

CE 561, Exam 1, October 27, 1998

The exam consists of one long problem, with 21 parts (labeled (a) through (u)). Some, but not all of the parts depend on previous parts. Carefully explain any assumptions you make, label what part of the problem you are working on, and define the symbols that you use. The point value of each part is indicated – budget your effort accordingly. Good luck.

Consider the consecutive, effectively irreversible, first-order reactions of gas phase molecules A, B, and C, occurring in a system where they are highly diluted in an inert gas:



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

In general, we can write a set of reactions as  $\underline{\underline{a}}A = \underline{0}$  where  $\underline{\underline{a}}$  is the stoichiometric matrix. In this case, we have

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

(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. (4 pts.)

The rate equations are

$$\frac{dC_A}{dt} = -k_1 C_A$$

$$\frac{dC_B}{dt} = 2k_1 C_A - k_2 C_B$$

$$\frac{dC_C}{dt} = 2k_2 C_B$$

Or, in matrix form

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

(c) Describe briefly how you would solve these equations using matrix methods (*you do not have to actually solve them*). (5 pts.)

In matrix form, the solution can be written as

$$\underline{C}(t) = \exp(\underline{\underline{M}}t) \underline{C}_o, \text{ where } \underline{\underline{M}} \text{ is the matrix of rate coefficients}$$

$$\underline{\underline{M}} = \begin{bmatrix} -k_1 & 0 & 0 \\ 2k_1 & -k_2 & 0 \\ 0 & 2k_2 & 0 \end{bmatrix}.$$

This can be written in terms of the eigenvalues and eigenvectors of  $\underline{\underline{M}}$  as

$$\underline{C}(t) = \underline{T} \exp(\underline{\Lambda}t) \underline{T}^{-1} \underline{C}_o$$

where  $\underline{\Lambda}$  is the diagonal matrix of eigenvalues of  $\underline{M}$  and  $\underline{T}$  is the matrix whose columns are the corresponding eigenvectors. The eigenvalues of  $\underline{M}$  are the roots of the equation

$$\det(\underline{M} - \underline{I}\lambda) = (-k_1 - \lambda)(-k_2 - \lambda)(-\lambda) = 0$$

so  $\lambda_1 = -k_1$ ,  $\lambda_2 = -k_2$ , and  $\lambda_3 = 0$ .

Solving for the eigenvectors gives the matrix  $\underline{T}$  as

$$\underline{T} = \begin{bmatrix} 1 & 0 & 0 \\ \frac{-2k_1}{k_1 - k_2} & 1 & 0 \\ \frac{4k_2}{k_1 - k_2} & -2 & 1 \end{bmatrix}$$

and taking the inverse (readily done by hand since there are so many zero elements) gives

$$\underline{T}^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ \frac{2k_1}{k_1 - k_2} & 1 & 0 \\ 4 & 2 & 0 \end{bmatrix}$$

The matrix  $\exp(\underline{\Lambda}t)$  is simply

$$\exp(\underline{\Lambda}t) = \begin{bmatrix} e^{-k_1 t} & 0 & 0 \\ 0 & e^{-k_2 t} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Multiplying things out gives

$$\underline{C}(t) = \begin{bmatrix} 1 & 0 & 0 \\ \frac{-2k_1}{k_1 - k_2} & 1 & 0 \\ \frac{4k_2}{k_1 - k_2} & -2 & 1 \end{bmatrix} \begin{bmatrix} e^{-k_1 t} & 0 & 0 \\ 0 & e^{-k_2 t} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ \frac{2k_1}{k_1 - k_2} & 1 & 0 \\ 4 & 2 & 0 \end{bmatrix} \underline{C}_o$$

$$\underline{C}(t) = \begin{bmatrix} e^{-k_1 t} & 0 & 0 \\ \frac{2k_1}{k_1 - k_2} (e^{-k_2 t} - e^{-k_1 t}) & e^{-k_2 t} & 0 \\ \frac{4k_2 (1 - e^{-k_1 t}) + 4k_1 (e^{-k_2 t} - 1)}{k_1 - k_2} & 2(1 - e^{-k_2 t}) & 1 \end{bmatrix} \underline{C}_o$$

You didn't have to actually do all of this, just say that this is what could be done.

- (d) Describe briefly how you would solve these equations using Laplace transform methods. (you do not have to actually solve them). (5 pts.)

Taking the Laplace transform of the rate equations would give:

$$sC_A - C_{Ao} = -k_1c_A$$

$$sC_B - C_{Bo} = 2k_1c_A - k_2c_B$$

$$sC_C - C_{Co} = 2k_2c_B$$

where the lowercase letters indicate the Laplace transforms of the corresponding concentrations. Solving these gives

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

$$c_B = \frac{C_{Bo} + 2k_1c_A}{s + k_2} = \frac{C_{Bo}}{s + k_2} + \frac{k_1C_{Ao}}{(s + k_2)(s + k_1)}$$

$$c_C = \frac{C_{Co} + 2k_2c_B}{s} = \frac{C_{Co}}{s} + \frac{2k_2C_{Bo}}{s(s + k_2)} + \frac{2k_1k_2C_{Ao}}{s(s + k_2)(s + k_1)}$$

To obtain the concentrations, these would be expanded in partial fractions and then the inverse Laplace transforms would be taken.

- (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. (5 pts.)

The simplest numerical method that we know is the explicit Euler method. For this problem, the algorithm would be something like:

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For I=1,nsteps
  CA(I+1)=CA(I)-k1*CA(I)*dt
  CB(I+1)=CB(I)+(2*k1*CA(I)-k2*CB(I))*dt
  CC(I+1)=CC(I)+2*k2*CB(I)*dt
  t(I+1)=t+dt
end
  
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where dt is a small time interval.

Advantages of this method are that it is easy to implement, easy to remember, and can readily be used in a spreadsheet.

Disadvantages are that it becomes unstable for time steps larger than some critical size and it has a relatively low degree of accuracy (error proportional to dt).

- (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  $C_A = C_{Ao}$ ,  $C_B = C_C = 0$ . (5 pts.)

Probably the easiest thing to do is to just integrate them sequentially. This is possible because the reactions are irreversible. We know from memory that the concentration of A is given by

$$C_A = C_{A_0} \exp(-k_1 t)$$

Substituting this into the rate equation for B gives

$$\frac{dC_B}{dt} + k_2 C_B = 2k_1 C_{A_0} \exp(-k_1 t)$$

We guess that the solution is of the form  $C_B = f(t) \exp(-k_2 t)$ . Substituting this into the differential equation gives

$$-k_2 f(t) \exp(-k_2 t) + f'(t) \exp(-k_2 t) + k_2 f(t) \exp(-k_2 t) = 2k_1 C_{A_0} \exp(-k_1 t)$$

$$\text{from which } f'(t) = 2k_1 C_{A_0} \exp((k_2 - k_1)t)$$

Integrating this gives

$$f(t) = \frac{2k_1 C_{A_0}}{k_2 - k_1} \exp((k_2 - k_1)t) + \text{CONST}$$

At  $t = 0$ ,  $C_B = 0$ , so  $f(0) = 0$ , so the integration constant is

$$\text{CONST} = -\frac{2k_1 C_{A_0}}{k_2 - k_1}$$

This gives the final expression for  $C_B$  (after some rearrangement) as

$$C_B = \frac{2k_1 C_{A_0}}{k_1 - k_2} (\exp(-k_2 t) - \exp(-k_1 t))$$

Finally, from stoichiometry,  $C_C = 4C_{A_0} - 4C_A - 2C_B$ , from which we get

$$C_C = 4C_{A_0} \frac{k_2(1 - e^{-k_1 t}) + k_1(e^{-k_2 t} - 1)}{k_1 - k_2}$$

- (g) What reaction time maximizes the yield of B (moles of B produced per mole of A initially present)? Give your solution in terms of the initial concentration of A and the rate constants for the two reactions. (5 pts.)

The concentration of B (proportional to the yield of B) goes through a maximum when its 1<sup>st</sup> derivative is zero. From the equation for the concentration of B given above, this is the solution of

$$\frac{dC_B}{dt} = \frac{2k_1 C_{A_0}}{k_1 - k_2} (-k_2 \exp(-k_2 t) + k_1 \exp(-k_1 t)) = 0$$

which is

$$t_{\max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2}$$

- (h) What is the maximum attainable yield of B? Again, give your result in terms of the rate constant and initial concentration of A. (3 pts.)

Substituting the above time into the expression for the concentration of B gives

$$C_{B \max} = \frac{2k_1 C_{A0}}{k_1 - k_2} \left( \exp \left( -\frac{k_2 \ln \left( \frac{k_1}{k_2} \right)}{k_1 - k_2} \right) - \exp \left( -\frac{k_1 \ln \left( \frac{k_1}{k_2} \right)}{k_1 - k_2} \right) \right)$$

$$C_{B \max} = \frac{2k_1 C_{A0}}{k_1 - k_2} \left( \left( \frac{k_1}{k_2} \right)^{-\frac{k_2}{k_1 - k_2}} - \left( \frac{k_1}{k_2} \right)^{-\frac{k_1}{k_1 - k_2}} \right)$$

The yield of B is defined here as  $yield = C_B/C_{A0}$ . The way that it is defined here, the maximum possible yield (all A converted to B, when  $k_1/k_2$  goes to infinity) would be 2. For particular rate constants the maximum yield is

$$yield_{\max} = \frac{2k_1}{k_1 - k_2} \left( \left( \frac{k_1}{k_2} \right)^{-\frac{k_2}{k_1 - k_2}} - \left( \frac{k_1}{k_2} \right)^{-\frac{k_1}{k_1 - k_2}} \right)$$

- (i) Derive an equation for the *scaled sensitivity* of the concentration of species A to the rate constant for the reaction  $A \rightarrow 2 B$ . (5 pts.)

The scaled sensitivity of  $C_A$  to  $k_1$  is defined as

$$\mathbf{s} = \frac{k_1}{C_A} \frac{\partial C_A}{\partial k_1}$$

Applying this to  $C_A = C_{A0} \exp(-k_1 t)$  gives

$$\mathbf{s} = \frac{k_1}{C_{A0} \exp(-k_1 t)} (-t C_{A0} \exp(-k_1 t)) = -k_1 t$$

The scaled sensitivity goes to infinity at long times, because the concentration of A goes to zero at long times.

**For parts (j) through (m), assume that the reactions that we have been working with are catalyzed by a solid surface. The sequence of elementary steps by which they occur are:**

- (1s)  $A + S \leftrightarrow A-S$   
 (2s)  $A-S + S \rightarrow 2 B-S$   
 (3s)  $B-S \leftrightarrow B + S$   
 (4s)  $B-S + S \rightarrow 2 C-S$   
 (5s)  $C-S \leftrightarrow C + S$

**Where S represents a vacant surface site.**

- (j) Assuming that steps (2s) and (4s) are irreversible and rate-limiting, so that the other three steps are in quasi-equilibrium (obeying a Langmuir adsorption isotherm), derive expressions for the rates of the overall reactions ( $A \rightarrow 2 B$  and  $B \rightarrow 2 C$ ), in terms of rate constants and equilibrium constants for the 5 elementary steps ((1s) through (5s)) and the gas phase concentrations. (10 pts.)

If steps 1s, 3s, and 5s are in equilibrium, so that we have competitive adsorption obeying the Langmuir isotherm, then the fractional surface coverages will be

$$q_A = \frac{K_A C_A}{1 + K_A C_A + K_B C_B + K_C C_C}$$

$$q_B = \frac{K_B C_B}{1 + K_A C_A + K_B C_B + K_C C_C}$$

$$q_C = \frac{K_C C_C}{1 + K_A C_A + K_B C_B + K_C C_C}$$

$$q_S = \frac{1}{1 + K_A C_A + K_B C_B + K_C C_C}$$

where  $K_A$ ,  $K_B$ , and  $K_C$  are the Langmuir adsorption equilibrium constants for A, B, and C. These can be derived by setting the rates of steps 1s, 3s, and 5s equal to zero, then solving these equations, along with the equation for conservation of the total number of sites, to get the surface coverages in terms of the equilibrium constants and gas phase concentrations. The rate of the reaction  $A \rightarrow 2B$  is then given by the rate of step 2s as

$$r_1 = k_{2s} q_S q_A C_t^2 = \frac{k_{2s} K_A C_A}{(1 + K_A C_A + K_B C_B + K_C C_C)^2}$$

where  $C_t$  is the total concentration of surface sites. Likewise, the rate of  $B \rightarrow 2C$  is

$$r_2 = k_{4s} q_S q_B C_t^2 = \frac{k_{4s} K_B C_B}{(1 + K_A C_A + K_B C_B + K_C C_C)^2}$$

**In experiments on a single-crystal, flat catalyst surface at 298 K, the reaction rates were found to be**

**Rate of  $A \rightarrow 2B = r_1$  (moles  $\text{cm}^{-2} \text{s}^{-1}$ ) =  $3.0 \times 10^{-4}$  (cm/s)  $\times C_A$  (moles/cm<sup>3</sup>)**

**Rate of  $B \rightarrow 2C = r_2$  (moles  $\text{cm}^{-2} \text{s}^{-1}$ ) =  $1.5 \times 10^{-4}$  (cm/s)  $\times C_B$  (moles/cm<sup>3</sup>)**

- (k) What does the fact that the reactions are both apparently first order tell us about the surface coverages of the reactants and products? (3 pts.)

Comparing these observations to the above Langmuir-Hinshelwood rate expression and Langmuir isotherm surface coverages, we see that the reactions will be first order if the term  $(1 + K_A C_A + K_B C_B + K_C C_C)^2$  is approximately equal to one. This will be the case when all of the products of gas phase concentration and Langmuir adsorption equilibrium constants are much less than one ( $K_A C_A \ll 1$ ,  $K_B C_B \ll 1$ ,  $K_C C_C \ll 1$ ). This is equivalent to saying that the surface coverages are all small ( $q_A \ll 1$ ,  $q_B \ll 1$ ,  $q_C \ll 1$ ,  $q_S \cong 1$ ).

- (l) If the diffusion coefficients of A, B, and C in the inert gas are all about 0.3 cm<sup>2</sup>/s and we plan to use the catalyst in a very thin film on an alumina support with a porosity of 0.4, a pellet density of 2.4 g/cm<sup>3</sup>, and a surface area of 120 m<sup>2</sup>/g, about how large can we make the catalyst pellets before pore diffusion will begin to affect the reaction rate? Show how you have made your estimate (no credit for just guessing). (5 pts.)

Diffusion limitations will affect the reaction of A before they affect the reaction of B because  $A \rightarrow 2B$  has a larger rate constant than  $B \rightarrow 2C$ , and because B is produced *inside the pores*, so it has to diffuse in to a lesser extent. Therefore, we can just worry about diffusion effects on the 1<sup>st</sup> reaction,  $A \rightarrow 2B$ . Diffusion effects will become important when the Thiele modulus is about 1. For a sphere, we define the Thiele modulus as

$$f = \frac{R}{3} \sqrt{\frac{S_g r_c k_r t}{D_A e_s^2}}$$

For this catalyst,  $S_g = 120 \text{ m}^2/\text{g} = 1.2 \times 10^6 \text{ cm}^2/\text{g}$ ,  $r_c = 2.4 \text{ g/cm}^3$ ,  $k_r = 3.0 \times 10^{-4} \text{ cm/s}$ ,  $D_A = 0.3 \text{ cm}^2/\text{s}$ , and  $e_s = 0.4$ . We don't know anything about the tortuosity ( $\tau$ ), so we'll take a guess and call it 3. In that case

$$f = \frac{R}{3} \sqrt{\frac{(1.2 \times 10^6)(2.4)(3 \times 10^{-4})(3)}{(0.3)(0.4)^2}} = 77R, \text{ with } R \text{ in cm.}$$

So, the Thiele modulus is one, when  $R$  is about  $1/77 \text{ cm} = 0.13 \text{ mm}$ . So, the pellets can only be about  $1/4$  millimeter in diameter. This is a pretty small catalyst pellet, and is probably not practical for many reactor types (consider trying to flow a large volume of gas through a bed of 0.26 mm diameter spheres).

- (m) How would pore diffusion limitations effect the yield of B? (3 pts.)

Pore diffusion limitations will decrease the yield of B, since the step that produces B will be slowed down more than the step that consumes B (as stated in the previous part).

**At sufficiently high temperatures, these same reactions will occur in the gas phase without a catalyst.**

**For parts (n) through (s), let A, B, and C, be cyclooctane ( $C_8H_{16}$ ), cyclobutane ( $C_4H_8$ ), and ethylene ( $C_2H_4$ ), respectively. For these problems, the reactions  $A \rightarrow 2B$  and  $B \rightarrow 2C$  are assumed to be elementary gas phase reactions, occurring in a nitrogen ( $N_2$ ) bath gas. The mole fractions of A, B, and C are very small.**

- (n) How many vibrational, rotational, and translational degrees of freedom do each of the three molecules have? (3 pts.)

They are all non-linear molecules, so they each have 3 translational degrees of freedom, 3 rotational degrees of freedom, and  $3N-6$  vibrational degrees of freedom, where  $N$  is the number of atoms in the molecule.  $C_8H_{16}$  has 24 atoms, and therefore 66 vibrational frequencies.  $C_4H_8$  has 12 atoms, and therefore 30 vibrational frequencies.  $C_2H_4$  has 6 atoms, and therefore 12 vibrational frequencies.

- (o) Will the entropy of reaction for each of the two reactions be positive, negative, or nearly zero? Why? (3 pts.)

For both reaction steps, the entropy of reaction will be positive because we are creating two molecules from one. This converts 6 vibrational degrees of freedom (that contribute

little to the entropy) to 3 rotational and 3 translational degrees of freedom (that make much greater contributions to the entropy).

- (p) Write the simplest rate expressions that you can that qualitatively describe the pressure dependence of the two reactions. Sketch a log-log plot of the unimolecular rate constant vs. total pressure. What are the limiting values of the unimolecular rate constant at high and low pressures? (10 pts.)

The simplest theory of the pressure dependence of unimolecular reactions that is qualitatively correct is the Lindemann-Hinshelwood theory. This is derived from the simple mechanism



Applying the pseudo-steady-state approximation to the energized reactant,  $A^*$ , gives the overall reaction rate for  $A \rightarrow \text{products}$  as

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

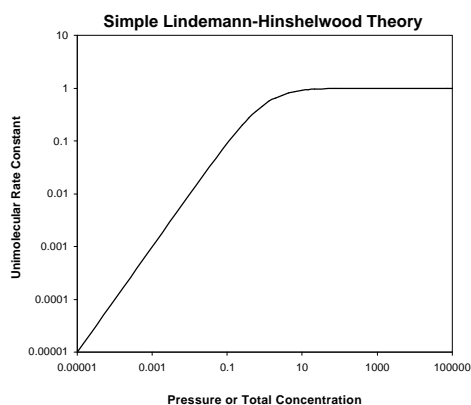
where the rate parameters are as defined in the Lindemann-Hinshelwood mechanism presented above. So, the apparent unimolecular rate coefficient is

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

At high pressures ( $k_{-1}[M] \gg k_2$ ), this becomes  $k_{uni} = k_{\infty} = k_1 k_2 / k_{-1}$ , and the reaction rate is independent of pressure (total concentration  $[M]$ ).

At low pressures ( $k_{-1}[M] \ll k_2$ ), the rate constant becomes  $k_{uni} = k_1 [M]$ , and the reaction rate is directly proportional to total pressure (total concentration).

A log-log plot of the pressure dependence of the rate constant looks like



This pressure dependence applies to both reaction steps ( $A \rightarrow 2B$  and  $B \rightarrow 2C$ )

- (q) If the two reactions have the same activation energy, which one will exhibit pressure dependence at higher pressures and why? How might this effect the yield of B? (4 pts.)  
 The second reaction step ( $B \rightarrow 2C$ , cyclobutane  $\rightarrow$  2 ethylene) will show pressure dependence at higher pressures than the first step. This is because the reactant in the second step (cyclobutane) has less degrees of freedom in which it can distribute its

internal energy than the reactant in the first step (cyclooctane). Therefore, the probability of it locating the critical energy in the particular motion that corresponds to the reaction coordinate is higher for cyclobutane than for cyclooctane (all other things being equal). Therefore, its elementary rate constant for product formation ( $k_2$  in the Lindemann-Hinshelwood scheme from the previous part) will become larger than the collision rate at higher pressures than for cyclooctane. Rule of thumb: The bigger the reactant molecule, the less susceptible the reaction is to falloff effects.

- (r) At 298 K and 1 atmosphere total pressure, about how many collisions per second will a particular A molecule have with the nitrogen bath gas molecules? Assume that the effective hard-sphere collision diameters for  $C_8H_{16}$  and  $N_2$  are 7.0 Å and 3.6 Å, respectively. (5 pts.)

We derived the hard-sphere total collision rate as

$$Z_{AB} = s_{AB} \left( \frac{8kT}{\rho m} \right)^{1/2} N_A N_B$$

The collision rate per A molecule is then

$$w = s_{AB} \left( \frac{8kT}{\rho m} \right)^{1/2} N_B$$

For this case,  $s_{AB} = \pi((7.0+3.6)/2 \times 10^{-10} \text{ m})^2 = 8.8 \times 10^{-19} \text{ m}^2$

and  $m = (28 \times 112)/(28+112) = 22.4 \text{ g/mol} = 3.72 \times 10^{-26} \text{ kg/molecule}$

Using these values, we calculate the collision rate per A molecule to be

$$w = 8.8 \times 10^{-19} \left( \frac{8 * 1.38 \times 10^{-23} * 298}{\rho * 3.72 \times 10^{-26}} \right)^{1/2} \left( \frac{101325}{8.314 * 298} * 6.022 \times 10^{23} \right) = 1.1 \times 10^{10} \text{ collisions/s}$$

- (s) Based on transition state theory, and neglecting contributions from the vibrational partition functions, what is the expected temperature dependence of the pre-exponential factor for each of the reactions? (4 pts.)

The transition-state-theory expression for the rate constant is

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

Any temperature dependence from the partition functions cancels out, so that we expect the pre-exponential factor to be proportional to  $T$ , from the 'universal frequency factor',  $kT/h$ .

**For the rest of the problem (parts (t) and (u)), assume that the reactions are occurring in an organic solvent rather than in the gas phase (still with no catalyst).**

- (t) As the temperature is increased, the solution reaction changes its apparent activation energy from about 30 kcal/mol at 298 K to only 3 kcal/mol above 370 K. Explain this temperature dependence of the reaction rate. (5 pts.)

The reaction appears to become diffusion limited at higher temperatures. A low activation energy like 3 kcal/mol is comparable to the expected temperature dependence of a diffusion coefficient, while the high activation energy at low temperatures is what we would expect for a reaction rate limited process.

At first, this seems odd, since these are unimolecular reactions – no reactants have to diffuse together, so how could the reaction be diffusion limited? However, even though the reactants don't have to diffuse together, the products *do* have to diffuse apart. If we write the overall process as reversible decomposition of A to give an 'encounter pair' {BB} that then irreversibly diffuses apart, we get:



Applying the pseudo-steady-state approximation on the encounter pair gives

$$[\{BB^*\}] = \frac{k_1[A]}{k_{-1} + k_2} \text{ from which the overall rate is } r = \frac{k_1 k_2 [A]}{k_{-1} + k_2} \text{ and the effective first-order}$$

rate constant is  $k_{eff} = \frac{k_1 k_2}{k_{-1} + k_2}$ .  $k_2$  can be identified as a diffusion rate constant, while  $k_1$

and  $k_{-1}$  are the forward and reverse reaction rate constants for decomposition of A into the 'encounter pair'. When diffusion is faster than the reverse reaction ( $k_2 \gg k_{-1}$ ) then the effective rate constant becomes  $k_{eff} = k_1$ , the forward reaction rate constant. When reaction is faster than diffusion, the reaction becomes diffusion limited and the effective rate constant becomes  $k_{eff} = (k_1/k_{-1})k_2 = K_1 k_2$  where  $K_1$  is the equilibrium constant for  $A \leftrightarrow \{BB^*\}$ . If  $K$  is the equilibrium constant for the overall process -  $A \leftrightarrow 2 B$ , and  $K_2$  is the equilibrium coefficient for destruction of the encounter pair ( $\{BB^*\} \leftrightarrow 2 B$ ) then this can be rewritten as  $k_{eff} = K k_2 / K_2 = K k_{-2}$ . The rate constant  $k_{-2}$  can be identified as the usual diffusion limited rate constant for formation of an encounter pair. Notice that in addition to the temperature dependence of the diffusion coefficient, there is also temperature dependence of the equilibrium constant. So, in this case, it would appear that the equilibrium constant is nearly temperature independent.

- (u) In the regime where the apparent activation energy is 3 kcal/mol, the reaction is carried out in a series of solvents. They are all mixtures of linear alkanes, but they have different average molecular weights, and therefore different viscosities, ranging from 10 cP to 1000 cP. How do you expect the reaction rate to depend on the solvent viscosity? (5 pts.)

As seen above, the rate constant is diffusion limited in this regime. All other things being equal, an increase in solvent viscosity will lead to a decrease in the diffusion coefficients (diffusion coefficients in liquids are roughly inversely proportional to viscosity). So, increasing the solvent viscosity will decrease the observed reaction rate.