1971
Ethyl iodide reacts with a solution of sodium hydroxide to give ethyl alcohol according to the equation.

\[ \text{CH}_3\text{CH}_2\text{I} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{I}^- \]

The reaction is first order with respect to both ethyl iodide and hydroxide ion, and the overall rate expression for the reaction is as follows:

\[ \text{rate} = k[\text{CH}_3\text{CH}_2\text{I}][\text{OH}^-] \]

What would you do in the laboratory to obtain data to confirm the order in the rate expression for either of the reactants?

Answer:
The molar concentration of the hydroxide ion [OH\(^-\)] can be determined by conducting the above reaction with a pH meter monitoring it. \([\text{OH}^-] = 1 \times 10^{14} - \log \text{pH}.\) By measuring [OH\(^-\)] over time and plotting ln[OH\(^-\)] vs time, if a straight line results, the reaction is first order with respect to [OH\(^-\)].

1972

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[A]</th>
<th>[B]</th>
<th>Initial Rate of Formation of C (mole liter(^{-1}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.60</td>
<td>0.15</td>
<td>6.3 \times 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
<td>0.60</td>
<td>2.8 \times 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>0.20</td>
<td>0.15</td>
<td>7.0 \times 10^{-4}</td>
</tr>
</tbody>
</table>

Use the information written above to answer the following questions.

(a) What is the rate equation for the reaction?

(b) What is the numerical value of the rate constant \(k\)? What are its dimensions?

(c) Propose a reaction mechanism for this reaction.

Answer:
(a) \(\text{rate} = k [A]^2[B]^1\)

(b) \(k = \frac{6.3 \times 10^{-3} \text{ mol} \text{ L}^{-1} \text{ min}^{-1}}{[0.60 \text{ mol L}^{-1}]^2[0.15 \text{ mol L}^{-1}]^1} = 0.12 \text{ mol}^2 \text{ L}^{-1} \text{ min}^{-3}\)

(c) \(A + A \rightarrow A_2 \quad \text{(fast)}
A_2 + B \rightarrow C + Q \quad \text{(slow)}
Q + B \rightarrow D \quad \text{(fast)}\)
Some alkyl halides, such as (CH₃)₃CCl, (CH₃)₃CBr, and (CH₃)₃CI, represented by RX are believed to react with water according to the following sequence of reactions to produce alcohols:

\[ RX \rightarrow R^+ + \text{X}^- \quad \text{(slow reaction)} \\
R^+ + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{H}^+ \quad \text{(fast reaction)} \\

(a) For the hydrolysis of RX, write a rate expression consistent with the reaction sequence above.

(b) When the alkyl halides RCl, RBr, and RI are added to water under the same experimental conditions, the rates are in the order RI > RBr > RCl. On one set of axes, construct properly labeled potential energy diagrams that are consistent with the information on the rates of hydrolysis of the three alkyl halides. Assume that the reactions are exothermic.

Answer:
(a) \[ \text{rate} = k \ [\text{RX}] \]

(b) Potential energy diagrams with reaction coordinates and labeled with RX, Cl⁻, ClO⁻, ROH, H⁺, and H₂O, showing exothermic reactions.

2002 D

An environmental concern is the depletion of O₃ in Earth's upper atmosphere, where O₃ is normally in equilibrium with O₂ and O. A proposed mechanism for the depletion of O₃ in the upper atmosphere is shown below.

Step I \[ \text{O}_3 + \text{Cl} \rightarrow \text{O}_2 + \text{ClO} \]
Step II \[ \text{ClO} + \text{O} \rightarrow \text{Cl} + \text{O}_2 \]

(a) Write a balanced equation for the overall reaction represented by Step I and Step II.
(b) Clearly identify the catalyst in the above mechanism. Justify your answer.
(c) Clearly identify the intermediate in the above mechanism. Justify your answer.
(d) If the rate law for the overall reaction is found to be rate = \[ k[\text{O}_3][\text{Cl}] \], determine the following.

(i) The overall order of the reaction.
(ii) Appropriate units for the rate constant, \( k \).
(iii) The rate-determining step of the reaction, along with justification for your answer.

Answer:
(a) \[ \text{O}_3 + \text{O} \rightarrow 2 \text{O}_2 \]
(b) Cl; used in step I and regenerated in step II, the amount at the end is the same as the beginning
(c) ClO⁻; product of step I and used in step II, an intermediate is a material the is produced by a step and consumed later, it does not show as either a product or reactant in the overall equation.
(d) (i) second order overall
(ii) \( k \) unit is \( M^4\text{time}^{-1}\frac{\text{mol}}{L^4}\text{s}^{-1} \)
(iii) step 1. the rate law applies to the concentration of the materials in the slowest step, the rate determining step.
**Kinetics – Free Response Sample Questions**

2003 B

5 Br\(^{-}\)(aq) + BrO\(_3\)^{3-}(aq) + 6 H\(^+\)(aq) → 3 Br\(_2\)(l) + 3 H\(_2\)O(l)

In a study of the kinetics of the reaction represented above, the following data were obtained at 298 K.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Initial [Br(^-)] (mol L(^{-1}))</th>
<th>Initial [BrO(_3)^{3-}] (mol L(^{-1}))</th>
<th>Initial [H(^+)] (mol L(^{-1}))</th>
<th>Rate of Disappearance of BrO(_3)^{3-} (mol L(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00100</td>
<td>0.00500</td>
<td>0.100</td>
<td>2.50×10(^{-4})</td>
</tr>
<tr>
<td>2</td>
<td>0.00200</td>
<td>0.00500</td>
<td>0.100</td>
<td>5.00×10(^{-4})</td>
</tr>
<tr>
<td>3</td>
<td>0.00100</td>
<td>0.00750</td>
<td>0.100</td>
<td>3.75×10(^{-4})</td>
</tr>
<tr>
<td>4</td>
<td>0.00100</td>
<td>0.01500</td>
<td>0.200</td>
<td>3.00×10(^{-3})</td>
</tr>
</tbody>
</table>

(a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

(i) Br\(^-\)

(ii) BrO\(_3\)^{3-}

(iii) H\(^+\)

(b) Write the rate law for the overall reaction.

(c) Determine the value of the specific rate constant for the reaction at 298 K. Include the correct units.

(d) Calculate the value of the standard cell potential, \(E^\circ\), for the reaction using the information in the table below.

<table>
<thead>
<tr>
<th>Half-reaction</th>
<th>(E^\circ) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(_2)(l) + 2e(^-) → 2 Br(^-)(aq)</td>
<td>+1.065</td>
</tr>
<tr>
<td>BrO(_3)^{3-}(aq) + 6 H(^+)(aq) + 5e(^-) → (\frac{1}{2}) Br(_2)(l) + 3 H(_2)O(l)</td>
<td>+1.52</td>
</tr>
</tbody>
</table>

(e) Determine the total number of electrons transferred in the overall reaction.

Answers:

(a) i) Br\(^-\) \[\frac{rate_2}{rate_1} = k[Br\(^-\)]^m[BrO\(_3\)^{3-}]^n[H\(^+\)]^p \Rightarrow 0.000500 = \frac{0.00200^m}{0.00100^n} \Rightarrow 2 = 2^m \Rightarrow 1 = m\]

ii) BrO\(_3\)^{3-} \[\frac{rate_3}{rate_1} = k[Br\(^-\)]^m[BrO\(_3\)^{3-}]^n[H\(^+\)]^p \Rightarrow 0.000375 = \frac{0.00750^m}{0.00500^n} \Rightarrow 1.5 = 1.5^m \Rightarrow 1 = n\]

iii) H\(^+\) \[\frac{rate_4}{rate_3} = k[Br\(^-\)]^m[BrO\(_3\)^{3-}]^n[H\(^+\)]^p \Rightarrow 0.00300 = \frac{0.01500^m[0.200]^p}{0.00750^m[0.100]^p} \Rightarrow 4 = 2^m \Rightarrow 2 = m\]

(b) \[rate = k[Br\(^-\)]^m[BrO\(_3\)^{3-}]^n[H\(^+\)]^p\]

(c) \[rate = k[Br\(^-\)]^m[BrO\(_3\)^{3-}]^n[H\(^+\)]^p \Rightarrow 0.00300 = k[0.00100]^m[0.01500]^n[0.200]^p \Rightarrow 5.00×10\(^{-3}\) \frac{k}{mol\(^{-1}\)s\(^{-1}\)} = k\]

(d) \(E^\circ = 1.52 + -1.065\) V = 0.455 V

(e) the overall reaction can be made by reversing the first half-reaction and multiplying by 2.5, therefore, there are 5 electrons transferred.
2005 B

Answer the following questions related to the kinetics of chemical reactions.

\[
\text{I}^- (aq) + \text{ClO}^- (aq) \xrightarrow{\text{OH}^-}\text{IO}^- (aq) + \text{Cl}^- (aq)
\]

Iodide ion, I\(^-\), is oxidized to hypoiodite ion, IO\(^-\), by hypochlorite, ClO\(^-\), in basic solution according to the equation above. Three initial-rate experiments were conducted; the results shown in the following table.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[I(^-)] (mol L(^-1))</th>
<th>[ClO(^-)] (mol L(^-1))</th>
<th>Initial Rate of Formation of IO(^-) (mol L(^-1) s(^-1))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.017</td>
<td>0.015</td>
<td>0.156</td>
</tr>
<tr>
<td>2</td>
<td>0.052</td>
<td>0.015</td>
<td>0.476</td>
</tr>
<tr>
<td>3</td>
<td>0.016</td>
<td>0.061</td>
<td>0.596</td>
</tr>
</tbody>
</table>

(a) Determine the order of the reaction with respect to each reactant listed below. Show your work.
   (i) \( I^- (aq) \)
   (ii) \( \text{ClO}^- (aq) \)
(b) For the reaction,
   (i) Write the rate law that is consistent with the calculations in part (a);
   (ii) Calculate the value of the specific rate constant, \( k \), and specify units.

The catalyzed decomposition of hydrogen peroxide, \( \text{H}_2\text{O}_2(aq) \), is represented by the following equation.

\[
2 \text{H}_2\text{O}_2(aq) \xrightarrow{\text{catalyst}} 2 \text{H}_2\text{O}(l) + \text{O}_2(g)
\]

The kinetics of the decomposition reaction were studied and the analysis of the results show that it is a first-order reaction. Some of the experimental data are shown in the table below.

<table>
<thead>
<tr>
<th>[H(_2)O(_2)] (mol L(^-1))</th>
<th>Time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00</td>
<td>0.0</td>
</tr>
<tr>
<td>0.78</td>
<td>5.0</td>
</tr>
<tr>
<td>0.61</td>
<td>10.0</td>
</tr>
</tbody>
</table>

(c) During the analysis of the data, the graph below was produced.

(i) Label the vertical axis of the graph
(ii) What are the units of the rate constant, \( k \), for the decomposition of \( \text{H}_2\text{O}_2(aq) \)?
(iii) On the graph, draw the line that represents the plot of the uncatalyzed first-order decomposition of 1.00 \( M \) \( \text{H}_2\text{O}_2(aq) \).

Answer:

(a) (i) \[
\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[I^-]^2[\text{ClO}^-]^2}{k[I^-][\text{ClO}^-]^1} \]
   (ii) \[
\frac{\text{rate}_3}{\text{rate}_1} = \frac{k[I^-]^3[\text{ClO}^-]^3}{k[I^-][\text{ClO}^-]^1} \]

Kinetics – Free Response Sample Questions

\[
\begin{align*}
0.476 &= k(0.052)^m(0.015)^n \\
0.156 &= k(0.017)^m(0.015)^n \\
3.05 &= 3.05^n \rightarrow 1 = m \\
0.596 &= k(0.016)^m(0.061)^n \\
0.156 &= k(0.017)^m(0.015)^n \\
4.06 &= 4.07^n \rightarrow 1 = n
\end{align*}
\]

(b) (i) rate = \( k[I^-][ClO^-] \)

(ii) \( k = \frac{\text{rate}}{[I^-][ClO^-]} = \frac{0.156 \text{ mol L}^{-1} \text{ s}^{-1}}{(0.017 \text{ mol L}^{-1})(0.015 \text{ mol L}^{-1})} = 610 \text{ L mol}^{-1} \text{ s}^{-1} \)

(c) (i) vertical axis is “\( \ln [H_2O_2] \)”

(ii) units for \( k \) are \( \text{min}^{-1} \)

\[
\begin{array}{c|c|c}
\text{Time (minutes)} & \text{uncatalyzed} & \text{catalyzed} \\
\hline
0 & \text{absorbance} & \text{absorbance} \\
10 & \text{absorbance} & \text{absorbance} \\
20 & \text{absorbance} & \text{absorbance} \\
30 & \text{absorbance} & \text{absorbance} \\
40 & \text{absorbance} & \text{absorbance} \\
\end{array}
\]

2004 B

The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of \( 5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1} \) and the path-length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below.

<table>
<thead>
<tr>
<th>[X] (M)</th>
<th>Absorbance</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>?</td>
<td>0.600</td>
<td>0.0</td>
</tr>
<tr>
<td>4.00×10^{-5}</td>
<td>0.200</td>
<td>35.0</td>
</tr>
<tr>
<td>3.00×10^{-5}</td>
<td>0.150</td>
<td>44.2</td>
</tr>
<tr>
<td>1.50×10^{-5}</td>
<td>0.075</td>
<td>?</td>
</tr>
</tbody>
</table>

(a) Calculate the initial concentration of the unknown species.

{hint: use Beer’s Law}

(b) Calculate the rate constant for the first order reaction using the values given for concentration and time. Include units with your answers.

(c) Calculate the minutes it takes for the absorbance to drop from 0.600 to 0.075.

(d) Calculate the half-life of the reaction. Include units with your answer.

(e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where \( T \) is temperature. This graph can be used to determine \( E_a \), the activation energy.

(i) Label the vertical axis of the graph

(ii) Explain how to calculate the activation energy from this graph.
**Kinetics – Free Response Sample Questions**

**Answer:**

(a) \[ A = abc; \ 0.600 = (5000 \text{ cm}^{-1} \text{M}^{-1})(1.00 \text{ cm}) \]
\[ c = 1.20 \times 10^{-4} \text{ M} \]
\[ k(35 \text{ min}) \]

(c) \[ \ln[X]_i - \ln[X]_0 = -kt \]
\[ \ln[1.50 \times 10^{-5}] - \ln[1.20 \times 10^{-4}] = -0.0314 \text{ min}^{-1} t \]
\[ t = 66.2 \text{ min}. \]

(b) \[ \ln[X]_i - \ln[X]_0 = -kt \]
\[ \ln(4.00 \times 10^{-5}) - \ln(1.20 \times 10^{-4}) = - \]
\[ k = 0.0314 \text{ min}^{-1} \]

(d) \[ t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0314} = 22.1 \text{ min} \]

(e) (i) \[ \ln k \]
\[ \frac{1}{T} \]

(ii) \[ -\frac{E_a}{R} = \text{slope}, \text{ multiply the slope by} \]
**Kinetics – Free Response Sample Questions**

2001 D

\[ 3 \text{I}^{-} (aq) + \text{S}_2\text{O}_8^{2-} (aq) \rightarrow \text{I}_3^- (aq) + 2 \text{SO}_4^{2-} (aq) \]

Iodide ion, \( \text{I}^{-} (aq) \), reacts with peroxydisulfate ion, \( \text{S}_2\text{O}_8^{2-} (aq) \), according to the equation above. Assume that the reaction goes to completion.

(a) Identify the type of reaction (combustion, disproportionation, neutralization, oxidation-reduction, precipitation, etc.) represented by the equation above. Also, give the formula of another substance that could convert \( \text{I}^{-} (aq) \) to \( \text{I}_3^- (aq) \).

(b) In an experiment, equal volumes of 0.0120 \( M \) \( \text{I}^{-} (aq) \) and 0.0040 \( M \) \( \text{S}_2\text{O}_8^{2-} (aq) \) are mixed at 25°C. The concentration of \( \text{I}_3^- (aq) \) over the following 80 minutes is shown in the graph below.

(i) Indicate the time at which the reaction first reaches completion by marking an “X” on the curve above at the point that corresponds to this time. Explain your reasoning.

(ii) Explain how to determine the instantaneous rate of formation of \( \text{I}_3^- (aq) \) at exactly 20 minutes. Draw on the graph above as part of your explanation.

(c) Describe how to change the conditions of the experiment in part (b) to determine the order of the reaction with respect to \( \text{I}^{-} (aq) \) and with respect to \( \text{S}_2\text{O}_8^{2-} (aq) \).

(d) State clearly how to use the information from the results of the experiments in part (c) to determine the value of the rate constant, \( k \), for the reaction.

(e) On the graph below (which shows the results of the initial experiment as a dashed curve), draw in a curve for the results you would predict if the initial experiment were to be carried out at 35°C rather than at 25°C.

**Answer:**

(a) redox; \( \text{H}_2\text{O}_2, \text{MnO}_4^- \), \( \text{Cr}_2\text{O}_7^{2-} \), \( \text{I}_2 \)

(b) (i) 35-40 minutes. When mixed in equal amounts of solution, the maximum \([\text{I}_3^-]\) that can be reached is \( 2.00 \times 10^{-3} \) \( M \). No further can occurs after this time.
Kinetics – Free Response Sample Questions

(ii) determine the slope of the tangent to the curve at 20 minutes.

(c) set up a series of reactions in which the concentrations of each ion is changed and measure the initial reaction rate for each. Such as

\[
\begin{array}{|c|c|c|c|}
\hline
\text{expt.} & [I^-] & [S_2O_8^{2-}] & \text{Initial rate} \\
\hline
1 & 0.0120 & 0.0040 & R_1 \\
2 & 0.0240 & 0.0040 & R_2 \\
3 & 0.0120 & 0.0080 & R_3 \\
\hline
\end{array}
\]

to determine the order with respect to \([S_2O_8^{2-}]\), solve for \(n\), when:

\[
\frac{R_1}{[S_2O_8^{2-}]} = \frac{R_2}{[S_2O_8^{2-}]} \]

to determine the order with respect to \([I^-]\), solve for \(m\), when:

\[
\frac{R_1}{[I^-]^m} = \frac{R_2}{[I^-]^m} \]

(d) \(R_1 = k[I^-][S_2O_8^{2-}]\); \(k = \frac{R_1}{[I^-]^m [S_2O_8^{2-}]^n}\)

(e)