Assignment #2

TOPICS & READINGS
Finish Chapter 13, except pp. 465-6 (steady-state approximation), and enzyme catalysis (pp. 477-8).
The steady-state approximation is important, particularly because of its application in biology (enzyme catalysis) but we just don't have enough time to cover it. If you're interested, the corresponding problems are 31, 33, 45, 57, 67.

Problem Assignment: Week #2

Oxtoby Chapter 13: odd-numbered problems 35-41, 47, 55, 59-65
Lecture Problems II: #1,2,3,4.

Lecture Problems II

1. The following mechanism has been proposed for the decomposition of O₃(g) to O₂(g):

   (i) O₃ → O₂ + O (fast, at equilibrium); K = k₁/k₋₁

   (ii) O + O₃ → 2 O₂ (slow)

   Identify the rds, derive an expression for the overall rate of production of O₂, and hence express the experimental rate constant kₑxp in terms of the rate constants for the elementary processes.

2. The following data were obtained in a study of the temperature dependence of the rate constant for the reaction: N₂O₅ → 2 NO₂ + (1/2) O₂. Plot these data and calculate the activation energy for this process.

   \[
   \begin{array}{ccc}
   T (K) & k (sec^{-1}) & T (K) & k (sec^{-1}) \\
   338 & 4.87 \times 10^{-3} & 308 & 1.35 \times 10^{-4} \\
   328 & 1.50 \times 10^{-3} & 298 & 3.46 \times 10^{-5} \\
   318 & 4.98 \times 10^{-4} & 273 & 7.87 \times 10^{-7} \\
   \end{array}
   \]

3. [Taken from Atkins, Physical Chemistry, p. 700] The rate of the second-order decomposition of acetaldehyde (ethanal), CH₃CHO was measured over the temperature range 700 - 1000 K, and the rate constants are reported in the table below. By plotting these data determine (a) the activation energy Eₐ and (b) the pre-exponential (frequency) factor A.
4. [Taken from Porile #45 p. 548] I'll probably do this in class, but see if you can do it without looking at your lecture notes. The mechanism for the reaction

\[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \]

is believed to involve the following steps:

1. \[ 2\text{NO} \xrightleftharpoons[k_1]{k_{-1}} \text{N}_2\text{O}_2 \text{ fast} \]
2. \[ \text{N}_2\text{O}_2 + \text{O}_2 \xrightarrow{k_2} 2\text{NO}_2 \text{ slow} \]

(a) Derive a 3rd-order rate law consistent with this mechanism.

(b) The rate of the reaction \textit{decreases} with increasing temperature. Explain this unusual behavior on the basis of the postulated mechanism, the derived rate law, and the fact that the reaction in Step 1 is exothermic.