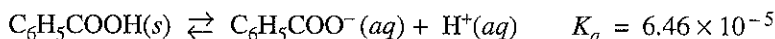


AP[®] CHEMISTRY
2006 SCORING GUIDELINES (Form B)

Question 1



1. Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, dissociates in water as shown in the equation above. A 25.0 mL sample of an aqueous solution of pure benzoic acid is titrated using standardized 0.150 M NaOH.

- (a) After addition of 15.0 mL of the 0.150 M NaOH, the pH of the resulting solution is 4.37. Calculate each of the following.

- (i) $[\text{H}^+]$ in the solution

$[\text{H}^+] = 10^{-4.37} M = 4.3 \times 10^{-5} M$	One point is earned for the correct answer.
--	---

- (ii) $[\text{OH}^-]$ in the solution

$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14} M^2}{4.3 \times 10^{-5} M} = 2.3 \times 10^{-10} M$	One point is earned for the correct answer.
---	---

- (iii) The number of moles of NaOH added

$\text{mol OH}^- = 0.0150 \text{ L} \times 0.150 \text{ mol L}^{-1} = 2.25 \times 10^{-3} \text{ mol}$	One point is earned for the correct answer.
--	---

- (iv) The number of moles of $\text{C}_6\text{H}_5\text{COO}^-(aq)$ in the solution

$\text{mol OH}^- \text{ added} = \text{mol C}_6\text{H}_5\text{COO}^-(aq) \text{ generated, thus}$ $\text{mol C}_6\text{H}_5\text{COO}^-(aq) \text{ in solution} = 2.25 \times 10^{-3} \text{ mol}$	One point is earned for the correct answer.
--	---

- (v) The number of moles of $\text{C}_6\text{H}_5\text{COOH}$ in the solution

$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} \Rightarrow [\text{C}_6\text{H}_5\text{COOH}] = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{COO}^-]}{K_a}$ $[\text{C}_6\text{H}_5\text{COOH}] = \frac{(4.3 \times 10^{-5} M) \times \frac{2.25 \times 10^{-3} \text{ mol}}{0.040 \text{ L}}}{6.46 \times 10^{-5}} = 3.7 \times 10^{-2} M$ $\text{thus, mol C}_6\text{H}_5\text{COOH} = (0.040 \text{ L})(3.7 \times 10^{-2} M) = 1.5 \times 10^{-3} \text{ mol}$	One point is earned for the correct molarity. One point is earned for the correct answer.
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Question 1 (continued)

Alternative solution for part (a)(v):

$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]}$ $\Rightarrow \text{pH} - \text{p}K_a = \log [\text{C}_6\text{H}_5\text{COO}^-] - \log [\text{C}_6\text{H}_5\text{COOH}]$ $\Rightarrow \log [\text{C}_6\text{H}_5\text{COOH}] = \log [\text{C}_6\text{H}_5\text{COO}^-] - (\text{pH} - \text{p}K_a)$ $= \log \left(\frac{2.25 \times 10^{-3} \text{ mol}}{0.040 \text{ L}} \right) - (4.37 - 4.190)$ $= -1.25 - 0.18 = -1.43$ $\Rightarrow [\text{C}_6\text{H}_5\text{COOH}] = 10^{-1.43} = 3.7 \times 10^{-2} \text{ M}$ <p>thus, mol $\text{C}_6\text{H}_5\text{COOH} = (0.040 \text{ L})(3.7 \times 10^{-2} \text{ M}) = 1.5 \times 10^{-3} \text{ mol}$</p>	
--	--

(b) State whether the solution at the equivalence point of the titration is acidic, basic, or neutral. Explain your reasoning.

<p>At the equivalence point the solution is <u>basic</u> due to the presence of $\text{C}_6\text{H}_5\text{COO}^-$ (the conjugate base of the weak acid) that hydrolyzes to produce a basic solution as represented below.</p> $\text{C}_6\text{H}_5\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_5\text{COOH} + \text{OH}^-$	<p>One point is earned for the prediction <u>and</u> the explanation.</p>
--	---

In a different titration, a 0.7529 g sample of a mixture of solid $\text{C}_6\text{H}_5\text{COOH}$ and solid NaCl is dissolved in water and titrated with 0.150 M NaOH . The equivalence point is reached when 24.78 mL of the base solution is added.

(c) Calculate each of the following.

(i) The mass, in grams, of benzoic acid in the solid sample

$\text{mol } \text{C}_6\text{H}_5\text{COOH} = (0.02478 \text{ L}) \times (0.150 \text{ mol OH}^- \text{ L}^{-1}) \times \frac{1 \text{ mol } \text{C}_6\text{H}_5\text{COOH}}{1 \text{ mol OH}^-}$ $= 3.72 \times 10^{-3} \text{ mol } \text{C}_6\text{H}_5\text{COOH}$ $\text{mass } \text{C}_6\text{H}_5\text{COOH} = 3.72 \times 10^{-3} \text{ mol } \text{C}_6\text{H}_5\text{COOH} \times \frac{122 \text{ g } \text{C}_6\text{H}_5\text{COOH}}{1 \text{ mol } \text{C}_6\text{H}_5\text{COOH}}$ $= 0.453 \text{ g } \text{C}_6\text{H}_5\text{COOH}$	<p>One point is earned for the correct answer.</p>
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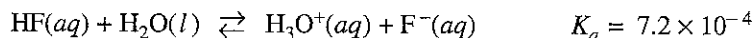
Question 1 (continued)

(ii) The mass percentage of benzoic acid in the solid sample

$\text{mass \% C}_6\text{H}_5\text{COOH} = \frac{0.453 \text{ g C}_6\text{H}_5\text{COOH}}{0.7529 \text{ g}} \times 100$ $= 60.2\%$	One point is earned for the correct answer.
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2007 SCORING GUIDELINES

Question 1



Hydrofluoric acid, $\text{HF}(aq)$, dissociates in water as represented by the equation above.

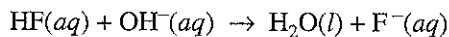
- (a) Write the equilibrium-constant expression for the dissociation of $\text{HF}(aq)$ in water.

$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$	One point is earned for the correct expression.
--	---

- (b) Calculate the molar concentration of H_3O^+ in a 0.40 M $\text{HF}(aq)$ solution.

$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} = \frac{(x)(x)}{0.40 - x} = 7.2 \times 10^{-4}$ <p>Assume $x \ll 0.40$, then $x^2 = (0.40)(7.2 \times 10^{-4})$</p> $x = [\text{H}_3\text{O}^+] = 0.017 \text{ M}$	One point is earned for the correct setup (or the setup consistent with part (a)). One point is earned for the correct concentration.
--	---

$\text{HF}(aq)$ reacts with $\text{NaOH}(aq)$ according to the reaction represented below.



A volume of 15 mL of 0.40 M $\text{NaOH}(aq)$ is added to 25 mL of 0.40 M $\text{HF}(aq)$ solution. Assume that volumes are additive.

- (c) Calculate the number of moles of $\text{HF}(aq)$ remaining in the solution.

$\begin{aligned} \text{mol HF}(aq) &= \text{initial mol HF}(aq) - \text{mol NaOH}(aq) \text{ added} \\ &= (0.025 \text{ L})(0.40 \text{ mol L}^{-1}) - (0.015 \text{ L})(0.40 \text{ mol L}^{-1}) \\ &= 0.010 \text{ mol} - 0.0060 \text{ mol} = 0.004 \text{ mol} \end{aligned}$	One point is earned for determining the initial number of moles of HF and OH^- . One point is earned for setting up and doing correct subtraction.
---	---

- (d) Calculate the molar concentration of $\text{F}^-(aq)$ in the solution.

$\begin{aligned} \text{mol F}^-(aq) \text{ formed} &= \text{mol NaOH}(aq) \text{ added} = 0.0060 \text{ mol F}^-(aq) \\ \frac{0.0060 \text{ mol F}^-(aq)}{(0.015 + 0.025) \text{ L of solution}} &= 0.15 \text{ M F}^-(aq) \end{aligned}$	One point is earned for determining the number of moles of $\text{F}^-(aq)$. One point is earned for dividing the number of moles of $\text{F}^-(aq)$ by the correct total volume.
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Question 1 (continued)

(e) Calculate the pH of the solution.

$$[\text{HF}] = \frac{0.004 \text{ mol HF}}{0.040 \text{ L}} = 0.10 \text{ M HF}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]} \Rightarrow \frac{[\text{HF}] \times K_a}{[\text{F}^-]} = [\text{H}_3\text{O}^+]$$

$$\Rightarrow \frac{0.10 \text{ M} (7.2 \times 10^{-4})}{0.15 \text{ M}} = 4.8 \times 10^{-4}$$

$$\Rightarrow \text{pH} = -\log(4.8 \times 10^{-4}) = 3.32$$

OR

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

$$= -\log(7.2 \times 10^{-4}) + \log \frac{0.15 \text{ M}}{0.10 \text{ M}}$$

$$= 3.14 + 0.18$$

$$= 3.32$$

One point is earned for indicating that the resulting solution is a buffer (e.g., by showing a ratio of $[\text{F}^-]$ to $[\text{HF}]$ or moles of F^- to HF).

One point is earned for the correct calculation of pH.

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Question 1 (10 points)

Answer the following questions that relate to the chemistry of halogen oxoacids.

- (a) Use the information in the table below to answer part (a)(i).

Acid	K_a at 298 K
HOCl	2.9×10^{-8}
HOBr	2.4×10^{-9}

- (i) Which of the two acids is stronger, HOCl or HOBr? Justify your answer in terms of K_a .

HOCl is the stronger acid because its K_a value is greater than the K_a value of HOBr.	One point is earned for the correct answer with justification.
--	--

- (ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).

$\text{H}:\ddot{\text{O}}:\ddot{\text{Cl}}:$	One point is earned for a correct diagram.
--	--

- (iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

<p>HOI is a weaker acid than HOCl because the O–H bond in HOI is stronger than the O–H bond in HOCl. The lower electronegativity (electron-drawing ability) of I compared with that of Cl results in an electron density that is higher (hence a bond that is stronger) between the H and O atoms in HOI compared with the electron density between the H and O atoms in HOCl.</p> <p>OR</p> <p>The conjugate base OCI^- is more stable than OI^- because Cl, being more electronegative, is better able to accommodate the negative charge.</p>	<p>One point is earned for predicting that HOI is a weaker acid than HOCl <u>and</u> stating that iodine has a lower electronegativity than chlorine and EITHER</p> <ul style="list-style-type: none"> • stating that this results in a stronger O–H bond in HOI <p>OR</p> <ul style="list-style-type: none"> • stating that this decreases the stability of the OI^- ion in solution.
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Question 1 (continued)

(b) Write the equation for the reaction that occurs between hypochlorous acid and water.

$\text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{OCl}^- + \text{H}_3\text{O}^+$ <p style="text-align: center;">OR</p> $\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	<p style="text-align: center;">One point is earned for the correct equation.</p>
---	--

(c) A 1.2 M NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $\text{OCl}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HOCl}(aq) + \text{OH}^-(aq)$ occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between $\text{OCl}^-(aq)$ and $\text{H}_2\text{O}(l)$.

$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]}$	<p style="text-align: center;">One point is earned for the correct expression.</p>
---	--

(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.

$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.4 \times 10^{-7}$	<p style="text-align: center;">One point is earned for the correct value with supporting work.</p>
---	--

(iii) Calculate the value of $[\text{OH}^-]$ in the 1.2 M NaOCl solution at 298 K.

<table border="1" style="margin-left: auto; margin-right: auto; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>$[\text{OCl}^-]$</th> <th>$[\text{HOCl}]$</th> <th>$[\text{OH}^-]$</th> </tr> </thead> <tbody> <tr> <td>initial value</td> <td>1.2</td> <td>0</td> <td>≈ 0</td> </tr> <tr> <td>change</td> <td>$-x$</td> <td>x</td> <td>x</td> </tr> <tr> <td>equilibrium value</td> <td>$1.2 - x$</td> <td>x</td> <td>x</td> </tr> </tbody> </table> $K_{\text{hyd}} = 3.4 \times 10^{-7} = \frac{[\text{OH}^-][\text{HOCl}]}{[\text{OCl}^-]} = \frac{(x)(x)}{(1.2 - x)} \approx \frac{x^2}{1.2}$ $\Rightarrow (1.2)(3.4 \times 10^{-7}) = x^2 \Rightarrow$ $x = [\text{OH}^-] = 6.4 \times 10^{-4} M$		$[\text{OCl}^-]$	$[\text{HOCl}]$	$[\text{OH}^-]$	initial value	1.2	0	≈ 0	change	$-x$	x	x	equilibrium value	$1.2 - x$	x	x	<p style="text-align: center;">One point is earned for the correct setup.</p> <p style="text-align: center;">One point is earned for the correct answer with supporting calculations.</p>
	$[\text{OCl}^-]$	$[\text{HOCl}]$	$[\text{OH}^-]$														
initial value	1.2	0	≈ 0														
change	$-x$	x	x														
equilibrium value	$1.2 - x$	x	x														

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Question 1 (continued)

- (d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of the buffer solution is determined to be 6.48.

- (i) Calculate the value of $[H_3O^+]$ in the buffer solution.

$[H^+] = 10^{-6.48} = 3.3 \times 10^{-7} M$	One point is earned for the correct value.
---	--

- (ii) Indicate which of HOCl(aq) or OCl⁻(aq) is present at the higher concentration in the buffer solution. Support your answer with a calculation.

$[H^+] = 3.3 \times 10^{-7} M$ and K_a for HOCl = 2.9×10^{-8} $K_a = \frac{[H^+][OCl^-]}{[HOCl]}$ $2.9 \times 10^{-8} = \frac{(3.3 \times 10^{-7})[OCl^-]}{[HOCl]}$ $\frac{[OCl^-]}{[HOCl]} = \frac{2.9 \times 10^{-8}}{3.3 \times 10^{-7}} = 0.088 \Rightarrow [HOCl] > [OCl^-]$	One point is earned for the correct answer with supporting buffer calculations.
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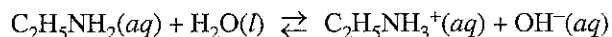
Question 1 (10 points)

A pure 14.85 g sample of the weak base ethylamine, $C_2H_5NH_2$, is dissolved in enough distilled water to make 500. mL of solution.

- (a) Calculate the molar concentration of the $C_2H_5NH_2$ in the solution.

$n_{C_2H_5NH_2} = 14.85 \text{ g } C_2H_5NH_2 \times \frac{1 \text{ mol } C_2H_5NH_2}{45.09 \text{ g } C_2H_5NH_2}$ $= 0.3293 \text{ mol } C_2H_5NH_2$ $M_{C_2H_5NH_2} = \frac{0.3293 \text{ mol } C_2H_5NH_2}{0.500 \text{ L}} = \mathbf{0.659 \text{ M}}$	<p>One point is earned for the correct number of moles.</p> <p>One point is earned for the correct concentration.</p>
---	---

The aqueous ethylamine reacts with water according to the equation below.



- (b) Write the equilibrium-constant expression for the reaction between $C_2H_5NH_2(aq)$ and water.

$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]}$	<p>One point is earned for the correct expression.</p>
---	--

- (c) Of $C_2H_5NH_2(aq)$ and $C_2H_5NH_3^+(aq)$, which is present in the solution at the higher concentration at equilibrium? Justify your answer.

<p>$C_2H_5NH_2$ is present in the solution at the higher concentration at equilibrium. Ethylamine is a weak base, and thus it has a small K_b value. Therefore only partial dissociation of $C_2H_5NH_2$ occurs in water, and $[C_2H_5NH_3^+]$ is thus less than $[C_2H_5NH_2]$.</p>	<p>One point is earned for the correct answer with justification.</p>
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Question 1 (continued)

- (d) A different solution is made by mixing 500. mL of 0.500 M C₂H₅NH₂ with 500. mL of 0.200 M HCl. Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

- (i) Calculate the concentration of OH⁻(aq) in the solution.

$\text{pH} = -\log[\text{H}^+]$ $[\text{H}^+] = 10^{-10.93} = 1.17 \times 10^{-11}$ $[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.00 \times 10^{-14}}{1.17 \times 10^{-11}} = 8.5 \times 10^{-4} \text{ M}$ <p>OR</p> $\text{pOH} = 14 - \text{pH} = 14 - 10.93 = 3.07$ $\text{pOH} = -\log[\text{OH}^-]$ $[\text{OH}^-] = 10^{-3.07} = 8.5 \times 10^{-4} \text{ M}$	One point is earned for the correct concentration.
--	--

- (ii) Write the net-ionic equation that represents the reaction that occurs when the C₂H₅NH₂ solution is mixed with the HCl solution.

$\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_3\text{O}^+ \rightarrow \text{C}_2\text{H}_5\text{NH}_3^+ + \text{H}_2\text{O}$	One point is earned for the correct equation.
---	---

- (iii) Calculate the molar concentration of the C₂H₅NH₃⁺(aq) that is formed in the reaction.

$\text{moles of C}_2\text{H}_5\text{NH}_2 = 0.500 \text{ L} \times \frac{0.500 \text{ mol}}{1.00 \text{ L}} = 0.250 \text{ mol}$ $\text{moles of H}_3\text{O}^+ = 0.500 \text{ L} \times \frac{0.200 \text{ mol}}{1.00 \text{ L}} = 0.100 \text{ mol}$ <table border="1" style="margin: 10px auto; border-collapse: collapse; text-align: center;"> <thead> <tr> <th></th> <th>[C₂H₅NH₂]</th> <th>[H₃O⁺]</th> <th>[C₂H₅NH₃⁺]</th> </tr> </thead> <tbody> <tr> <td>initial value</td> <td>0.250</td> <td>0.100</td> <td>~ 0</td> </tr> <tr> <td>change</td> <td>-0.100</td> <td>-0.100</td> <td>+0.100</td> </tr> <tr> <td>final value</td> <td>0.150</td> <td>~ 0</td> <td>0.100</td> </tr> </tbody> </table> $[\text{C}_2\text{H}_5\text{NH}_3^+] = \frac{0.100 \text{ mol C}_2\text{H}_5\text{NH}_3^+}{1.00 \text{ L}} = 0.100 \text{ M}$		[C ₂ H ₅ NH ₂]	[H ₃ O ⁺]	[C ₂ H ₅ NH ₃ ⁺]	initial value	0.250	0.100	~ 0	change	-0.100	-0.100	+0.100	final value	0.150	~ 0	0.100	One point is earned for the correct number of moles of C ₂ H ₅ NH ₂ and H ₃ O ⁺ . One point is earned for the correct concentration.
	[C ₂ H ₅ NH ₂]	[H ₃ O ⁺]	[C ₂ H ₅ NH ₃ ⁺]														
initial value	0.250	0.100	~ 0														
change	-0.100	-0.100	+0.100														
final value	0.150	~ 0	0.100														

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Question 1 (continued)

(iv) Calculate the value of K_b for $C_2H_5NH_2$.

$$[C_2H_5NH_2] = \frac{0.150 \text{ mol } C_2H_5NH_2}{1.00 \text{ L}} = 0.150 \text{ M}$$

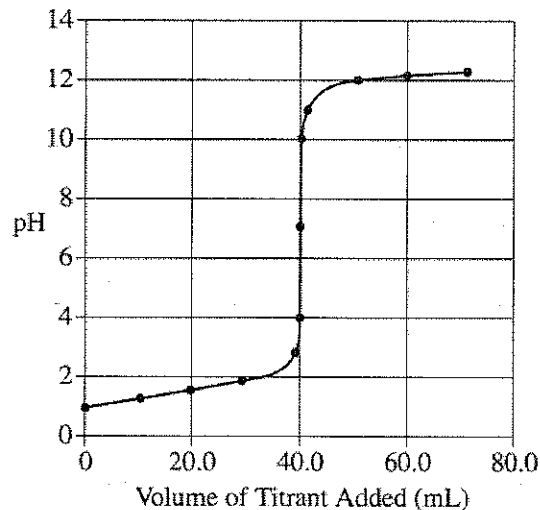
$$K_b = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{(0.100)(8.5 \times 10^{-4})}{0.150} = 5.67 \times 10^{-4}$$

One point is earned for the correct calculation of the molarity of $C_2H_5NH_2$ after neutralization.

One point is earned for the correct value.

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Question 5
(9 points)



A solution of 0.100 M HCl and a solution of 0.100 M NaOH are prepared. A 40.0 mL sample of one of the solutions is added to a beaker and then titrated with the other solution. A pH electrode is used to obtain the data that are plotted in the titration curve shown above.

- (a) Identify the solution that was initially added to the beaker. Explain your reasoning.

The solution in the beaker was the 0.100 M HCl because the initial pH was 1 (the pH of 0.100 M HCl).	One point is earned for the correct identification with rationale.
--	--

- (b) On the titration curve above, circle the point that corresponds to the equivalence point.

The point with coordinates (40.0, 7) is circled.	One point is earned for the correct choice of point.
--	--

- (c) At the equivalence point, how many moles of titrant have been added?

$0.0400 \text{ L} \times \frac{0.100 \text{ mol NaOH}}{1.00 \text{ L}} = 0.00400 \text{ mol NaOH}$	One point is earned for the correct numerical answer.
--	---

- (d) The same titration is to be performed again, this time using an indicator. Use the information in the table below to select the best indicator for the titration. Explain your choice.

Methyl red would be best because its color change will occur closest to the equivalence point (when the pH changes from about 4 to 10).	One point is earned for the correct selection of indicator. One point is earned for the explanation.
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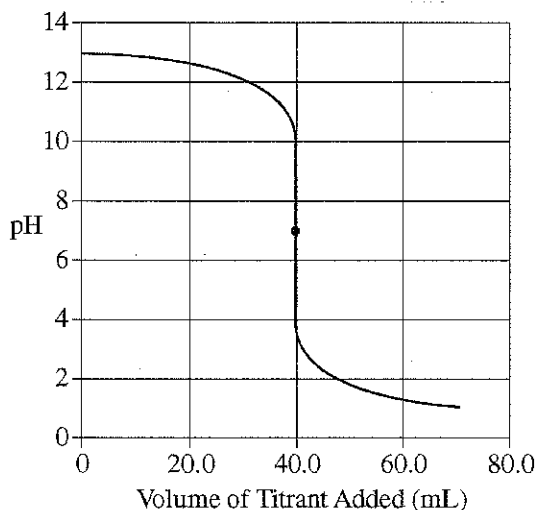
Question 5 (continued)

Indicator	pH Range of Color Change
Methyl violet	0 – 1.6
Methyl red	4 – 6
Alizarin yellow	10 – 12

- (e) What is the difference between the equivalence point of a titration and the end point of a titration?

<p>The equivalence point in a titration occurs when the number of moles of titrant added is exactly sufficient to react completely with the number of moles of the titrated species present in the sample being titrated.</p> <p>The end point of a titration is the point in a titration at which the indicator undergoes its color change.</p>	<p>One point is earned for each correct definition.</p>
--	---

- (f) On the grid provided below, sketch the titration curve that would result if the solutions in the beaker and buret were reversed (i.e., if 40.0 mL of the solution used in the buret in the previous titration were titrated with the solution that was in the beaker).



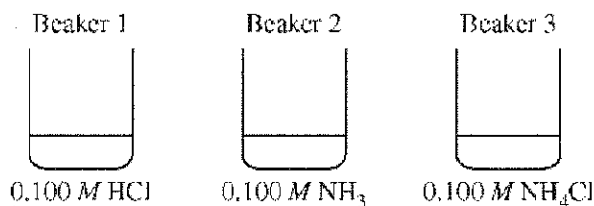
One point is earned for starting between pH 12 and 14 and for finishing below pH 2.

One point is earned for locating the equivalence point at pH 7 and volume 40.0 mL.

One point is earned for the overall shape of the curve.

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2011 SCORING GUIDELINES

Question 1



1. Each of three beakers contains 25.0 mL of a 0.100 M solution of HCl, NH₃, or NH₄Cl, as shown above. Each solution is at 25°C.

(a) Determine the pH of the solution in beaker 1. Justify your answer.

$\text{pH} = -\log[\text{H}^+] = -\log(0.100) = 1.000$	1 point is earned for the correct pH.
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- (b) In beaker 2, the reaction $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ occurs. The value of K_b for $\text{NH}_3(\text{aq})$ is 1.8×10^{-5} at 25°C.

(i) Write the K_b expression for the reaction of $\text{NH}_3(\text{aq})$ with $\text{H}_2\text{O}(\text{l})$.

$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$	1 point is earned for the correct expression.
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(ii) Calculate the $[\text{OH}^-]$ in the solution in beaker 2.

<p>Let $[\text{OH}^-] = x$, then $K_b = \frac{(x)(x)}{(0.100 - x)}$</p> <p>Assume that $x \ll 0.100$ M, then</p> $1.8 \times 10^{-5} = \frac{x^2}{0.100} \Rightarrow x = [\text{OH}^-] = 1.3 \times 10^{-3} \text{ M}$	<p>1 point is earned for the correct setup.</p> <p>1 point is earned for the correct answer.</p>
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- (c) In beaker 3, the reaction $\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$ occurs.

(i) Calculate the value of K_a for $\text{NH}_4^+(\text{aq})$ at 25°C.

$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$	1 point is earned for the correct answer.
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Question 1 (continued)

- (ii) The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

<p>In the resulting solution, $[\text{NH}_3] = [\text{NH}_4^+]$;</p> $K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$ <p>Thus $[\text{H}_3\text{O}^+] = 5.6 \times 10^{-10}$; $\text{pH} = -\log(5.6 \times 10^{-10}) = 9.25$</p>	<p>– 1 point is earned for noting that the solution is a buffer with $[\text{NH}_3] = [\text{NH}_4^+]$.</p> <p>1 point is earned for the correct pH.</p>
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- (d) The contents of beaker 1 are poured into the solution made in part (c)(ii). The resulting solution is stirred. Assume that volumes are additive.

- (i) Is the resulting solution an effective buffer? Justify your answer.

<p>The resulting solution is not an effective buffer. Virtually all of the NH_3 in the solution formed in (c)(ii) will react with the H_3O^+ from solution 1:</p> $\text{NH}_3 + \text{H}_3\text{O}^+ \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$ <p>leaving mostly NH_4^+ in the final solution. Since only one member of the $\text{NH}_4^+/\text{NH}_3$ conjugate acid-base pair is left, the solution cannot buffer both base and acid.</p>	<p>1 point is earned for the correct response with an acceptable justification.</p>
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- (ii) Calculate the final $[\text{NH}_4^+]$ in the resulting solution at 25°C.

<p>moles = (volume)(molarity)</p> <p>moles H_3O^+ in sol. 1 = $(0.0250)(0.100) = 0.00250$ mol</p> <p>moles NH_3 in sol. 2 = $(0.0250)(0.100) = 0.00250$ mol</p> <p>moles NH_4^+ in sol. 3 = $(0.0250)(0.100) = 0.00250$ mol</p> <p>When the solutions are mixed, the H_3O^+ and NH_3 react to form NH_4^+, resulting in a total of 0.00500 mol NH_4^+. The final volume is the sum $(25.0 + 25.0 + 25.0) = 75.0$ mL.</p> <p>The final concentration of $\text{NH}_4^+ = (0.00500 \text{ mol}/0.0750 \text{ L}) = 0.0667 \text{ M}$.</p>	<p>1 point is earned for the correct calculation of moles of NH_4^+.</p> <p>1 point is earned for the correct calculation of the final volume <u>and</u> concentration.</p>
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Question 5
(9 points)

A student is instructed to prepare 100.0 mL of 1.250 M NaOH from a stock solution of 5.000 M NaOH. The student follows the proper safety guidelines.

- (a) Calculate the volume of 5.000 M NaOH needed to accurately prepare 100.0 mL of 1.250 M NaOH solution.

$M_1V_1 = M_2V_2$ $V_1 = \frac{M_2V_2}{M_1} = \frac{(1.250\text{ M})(100.0\text{ mL})}{5.000\text{ M}} = 25.00\text{ mL}$	<p>1 point is earned for the correct volume.</p>
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- (b) Describe the steps in a procedure to prepare 100.0 mL of 1.250 M NaOH solution using 5.000 M NaOH and equipment selected from the list below.

Balance	25 mL Erlenmeyer flask	100 mL graduated cylinder	100 mL volumetric flask
50 mL buret	100 mL Florence flask	25 mL pipet	100 mL beaker
Eyedropper	Drying oven	Wash bottle of distilled H ₂ O	Crucible

<p>Pipet 25.00 mL of 5.000 M NaOH solution into the 100 mL volumetric flask.</p> <p>Fill the volumetric flask to the calibration line with distilled water; using an eyedropper for the last few drops is advised.</p> <p>Cap the volumetric flask and invert several times to ensure homogeneity.</p>	<p>1 point is earned for descriptions of any <u>two</u> of the three steps.</p> <p>An additional point is earned if all <u>three</u> steps are described.</p>
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- (c) The student is given 50.0 mL of a 1.00 M solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 M NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)

- (i) Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.

<p>When a weak acid is titrated with a strong base, the reaction forms water and the A⁻ ion.</p> $\text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O}$ <p>The A⁻ ion formed in the titration reacts with the solvent water to release OH⁻ ions, making the solution basic at the equivalence point.</p> $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$	<p>1 point is earned for either the correct equation or a clear statement that the conjugate base, A⁻, is a (weak) base.</p> <p>1 point is earned for indicating that the solution is basic because of the formation of OH⁻.</p>
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Question 5 (continued)

(ii) Identify the indicator in the table below that would be best for the titration. Justify your choice.

Indicator	pK_a
Methyl red	5
Bromothymol blue	7
Phenolphthalein	9

Because the pH is basic at the equivalence point, it is best to use an indicator that changes color in basic solution. Therefore, phenolphthalein would be the best indicator for the titration.

1 point is earned for an answer consistent with the answer to part (c)(i) with justification.

(d) The student is given another 50.0 mL sample of 1.00 M HA, which the student adds to the solution that had been titrated to the endpoint in part (c). The result is a solution with a pH of 5.0.

(i) What is the value of the acid-dissociation constant, K_a , for the weak acid? Explain your reasoning.

The resulting solution is at the half-equivalence-point, where $[HA] = [A^-]$, thus $pH = pK_a = 5.0 \Rightarrow K_a = 1 \times 10^{-5}$.

1 point is earned for showing that the system is at the half-equivalence point.

1 point is earned for the correct value of K_a .

(ii) Explain why the addition of a few drops of 1.250 M NaOH to the resulting solution does not appreciably change its pH.

The resulting solution is a buffer; therefore adding a few drops of acid or base does not appreciably change the pH.

1 point is earned for indicating that the solution is a buffer.

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Question 1
(10 points)

A 1.22 g sample of a pure monoprotic acid, HA, was dissolved in distilled water. The HA solution was then titrated with 0.250 M NaOH. The pH was measured throughout the titration, and the equivalence point was reached when 40.0 mL of the NaOH solution had been added. The data from the titration are recorded in the table below.

Volume of 0.250 M NaOH Added (mL)	pH of Titrated Solution
0.00	?
10.0	3.72
20.0	4.20
30.0	?
40.0	8.62
50.0	12.40

(a) Explain how the data in the table above provide evidence that HA is a weak acid rather than a strong acid.

The pH at the equivalence point is above 7, which indicates that HA is a weak acid.	1 point is earned for the correct explanation.
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(b) Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA.

$\text{HA}(aq) + \text{OH}^-(aq) \rightarrow \text{A}^-(aq) + \text{H}_2\text{O}(l)$	1 point is earned for writing the net-ionic equation balanced for mass and charge.
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(c) Calculate the number of moles of HA that were titrated.

At the equivalence point, the number of moles of base added equals the number of moles of acid initially present. $0.0400 \text{ L} \times \frac{0.250 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol HA}}{1 \text{ mol NaOH}} = 0.0100 \text{ mol HA}$	1 point is earned for the correct number of moles.
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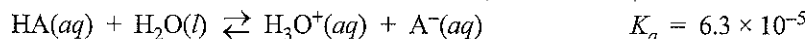
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Question 1 (continued)

(d) Calculate the molar mass of HA.

$\text{MM} = \frac{\text{mass of acid}}{\text{moles of acid}} = \frac{1.22 \text{ g}}{0.0100 \text{ mol}} = 122 \text{ g/mol}$	<p>1 point is earned for the correct molar mass.</p>
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The equation for the dissociation reaction of HA in water is shown below.



(e) Assume that the initial concentration of the HA solution (before any NaOH solution was added) is 0.200 M. Determine the pH of the initial HA solution.

$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$ $6.3 \times 10^{-5} = \frac{(x)(x)}{(0.200 - x)}; \text{ assume that } x \ll 0.200 \text{ M.}$ $x = [\text{H}_3\text{O}^+] = 3.5 \times 10^{-3} \text{ M}$ $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.5 \times 10^{-3}) = 2.45$	<p>1 point is earned for the appropriate substitution into the K_a expression.</p> <p>1 point is earned for the correct $[\text{H}_3\text{O}^+]$.</p> <p>1 point is earned for the calculation of pH.</p>
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(f) Calculate the value of $[\text{H}_3\text{O}^+]$ in the solution after 30.0 mL of NaOH solution is added and the total volume of the solution is 80.0 mL.

$\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$ <p>mol before rxn: 0.0100 0.00750 0.00000</p> <p>mol after rxn: 0.00250 0.00000 0.00750</p> $[\text{HA}] = \frac{0.00250 \text{ mol}}{0.0800 \text{ L}} = 3.13 \times 10^{-2} \text{ M}$ $[\text{A}^-] = \frac{0.00750 \text{ mol}}{0.0800 \text{ L}} = 9.38 \times 10^{-2} \text{ M}$ $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$ $6.3 \times 10^{-5} = \frac{(x)(9.38 \times 10^{-2} + x)}{(3.13 \times 10^{-2} - x)}$ <p>Assume that $x \ll 9.38 \times 10^{-2} \text{ M}$ and $3.13 \times 10^{-2} \text{ M}$,</p> $\text{then } 6.3 \times 10^{-5} = \frac{(x)(9.38 \times 10^{-2})}{(3.13 \times 10^{-2})}$ $x = [\text{H}_3\text{O}^+] = 2.10 \times 10^{-5} \text{ M.}$	<p>1 point is earned for the correct calculation of moles of A^- and HA after the reaction.</p> <p>1 point is earned for the appropriate substitution into the equilibrium expression.</p> <p>1 point is earned for the correct calculation of $[\text{H}_3\text{O}^+]$.</p>
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