Chem 104
Test 3 Practice Problems
Solutions

1. Complete the following table by calculating the missing entries and indicating whether the solution is acidic or basic.

$[H_3O^+]$	$[OH^-]$	pH	pOH	acidic or basic?
5.0×10^{-8} M	2.0×10^{-7} M	7.30	**6.70**	basic

2. Using the Table of Conjugate Acid-Base Pairs, decide whether each of the following equilibria lies to the left or right.

$H_2C_2O_4(aq) + SO_4^{2-}(aq) \rightleftharpoons HC_2O_4^-(aq) + HSO_4^-(aq)$	right
$HC_2O_4^-(aq) + SO_4^{2-}(aq) \rightleftharpoons C_2O_4^{2-}(aq) + HSO_4^-(aq)$	left
$HC_2O_4^-(aq) + OCl^-(aq) \rightleftharpoons C_2O_4^{2-}(aq) + HOCl(aq)$	right
$HOBr(aq) + OCl^-(aq) \rightleftharpoons OBr^-(aq) + HOCl(aq)$	left

3. Using the Table of Conjugate Acid-Base Pairs, decide whether a solution of $NaHC_2O_4(aq)$ is acidic or basic.

$HC_2O_4^- + H_2O \rightleftharpoons C_2O_4^{2-} + H_3O^+$ $\quad K_a = 6.40 \times 10^{-5}$ (from table)

$HC_2O_4^- + H_2O \rightleftharpoons H_2C_2O_4 + OH^-$ $\quad K_b = ?$

Calculate K_b for $HC_2O_4^-$ from the K_a of its conjugate acid, $H_2C_2O_4$.

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{5.90 \times 10^{-2}} = 1.69 \times 10^{-13}$$

$K_a >> K_b$, therefore the solution is acidic.

4. Vitamin C is ascorbic acid, a diprotic acid for which $K_1 = 8.0 \times 10^{-5}$ and $K_2 = 1.6 \times 10^{-12}$.
   (a) Using the abbreviation H_2Asc for ascorbic acid, write the hydrolysis equilibria that correspond to K_1 and K_2.

$$H_2Asc + H_2O \rightleftharpoons HAsc^- + H_3O^+ \qquad K_1 = 8.0 \text{ x } 10^{-5}$$
$$HAsc^- + H_2O \rightleftharpoons Asc^{2-} + H_3O^+ \qquad K_2 = 1.6 \text{ x } 10^{-12}$$

   (b) Consider a 0.10 M solution of ascorbic acid. Calculate $[H_3O^+]$, pH, and the percent dissociation of the acid in this solution.

   Assume the first dissociation is the only important source of hydronium ion in the solution; i.e., $[H_3O^+] = [HAsc^-]$ (Assumption I). The analytical concentration of the acid is much greater than K_1. Therefore, ignore acid hydrolysis (Assumption II); i.e., $[H_2Asc] = 0.10$ M.

$$[H_3O^+] = \sqrt{(0.10)(8.0\times10^{-5})} = 2.8_3\times10^{-3}\,\text{M} = [HAsc^-]$$

$$\text{pH} = 2.55$$

$$\%\ \text{dissoc.} = \frac{2.8_3\times10^{-3}}{0.10}\times100\% = 2.8\%$$

   (c) What is the concentration of ascorbate ion, $[Asc^{2-}]$, in a 0.10 M ascorbic acid solution?

   From the initial calculation, $[H_3O^+] = [HAsc^-]$. Therefore, they cancel when substituted into the K_2 expression, and $[Asc^{2-}] = K_2 = 1.6 \text{ x } 10^{-12}$.

5. Consider the titration of 25.0 mL of 0.120 M acetic acid (CH_3CO_2H, $K_a = 1.76 \times 10^{-5}$) with 0.100 M NaOH(*aq*).
   (a) How much 0.100 M NaOH(*aq*) must be added to reach the equivalence point?

$$V_b = \frac{M_a V_a}{M_b} = \frac{(0.120\,\text{M})(25.00\,\text{mL})}{0.100\,\text{M}} = 30.0\,\text{mL}$$

   (b) How many millimoles of CH_3CO_2H are present in the initial sample?

$$\text{mmol } CH_3CO_2H = (0.120 \text{ M})(25.0 \text{ mL}) = 3.00 \text{ mmol}$$

   (c) What is the initial pH of the sample solution?

   Use Assumptions I and II.

$$[H_3O^+] = \sqrt{(0.120)(1.76\times10^{-5})} = 1.45\times10^{-3}$$

$$\text{pH} = 2.838$$

(d) What is the pH of the solution after adding 5.00 mL of 0.100 M NaOH(*aq*)?

mmol OH^- added = 5.00 mL x 0.10 M = 0.50 mmol

	CH_3CO_2H	+	OH^-	⇌	H_2O	+	$CH_3CO_2^-$
Add	3.00		0.50				
Get	2.50		~0				0.50

Use K_a to calculate the concentration of hydronium ion in equilibrium with these amounts of acid and conjugate base.

$$K_a = 1.76 \times 10^{-5} = \frac{[H_3O^+](0.50)}{2.50}$$

$$[H_3O^+] = 8.8 \text{ x } 10^{-5} \text{ M}$$

$$pH = 4.05_{56} = 4.06$$

(e) What is the pH of the solution after adding 15.0 mL of 0.100 M NaOH(*aq*)?

mmol OH^- added = 15.0 mL x 0.10 M = 1.50 mmol

	CH_3CO_2H	+	OH^-	⇌	H_2O	+	$CH_3CO_2^-$
Add	3.00		1.50				
Get	1.50		~0				1.50

This is the half-titration point, where equal amounts of acid and conjugate base exit in the solution.

$$K_a = 1.76 \times 10^{-5} = \frac{[H_3O^+](1.50)}{1.50}$$

Therefore, $[H_3O^+] = K_a$ and pH = pK_a

$$pH = -\log (1.76 \text{ x } 10^{-5}) = 4.754$$

(f) What is the pH at the equivalence point?

All the acid has been converted to conjugate base. Therefore, calculate the K_b for acetate ion, calculate the analytical concentration of the acetate ion in the resulting solution, and use K_b to calculate the concentration of hydroxide ion. Then, calculate pOH, and by subtraction from 14.00 calculate pH.

	CH_3CO_2H	+	OH^-	$\rightleftharpoons$	H_2O	+	$CH_3CO_2^-$
Add	3.00		3.00				
Get	~0		~0				3.00

$$K_b = \frac{1.00 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

volume = (25.0 + 35.0) mL = 55.0 mL

$$c = \frac{3.00\,\text{mmol}}{55.0\,\text{mL}} = 0.0545_{45}\,\text{M}$$

$$[\text{OH}^-] = \sqrt{(0.0545)(5.68 \times 10^{-10})} = 5.57 \times 10^{-6}\,\text{M}$$

pOH = 5.254 ⇒ pH = 8.746

(g) What is the pH when 5.00 mL of 0.100 M NaOH(*aq*) has been added beyond the equivalence point?

This is after adding 35.0 mL of 0.100 M NaOH, which supplies 3.50 mmol OH^-.

	CH_3CO_2H	+	OH^-	$\rightleftharpoons$	H_2O	+	$CH_3CO_2^-$
Add	3.00		3.50				
Get	~0		0.50				3.00

Only the excess sodium hydroxide is an important source of hydroxide ion.

volume = (25.0 + 35.0) mL = 60.0 mL

$$[\text{OH}^-] = \frac{0.50\,\text{mmol}}{60.0\,\text{mL}} = 8.3 \times 10^{-3}\,\text{M}$$

pOH = 2.08 ⇒ pH = 11.92