# AP® Chemistry
# 2003 Sample Student Responses

3A, 1

$$5\,Br^-(aq) + BrO_3^-(aq) + 6\,H^+(aq) \rightarrow 3\,Br_2(l) + 3\,H_2O(l)$$

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

| Experiment | Initial $[Br^-]$ (mol $L^{-1}$) | Initial $[BrO_3^-]$ (mol $L^{-1}$) | Initial $[H^+]$ (mol $L^{-1}$) | Rate of Disappearance of $BrO_3^-$ (mol $L^{-1}$ $s^{-1}$) |
|---|---|---|---|---|
| 1 | 0.00100 | 0.00500 | 0.100 | $2.50 \times 10^{-4}$ |
| 2 | 0.00200 | 0.00500 | 0.100 | $5.00 \times 10^{-4}$ |
| 3 | 0.00100 | 0.00750 | 0.100 | $3.75 \times 10^{-4}$ |
| 4 | 0.00100 | 0.01500 | 0.200 | $3.00 \times 10^{-3}$ |

×2 ×1.5 ×2 ×3 ×4 ×2 × 1.5

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

(i) $Br^-$ first order

(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, $E°$, for the reaction using the information in the table below.

| Half-reaction | $E°$ (V) |
|---|---|
| $Br_2(l) + 2\,e^- \rightarrow 2\,Br^-(aq)$ | +1.065 |
| $BrO_3^-(aq) + 6\,H^+(aq) + 5\,e^- \rightarrow \frac{1}{2}\,Br_2(l) + 3\,H_2O(l)$ | +1.52 |

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

a)(i) The order for $[Br^-]$ is first order because from Experiment one to experiment two, the concentration of $Br^-$ is doubled from .00100 to .00200, while the other concentrations remain the same. The doubling in the concentration of $Br^-$, caused the rate to double from $2.50 \times 10^{-4}$ to $5.00 \times 10^{-4}$. Thus, $Br^-$ is first order in the reaction.

(ii) The order for $BrO_3^-$ is also first order. We know this because from experiment one to experiment three, the concentration

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of $BrO_3^-$ increases by a multiplication of 1.5, (from .00500 to .00750) 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 $2.5 \times 10^{-4}$ to $3.75 \times 10^{-4}$) thus making $[BrO_3^-]$ first order in the reaction.

(iii) $H^+$ in the reaction is 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 tripled. Since we already know $[BrO_3^-]$ is first order, the tripling would cause the rate to triple from $2.50 \times 10^{-4}$ in the first experiment to $7.5 \times 10^{-4}$ in the fourth experiment. This means that $H^+$ must be second order because quadrupling $7.5 \times 10^{-4}$ gives a rate of .003, which is the correct answer. Therefore while the $[H^+]$ doubled from experiment one to four, the rate quadrupled making $H^+$ second order

(b) rate = $k[Br^-][BrO_3^-][H^+]^2$

(c) rate = $k[Br^-][BrO_3^-][H^+]^2$

$2.5 \times 10^{-4}$ mol = $k(.00100)(.00500)(.100)^2$

$2.5 \times 10^{-4} \frac{mol}{LS} = k\, 5 \times 10^{-8}\, M^4$

$\boxed{k = 5000\ 1/M^3S}$

(d) $E° = -1.065 + 1.52 = .455$ V

$\boxed{E° = .455V}$

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 5e- will become 10e-.

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3B 1

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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.

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

a) (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 3 and 4 the rate becomes 8 times more, it doubles because $BrO_3^-$ doubles. since that is first order

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3B2

that leaves a change of 4 times when H+ is doubled, so H+ is second order

b) rate = $k[Br^-][BrO_3][H^+]^2$

c) $2.5 \times 10^{-4} = k(.001M)(.005M)(.1M)^2$

$2.5 \times 10^{-4} = k \; 5.00 \times 10^{-8} M^4$

$\dfrac{2.5 \times 10^{-4} \frac{mol}{L \cdot s}}{5.00 \times 10^{-8} \frac{mol^{4}}{L^{4}}} = k$

$5.00 \times 10^{3} \dfrac{L^3}{mol^3 s} = k$

d) $E^o$ = $E^o$ reduced − $E^o$ oxidized

1.52 − 1.065

$E^o = .46 V$

e) $2.5(2Br^- \rightarrow Br_2 + 2e^-)$

$1(BrO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}Br_2 + 3H_2O)$

5 electrons are transferred in each halfreaction for a total of 10 electrons transferred

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3C 1

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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.

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

a) $R = k[Br^-]^x[BrO_3^-]^y[H^+]^z$

(i) $\frac{2.50\times10^{-4}}{5.00\times10^{-4}} = \frac{k(.001)^x(.005)^y(.1)^z}{k(.002)^x(.005)^y(.1)^z}$ $\quad \frac{1}{2} = \left(\frac{1}{2}\right)^x$ $\quad x = 1$ $\quad$ first order for $Br^-$

(ii) $\frac{2.50\times10^{-4}}{3.75\times10^{-4}} = \frac{k(.001)^x(.005)^y(.1)^z}{k(.001)^x(.0075)^y(.1)^z}$ $\quad \frac{2}{3} = \left(\frac{2}{3}\right)^y$ $\quad y = 1$ $\quad$ first order for $BrO_3^-$

(iii) $\frac{2.50\times10^{-4}}{3.00\times10^{-3}} = \frac{k(.001)^1(.005)^1(.1)^2}{k(.001)^1(.015)^1(.2)^2}$ $\quad .083 = .33(.5)^2$ $\quad \frac{1}{4} = \left(\frac{1}{2}\right)^2$ $\quad z = 2$ $\quad$ Second order for $H^+$

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b) $R = k[Br^-][BrO_3^-][H^+]^2$

c) $2.50 \times 10^{-4} = k(.001)(.005)(.1)^2$ $\frac{mol}{Ls} = \left(\frac{mol}{L}\right)^4$

$2.50 \times 10^{-4} = k(5 \times 10^{-8})$

$\boxed{5.00 \times 10^{3}\ mol^{-3}L^{-1}} = k$

d) $2Br^- \rightarrow 2e^- + Br_2$ $E^\circ = -1.065$

$+\ BrO_3^- + 6H^+ + 3e^- \rightarrow \frac{1}{2}Br_2 + 3H_2O$ $E^\circ = +1.52$

$BrO_3^- + 2Br^- + 6H^+ + 3e^- \rightarrow \frac{3}{2}Br_2 + 3H_2O$ $\boxed{-.455\ V}$

e) $6\ e^-$

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