## SCH 224 Assignments 1

Q1. The rate of the following reaction in aqueous solution is monitored by measuring the number of moles of $\mathrm{Hg}_{2} \mathrm{Cl}_{2}$ that precipitate per liter per minute. The data obtained are listed in the table.
$2 \mathrm{HgCl}_{2(a q)}+\mathrm{C}_{2} \mathrm{O}_{4}^{2-}{ }_{(a q)} \rightarrow 2 \mathrm{Cl}_{(a q)}^{-}+2 \mathrm{CO}_{2(g)}+\mathrm{Hg}_{2} \mathrm{Cl}_{2(s)}$

| Experiment | $\left[\mathrm{HgCl}_{2}\right](\mathrm{M})$ | $\left[\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2}\right](\mathrm{M})$ | Initial rate $\left(\mathrm{mol} \mathrm{L}^{-}\right.$ <br> $\left.{ }^{1} \mathrm{~min}^{-1}\right)$ |
| :--- | :--- | :--- | :---: |
| 1 | 0.105 | 0.15 | $1.8 \times 10^{-5}$ |
| 2 | 0.105 | 0.15 | $1.8 \times 10^{-5}$ |
| 3 | 0.052 | 0.30 | $7.1 \times 10^{-5}$ |
| 4 | 0.052 | 0.15 | $8.9 \times 10^{-6}$ |

(a) Determine the order of reaction with respect to $\mathrm{HgCl}_{2}$, with respect to $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ and overall.
(3 Marks)
(b) What is the value of the rate constant $k$ ?
(2 Marks)
(c) What would be the initial rate of reaction if $\left[\mathrm{HgCl}_{2}\right]=0.094 \mathrm{M}$ and $\left[\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}\right]=0.19 \mathrm{M}$ ?
(2 Marks)
(d) Are all four experiments necessary to answer parts (a) - (c)? Explain.
(1 Mark)

Q2). The decomposition of carbon disulfide, $\mathrm{CS}_{2}$, to carbon monosulfide, CS , and sulfur is first order with $\mathrm{k}=2.8 \times 10^{-7} \mathrm{~s}^{-1}$ at $1000^{\circ} \mathrm{C}$.

$$
\mathrm{CS}_{2} \rightarrow \mathrm{CS}+\mathrm{S}
$$

What is the half-life of this reaction at $1000^{\circ} \mathrm{C}$ ?
(2Marks)

Q3). Suppose the reaction: $A+2 B \rightarrow A B_{2}$ occurs by the following mechanism:
Step $1 \quad \mathrm{~A}+\mathrm{B} \rightarrow \mathrm{AB}$ slow
Step $2 \mathrm{AB}+\mathrm{B} \rightarrow \mathrm{AB}_{2}$ fast
Overall $\mathrm{A}+2 \mathrm{~B} \rightarrow \mathrm{AB}_{2}$
(i) Identify the rate determining step
(ii) Identify the reaction intermediate
(1 Mark)
(iii) Determine the reaction rate law
(2 Marks)

Q4) At 300 K , the following reaction is found to obey the rate law: Rate $=\mathrm{k}[\mathrm{NOCl}]^{2}$ :

$$
2 \mathrm{NOCl} \rightarrow 2 \mathrm{NO}+\mathrm{Cl}_{2}
$$

Consider the three postulated mechanisms given below. Then choose the response that lists all those that are possibly correct and no others.
(2 Marks)

$$
\begin{array}{lll}
\text { Mechanism } 1 & \mathrm{NOCl} \rightarrow \mathrm{NO}+\mathrm{Cl} & \text { slow } \\
& \mathrm{Cl}+\mathrm{NOCl} \rightarrow \mathrm{NOCl}_{2} & \text { fast } \\
& \mathrm{NOCl}_{2}+\mathrm{NO} \rightarrow 2 \mathrm{NO}+\mathrm{Cl}_{2} & \text { fast } \\
& \text { Overall: } 2 \mathrm{NOCl} \rightarrow 2 \mathrm{NO}+\mathrm{Cl}_{2} & \\
\text { Mechanism 2 } & 2 \mathrm{NOCl} \rightarrow \mathrm{NOCl} l_{2}+\mathrm{NO} & \text { slow } \\
& \mathrm{NOCl}_{2} \rightarrow \mathrm{NO}+\mathrm{Cl}_{2} & \text { fast } \\
& \text { Overall: } 2 \mathrm{NOCl} \rightarrow 2 \mathrm{NO}+\mathrm{Cl}_{2} & \\
\text { Mechanism 3 } & \mathrm{NOCl} \rightleftharpoons \mathrm{NO}+\mathrm{Cl} & \text { fast, equilibrium } \\
& \mathrm{NOCl}+\mathrm{Cl} \rightarrow \mathrm{NO}+\mathrm{Cl}_{2} & \text { slow } \\
& \text { Overall: } 2 \mathrm{NOCl} \rightarrow 2 \mathrm{NO}+\mathrm{Cl}_{2}
\end{array}
$$

Q5). Hydrolysis of ethyl acetate by NaOH using equal concentration of the reactants was studied by titrating 25 ml of the reaction mixture at different time intervals against standard acid. From the data given below, establish that this is a second order reaction.
(4Marks)

| $t$ (minutes) | 0 | 5 | 15 | 25 |
| :--- | :---: | :---: | :---: | :--- |
| ml acid used | 16.00 | 10.24 | 6.13 | 4.32 |

