Chem 1515 Name\_\_\_\_\_ Problem Set #6 TA Name \_\_\_\_\_ Fall 2001

Lab Section #\_\_\_\_\_

ALL work must be shown to receive full credit. Due at the beginning of lecture on Monday, October 15, 2001.

PS6.1. The rate of the reaction

 $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ 

was followed over a range of temperatures and the following data was collected;

Temperature (C)	Rate Constant (s <sup>-1</sup> )
25	3.65 x 10 <sup>-5</sup>
45	5.08 x 10 <sup>-4</sup>
55 65	1.7 x 10 <sup>-3</sup>
	5.17 x 10 <sup>-3</sup>

Plot the data ln k (y-axis) versus  $\frac{1}{T}$  (x-axis) and determine the activation energy for the reaction.

PS6.2. Using the data from PS6.1 determine the rate constant for the reaction at 333 K?

PS6.3. Using the data in PS6.1, estimate the temperature at which the rate constant is  $8.45 \times 10^{-4} \cdot \text{sec}^{-1}$ .

PS6.4. A chemist was able to determine that the rate of a particular reaction at 200 °C was three times faster than at 75 °C. Calculate the approximate energy of activation for such a reaction.

PS6.5. Explain why reactions proceed faster at higher temperatures.

PS6.6a. Consider the simple reaction,

 $A(g) \rightarrow \text{products}$ Determine what the order of the reaction must be if the initial concentration of A is doubled and the initial rate increase by a factor of eight.

b) Consider the simple reaction,

 $B(g) \rightarrow \text{products}$ Determine what the order of the reaction must be if the half-life for the disappearance of B is inversely proportional to the initial concentration of B.

c) Consider the simple reaction,

 $C(g) \rightarrow \text{products}$ Determine what the order of the reaction must be if the time required for the concentration of A to decrease to from  $[C]_0$  to  $\frac{[C]_0}{2}$  is equal to the time required for [A] to decrease from  $\frac{[C]_0}{2}$  to  $\frac{[C]_0}{4}$ .

PS6.7. Given the following reaction mechanism

$$CO_{2}(aq) + OH^{-}(aq) \longrightarrow HCO_{3}^{-}(aq) \qquad \text{slow}$$
$$HCO_{3}^{-}(aq) + OH^{-}(aq) \longrightarrow CO_{3}^{2-}(aq) + H_{2}O(g) \qquad \text{fast}$$

What is the overall reaction? Write the rate law for the reaction.

PS6.8. Draw a picture of the activated complex of the second step of the mechanism in PS6.7.

PS6.9. The following reaction between nitrogen dioxide and fluorine

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

has the experimental rate law is rate =  $k[NO_2][F_2]$ . Suggest a mechanism for this reaction.

Step 1	$\operatorname{Ce}^{4+}(aq) + \operatorname{Mn}^{2+}(aq) \rightarrow \operatorname{Mn}^{3+}(aq) + \operatorname{Ce}^{3+}(aq)$	slow
Step 2	$Ce^{4+}(aq) + Mn^{3+}(aq) \rightarrow Mn^{4+}(aq) + Ce^{3+}(aq)$	fast
Step 3	$\mathrm{Tl}^+(aq) + \mathrm{Mn}^{4+}(aq) \rightarrow \mathrm{Mn}^{2+}(aq) + \mathrm{Tl}^{3+}(aq)$	fast

Identify a specie(s), if any, which is acting as a catalyst and a specie(s) which is acting as an intermediate. Write the overall reaction.