Chem 1515
Problem Set \#6 Fall 2001

Name $\qquad$
TA Name $\qquad$
Lab Section \# $\qquad$

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

$$
2 \mathrm{~N}_{2} \mathrm{O}_{5}(g) \rightarrow 4 \mathrm{NO}_{2}(g)+\mathrm{O}_{2}(g)
$$

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

| Temperature (C) | Rate Constant $\left(\mathrm{s}^{-1}\right)$ |
| :---: | :---: |
| 25 | $3.65 \times 10^{-5}$ |
| 45 | $5.08 \times 10^{-4}$ |
| 55 | $1.7 \times 10^{-3}$ |
| 65 | $5.17 \times 10^{-3}$ |

Plot the data $\ln \mathrm{k}$ ( $y$-axis) versus $\frac{1}{\mathrm{~T}}$ ( $x$-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 $8.45 \times 10^{-4} \cdot \mathrm{sec}^{-1}$.

PS6.4. A chemist was able to determine that the rate of a particular reaction at $200^{\circ} \mathrm{C}$ was three times faster than at $75^{\circ} \mathrm{C}$. 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,
$\mathrm{A}(\mathrm{g}) \rightarrow$ 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,

$$
\mathrm{B}(\mathrm{~g}) \rightarrow \text { products }
$$

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,

$$
\mathrm{C}(\mathrm{~g}) \rightarrow \text { products }
$$

Determine what the order of the reaction must be if the time required for the concentration of A to decrease to from $[\mathrm{C}]_{0}$ to $\frac{[\mathrm{C}]_{0}}{2}$ is equal to the time required for $[\mathrm{A}]$ to decrease from $\frac{[\mathrm{C}]_{0}}{2}$ to $\frac{[C]_{0}}{4}$.

PS6.7. Given the following reaction mechanism

$$
\begin{array}{rll}
\mathrm{CO}_{2}(a q)+\mathrm{OH}^{-}(a q) & \rightarrow \mathrm{HCO}_{3}^{-}(a q) & \text { slow } \\
\mathrm{HCO}_{3}^{-}(a q)+\mathrm{OH}^{-}(a q) & \rightarrow \mathrm{CO}_{3}^{2-}(a q)+\mathrm{H}_{2} \mathrm{O}(g) & \text { fast }
\end{array}
$$

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

$$
2 \mathrm{NO}_{2}(g)+\mathrm{F}_{2}(g) \rightarrow 2 \mathrm{NO}_{2} \mathrm{~F}(g)
$$

has the experimental rate law is rate $=\mathrm{k}\left[\mathrm{NO}_{2}\right]\left[\mathrm{F}_{2}\right]$. Suggest a mechanism for this reaction.

PS6.10. The suggested mechanism for the reaction between cerium (IV) and thallium (I),

Step $1 \quad \mathrm{Ce}^{4+}(a q)+\mathrm{Mn}^{2+}{ }_{(a q)} \rightarrow \mathrm{Mn}^{3+}{ }_{(a q)}+\mathrm{Ce}^{3+}(a q) \quad$ slow
Step $2 \mathrm{Ce}^{4+}{ }_{(a q)}+\mathrm{Mn}^{3+}{ }_{(a q)} \rightarrow \mathrm{Mn}^{4+}{ }_{(a q)}+\mathrm{Ce}^{3+}{ }_{(a q)}$ fast
Step $3 \mathrm{Tl}^{+}(a q)+\mathrm{Mn}^{4+}(a q) \rightarrow \mathrm{Mn}^{2+}(a q)+\mathrm{Tl}^{3+}(a q) \quad$ 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.

