Chem 1515
Problem Set #6
Fall 2001

Name______________________________

TA Name __________________________

Lab Section #______

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

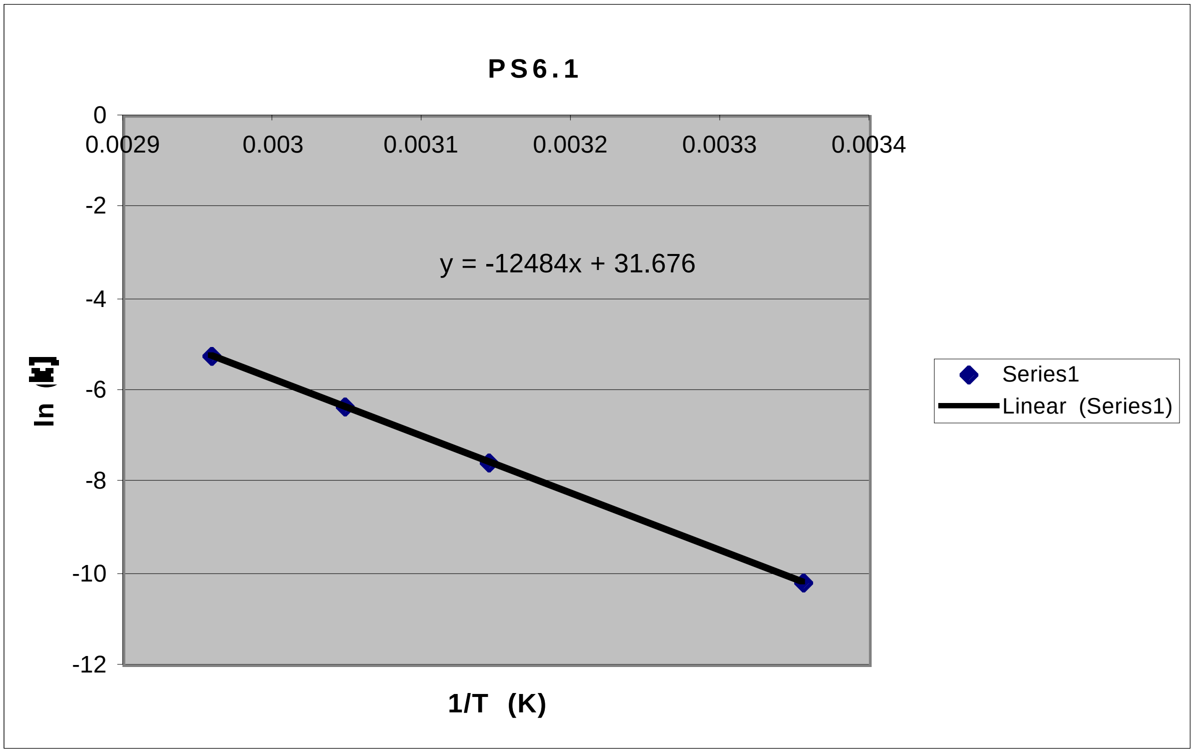
PS6.1. The rate of the reaction

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

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

Temperature (C)	Rate Constant (s^{-1})
25	3.65×10^{-5}
45	5.08×10^{-4}
55	1.7×10^{-3}
65	5.17×10^{-3}

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



$$\textbf{Slope} = -1.25 \times 10^4 = -\frac{E_a}{R}$$

$$E_a = 1.25 \times 10^4\ K \cdot\ 8.314\ \frac{J}{mol \cdot K} = \boxed{104\ \frac{kJ}{mol}}$$

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

The equation for the line in PS6.1 is $\ln(k) = -1.25 \times 10^4 \cdot \frac{1}{T} + 31.68$

$$\ln(k) = -1.25 \times 10^4 \cdot \frac{1}{333} + 31.68 = -5.86$$

$$k = 2.86 \times 10^{-3}\ s^{-1}$$

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

$$\ln(8.45 \times 10^{-4}) = -1.25 \times 10^4 \cdot \frac{1}{T} + 31.68$$

$$-7.08 - 31.68 = -1.25 \times 10^4 \cdot \frac{1}{T}$$

$$T = \frac{-1.25 \times 10^4}{-38.8} = 322\ K$$

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.

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

k_2 at 473 K is $3k_1$ at 348 K so $k_2 = 3k_1$.

$$\ln \frac{k_1}{3k_1} = \frac{E_a}{8.314 \frac{J}{mol \cdot K}}\left(\frac{1}{473} - \frac{1}{348}\right)$$

$$\ln 0.333 = \frac{E_a}{8.314 \frac{J}{mol \cdot K}} (-7.59 \times 10^{-4})$$

$$-1.11 = E_a\ (-9.13 \times 10^{-5})$$

$$\frac{-1.11}{-9.13 \times 10^{-5} \frac{mol}{J}} = E_a$$

$$1.22 \times 10^4 \frac{J}{mol} = E_a$$

$$\boxed{12.2 \frac{kJ}{mol} = E_a}$$

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

At high temperature molecules have a higher average kinetic energy compared to molecules at lower temperatures. At a higher temperature there are a higher fraction of reactant molecules with an energy that exceeds the activation energy of the reaction. Therefore, collisions between reactant molecules are more likely to overcome the barrier to activation and continue to products.

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.

For the reaction

$$\mathbf{A \rightarrow products}$$

the rate law is

rate = k[A]^m

If doubling the [A] increases the rate by a factor of 8 then

rate$_2$ = 8·rate$_1$, when [A]$_2$ = 2[A]$_1$

Taking the ratio of the 2 experiments

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[A]_2^n}{k_1[A]_1^n}$$

$$\frac{8 \cdot \cancel{\text{rate}_1}}{\cancel{\text{rate}_1}} = \left(\frac{[2\cancel{[A]}]_1^n}{\cancel{[A]}_1^n}\right)$$

$$8 = 2^n$$

$$3 = n: \quad \boxed{\text{reaction is 3rd order}}$$

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.

If $t_{1/2} \propto \dfrac{1}{[B]_o}$**, then** $\boxed{\text{the reaction is 2nd order}}$

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 C to decrease to from $[C]_o$ to $\dfrac{[C]_o}{2}$ is equal to the time required for [C] to decrease from $\dfrac{[C]_o}{2}$ to $\dfrac{[C]_o}{4}$.

If the time required for an equal change in concentration is independent of the initial concentration,

$\boxed{\text{the reaction is 1st order.}}$

PS6.7. Given the following reaction mechanism

$CO_2(aq) + OH^-(aq)$	$\rightarrow HCO_3^-(aq)$	slow
$HCO_3^-(aq) + OH^-(aq)$	$\rightarrow CO_3^{2-}(aq) + H_2O(g)$	fast

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

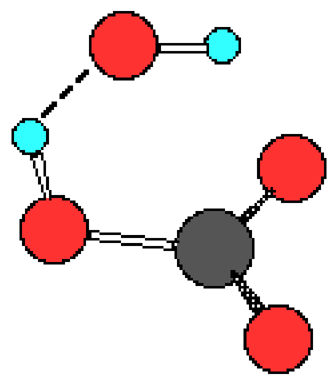
The overall reaction is obtained by adding the elementary steps of the mechanism. The equation is,

$$CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(g)$$

The rate law, as given in the slow step of the mechanism, is

$$\boxed{\text{rate} = k[CO_2]^1[OH^-]^1}$$

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



The O–H bond on HCO_3^- is breaking and an H–O bond forming with the OH^-.

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.

The mechanism for this reaction must be a two step mechanism. The reason for this should be apparent from the discussion below.

According to the experimental rate law, rate = $k[NO_2][F_2]$, the reactants in the slow step of the mechanism are;

Step 1: $1NO_2(g) + 1F_2(g) \rightarrow$?

Since the overall reaction has two $2NO_2(g)$ we will need a second step to the mechanism.

Step 2: $1NO_{2}(g)$ + ? $\rightarrow$?

Now we must use our intuition to determine the rest of the species. Since there are two steps to the mechanism there must be an intermediate. An intermediate appears as a product in a step of the mechanism and re-appears as a reactant in a subsequent (later) step.

Step 1: $1NO_{2}(g)$ + $1F_{2}(g)$ $\rightarrow$?

Step 2: $1NO_{2}(g)$ + ? $\rightarrow$?

It would reasonable to think that the first step of the mechanism produces one of the product compounds and an intermediate. Since the product is $NO_{2}F(g)$ the only species remaining is an F atom. We do not want to have an anion of fluoride, F^{-}, because that would mean the $NO_{2}F(g)$ would have to be charged, but it is not in the overall balanced equation.

Step 1: $1NO_{2}(g)$ + $1F_{2}(g)$ $\rightarrow$ $NO_{2}F(g)$ + $F(g)$

Then the intermediate appears as a reactant in Step 2:

Step 2: $1NO_{2}(g)$ + F $\rightarrow$ $NO_{2}F(g)$

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

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

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

Overall $2Ce^{4+}(aq) + Tl^{+}(aq) \rightarrow Tl^{3+}(aq) + 2Ce^{3+}(aq)$

$Mn^{2+}(aq)$ is acting as a catalyst

$Mn^{3+}(aq)$ and $Mn^{4+}(aq)$ are acting as intermediates.

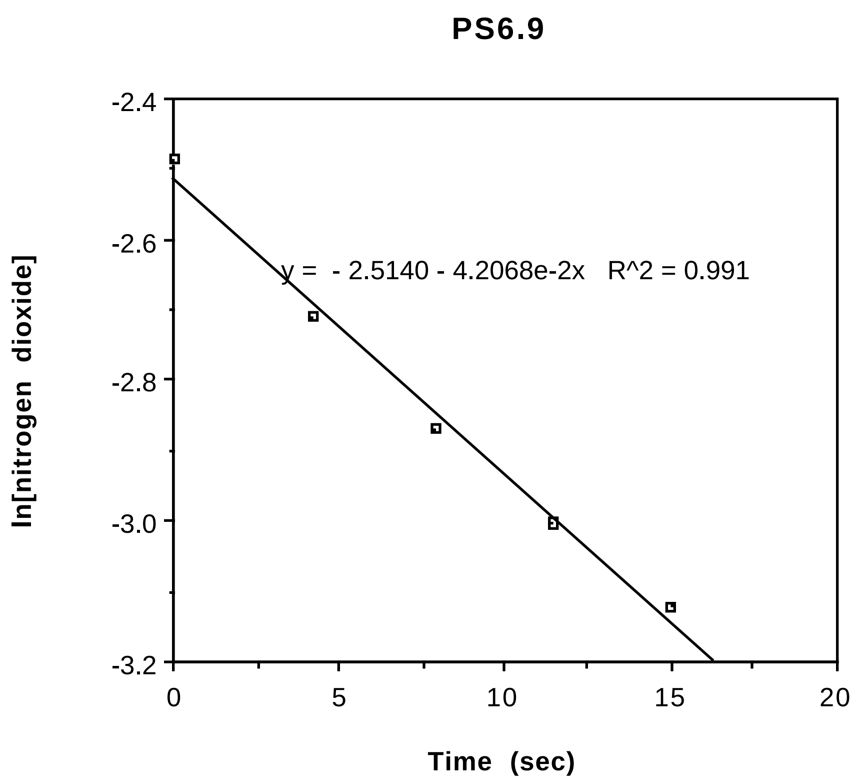
PS5.9. In the reaction

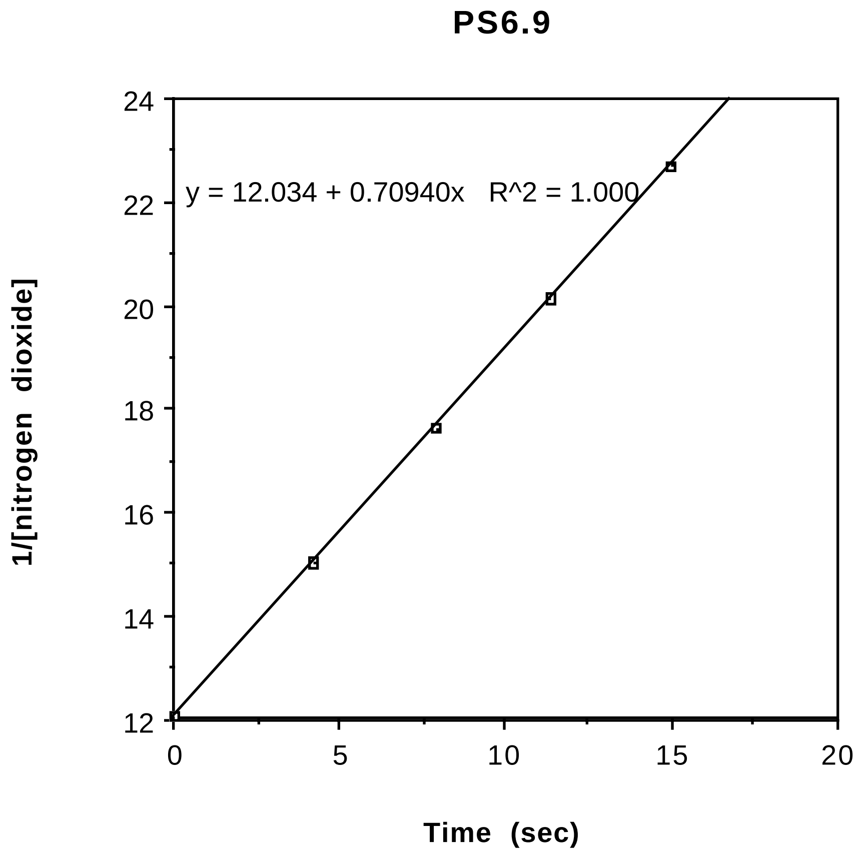
$$NO_{2(g)} \rightarrow NO_{(g)} + \frac{1}{2}O_{2(g)}$$

the $[NO_2]$ was followed with time and the data shown below was obtained.

Time(s)	$[NO_2]$(M)
0	0.0831
4.2	0.0666
7.9	0.0567
11.4	0.0497
15	0.0441

Determine the order of the reaction and its half-life. (Include graphs of your data to support your conclusion. Be sure <u>all</u> plots are included.)





The reaction follows second order kinetics with k = 0.709 $M^{-1} \cdot s^{-1}$ and the half-life of 17.0 s.

$$t_{1/2} = \frac{1}{k[NO_2]_0}$$

$$t_{1/2} = \frac{1}{0.709\ M^{-1} \cdot s^{-1}(0.0831\ M)} = 17.0\ s$$