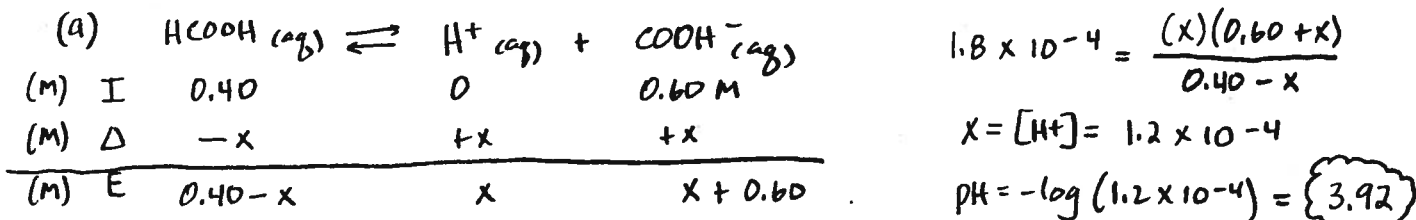


AP Chemistry Buffer/Titration Question (1982)

A buffer solution contains 0.40 mole of formic acid, HCOOH, and 0.60 mole of sodium formate, HCOONa, in 1.00 liter of solution. The ionization constant,  $K_a$ , of formic acid is  $1.8 \times 10^{-4}$ .

- Calculate the pH of this solution.
- If 100. mL of this buffer solution is diluted to a volume of 1.00 liter with pure water, the pH does not change. Discuss why the pH does not change on dilution.
- A 5.00 mL sample of 1.00 molar HCl is added to 100. mL of the original buffer solution. Calculate the  $[H_3O^+]$  of the resulting solution.
- A 800. milliliter sample of 2.00 molar formic acid is mixed with 200. milliliters of 4.80-molar NaOH. Calculate the  $[H_3O^+]$  of the resulting solution.



OR HEND. - HASS.  $pH = pK_a + \log \frac{[COOH^-]}{[HCOOH]}$ ;  $pH = -\log(1.8 \times 10^{-4}) + \log \frac{0.60}{0.40} = 3.92$

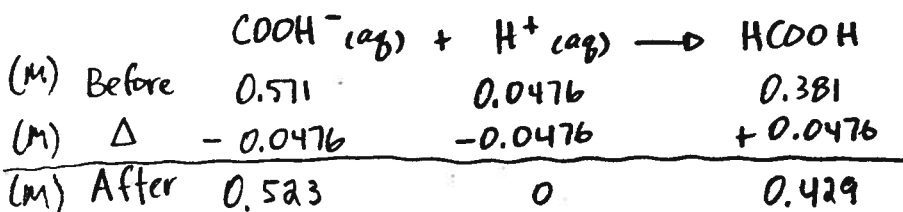
(b) The pH does not change because the amounts of HCOOH & COOH<sup>-</sup> do not change. The ratio of  $[COOH^-] : [HCOOH]$  is constant. The ions are simply "spread out."

(c) NEW VOLUME = 105 mL

$$[COOH^-] = \frac{\text{mol}}{L} = \frac{(0.60 \text{ M})(0.100 \text{ L})}{0.105 \text{ L}} = 0.571 \text{ M } COOH^-$$

$$[HCOOH] = \frac{\text{mol}}{L} = \frac{(0.40 \text{ M})(0.100 \text{ L})}{0.105 \text{ L}} = 0.381 \text{ M } HCOOH$$

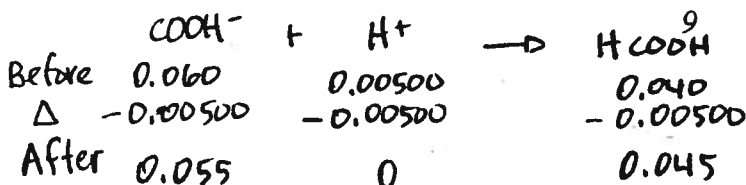
$$[HCl] = \frac{\text{mol}}{L} = \frac{(1.00 \text{ M})(0.00500 \text{ L})}{0.105 \text{ L}} = 0.0476 \text{ M } HCl$$



$$pH = pK_a + \log \frac{[COOH^-]}{[HCOOH]}$$

$$pH = -\log(1.8 \times 10^{-4}) + \log \frac{0.523}{0.429}$$

$pH = 3.83$        $10^{-3.83} = 1.5 \times 10^{-4} \text{ M}$



$$pH = -\log(1.8 \times 10^{-4}) + \log \frac{0.055}{0.045} = 3.8$$

$$(d) \quad [\text{NaOH}] = \frac{\text{mol}}{\text{L}} = \frac{(4.80 \text{ M})(0.200 \text{ L})}{1 \text{ L}} = 0.960 \text{ M NaOH}$$

$$[\text{HCOOH}] = \frac{\text{mol}}{\text{L}} = \frac{(2.00 \text{ M})(0.800 \text{ L})}{1 \text{ L}} = 1.60 \text{ M HCOOH}$$

	$\text{HCOOH (aq)}$	$+ \text{OH}^- \text{(aq)}$	$\rightarrow$	$\text{COOH}^- \text{(aq)}$	$+ \text{H}_2\text{O (l)}$
Initial	1.60 M	0.960 M		0	
$\Delta$	-0.960 M	-0.960 M		+0.960 M	
	0.64 M	0		0.960 M	

$$\text{pH} = \text{p}K_a + \log \frac{[\text{COOH}^-]}{[\text{HCOOH}]}$$

$$\text{pH} = -\log(1.8 \times 10^{-4}) + \log \frac{0.960}{0.64} = 3.92 \quad \begin{matrix} [\text{H}^+] = 10^{-3.92} \\ [\text{H}^+] = 1.2 \times 10^{-4} \text{ M} \end{matrix}$$

OR

	$\text{HCOOH (aq)}$	$\rightleftharpoons$	$\text{H}^+ \text{(aq)}$	$+ \text{COOH}^- \text{(aq)}$
I	0.64		0	0.960
$\Delta$	-x		+x	+x
E	0.64 - x		x	0.960 + x

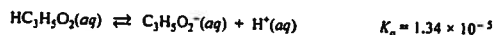
$$K_a = 1.8 \times 10^{-4} = \frac{(x)(0.960 + x)}{0.64 - x} \approx \frac{(x)(0.960)}{0.64}$$

$$x = [\text{H}^+] = 1.2 \times 10^{-4} \text{ M}$$

$$\text{pH} = -\log(1.2 \times 10^{-4}) = 3.92$$

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2005 SCORING GUIDELINES

Question 1



Propanoic acid,  $\text{HC}_3\text{H}_5\text{O}_2$ , ionizes in water according to the equation above.

(a) Write the equilibrium-constant expression for the reaction.

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]}$$

Notes: Correct expression without  $K_a$  earns 1 point.  
Entering the value of  $K_a$  is acceptable.  
Charges must be correct to earn 1 point.

One point is earned for the correct equilibrium expression.

(b) Calculate the pH of a 0.265 M solution of propanoic acid.



I	0.265	0	-0
C	-x	+x	+x
E	0.265 - x	+x	+x

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(x)(x)}{(0.265 - x)}$$

Assume that  $0.265 - x = 0.265$ ,

$$\text{then } 1.34 \times 10^{-5} = \frac{x^2}{0.265}$$

$$(1.34 \times 10^{-5})(0.265) = x^2$$

$$3.55 \times 10^{-6} = x^2$$

$$x = [\text{H}^+] = 1.88 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(1.88 \times 10^{-3})$$

$$\text{pH} = 2.725$$

One point is earned for recognizing that  $[\text{H}^+]$  and  $[\text{C}_3\text{H}_5\text{O}_2^-]$  have the same value in the equilibrium expression.

One point is earned for calculating  $[\text{H}^+]$ .

One point is earned for calculating the correct pH.

(c) A 0.496 g sample of sodium propanoate,  $\text{NaC}_3\text{H}_5\text{O}_2$ , is added to a 50.0 mL sample of a 0.265 M solution of propanoic acid. Assuming that no change in the volume of the solution occurs, calculate each of the following.

(i) The concentration of the propanoate ion,  $\text{C}_3\text{H}_5\text{O}_2^-(\text{aq})$  in the solution

$$\text{mol NaC}_3\text{H}_5\text{O}_2 = 0.496 \text{ g NaC}_3\text{H}_5\text{O}_2 \times \frac{1 \text{ mol NaC}_3\text{H}_5\text{O}_2}{96.0 \text{ g NaC}_3\text{H}_5\text{O}_2}$$

$$\text{mol NaC}_3\text{H}_5\text{O}_2 = 5.17 \times 10^{-3} \text{ mol NaC}_3\text{H}_5\text{O}_2 = \text{mol C}_3\text{H}_5\text{O}_2^-$$

$$[\text{C}_3\text{H}_5\text{O}_2^-] = \frac{\text{mol C}_3\text{H}_5\text{O}_2^-}{\text{volume of solution}} = \frac{5.17 \times 10^{-3} \text{ mol C}_3\text{H}_5\text{O}_2^-}{0.050 \text{ L}} = 0.103 \text{ M}$$

One point is earned for calculating the number of moles of  $\text{NaC}_3\text{H}_5\text{O}_2$ .

One point is earned for the molarity of the solution.

(ii) The concentration of the  $\text{H}^+(\text{aq})$  ion in the solution



I	0.265	0.103	-0
C	-x	+x	+x
E	0.265 - x	0.103 + x	+x

$$K_a = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_2^-]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(x)(0.103 + x)}{(0.265 - x)}$$

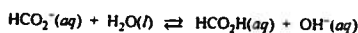
Assume that  $0.103 + x = 0.103$  and  $0.265 - x = 0.265$

$$K_a = 1.34 \times 10^{-5} = \frac{(x)(0.103)}{0.265}$$

$$x = [\text{H}^+] = (1.34 \times 10^{-5}) \times \frac{0.265}{0.103} = 3.45 \times 10^{-5} \text{ M}$$

One point is earned for calculating the value of  $[\text{H}^+]$ .

The methanoate ion,  $\text{HCO}_2^-(\text{aq})$ , reacts with water to form methanoic acid and hydroxide ion, as shown in the following equation.

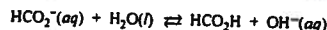


(d) Given that  $[\text{OH}^-]$  is  $4.18 \times 10^{-6} \text{ M}$  in a 0.309 M solution of sodium methanoate, calculate each of the following.

2005

FORMA

(i) The value of  $K_b$  for the methanoate ion,  $\text{HCO}_2^-(\text{aq})$



I	0.309	-	0	-0
C	-x	-	+x	+x
E	0.309 - x	-	+x	+x

$$x = [\text{OH}^-] = 4.18 \times 10^{-6} \text{ M}$$

$$K_b = \frac{[\text{OH}^-][\text{HCO}_2\text{H}]}{[\text{HCO}_2^-]} = \frac{(x)(x)}{(0.309 - x)} = \frac{(4.18 \times 10^{-6})^2}{(0.309 - x)}$$

$x$  is very small ( $4.18 \times 10^{-6} \text{ M}$ ), therefore  $0.309 - x \approx 0.309$

$$K_b = \frac{(4.18 \times 10^{-6})^2}{0.309} = 5.65 \times 10^{-11}$$

One point is earned for substituting  $4.18 \times 10^{-6}$  for both  $[\text{OH}^-]$  and  $[\text{HCO}_2\text{H}]$ , and for calculating the value of  $K_b$ .

(ii) The value of  $K_a$  for methanoic acid,  $\text{HCO}_2\text{H}$

$$K_w = K_a \times K_b$$

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{5.65 \times 10^{-11}}$$

$$K_a = 1.77 \times 10^{-4}$$

One point is earned for calculating a value of  $K_a$  from the value of  $K_b$  determined in part (d)(i).

(e) Which acid is stronger, propanoic acid or methanoic acid? Justify your answer.

$K_a$  for propanoic acid is  $1.34 \times 10^{-5}$ , and  $K_a$  for methanoic acid is  $1.77 \times 10^{-4}$ . For acids, the larger the value of  $K_a$ , the greater the strength; therefore methanoic acid is the stronger acid because  $1.77 \times 10^{-4} > 1.34 \times 10^{-5}$ .

One point is earned for the correct choice and explanation based on the  $K_a$  calculated for methanoic acid in part (d)(ii).

# 2005 Form B

AP<sup>®</sup> CHEMISTRY  
2005 SCORING GUIDELINES (Form B)

Question 1

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = 3.2 \times 10^{-8}$$

Hypochlorous acid, HOCl, is a weak acid in water. The  $K_a$  expression for HOCl is shown above.  
(a) Write a chemical equation showing how HOCl behaves as an acid in water.

$\text{HOCl}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{OCl}^-(aq) + \text{H}_3\text{O}^+(aq)$	One point is earned for the correct chemical equation.
---	--

(b) Calculate the pH of a 0.175 M solution of HOCl.

$\text{HOCl}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{OCl}^-(aq) + \text{H}_3\text{O}^+(aq)$ <table style="margin-left: 20px;"> <tr><td>I</td><td>0.175</td><td>-</td><td>0</td><td>-0</td></tr> <tr><td>C</td><td>-x</td><td>-</td><td>+x</td><td>+x</td></tr> <tr><td>E</td><td>0.175 - x</td><td>-</td><td>+x</td><td>+x</td></tr> </table> $K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(x)(x)}{(0.175 - x)}$ <p>Assume that <math>0.175 - x \approx 0.175</math></p> $3.2 \times 10^{-8} = \frac{x^2}{0.175}$ $x^2 = (3.2 \times 10^{-8})(0.175) = 5.6 \times 10^{-9}$ $x = [\text{H}_3\text{O}^+] = 7.5 \times 10^{-5} M$ $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.5 \times 10^{-5}) = 4.13$	I	0.175	-	0	-0	C	-x	-	+x	+x	E	0.175 - x	-	+x	+x	<p>One point is earned for calculating the value of <math>[\text{H}_3\text{O}^+]</math>.</p> <p>One point is earned for calculating the pH.</p>
I	0.175	-	0	-0												
C	-x	-	+x	+x												
E	0.175 - x	-	+x	+x												

(c) Write the net ionic equation for the reaction between the weak acid HOCl(aq) and the strong base NaOH(aq).

$\text{HOCl}(aq) + \text{OH}^-(aq) \rightarrow \text{OCl}^-(aq) + \text{H}_2\text{O}(l)$	<p>One point is earned for both of the correct reactants.</p> <p>One point is earned for both of the correct products.</p>
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(d) In an experiment, 20.00 mL of 0.175 M HOCl(aq) is placed in a flask and titrated with 6.55 mL of 0.435 M NaOH(aq).

(i) Calculate the number of moles of NaOH(aq) added.

$\text{mol}_{\text{NaOH}} = 6.55 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} \times \frac{0.435 \text{ mol NaOH}}{1 \text{ L}}$ $\text{mol}_{\text{NaOH}} = 2.85 \times 10^{-3} \text{ mol NaOH}$	One point is earned for the correct number of moles of NaOH.
--	--

(ii) Calculate  $[\text{H}_3\text{O}^+]$  in the flask after the NaOH(aq) has been added.

$\text{mol}_{\text{HOCl}} = 20.00 \text{ mL} \times \frac{1 \text{ L}}{1,000 \text{ mL}} \times 0.175 \text{ mol NaOH} = 3.50 \times 10^{-3} \text{ mol}$ <p>OH<sup>-</sup>(aq) is the limiting reactant, therefore all of it reacts</p> <table style="margin-left: 20px;"> <tr><td>HOCl(aq)</td><td>+ OH<sup>-</sup>(aq)</td><td>→</td><td>OCl<sup>-</sup>(aq)</td><td>+ H<sub>2</sub>O(l)</td></tr> <tr><td>I</td><td>0.00350</td><td></td><td>0</td><td>-</td></tr> <tr><td>C</td><td>-0.00285</td><td></td><td>+0.00285</td><td>-</td></tr> <tr><td>E</td><td>0.00065</td><td></td><td>0</td><td>0.00285</td></tr> </table> $M_{\text{HOCl}} = \frac{0.00065 \text{ mol}}{0.02655 \text{ L}} = 0.0245 \text{ M}$ $M_{\text{OCl}^-} = \frac{0.00285 \text{ mol}}{0.02655 \text{ L}} = 0.107 \text{ M}$ <table style="margin-left: 20px;"> <tr><td>HOCl(aq)</td><td>+ H<sub>2</sub>O(l)</td><td>↔</td><td>H<sub>3</sub>O<sup>+</sup>(aq)</td><td>+ OCl<sup>-</sup>(aq)</td></tr> <tr><td>I</td><td>0.0245</td><td></td><td>-0</td><td>0.107</td></tr> <tr><td>C</td><td>-x</td><td></td><td>+x</td><td>+x</td></tr> <tr><td>E</td><td>0.0245 - x</td><td></td><td>+x</td><td>0.107 + x</td></tr> </table> $K_a = \frac{[\text{H}_3\text{O}^+][\text{OCl}^-]}{[\text{HOCl}]} = \frac{(x)(0.107 + x)}{(0.0245 - x)}$ <p>Assume that <math>0.107 + x \approx 0.107</math> and that <math>0.0245 - x \approx 0.0245</math></p> $3.2 \times 10^{-8} = \frac{(x)(0.107)}{(0.0245)}$ $x = [\text{H}_3\text{O}^+] = 7.3 \times 10^{-9} M$	HOCl(aq)	+ OH <sup>-</sup> (aq)	→	OCl <sup>-</sup> (aq)	+ H <sub>2</sub> O(l)	I	0.00350		0	-	C	-0.00285		+0.00285	-	E	0.00065		0	0.00285	HOCl(aq)	+ H <sub>2</sub> O(l)	↔	H <sub>3</sub> O <sup>+</sup> (aq)	+ OCl <sup>-</sup> (aq)	I	0.0245		-0	0.107	C	-x		+x	+x	E	0.0245 - x		+x	0.107 + x	<p>One point is earned for calculating the initial number of moles of HOCl.</p> <p>One point is earned for the concentration or number of moles of HOCl and OCl<sup>-</sup> after the neutralization reaction.</p> <p>One point is earned for the correct <math>[\text{H}_3\text{O}^+]</math>.</p>
HOCl(aq)	+ OH <sup>-</sup> (aq)	→	OCl <sup>-</sup> (aq)	+ H <sub>2</sub> O(l)																																					
I	0.00350		0	-																																					
C	-0.00285		+0.00285	-																																					
E	0.00065		0	0.00285																																					
HOCl(aq)	+ H <sub>2</sub> O(l)	↔	H <sub>3</sub> O <sup>+</sup> (aq)	+ OCl <sup>-</sup> (aq)																																					
I	0.0245		-0	0.107																																					
C	-x		+x	+x																																					
E	0.0245 - x		+x	0.107 + x																																					

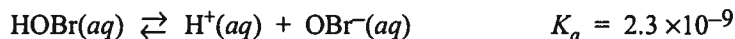
(iii) Calculate  $[\text{OH}^-]$  in the flask after the NaOH(aq) has been added.

$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} = K_w$ $[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{7.3 \times 10^{-9}} = 1.4 \times 10^{-6} M$	One point is earned for the correct concentration of OH <sup>-</sup> .
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2002 SCORING GUIDELINES**

**Question 1**

**Total Score 10 Points**



1. Hypobromous acid, HOBr, is a weak acid that dissociates in water, as represented by the equation above.

(a) Calculate the value of  $[\text{H}^+]$  in an HOBr solution that has a pH of 4.95.

$\begin{aligned} \text{pH} &= -\log [\text{H}^+] \\ [\text{H}^+] &= 10^{-4.95} \\ [\text{H}^+] &= 1.1 \times 10^{-5} M \end{aligned}$	1 point earned for correct calculation
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(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  $[\text{H}^+]$  equal to  $1.8 \times 10^{-5} M$ .

$K_a = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]}$	1 point earned for correct expression for $K_a$
If $[\text{H}^+] = 1.8 \times 10^{-5} M$ , then $[\text{OBr}^-] = 1.8 \times 10^{-5} M$ . Substituting,	1 point earned for $[\text{H}^+] = [\text{OBr}^-]$
$2.3 \times 10^{-9} = \frac{[\text{H}^+][\text{OBr}^-]}{[\text{HOBr}]} = \frac{[1.8 \times 10^{-5} M][1.8 \times 10^{-5} M]}{[\text{HOBr}]}$	1 point earned for correct $[\text{HOBr}]$
$[\text{HOBr}] = \frac{[1.8 \times 10^{-5} M][1.8 \times 10^{-5} M]}{2.3 \times 10^{-9}} = 0.14 M$	

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**2002 SCORING GUIDELINES**

**Question 1 (cont'd.)**

(c) A solution of  $\text{Ba}(\text{OH})_2$  is titrated into a solution of  $\text{HOBr}$ .

- (i) Calculate the volume of  $0.115\text{ M Ba}(\text{OH})_2(\text{aq})$  needed to reach the equivalence point when titrated into a  $65.0\text{ mL}$  sample of  $0.146\text{ M HOBr}(\text{aq})$ .

$0.0650\text{ L} \left( \frac{0.146\text{ mol HOBr}}{1\text{ L}} \right) \left( \frac{1\text{ mol Ba}(\text{OH})_2}{2\text{ mol HOBr}} \right) \left( \frac{1\text{ L}}{0.115\text{ mol Ba}(\text{OH})_2} \right)$ <p>= 0.0413 L or 41.3 mL</p> <p>Another possible correct method for calculating the volume starts with the expression <math>\frac{V_b M_b}{V_a M_a} = \frac{1}{2}</math>.</p>	<p>1 point earned for stoichiometric ratio</p> <p>1 point earned for correct substitution and calculation</p>
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- (ii) Indicate whether the pH at the equivalence point is less than 7, equal to 7, or greater than 7. Explain.

<p>The pH is greater than 7.  <math>\text{HOBr}</math> is a weak acid and <math>\text{OBr}^-</math> is a weak base.          At the equivalence point, the <math>\text{OBr}^-</math> in solution is the pH-determining species and the hydrolysis reaction produces hydroxide ion:</p> $\text{OBr}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOBr} + \text{OH}^-$ <p><b>OR</b></p> $K_b(\text{OBr}^-) = \left( \frac{K_w}{K_a(\text{HOBr})} \right) = \left( \frac{1.0 \times 10^{-14}}{2.3 \times 10^{-9}} \right) = 4.3 \times 10^{-6}$ <p><b>OR</b></p> <p>the calculated pH = 10.79</p>	<p>1 point earned for explanation</p>
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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.

$K_a = \frac{[H^+][OBr^-]}{[HOBr]}$	<p>1 point earned for <math>[OBr^-]</math>, the set-up, and the substitution</p>
$[OBr^-] = \frac{[HOBr] \cdot K_a}{[H^+]} = \frac{(0.160 M)(2.3 \times 10^{-9})}{5.00 \times 10^{-9} M}$	<p>1 point earned for mol NaOBr</p>
$[OBr^-] = 0.074 M$	
$n_{NaOBr} = 0.125 L \left( \frac{0.074 \text{ mol } OBr^-}{1 L} \right) = 9.2 \times 10^{-3} \text{ mol}$	

- (e) HOBr is a weaker acid than HBrO<sub>3</sub>. Account for this fact in terms of molecular structure.

<p>The H-O bond is weakened or increasingly polarized by the additional oxygen atoms bonded to the central bromine atom in HBrO<sub>3</sub>.</p>	<p>1 point earned for a correct explanation</p>
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