CHM3910 Homework Assignment #10  
Due by 5 pm on Friday December 8th 2006  
No late assignments will be accepted.

Make sure you include the correct units and significant figures in your answers or you will lose points. Please show all your work.

1. (a) Determine the rate law for the mechanism shown below, assuming that the concentration of the intermediate (B) is small compared to the concentrations of A, C, and D. Hint: you can use the steady-state approximation to solve for [B].

\[
\begin{align*}
A & \quad \underset{k_2}{\xrightarrow{k_1}} B \\
B + C & \quad \xrightarrow{k_3} D 
\end{align*}
\]

(b) Prove that the overall reaction will follow a first-order rate law for high reactant pressures and a second-order rate law for low reactant pressures.

2. Using the values of the pre-exponential factor \( A = 4 \times 10^{13} \text{ s}^{-1} \) and the activation energy \( E_a = 160 \text{ kJ mol}^{-1} \) estimate the values for \( \Delta^\ddagger H \), \( \Delta^\ddagger S \) and \( \Delta^\ddagger G \) for the isomerization reaction \( \text{CH}_3\text{NC} \rightleftharpoons \text{CH}_3\text{CN} \) at 300 K. Hint: this is a unimolecular process.  

**Important note:** equation (9.97) on page 393 is the correct form of the expression you will need. In class, I incorrectly wrote the first part of this expression such that it implies that \( e \) is raised to the power of \( (k_bT/h) \) rather than the numerical value of \( e \) (2.718) multiplied by the term \( (k_bT/h) \). So, you should view equation (9.97) as reading

\[
k = (2.718281828...) \left( \frac{k_bT}{h} \right) e^{\Delta S^R/RT} e^{-E_a/RT} \text{ where the 2.718… is the numerical value of } e.\]
3. The hydrolysis of the species A (shown to the right) is found to follow first-order kinetics. The values for rate constants at a series of different temperatures are given below.

<table>
<thead>
<tr>
<th>T / °C</th>
<th>k / s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.06 × 10⁻⁵</td>
</tr>
<tr>
<td>25</td>
<td>3.19 × 10⁻⁴</td>
</tr>
<tr>
<td>35</td>
<td>9.86 × 10⁻⁴</td>
</tr>
<tr>
<td>45</td>
<td>2.92 × 10⁻³</td>
</tr>
</tbody>
</table>

By making an appropriate plot of this data, calculate
(a) the activation energy (Eₐ)
(b) the pre-exponential factor (A)
(c) the half-life of the reaction (at 0°C)
(d) using your answer to part (c), determine how long it will take for the reaction to go to 90% completion (i.e. for 90% of the reactants to be consumed).

4. The series of consecutive first-order reactions A → B → C has rate constants k₁ and k₂ for the two reactions A → B and B → C, respectively.
(a) Write expressions for \( \frac{d[A]}{dt} \), \( \frac{d[B]}{dt} \), \( \frac{d[C]}{dt} \)
(b) The integrated forms of the rates of consumption or production are given by
\[ [A] = a_0 e^{-k_1 t}; \quad [B] = \frac{k_1}{k_2 - k_1} a_0 (e^{-k_2 t} - e^{-k_1 t}) \] and \([C] = k_2 [B]\)
where \(a_0\) is the initial concentration of species A. (It’s relatively easy to show the first and last but the expression for [B] involves some calculus).
Using these expressions, prove that the rate of formation of C is determined by \(k_1\) when \(k_1 \ll k_2\) and by \(k_2\) when \(k_2 \ll k_1\). This illustrates the concept of the rate limiting step.

5. Devise the rate law for the decomposition of N₂O₅
(i.e. write the expression for \( \frac{d[N_2O_5]}{dt} \)).
N₂O₅ (g) → 4NO₂ (g) + O₂ (g)
Based on the following mechanism:
N₂O₅ → NO₂ + NO₃ \( k_d \)
NO₂ + NO₃ → N₂O₅ \( k_d' \)
NO₂ + NO₃ → NO₂ + O₂ + NO \( k_b \)
NO + N₂O₅ → NO₂ + NO₂ + NO₂ \( k_c \)
The intermediates are NO and NO₃ so you can use the steady-state approximation to set the change of concentration of these two species equal to zero.