The nitration of benzene to form nitrobenzene may be written with the following stoichiometry.

\[
\text{C}_6\text{H}_6 + \text{HNO}_3 \rightarrow \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O}
\]

The reaction was performed in the presence of excess concentrated sulfuric acid and the following data were obtained.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>initial [benzene] (M)</th>
<th>initial [nitric acid] (M)</th>
<th>[nitrobenzene] (M) after 100 s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.010</td>
<td>1.0</td>
<td>(1.2 \times 10^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.020</td>
<td>1.0</td>
<td>(2.4 \times 10^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>0.020</td>
<td>0.50</td>
<td>(1.2 \times 10^{-4})</td>
</tr>
</tbody>
</table>

Determine the rate of the reaction for Experiment 1.

\[
\text{rate} = \frac{\text{change in concentration}}{\text{change in time}} = \frac{\Delta[\text{nitrobenzene}]}{\Delta t}, \text{ for experiment 1:}
\]

\[
\text{rate} = \frac{[\text{nitrobenzene}]_t - [\text{nitrobenzene}]_i}{(t_2 - t_1)} = \frac{(1.2 \times 10^{-4} - 0)}{(100 - 0)} = 1.2 \times 10^{-6} \text{ M s}^{-1}
\]

Answer: \(1.2 \times 10^{-6} \text{ M s}^{-1}\)

What is the rate equation for this reaction?

Between experiments 1 and 2, [nitric acid] is kept constant. [Benzene] is doubled and this leads to a doubling in the [nitrobenzene] produced after 100 s. Between experiments 2 and 3, [benzene] is kept constant. [Nitric acid] is halved and this leads to a halving in the [nitrobenzene] produced after 100 s. Thus,

\[
\text{rate} \propto [\text{benzene}][\text{nitreric acid}] = k[\text{benzene}][\text{nitreric acid}]
\]

Rate = \(k[\text{benzene}][\text{nitreric acid}]\)

What is the value of the rate constant?

As rate = \(k[\text{benzene}][\text{nitreric acid}]\), for experiment 1 so k and its units are:

\[
1.2 \times 10^{-6} = k \times (0.010) \times (1.0) \text{ so } k = 1.2 \times 10^{-4}
\]

\((\text{M s}^{-1}) = (\text{units of k}) \times (\text{M}) \times (\text{M}) \text{ so the units of k are M}^{-1} \text{ s}^{-1}\)

\[
k = 1.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}
\]

THIS QUESTION CONTINUES ON THE NEXT PAGE
Show that the observed kinetics are consistent with the following mechanism.

\[
\text{HNO}_3 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O} \quad \text{(fast)}
\]

\[
\begin{align*}
\text{benzene} & + \text{NO}_2^+ \rightarrow \text{benzene}(\text{HNO}_2) \quad \text{(slow)} \\
\text{benzene}(\text{NO}_2^+) & \rightarrow \text{benzene(NO}_2) + \text{H}^+ \quad \text{(fast)}
\end{align*}
\]

As the second reaction is slow, it is rate determining. From the mechanism, the rate of this step is given by:

\[
\text{rate} = k_2[\text{benzene}][\text{NO}_2^+]
\]

As \(\text{NO}_2^+\) is a highly reactive intermediate, its concentration cannot be included in the rate equation which is to be experimental tested. As the first step is fast, the equilibrium between \(\text{HNO}_3 + \text{H}_2\text{SO}_4\) and \(\text{NO}_2^+ + \text{HSO}_4^- + \text{H}_2\text{O}\) will be set up rapidly and maintained for most of the reaction. For an equilibrium,

rate forward reaction = rate backward reaction

\[
k_1[\text{HNO}_3][\text{H}_2\text{SO}_4] = k_{-1}[\text{NO}_2^+][\text{HSO}_4^-][\text{H}_2\text{O}]
\]

or \([\text{NO}_2^+] = \frac{k_1}{k_{-1}} \frac{[\text{HNO}_3][\text{H}_2\text{SO}_4]}{[\text{HSO}_4^-][\text{H}_2\text{O}]}
\]

Hence,

\[
\text{rate} = k_2[\text{benzene}][\text{NO}_2^+] = k_2[O_3] \times \frac{k_1}{k_{-1}} \frac{[\text{HNO}_3][\text{H}_2\text{SO}_4]}{[\text{HSO}_4^-][\text{H}_2\text{O}]}
\]

\[
= \frac{k_1k_2}{k_{-1}} \frac{[\text{benzene}][\text{HNO}_3][\text{H}_2\text{SO}_4]}{[\text{HSO}_4^-][\text{H}_2\text{O}]} = k \frac{[\text{benzene}][\text{HNO}_3][\text{H}_2\text{SO}_4]}{[\text{HSO}_4^-][\text{H}_2\text{O}]}
\]

where \(k = \frac{k_1k_2}{k_{-1}}\). If \(\text{H}_2\text{SO}_4\) and \(\text{H}_2\text{O}\) are present in excess, the equilibrium between \(\text{H}_2\text{SO}_4\) and \(\text{HSO}_4^-\) will be maintained and \([\text{H}_2\text{SO}_4], [\text{HSO}_4^-]\) and \([\text{H}_2\text{O}]\) will be constant leading to:

\[
\text{rate} = k \frac{[\text{benzene}][\text{HNO}_3][\text{H}_2\text{SO}_4]}{[\text{HSO}_4^-][\text{H}_2\text{O}]} = k_{\text{eff}}[\text{benzene}][\text{HNO}_3]
\]

as observed in 2004-N-11.
Consider the following reaction.

\[
2\text{ClO}_2(aq) + 2\text{OH}^-(aq) \rightarrow \text{ClO}_3^-(aq) + \text{ClO}_2^-(aq) + \text{H}_2\text{O}(l)
\]

A series of experiments gave the rate data shown in the table below.

<table>
<thead>
<tr>
<th>Experiment number</th>
<th>initial [ClO(_2)] (M)</th>
<th>initial [OH(^-)] (M)</th>
<th>initial rate of decrease of [ClO(_2)] (M \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0500</td>
<td>0.100</td>
<td>5.75 \times 10^{-2}</td>
</tr>
<tr>
<td>2</td>
<td>0.100</td>
<td>0.100</td>
<td>2.30 \times 10^{-1}</td>
</tr>
<tr>
<td>3</td>
<td>0.100</td>
<td>0.050</td>
<td>1.15 \times 10^{-1}</td>
</tr>
</tbody>
</table>

Determine the rate expression for the above reaction.

Between experiments 1 and 2, [OH\(^-\)] is kept constant. [ClO\(_2\)] is doubled and this quadruples the rate: the reaction is second order with respect to [ClO\(_2\)]. Between experiments 2 and 3, [ClO\(_2\)] is kept constant. [OH\(^-\)] is halved and this halves the rate: the reaction is first order with respect to [OH\(^-\)]. Thus,

\[
\text{rate } \alpha \text{[ClO}_2^\text{2}[\text{OH}^-] = k[\text{ClO}_2^\text{2}[\text{OH}^-]}
\]

Rate = \(k[\text{ClO}_2]^2[\text{OH}^-]\)

What is the value of the rate constant? Include units in your answer.

Using experiment 1,

\[
\text{rate } = k[\text{ClO}_2]^2[\text{OH}^-]
\]

\[
(5.75 \times 10^{-2}) = k \times (0.0500)^2 \times (0.100) \quad \text{so } k = 230 \quad \text{(M s}^{-1}) = \text{(units of } k) \times (\text{M})^2 \times (\text{M}) \quad \text{so the units of } k \text{ are M}^2 \text{s}^{-1}
\]

\[
k = 230 \text{ M}^2 \text{s}^{-1}
\]

What is the relationship between the rate of decrease of [ClO\(_2\)] and the rate of increase of [ClO\(_3\)\(^-\)]?

From the chemical equation, two moles of ClO\(_2\) are lost for every mole of ClO\(_3\)\(^-\) formed. Thus, the rate of decrease of [ClO\(_2\)] is twice the rate of increase of [ClO\(_3\)\(^-\)] (or the rate of increase of [ClO\(_3\)\(^-\)] is half the rate of decrease of [ClO\(_2\)]).
It has been proposed that the reaction \( \text{Cl}_2(g) + \text{CHCl}_3(g) \rightarrow \text{HCl}(g) + \text{CCl}_4(g) \) proceeds by the following mechanism:

\[
\begin{align*}
\text{Cl}_2(g) & \xrightarrow{k_1, k_{-1}} \ 2\text{Cl}(g) & \text{(fast equilibrium)} \\
\text{Cl}(g) + \text{CHCl}_3(g) & \xrightarrow{k_2} \ \text{HCl}(g) + \text{CCl}_3(g) & \text{(slow)} \\
\text{CCl}_3(g) + \text{Cl}(g) & \xrightarrow{k_3} \ \text{CCl}_4(g) & \text{(fast)}
\end{align*}
\]

Derive the rate expression for this mechanism.

As the second reaction is slow, it is rate determining. From the mechanism, the rate of this step is given by:

\[
\text{rate} = k_2[\text{Cl}(g)][\text{CHCl}_3(g)]
\]

As Cl is a highly reactive intermediate, its concentration cannot be included in the rate equation which is to be experimental tested. As the first step is fast, the equilibrium between \( \text{Cl}_2(g) \) and \( \text{Cl}(g) \) will be set up rapidly and maintained for most of the reaction. For an equilibrium,

\[
\text{rate forward reaction} = \text{rate backward reaction}
\]

\[
\begin{align*}
\text{k}_1[\text{Cl}_2(g)] &= \text{k}_{-1}[\text{Cl}(g)]^2 \\
\text{or} \ [\text{Cl}(g)]^2 &= \frac{\text{k}_1}{\text{k}_{-1}}[\text{Cl}_2(g)]
\end{align*}
\]

Hence,

\[
\begin{align*}
\text{rate} &= k_2[\text{Cl}(g)][\text{CHCl}_3(g)] = k_2 \times \sqrt[1/2]{\frac{\text{k}_1}{\text{k}_{-1}}[\text{Cl}_2(g)]} \times [\text{CHCl}_3(g)] \\
&= k_2 \sqrt[1/2]{[\text{CHCl}_3(g)][\text{Cl}(g)]}^{1/2} = k[\text{CHCl}_3(g)][\text{Cl}(g)]^{1/2}
\end{align*}
\]

where \( k = k_2 \sqrt[1/2]{\frac{\text{k}_1}{\text{k}_{-1}}} \)

Answer: rate = \( k[\text{CHCl}_3(g)][\text{Cl}(g)]^{1/2} \)

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.