You must show all your working on the long answer problems to gain full credit.

Useful Physical Constants and Equations

\[ T_C = T_K - 273.15 \]

\[ R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \]

Zeroth Order reaction:
\[ [A] = [A]_0 - kt \]

half life \[ t_{1/2} = [A]_0 / (2k) \]

First Order reaction:
\[ \ln [A] = \ln [A]_0 - kt \]

half life \[ t_{1/2} = 0.693 / k \]

Second Order reaction:
\[ 1/[A] = 1/[A]_0 + kt \]

half life \[ t_{1/2} = 1 / (k [A]_0) \]

Arrhenius Equation:
\[ k = A \exp(-E_A/RT) \]

\[ \ln(k) = \ln(A) - \frac{E_A}{R} \left( \frac{1}{T} \right) \]
Multiple Choice and short answer questions:
(You need not show your working to receive full credit)

Question 1) If the reaction:

\[ 2 \text{N}_2\text{O}_5 \, (aq) \rightarrow 4 \text{NO}_2 \, (aq) + \text{O}_2 \, (g) \]

is first order and has a half life of 35 seconds at 110° C, what is the rate constant for the reaction, if [N₂O₅]₀ = 0.1 mol L⁻¹?

(a) 35 mol⁻¹ L s⁻¹
(b) 0.020 s⁻¹
(c) 0.020 mol⁻¹ L s⁻¹
(d) 0.29 s⁻¹
(e) 0.29 mol⁻¹ L s⁻¹

(5 points)

Question 2) A catalyst

(a) speeds up a reaction by increasing the temperature
(b) speeds up a reaction by increasing the reaction exothermicity
(c) has no effect on the rate of reaction
(d) speeds up the reaction by changing the activation energy
(e) none of the above.

(5 points)
Question 3)
The mechanism for the following reaction has 3 elementary steps:

\[ \text{C}_4\text{H}_9\text{Br} + 2\text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+ + \text{Br}^- \]

Mechanism:

\[ \begin{align*}
\text{C}_4\text{H}_9\text{Br} & \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^- \quad \text{(slow)} \\
\text{C}_4\text{H}_9^+ + 2\text{H}_2\text{O} & \rightarrow \text{C}_4\text{H}_9\text{OH}_2^+ + \text{H}_2\text{O} \quad \text{(fast)} \\
\text{C}_4\text{H}_9\text{OH}_2^+ + \text{H}_2\text{O} & \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+ \quad \text{(fast)}
\end{align*} \]

(a) Which step is rate determining? What is the molecularity of that step?

**Slow step (step #1) is rate determining**

Unimolecular step

(b) Identify the intermediate(s) in the mechanism given above (if any).

\[ \text{C}_4\text{H}_9^+ \]

(c) Write down the overall rate law for the production of \( \text{C}_4\text{H}_9\text{OH} \) from \( \text{C}_4\text{H}_9\text{Br} \) based on the proposed mechanism.

\[ \text{rate} = \frac{-\Delta [\text{C}_4\text{H}_9\text{Br}]}{\Delta t} = k [\text{C}_4\text{H}_9\text{Br}] \]

(10 points)
Long Questions (Show all your working for full credit):

Question 4) The reaction

\[ \text{NO (g) + O}_3 (g) \rightarrow \text{NO}_2 (g) + \text{O}_2 (g) \]

obeys the following rate law:

\[ -\frac{\Delta [\text{NO}]}{\Delta t} = (0.8 \text{ mol}^{-1} \text{ L s}^{-1}) [\text{O}_3]^2 \]

(a) In a given experiment, how long would it take for \([\text{NO}]\) to be reduced to one half of its initial value? Second order overall in \([\text{O}_3]\)

\[ \Rightarrow t_{1/2} = \frac{1}{k [\text{O}_3]_0} \]

\[ = \frac{1.25 \text{ mol L}^{-1} \text{ s}^{-1}}{[\text{O}_3]_0} \]

Partial credit for realizing \([\text{O}_3]_0\) is required

Depends on the initial concentration of \([\text{O}_3]\)

Four possible mechanisms for the decomposition are:

**I**

\[
\text{NO + O}_3 \rightarrow \text{NO}_2 + \text{O}_2
\]

**II**

\[
\begin{align*}
\text{O}_3 &\rightarrow \text{O} + \text{O}_2 \\
\text{NO + O} &\rightarrow \text{NO}_2
\end{align*}
\]

\[
\text{O}_3 + \text{NO} + \text{O} \rightarrow \text{O} + \text{O}_2 + \text{NO}_2 \checkmark
\]

**III**

\[
\begin{align*}
\text{NO + O}_3 &\rightarrow \text{NO}_4 \\
\text{O}_3 + \text{NO}_4 &\rightarrow \text{NO}_2 + 2 \text{O}_2 + \text{O}
\end{align*}
\]

\[
\text{NO}_2 + 2 \text{O}_3 + \text{NO}_4 \rightarrow \text{NO}_4 + \text{NO}_2 + 2 \text{O}_2 + \text{O}
\]

\[
\text{NO}_2 + 2 \text{O}_3 \rightarrow 2 \text{NO}_2 + 2 \text{O}_2 + \text{O} \checkmark
\]

**IV**

\[
\begin{align*}
\text{2O}_3 &\rightarrow \text{O}_6 \\
\text{NO + O}_6 &\rightarrow \text{NO}_2 + \text{O}_3 + \text{O}_2
\end{align*}
\]

\[
\text{2O}_3 + \text{NO} + \text{O} \rightarrow \text{O}_6 + \text{NO}_2 + \text{O}_3 + \text{O}_2 \checkmark
\]

(b) Which mechanisms are consistent with the overall balanced chemical equation? Show your reasoning.

Summing up II, III, IV we see that III does not give correct overall equation

I, II, IV are consistent with balanced overall equation.
(c) If the first step is assumed to be rate-determining for each suggested mechanism above, which is the most-likely mechanism? Why?

Only consider I, II, IV.

Overall rate law is determined by rate of elementary R.D.S.

I
r.d.s is only step, step #1
rate = \( k_1 [O_3] [NO] \)  \hspace{1cm} \text{bimolecular}

II
r.d.s. is first step
rate = \( k_1 [O_3] \)  \hspace{1cm} \text{unimolecular}

IV
r.d.s is first step
rate = \( k_1 [O_3]^2 \)  \hspace{1cm} \text{bimolecular}

Only IV is consistent with overall rate law and gives balanced overall equation.

Mechanism IV most likely

(20 points)
Question 5) At elevated temperatures, nitrous oxide decomposes according to the equation

$$2 \text{N}_2\text{O} (g) \rightarrow 2 \text{N}_2 (g) + \text{O}_2 (g)$$

Given the following data, plot the appropriate graphs using the sheet of graph paper on the next page, to determine the rate law for the reaction. Give both the differential and integrated rate law in your answer.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>60</th>
<th>90</th>
<th>120</th>
<th>180</th>
</tr>
</thead>
<tbody>
<tr>
<td>[N$_2$O]</td>
<td>0.25</td>
<td>0.218</td>
<td>0.204</td>
<td>0.190</td>
<td>0.166</td>
</tr>
</tbody>
</table>

To check for 1st order, plot $\ln([\text{N}_2\text{O}])$ versus time.

This is STRAIGHT LINE (see next page).

To check for 2nd order, plot $\frac{1}{[\text{N}_2\text{O}]}$ versus time.

This is not STRAIGHT LINE.

Reaction is FIRST ORDER

$$\text{Rate} = -\frac{\Delta [\text{N}_2\text{O}]}{\Delta t} = k [\text{N}_2\text{O}]$$

Integrated Rate Law:

$$[\text{N}_2\text{O}] = [\text{N}_2\text{O}]_0 \exp(-kt)$$
AT LEAST ONE (FIRST ORDER) PLOT ON GRAPH PAPER REQUIRED

Test for First Order Kinetics

\[
\ln \left( \frac{1}{[N_2O]} \right) = \text{straight line} \]

\[
\ln(1.025) - \ln(0.166) \]

\[
\text{Slope} = \frac{-0.409}{180} = -2.275 \times 10^{-3} \text{ min}^{-1}
\]

Test for Second order kinetics

\[
\frac{1}{[N_2O]} \text{ vs time (min)} \]

not straight line
(b) What is the rate constant for the reaction? (Make sure to include the units in your answer)

From slope of graph in part (a)

\[ \text{Slope} = -2.275 \times 10^{-3} \text{ min}^{-1} \]

\[ \Rightarrow k = 2.3 \times 10^{-3} \text{ min}^{-1} \] (2 sig figs)

(20 points)
(c) Give two reasons why the reaction rate constant for a chemical reaction increases when the temperature is raised.

i) The number of **activated collisions** increases as temperature is increased because distribution of molecular kinetic energies shifts to higher KE.

![Diagram showing number of molecules and KE vs. temperature]

ii) The number of collisions per unit time increases with temperature.

(20 points)
Question 7)

Given the initial rate data below, we may consider the rate law for the reaction

\[ 4 \text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4 \text{Fe}^{3+} + 2 \text{H}_2\text{O} \]

The initial rate, \(-\Delta [\text{O}_2] / \Delta t\), was determined for the following concentrations of each of the reactants in 4 experiments:

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[\text{Fe}^{2+}]_0 (mol L(^{-1}))</th>
<th>[\text{O}_2]_0 (mol L(^{-1}))</th>
<th>[\text{H}^+]_0 (mol L(^{-1}))</th>
<th>Initial rate (mol L(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(1 \times 10^{-3})</td>
<td>(1 \times 10^{-3})</td>
<td>0.1</td>
<td>(5 \times 10^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>(2 \times 10^{-3})</td>
<td>(2 \times 10^{-3})</td>
<td>0.1</td>
<td>(8 \times 10^{-3})</td>
</tr>
<tr>
<td>3</td>
<td>(2 \times 10^{-3})</td>
<td>(1 \times 10^{-3})</td>
<td>0.2</td>
<td>(8 \times 10^{-3})</td>
</tr>
<tr>
<td>4</td>
<td>(2 \times 10^{-3})</td>
<td>(2 \times 10^{-3})</td>
<td>0.2</td>
<td>(1.6 \times 10^{-2})</td>
</tr>
</tbody>
</table>

**Generic Rate Law:**

\[
\text{rate} = k \left[ \text{Fe}^{2+} \right]^x \left[ \text{O}_2 \right]^y \left[ \text{H}^+ \right]^z
\]

(a) What is the order of this reaction with respect to \text{Fe}^{2+}?

\[
\frac{\text{rate}_3}{\text{rate}_1} = \frac{k \left[ 2 \times 10^{-3} \right]^x \left[ 1 \times 10^{-3} \right]^y \left[ 0.2 \right]^z}{k \left[ 1 \times 10^{-3} \right]^x \left[ 1 \times 10^{-3} \right]^y \left[ 0.1 \right]^z} = \frac{8 \times 10^{-3}}{5 \times 10^{-4}} = 16
\]

\[
\left(\frac{2}{1}\right)^x \left(\frac{2}{1}\right)^z = 16
\]

Using result to part (c) for order w.r.t \text{[H}^+] first:

\[ z = 1 \]

so \[2^x = 8\]

\[
\Rightarrow x = 3
\]

and reaction is **THIRD ORDER w.r.t. \text{[Fe}^{2+}]**
Question 7 continued)

(b) Determine the order of the reaction with respect to $O_2$

\[
\frac{\text{rate} \_4}{\text{rate} \_2} = \frac{k \left[ 2 \times 10^{-3} \right]^3 \left[ 2 \times 10^{-3} \right]^y \left[ 0.2 \right]}{k \left[ 1 \times 10^{-3} \right]^3 \left[ 1 \times 10^{-4} \right]^2 \left[ 0.1 \right]} = \frac{8 \times 10^{-3}}{8 \times 10^{-4}} = 16
\]

\[\Rightarrow 2^3 \times 2^y = 16 \quad \Rightarrow \quad 2^y = 2\]

\[y = 1\]

Reactan is FIRST ORDER w.r.t. $[O_2]$

(c) Determine the order of reaction with respect to $H^+$

Choose lines 2 and 4 to extract order w.r.t. $[H^+]$

\[
\frac{\text{rate} \_4}{\text{rate} \_2} = \frac{k \left[ 2 \times 10^{-3} \right]^x \left[ 2 \times 10^{-3} \right]^y \left[ 0.2 \right]^2}{k \left[ 2 \times 10^{-3} \right]^x \left[ 2 \times 10^{-3} \right]^y \left[ 0.1 \right]^2} = \frac{2^y \times 4}{2^2} = \frac{1.6 \times 10^{-2}}{8 \times 10^{-3}} = 2
\]

\[\Rightarrow z = 1\]

Reactan is FIRST ORDER w.R.T $[H^+]$

(d) Write down the overall differential rate law for the reaction, based on your answers to parts (a) - (c).

\[
\text{rate} = k \left[ Fe^{2+} \right]^3 \left[ O_2 \right] \left[ H^+ \right]
\]
(e) Calculate the value of the rate constant, giving appropriate units.

Using data from any line:

e.g. line 1,

$$\text{rate} = 5 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1} = \frac{k (1 \times 10^{-3})^3 (1 \times 10^{-3}) (0.1)}{(\text{mol L}^{-1})^3 (\text{mol L}^{-1}) (\text{mol L}^{-1})}$$

$$\Rightarrow k = \frac{5 \times 10^{-4}}{10^{-13}} = 5 \times 10^9$$

Units are:

$$\frac{\text{mol L}^{-1} \text{ s}^{-1}}{(\text{mol L}^{-1})^3 (\text{mol L}^{-1}) (\text{mol L}^{-1})} = \text{mol}^{-4} \text{ L}^4 \text{ s}^{-1}$$

So

$$k = 5 \times 10^9 \text{ mol}^{-4} \text{ L}^4 \text{ s}^{-1}$$

(20 points)