AP® Chemistry
2003 Sample Student Responses

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\[5 \text{Br}^- (aq) + \text{BrO}_3^- (aq) + 6 \text{H}^+ (aq) \rightarrow 3 \text{Br}_2(l) + 3 \text{H}_2\text{O}(l)\]

3. 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 [\text{Br}^-] (mol L(^{-1}))</th>
<th>Initial [\text{BrO}_3^-] (mol L(^{-1}))</th>
<th>Initial [\text{H}^+] (mol L(^{-1}))</th>
<th>Rate of Disappearance of \text{BrO}_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 \times 10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>0.00200</td>
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<tr>
<td>3</td>
<td>0.00100</td>
<td>0.00750</td>
<td>0.100</td>
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</tr>
<tr>
<td>4</td>
<td>0.00100</td>
<td>0.01500</td>
<td>0.200</td>
<td>3.00 \times 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) \text{Br}^- 

(ii) \text{BrO}_3^- 

(iii) \text{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>
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<tbody>
<tr>
<td>(\text{Br}_2(l) + 2 \text{e}^- \rightarrow 2 \text{Br}^- (aq))</td>
<td>+1.065</td>
</tr>
<tr>
<td>(\frac{1}{2} \text{BrO}_3^- (aq) + 6 \text{H}^+ (aq) + \frac{5}{2} \text{e}^- \rightarrow \frac{1}{2} \text{Br}_2(l) + 3 \text{H}_2\text{O}(l))</td>
<td>+1.52</td>
</tr>
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</table>

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

\(\Delta \text{X} \) The order for \(\text{[Br}^-\) is first order because; from experiment one to experiment two, the concentration of \(\text{Br}^-\) is doubled from 0.001 to 0.002, while the other concentrations remain the same. The doubling in the concentration of \(\text{Br}^-\) causes the rate to double from 2.50 \times 10^{-4} to 5.00 \times 10^{-4}. Thus, \(\text{Br}^-\) is first order in the reaction.

(ii) The order for \(\text{BrO}_3^-\) is also first order. We know this because from experiment one to experiment three, the concentration...
ADDITIONAL PAGE FOR ANSWERING QUESTION 3.

of BrO_3^- increases by a multiplication of 1.5 (from 0.0500 to 0.0750) and the concentrations of Br^- and H^+ remain the same. From experiment one to experiment three, the rate also increased by a multiplication of 1.5 (from 2.5 x 10^-4 to 3.75 x 10^-4) thus making [BrO_3^-] first order in the reaction.

(iii) H^+ in the reaction is first order. This one was trickier but from experiment one to experiment four the concentration of H^+ is doubled, but the concentration of BrO_3^- is tripped. Since we already know [BrO_3^-] is first order, the tripling would cause the rate to triple from 2.5 x 10^-4 in the first experiment to 7.5 x 10^-4 in the fourth experiment. This means that H^+ must be second order because quadrupling 7.5 x 10^-4 gives a rate of 300, which is the correct answer. Therefore while the [H^+] doubled from experiment one to four, the rate quadrupled making H^+ second order.

(b) \[ \text{rate} = k [\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2 \]

(c) \[ \text{rate} = k [\text{Br}^-][\text{BrO}_3^-][\text{H}^+]^2 \]

\[ \frac{2.5 \times 10^{-4} \, \text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1} \times (0.0500 \, \text{mol} \cdot \text{L}^{-1})^2}{100 \, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} = k \times 10^{-8} \, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \]

\[ k = 5000 \, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \]

(d) \[ E^0 = -1.0985 + 1.57 = 0.455 \, \text{V} \]

\[ E^0 = 0.455 \, \text{V} \]

(e) The number of electrons transferred in the overall reaction will be 10e^- because the second reaction must be multiplied by 2 in order to clear the fraction, so the Se^- will become 10e^-.
\[ 5 \text{Br}^- (aq) + \text{BrO}_3^- (aq) + 6 \text{H}^+ (aq) \rightarrow 3 \text{Br}_2 (l) + 3 \text{H}_2\text{O}(l) \]

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

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<th>Experiment</th>
<th>Initial [Br(^-)] (mol L(^{-1}))</th>
<th>Initial [BrO(_3)^-] (mol L(^{-1}))</th>
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<th>Rate of Disappearance of BrO(_3)^- (mol L(^{-1}) s(^{-1}))</th>
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(a) From the data given above, determine the order of the reaction for each reactant listed below. Show your reasoning.

(i) Br\(^-\)

(ii) BrO\(_3\)^-

(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.

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<td>Br(_2) (l) + 2 e(^-) \rightarrow 2 Br(^-) (aq)</td>
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<tr>
<td>BrO(_3)^- (aq) + 6 H(^+) (aq) + 5 e(^-) \rightarrow \frac{1}{2} \text{Br}_2 (l) + 3 \text{H}_2\text{O}(l)</td>
<td>+1.52</td>
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</table>

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

(i) first, when the concentration of Br\(^-\) doubles and everything else is constant, the rate doubles

(ii) first, when the concentration of BrO\(_3\)^- is multiplied by 1.5 and everything else is constant, the rate multiplies by 1.5

(iii) second, between experiments 2 and 4, the rate becomes 8 times more, it doubles because BrO\(_3\)^- doubles, since that is first order
that leaves a change of 4 times when H⁺ is doubled, so H⁺ is second-order.

b) \( \text{rate} = k \left[ \text{Br}^- \right] \left[ \text{BrO}_3^- \right] \left[ \text{H}^+ \right]^2 \)

c) \( 2 \times 10^{-4} = k \left( \frac{0.001 \text{ M}}{2} \right) \left( \frac{0.005 \text{ M}}{2} \right) \left( \frac{1 \text{ M}}{2} \right)^2 \)
\( 2 \times 10^{-4} = k \times 5.00 \times 10^{-8} \text{ M}^4 \)
\( 2 \times 10^{-4} \text{ M}^4 = k \times 5.00 \times 10^{-8} \text{ M}^4 \)
\( 5.00 \times 10^3 \text{ M}^3 \text{ s}^{-1} = k \)

d) \( E^o = E^o \text{ reduced} - E^o \text{ oxidized} \)
\( 1.52 - 1.065 = 0.455 \text{ V} \)
\( E^o = 0.455 \text{ V} \)

e) \( 2 \times \left( 2 \text{Br}^- \rightarrow \text{Br}_2 + 2e^- \right) \)
\( \left( \text{BrO}_3^- + 6 \text{H}^+ + 6e^- \rightarrow \frac{3}{2} \text{Br}_2 + 3 \text{H}_2\text{O} \right) \)
5 electrons are transferred in each half-reaction for a total of 10 electrons transferred.
5 \text{Br}^{-}(aq) + \text{BrO}_3^{-}(aq) + 6 \text{H}^{+}(aq) \rightarrow 3 \text{Br}_2(l) + 3 \text{H}_2\text{O}(l)

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

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

(i) Br\textsuperscript{−}

(ii) BrO\textsubscript{3}\textsuperscript{−}

(iii) H\textsuperscript{+}

(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.

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

\[
\begin{align*}
\alpha & = k [\text{Br}^{-}]^x [\text{BrO}_3^{-}]^y [\text{H}^{+}]^z \\
(i) & = 2.5 \times 10^{-4} = \frac{1}{2} (0.01)^x (0.005)^y (0.1)^z \\
& \quad 1 = \frac{1}{2} \quad x = 1 \quad \text{first order for Br}^{-} \\
(ii) & = 2.5 \times 10^{-4} = \frac{1}{3} (0.005)^y (0.005)^z (0.1)^z \\
& \quad 2 = \frac{1}{3} \quad y = 1 \quad \text{first order for BrO}_3^{-} \\
(iii) & = 3.0 \times 10^{-3} = \frac{3}{2} (0.005)^z (0.005)^z (0.1)^z \\
& \quad 3 = \frac{3}{2} \quad z = 2 \quad \text{second order for H}^{+}
\end{align*}
\]
b) \[ P = k \left[ R_2 \right] \left[ BrO_3^- \right] \left[ H^+ \right] \]

c) \[ 2.30 \times 10^{-4} = k \left( 0.001 \times 0.005 \times 1 \right)^2 \]

\[ k = \frac{2.30 \times 10^{-4}}{0.001 \times 0.005 \times 1} \]

\[ k = \frac{2.30 \times 10^{-4}}{5 \times 10^{-8}} \]

\[ k = 5.00 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ mol} \]

d) \[ 2Br^- \rightarrow 2e^- + Br_2 \]

\[ \Delta G^o = -1.065 \text{ V} \]

\[ \text{Br}_2O_2^- + 6e^- + 6H^+ \rightarrow 2\text{Br}_2 + 3H_2O \]

\[ \Delta G^o = +1.52 \text{ V} \]

\[ \text{Br}_2O_2^- + 2\text{Br}^- + 6H^+ + 6e^- \rightarrow 2\text{Br}_2 + 3H_2O \]

\[ \Delta G^o = -(9.55 \text{ V}) \]

e) \[ 6 \text{ e}^- \]