2002 AP® CHEMISTRY FREE-RESPONSE QUESTIONS

CHEMISTRY

Section II

(Total time—90 minutes)

Part A

Time-40 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Question 1 below. The Section II score weighting for this question is 20 percent.

$$HOBr(aq) \rightleftharpoons H^+(aq) + OBr^-(aq)$$

$$K_a = 2.3 \times 10^{-9}$$

- 1. Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.
 - (a) Calculate the value of [H⁺] in an HOBr solution that has a pH of 4.95.
 - (b) Write the equilibrium constant expression for the ionization of HOBr in water, then calculate the concentration of HOBr(aq) in an HOBr solution that has [H⁺] equal to $1.8 \times 10^{-5} M$.
 - (c) A solution of Ba(OH)₂ is titrated into a solution of HOBr.
 - (i) Calculate the volume of 0.115 M Ba(OH)₂(aq) needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M HOBr(aq).
 - (ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.
 - (d) Calculate the number of moles of NaOBr(s) that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with $[H^+] = 5.00 \times 10^{-9} M$. Assume that volume change is negligible.
 - (e) HOBr is a weaker acid than HBrO₃. Account for this fact in terms of molecular structure.

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Question 1

Total Score 10 Points

$$HOBr(aq) \rightleftharpoons H^+(aq) + OBr^-(aq)$$

$$K_a = 2.3 \times 10^{-9}$$

- 1. Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.
 - (a) Calculate the value of [H⁺] in an HOBr solution that has a pH of 4.95.

$$pH = -\log [H^+]$$

$$[H^+] = 10^{-4.95}$$

$$[H^+] = 1.1 \times 10^{-5} M$$
1 point earned for correct calculation

(b) Write the equilibrium constant expression for the ionization of HOBr in water, then calculate the concentration of HOBr(aq) in an HOBr solution that has [H⁺] equal to $1.8 \times 10^{-5} M$.

$$K_{a} = \frac{[H^{+}][OBr^{-}]}{[HOBr]}$$
1 point earned for correct expression for K_{a}
1 point earned for K_{a}
1 point earned for K_{a}
2.3 × 10⁻⁹ = $\frac{[H^{+}][OBr^{-}]}{[HOBr]} = \frac{[1.8 \times 10^{-5} M][1.8 \times 10^{-5} M]}{[HOBr]}$
1 point earned for $[H^{+}] = [OBr^{-}]$
1 point earned for $[H^{+}] = [OBr^{-}]$
1 point earned for correct $[HOBr]$
1 point earned for correct $[HOBr]$

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Question 1 (cont'd.)

- (c) A solution of Ba(OH)₂ is titrated into a solution of HOBr.
 - (i) Calculate the volume of 0.115 M Ba(OH)₂(aq) needed to reach the equivalence point when titrated into a 65.0 mL sample of 0.146 M HOBr(aq).

$$0.0650 \text{ L} \left(\frac{0.146 \text{ mol HOBr}}{1 \text{ L}} \right) \left(\frac{1 \text{ mol Ba(OH)}_2}{2 \text{ mol HOBr}} \right) \left(\frac{1 \text{ L}}{0.115 \text{ mol Ba(OH)}_2} \right)$$

1 point earned for stoichiometric ratio

= 0.0413 L or 41.3 mL

1 point earned for correct substitution and calculation

Another possible correct method for calculating the volume starts with

the expression $\frac{V_b M_b}{V_a M_a} = \frac{1}{2}$

(ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.

The pH is greater than 7.

HOBr is a weak acid and OBr is a weak base.

At the equivalence point, the OBr in solution is the pH-determining species and the hydrolysis reaction produces hydroxide ion:

$$OBr^- + H_2O \rightleftharpoons HOBr + OH^-$$

1 point earned for explanation

ΩR

$$K_b(\text{OBr}^-) = \left(\frac{K_w}{K_a(\text{HOBr})}\right) = \left(\frac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}}\right) = 4.3 \times 10^{-6}$$

OR

the calculated pH = 10.79

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Question 1 (cont'd.)

(d) Calculate the number of moles of NaOBr(s) that would have to be added to 125 mL of 0.160 M HOBr to produce a buffer solution with $[H^+] = 5.00 \times 10^{-9} M$. Assume that volume change is negligible.

$$K_a = \frac{[\mathrm{H}^+][\mathrm{OBr}^-]}{[\mathrm{HOBr}]}$$

$$[\mathrm{OBr}^-] = \frac{[\mathrm{HOBr}] \cdot K_a}{[\mathrm{H}^+]} = \frac{(0.160 \, M)(2.3 \times 10^{-9})}{5.00 \times 10^{-9} M}$$

$$[\mathrm{OBr}^-] = 0.074 \, M$$

$$n_{\mathrm{NaOBr}} = 0.125 \, \mathrm{L} \left(\frac{0.074 \, \mathrm{mol} \, \mathrm{OBr}^-}{1 \, \mathrm{L}} \right) = 9.2 \times 10^{-3} \, \mathrm{mol}$$

(e) HOBr is a weaker acid than HBrO₃. Account for this fact in terms of molecular structure.

The H-O bond is weakened or increasingly polarized by the additional oxygen atoms bonded to the central bromine atom in HBrO₃.