frac{k_2}{k_3 - k_1}}{k_1} x_{1,2} = \frac{k_2 k_3 - k_1 k_2 - k_1 k_3 + k_1^2 - k_2 k_3}{k_1 (k_3 - k_1)} x_{1,2}$$

$$x_{1,1} = \frac{k_1 - k_2 - k_3}{k_3 - k_1} x_{1,2}$$

$$x_1 = \begin{bmatrix} k_1 - k_2 - k_3 \\ k_3 - k_1 \\ k_2 \end{bmatrix}$$

For $\lambda_2 = -k_2 - k_3$ this gives

$$\begin{bmatrix} -k_1 + k_2 + k_3 & 0 & 0 \\ k_1 & k_3 & k_3 \\ 0 & k_2 & k_2 \end{bmatrix} \begin{bmatrix} x_{2,1} \\ x_{2,2} \\ x_{2,3} \end{bmatrix} = 0$$

$$x_{2,1} = 0$$

$$x_{2,2} = -x_{2,3}$$

$$x_2 = \begin{bmatrix} 0 \\ 1 \\ -1 \end{bmatrix}$$

For $\lambda_3 = 0$ this gives

$$\begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & k_3 \\ 0 & k_2 & -k_3 \end{bmatrix} \begin{bmatrix} x_{3,1} \\ x_{3,2} \\ x_{3,3} \end{bmatrix} = 0$$

$$x_{3,1} = 0$$

$$x_{3,2} = \frac{k_3}{k_2} x_{3,3}$$

$$x_3 = \begin{bmatrix} 0 \\ k_3 \\ k_2 \end{bmatrix}$$

And finally, the matrix of eigenvectors (each column of which could be multiplied by an arbitrary constant) is

$$\underline{T} = \begin{bmatrix} k_1 - k_2 - k_3 & 0 & 0 \\ k_3 - k_1 & 1 & k_3 \\ k_2 & -1 & k_2 \end{bmatrix}$$

If we really want to insist on completing this, we can find the inverse of the matrix by augmenting it and performing row operations:

$$\left[\begin{array}{ccc|ccc} k_1 - k_2 - k_3 & 0 & 0 & 1 & 0 & 0 \\ k_3 - k_1 & 1 & k_3 & 0 & 1 & 0 \\ k_2 & -1 & k_2 & 0 & 0 & 1 \end{array} \right]$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ k_3 - k_1 & 1 & k_3 & 0 & 1 & 0 \\ k_2 & -1 & k_2 & 0 & 0 & 1 \end{array} \right]$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ 0 & 1 & k_3 & \frac{k_1 - k_3}{k_1 - k_2 - k_3} & 1 & 0 \\ k_2 & -1 & k_2 & 0 & 0 & 1 \end{array} \right]$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ 0 & 1 & k_3 & \frac{k_1 - k_3}{k_1 - k_2 - k_3} & 1 & 0 \\ 0 & -1 & k_2 & \frac{-k_2}{k_1 - k_2 - k_3} & 0 & 1 \end{array} \right]$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ 0 & 1 & k_3 & \frac{k_1 - k_3}{k_1 - k_2 - k_3} & 1 & 0 \\ 0 & 0 & k_3 + k_2 & \frac{k_1 - k_2 - k_3}{k_1 - k_2 - k_3} & 1 & 1 \end{array} \right]$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ 0 & 1 & k_3 & \frac{k_1 - k_3}{k_1 - k_2 - k_3} & 1 & 0 \\ 0 & 0 & 1 & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} \end{array} \right]$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ 0 & 1 & 0 & \frac{k_1 - k_3}{k_1 - k_2 - k_3} - \frac{k_3}{k_2 + k_3} & 1 - \frac{k_3}{k_2 + k_3} & -\frac{k_3}{k_2 + k_3} \\ 0 & 0 & 1 & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} \end{array} \right]$$

$$\left[\begin{array}{ccc|ccc} 1 & 0 & 0 & \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ 0 & 1 & 0 & \frac{k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} & \frac{k_2}{k_2 + k_3} & -\frac{k_3}{k_2 + k_3} \\ 0 & 0 & 1 & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} \end{array} \right]$$

So, at long last, we have

$$\underline{T}^{-1} = \begin{bmatrix} \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ \frac{k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} & \frac{k_2}{k_2 + k_3} & -\frac{k_3}{k_2 + k_3} \\ \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} \end{bmatrix}$$

To obtain an explicit solution, we would multiply out:

$$\begin{aligned} \underline{C}(t) &= (\underline{T} \exp(\underline{\Lambda}t) \underline{T}^{-1}) \underline{C}_o \\ \underline{C}(t) &= \begin{bmatrix} k_1 - k_2 - k_3 & 0 & 0 \\ k_3 - k_1 & 1 & k_3 \\ k_2 & -1 & k_2 \end{bmatrix} \begin{bmatrix} \exp(-k_1 t) & 0 & 0 \\ 0 & \exp(-(k_2 + k_3)t) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \frac{1}{k_1 - k_2 - k_3} & 0 & 0 \\ \frac{k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} & \frac{k_2}{k_2 + k_3} & -\frac{k_3}{k_2 + k_3} \\ \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} & \frac{1}{k_2 + k_3} \end{bmatrix} \begin{bmatrix} C_{Ao} \\ 0 \\ 0 \end{bmatrix} \\ \underline{C}(t) &= \begin{bmatrix} k_1 - k_2 - k_3 & 0 & 0 \\ k_3 - k_1 & 1 & k_3 \\ k_2 & -1 & k_2 \end{bmatrix} \begin{bmatrix} \frac{C_{Ao}}{k_1 - k_2 - k_3} \exp(-k_1 t) \\ \frac{C_{Ao} k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} \exp(-(k_2 + k_3)t) \\ \frac{C_{Ao}}{k_2 + k_3} \end{bmatrix} \\ \underline{C}(t) &= \begin{bmatrix} C_{Ao} \exp(-k_1 t) \\ \frac{C_{Ao} (k_3 - k_1)}{k_1 - k_2 - k_3} \exp(-k_1 t) + \frac{C_{Ao} k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} \exp(-(k_2 + k_3)t) + \frac{k_3 C_{Ao}}{k_2 + k_3} \\ \frac{C_{Ao} k_2}{k_1 - k_2 - k_3} \exp(-k_1 t) - \frac{C_{Ao} k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} \exp(-(k_2 + k_3)t) + \frac{k_2 C_{Ao}}{k_2 + k_3} \end{bmatrix} \end{aligned}$$

Of course, you did not have to use the matrix method and carry this all the way to the end to get full credit.

- (d) Show how you would find an analytical expression for the *scaled sensitivity coefficient* of the concentration of *B* to the forward rate constant for the second reaction (k_2). Set up the equations and provide a clear description of an appropriate method of solving the problem. Take your solution as far as you can in the time available. (10 points)

In general, the equation for the sensitivity coefficient of species *i* to rate constant *j* is

$$\frac{dZ_{ij}}{dt} = \frac{\partial g_i}{\partial k_j} + \sum_{l=1}^N \frac{\partial g_i}{\partial y_l} Z_{lj}$$

Where g_i is the rate equation for species *i*. Thus, the equation for the sensitivity coefficient of species *B* with respect to k_2 is

$$\frac{dZ_{B2}}{dt} = -C_B + k_1 Z_{A2} - k_2 Z_{B2} + k_3 Z_{C2}$$

From this equation we see that we have to simultaneously solve for the sensitivity coefficients of species A and C to k_2 . Those equations are

$$\frac{dZ_{A2}}{dt} = k_1 Z_{A2}$$

$$\frac{dZ_{C2}}{dt} = C_B + k_2 Z_{B2} - k_3 Z_{C2}$$

These three equations would have to be solved simultaneously. Usually, we would have to solve these along with the equations for the concentrations. However, since we have an explicit analytical expression for the concentrations, we would simply substitute the known expression for C_B into this equation. We also note that the equation for Z_{A2} does not depend on any concentrations or sensitivity coefficients. In fact, it is our favorite ODE, with solution $Z_{A2} = Z_{A2}(t=0)\exp(k_1 t)$. However, the initial condition for Z_{A2} is $Z_{A2}(t=0)=0$. Thus, we simply have $Z_{A2} = 0$, which is what we would expect, since reaction one is irreversible, and we know that the concentration of species A cannot have any dependence on k_2 . Thus, we finally have

$$\frac{dZ_{B2}}{dt} = - \left(\frac{C_{A0}(k_3 - k_1)}{k_1 - k_2 - k_3} \exp(-k_1 t) + \frac{C_{A0} k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} \exp(-(k_2 + k_3)t) + \frac{k_3 C_{A0}}{k_2 + k_3} \right) - k_2 Z_{B2} + k_3 Z_{C2}$$

$$\frac{dZ_{C2}}{dt} = \left(\frac{C_{A0}(k_3 - k_1)}{k_1 - k_2 - k_3} \exp(-k_1 t) + \frac{C_{A0} k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} \exp(-(k_2 + k_3)t) + \frac{k_3 C_{A0}}{k_2 + k_3} \right) + k_2 Z_{B2} - k_3 Z_{C2}$$

Comparing these, we see that

$$\frac{dZ_{B2}}{dt} + \frac{dZ_{C2}}{dt} = 0$$

$$Z_{B2} + Z_{C2} = \text{constant} = 0$$

$$Z_{C2} = -Z_{B2}$$

Substituting this into the equation for Z_{B2} we are left with a single equation for it:

$$\frac{dZ_{B2}}{dt} = - \left(\frac{C_{A0}(k_3 - k_1)}{k_1 - k_2 - k_3} \exp(-k_1 t) + \frac{C_{A0} k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} \exp(-(k_2 + k_3)t) + \frac{k_3 C_{A0}}{k_2 + k_3} \right) - (k_2 + k_3) Z_{B2}$$

Finally, we could solve this with the initial condition $Z_{B2} = 0$ at $t = 0$ to obtain an explicit analytical expression for Z_{B2} as a function of time. We could do so by assuming $Z_{B2} = f(t)\exp(-(k_2+k_3)t)$, substituting that into the equation, integrating, and applying the initial condition.

The above approach is akin to what we would do if we did not have an explicit equation for C_B . In this case, we could have simply taken a partial derivative of C_B with respect to k_2 :

$$Z_{B2} \equiv \frac{\partial C_B}{\partial k_2} = \frac{\partial}{\partial k_2} \left(\frac{C_{A0}(k_3 - k_1)}{k_1 - k_2 - k_3} \exp(-k_1 t) + \frac{C_{A0} k_1 k_2}{(k_1 - k_2 - k_3)(k_2 + k_3)} \exp(-(k_2 + k_3)t) + \frac{k_3 C_{A0}}{k_2 + k_3} \right)$$

Either taking this derivative or solving the above equation would be tedious but doable. The scaled sensitivity coefficient would then be obtained as

$$\sigma_{B2} = \frac{k_2}{C_B} Z_{B2}$$

- (e) 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. (5 points)

If the time interval is sufficiently short that, at most, one reaction occurs, then there are two possible ways to have $j+1$ B molecules: by reaction 1, with rate k_1i or by the reverse of reaction 2, with rate k_3k . So, the total probability of having $j+1$ B molecules at time $t+\Delta t$ is

$$P_{j+1}(t+\Delta t) = W_{j+1}(\Delta t) = k_1i\Delta t + k_3k\Delta t = (k_1i + k_3k) \Delta t$$

2. Consider the elementary gas phase reaction $\text{Al} + \text{H}_2 \leftrightarrow \text{AlH}_2$. Properties of the reactants, transition state, and products are given below. Boltzmann's constant is $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$, and Planck's constant is $h = 6.63 \times 10^{-34} \text{ J s}$.

	Al	H ₂	AlH ₂	Transition State
M (amu)	26.98	2.02	29.00	29.00
I (amu Å ²)		0.28	1.3; 3.9; 5.1	1.5; 4.5; 6.0
$\Delta H_f(0 \text{ K})$ (kJ/mol)	337.7	0.0	280.0	451.9
ν (cm ⁻¹)		4140	729; 1750; 1790	4003i; 758; 1346
g_{elec}	2	1	2	2
Hard Sphere Collision Diameter (Å)	3.0	2.9	3.5	

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

Al is an atom, with three translational, zero rotational, and zero vibrational degrees of freedom.

H₂ is a linear diatomic molecule, with three translational, two rotational, and one vibrational degree of freedom.

AlH₂ is a nonlinear triatomic molecule (we can tell it is nonlinear because it has three distinct moments of inertia). Thus, it has three translational, three rotational, and three vibrational degrees of freedom.

The transition state is also a nonlinear triatomic, with three translational, three rotational, and three vibrational degrees of freedom. The imaginary vibrational frequency corresponds to the reaction coordinate, and thus is not truly a vibrational degree of freedom. So, two vibrational degrees of freedom is an equally correct answer.

- (b) What is the hard-sphere collisional rate constant for collisions between Al and H₂ at 1000 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

$$\sigma = \pi \left(\frac{d_{Al} + d_{H_2}}{2} \right)^2 = \pi \left(\frac{3.0 + 2.9}{2} \times 10^{-10} \text{ m} \right)^2 = 2.73 \times 10^{-19} \text{ m}^2$$

and the reduced mass for the colliding molecules is

$$\mu = \frac{m_{Al} m_{H_2}}{m_{Al} + m_{H_2}} = \frac{26.98 \cdot 2.02}{26.98 + 2.02} \times \frac{1 \text{ kg}}{6.022 \times 10^{26} \text{ amu}} = 3.12 \times 10^{-27} \text{ kg}$$

so

$$k_{coll} = 2.73 \times 10^{-19} \text{ m}^2 \left(\frac{8(1.38 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})}{\pi(3.12 \times 10^{-27} \text{ kg})} \right)^{1/2} = 9.16 \times 10^{-16} \frac{\text{m}^3}{\text{molecule s}} = 5.52 \times 10^8 \frac{\text{m}^3}{\text{mol s}}$$

(c) Sketch the profile of enthalpy vs. reaction coordinate (at 0 K) for this reaction, clearly labeling the enthalpy of reaction and the forward and reverse enthalpy of activation. (5 pts)

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

The enthalpy of formation of the transition state at 0 K is 451.9 kJ/mol .

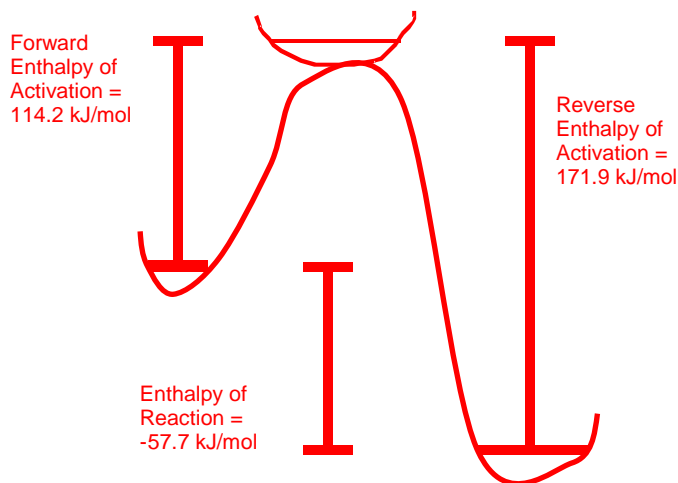
The enthalpy of formation of the product at 0 K is 280.0 kJ/mol .

Thus, the forward enthalpy of activation is $451.9 - 337.7 = 114.2 \text{ kJ/mol}$,

and the reverse enthalpy of activation is $451.9 - 280.0 = 171.9 \text{ kJ/mol}$,

and the enthalpy of reaction is $280.0 - 337.7 = -57.7 \text{ kJ/mol}$

A sketch of the reaction energetics therefore looks like this:



(d) Use transition state theory to calculate the forward rate constant for this reaction at 1000 K, for pressures sufficiently high that it is independent of pressure (15 points).

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

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

The partition functions are as follows:

For Al, an atom:

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

An atom has no vibrational or rotational motions.

$$Q_{elec} = 2$$

$$\text{so } Q_{Al}/V = 8.33 \times 10^{32} * 2 = 1.67 \times 10^{33} \text{ m}^{-3}$$

For H₂, a diatomic molecule,

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \left(\frac{2\pi(2.02/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2}\right)^{3/2} = 1.71 \times 10^{31} \text{ m}^{-3}$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} = \frac{8\pi^2 (0.28/6.022 \times 10^{46}) (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{2(6.626 \times 10^{-34} \text{ J s})^2} = 5.77$$

$$Q_{vib} = \frac{1}{1 - \exp\left(\frac{-hv}{kT}\right)} = \frac{1}{1 - \exp\left(\frac{-1.44 \text{ (cm K)} \bar{\nu}}{1000 \text{ K}}\right)} = \frac{1}{\left(1 - \exp\left(\frac{-1.44 * 4140}{1000}\right)\right)} = 1.00$$

$$Q_{elec} = 1$$

$$\text{so } Q_{H2}/V = 1.71 \times 10^{30} * 1.0 * 5.77 * 1 = 9.89 \times 10^{31} \text{ m}^{-3}$$

Finally, the transition state is a nonlinear polyatomic molecule (with 3 distinct moments of inertia and $3N - 6 = 3$ 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:

$$Q_{trans}/V = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} = \left(\frac{2\pi(29.00/6.022 \times 10^{26}) \text{ kg} (1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{(6.626 \times 10^{-34} \text{ J s})^2}\right)^{3/2} = 9.29 \times 10^{32} \text{ m}^{-3}$$

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

$$Q_{vib} = \frac{1}{\left(1 - \exp\left(\frac{-758}{694.4}\right)\right) \left(1 - \exp\left(\frac{-1346}{694.4}\right)\right)} = 1.76$$

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

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

$$Q_{rot} = 468.9 (1.5 \cdot 4.5 \cdot 6.0)^{1/2} = 2984$$

$$Q_{elec} = 2$$

$$\text{so } Q_{TS}/V = 9.29 \times 10^{32} \cdot 1.76 \cdot 2984 \cdot 2 = 9.76 \times 10^{36} \text{ m}^{-3}$$

So, the forward rate constant is:

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

$$k_f = \frac{(1.381 \times 10^{-23}) \text{ J K}^{-1} (1000) \text{ K}}{6.626 \times 10^{-34} \text{ J s}} \frac{9.76 \times 10^{36} \text{ m}^{-3}}{1.67 \times 10^{33} \text{ m}^{-3} \cdot 9.89 \times 10^{31} \text{ m}^{-3}} \exp\left(\frac{-114200 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} (1000) \text{ K}}\right)$$

$$k_f = 2.08 \times 10^{13} \text{ s}^{-1} \cdot 5.90 \times 10^{-29} \text{ m}^3 \cdot 1.083 \times 10^{-6} = 1.33 \times 10^{-21} \text{ m}^3 \text{ s}^{-1} = 1.33 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} = 8.00 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

(e) Sketch and qualitatively describe the expected pressure dependence of the forward rate constant for this reaction. (5 points)

The pressure dependence of a recombination reaction like this one (the reverse of a unimolecular decomposition, is just the same as that of the unimolecular decomposition. We can write something analogous to the Lindemann-Hinshelwood expression, as



Applying the pseudo-steady-state approximation for AlH_2^* , we have

$$k_1[\text{Al}][\text{H}_2] - k_{-1}[\text{AlH}_2^*] - k_2[\text{AlH}_2^*][\text{M}] = 0$$

$$[\text{AlH}_2^*] = k_1[\text{Al}][\text{H}_2] / (k_{-1} + k_2[\text{M}])$$

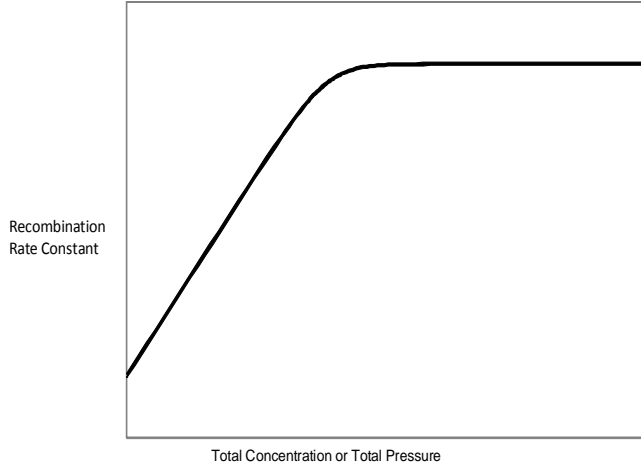
The overall reaction rate is then the rate of the second step

$$\text{Rate} = k_2[\text{AlH}_2^*][\text{M}] = k_1 k_2 [\text{M}][\text{Al}][\text{H}_2] / (k_{-1} + k_2[\text{M}])$$

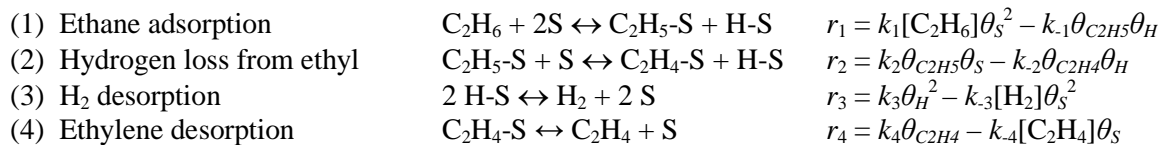
At low pressures, where $k_{-1} \gg k_2[\text{M}]$, the reaction behaves as if it were third order (the bimolecular rate constant is proportional to pressure), $k_{rec} = (k_1 k_2 / k_{-1})[\text{M}]$

At high pressures, where $k_2[\text{M}] \gg k_{-1}$, the rate becomes independent of pressure, and $k_{rec} = k_1$ (the rate constant that we calculated from TST above).

One can arrive at the same conclusion by noting that the equilibrium constant is independent of pressure, so the pressure dependence of the recombination rate constant must be the same as that of the unimolecular decomposition rate constant.



3. Consider the surface-catalyzed cracking of ethane to ethylene and hydrogen, by the following mechanism:



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

If step 3 is rate limiting, that means we assume that the other three steps are pseudo-equilibrated. As always, we also have the site balance equation. We want to use those four equations to determine the surface site fractions in terms of the gas phase concentrations and rate parameters.

$$\begin{aligned}
 k_1[C_2H_6]\theta_S^2 - k_{-1}\theta_{C_2H_5}\theta_H &= 0 \\
 k_2\theta_{C_2H_5}\theta_S - k_{-2}\theta_{C_2H_4}\theta_H &= 0 \\
 k_4\theta_{C_2H_4} - k_{-4}[C_2H_4]\theta_S &= 0 \\
 \theta_{C_2H_4} + \theta_{C_2H_5} + \theta_H + \theta_S &= 1
 \end{aligned}$$

From the third equation, $\theta_{C_2H_4} = (k_{-4}/k_4)[C_2H_4]\theta_S = K_4^{-1}[C_2H_4]\theta_S$, where K_4 is an adsorption equilibrium constant.

From the second equation, $\theta_{C_2H_5} = (k_{-2}/k_2) \theta_{C_2H_4}\theta_H/\theta_S = K_2^{-1}\theta_{C_2H_4}\theta_H/\theta_S$

Using the result of the previous equation, this becomes, $\theta_{C_2H_5} = K_2^{-1}K_4^{-1}[C_2H_4]\theta_H$

Substituting this into the first equation gives

$$k_1[C_2H_6]\theta_S^2 - k_{-1}K_2^{-1}K_4^{-1}[C_2H_4]\theta_H^2 = 0$$

From which

$$\theta_H = \sqrt{\frac{K_1K_2K_4[C_2H_6]}{[C_2H_4]}}\theta_S$$

And, using that result

$$\theta_{C_2H_5} = \sqrt{\frac{K_1[C_2H_6][C_2H_4]}{K_2K_4}}\theta_S$$

Substituting all of this into the overall site balance gives:

$$\sqrt{\frac{K_1 K_2 K_4 [C_2 H_6]}{[C_2 H_4]}} \theta_s + \sqrt{\frac{K_1 [C_2 H_6] [C_2 H_4]}{K_2 K_4}} \theta_s + \frac{[C_2 H_4]}{K_4} \theta_s + \theta_s = 1$$

$$\theta_s = \frac{1}{1 + \sqrt{\frac{K_1 K_2 K_4 [C_2 H_6]}{[C_2 H_4]}} + \sqrt{\frac{K_1 [C_2 H_6] [C_2 H_4]}{K_2 K_4}} + \frac{[C_2 H_4]}{K_4}}$$

Finally, then, the overall reaction rate is

$$r = k_3 \theta_s^2 - k_{-3} [H_2] \theta_s^2$$

$$r = \frac{k_3 \frac{K_1 K_2 K_4 [C_2 H_6]}{[C_2 H_4]} - k_{-3} [H_2]}{\left(1 + \sqrt{\frac{K_1 K_2 K_4 [C_2 H_6]}{[C_2 H_4]}} + \sqrt{\frac{K_1 [C_2 H_6] [C_2 H_4]}{K_2 K_4}} + \frac{[C_2 H_4]}{K_4} \right)^2}$$

4. Suppose a surface reaction with first-order kinetics occurs on the pore walls within a porous catalyst pellet that has been formed into long rods with a hexagonal cross-section, as illustrated below:



If the effective diffusion coefficient of the reactant within the catalyst is $0.1 \text{ cm}^2/\text{s}$, the catalyst specific surface area is $30 \text{ m}^2/\text{g}$, the catalyst pellet density is 0.8 g/cm^3 , and the rate constant for the first order surface reaction is 10 cm/s , estimate the rod width d for which diffusion limitations will reduce the overall reaction rate by a factor of 2 from the rate that would be observed in the absence of diffusion limitations.

The observed reaction rate is reduced by a factor of 2 when the effectiveness factor is 0.5. Using the generic (slab) version of the effectiveness factor as a function of Thiele modulus, we have

$$\frac{\tanh(\phi)}{\phi} = 0.5$$

This can be solved iteratively or by trial and error to get $\phi = 1.92$.

The Thiele modulus for a pellet of arbitrary shape is given by:

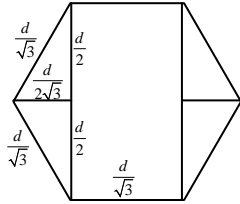
$$\phi = \frac{V}{S} \sqrt{\frac{S_g \rho_c k_r \tau}{D_A \varepsilon_s}}$$

We have numerical values for everything except V/S :

$$1.92 = \frac{V}{S} \sqrt{\frac{30 \times 10^4 * 0.8 * 0.1}{0.1}}$$

This gives $V/S = 3.92 \times 10^{-4} \text{ cm}$.

All that remains is to relate the surface to volume ratio of the pellet to the dimension d given. A little middle school geometry is required:



In the construction shown above, there is a rectangle with area $d * \frac{d}{\sqrt{3}}$ and four triangles that each

have area $\frac{1}{2} * \frac{d}{2} * \frac{d}{2\sqrt{3}}$. Thus, the total cross-sectional area is

$$A_c = \frac{d^2}{\sqrt{3}} + 4 * \frac{d^2}{8\sqrt{3}} = \frac{3d^2}{2\sqrt{3}} = \frac{\sqrt{3}}{2} d^2$$

The perimeter of the hexagon is

$$p = 6 * \frac{d}{\sqrt{3}} = 2\sqrt{3}d$$

Thus, for an arbitrary length l of the hexagonal rod, the volume to surface ratio is

$$\frac{V}{S} = \frac{\frac{\sqrt{3}}{2} d^2 l}{2\sqrt{3} d l} = \frac{d}{4}$$

Returning to the problem at hand, we have

$$d/4 = 3.92 \times 10^{-4} \text{ cm, or } d = 1.57 \times 10^{-3} \text{ cm} = 15.7 \text{ microns} = \text{too small to be practical}$$