

Ch 16 Acid-Base Equilibria (OpenStax Sections [14.3](#), [14.4](#), [14.5](#), [14.6](#), and [14.7](#))

Finding  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  for weak acids and bases involves equilibrium constants.

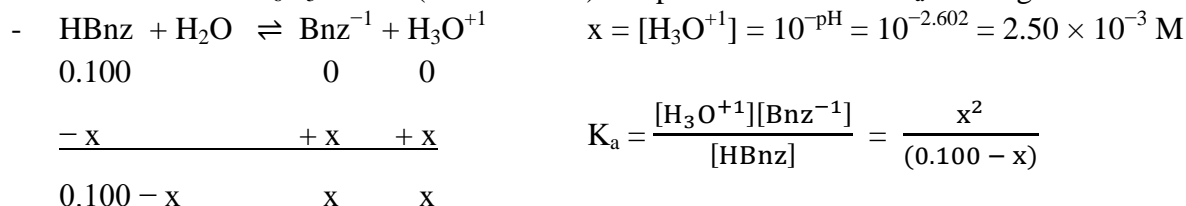
This is because they do not dissociate fully and they have a reversible [hydrolysis reaction](#).

- **Acid Ionization Constant**  $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$  is the expression for  $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$
- For acetic acid ( $\text{CH}_3\text{COOH}$ )  $K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.7 \times 10^{-5}$
- Correspondingly  $\text{p}K_a = -\log_{10}(K_a)$  and  $K_a = 10^{-\text{p}K_a}$
- For acetic acid  $\text{p}K_a = -\log(1.7 \times 10^{-5}) = 4.75$  and  $K_a = 10^{-(4.75)} = 1.7 \times 10^{-5}$
- This is similar to  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$  and  $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

$K_a$  must be determined experimentally (two general methods)

- Degree of ionization (or % ionization) is determined by measuring electrical conductivity or another colligative property (that depends only on total moles of all solutes).
- Measure pH or  $[\text{H}_3\text{O}^+]$  directly. Then, calculate all other concentrations with an eqm table.

Ex 16.01 0.100 M  $\text{C}_6\text{H}_5\text{COOH}$  (benzoic acid) has pH = 2.602. Find  $K_a$  and degree of ionization.



- Generally, variable in denominator ( $-x$ ) can be neglected for weak acid/base if  $\frac{[\text{HA}]_0}{K_a} > 100$ .

$x \ll 0.100$  So,  $0.100 - x \approx 0.100$

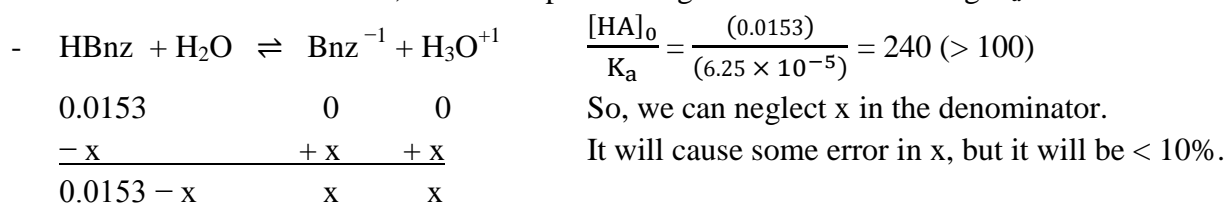
$$K_a = \frac{(2.50 \times 10^{-3})^2}{0.100} = 6.25 \times 10^{-5}$$

- Was it OK to neglect the  $-x$ ?  $\frac{[\text{HA}]_0}{K_a} = \frac{(1.00 \times 10^{-1})}{(6.25 \times 10^{-5})} = 1600 (> 100)$

- **Degree of Ionization** =  $\frac{[\text{A}^-]_{\text{eqm}}}{[\text{HA}]_0}$

$$[\text{Bnz}^-]_{\text{eqm}} \div [\text{HBnz}]_0 = x \div 0.100 = (2.50 \times 10^{-3}) \div (0.100) = 0.0250 \text{ (equivalent to 2.50 \%)}$$

Ex 16.02 For 0.0153 M HBnz, determine pH and degree of ionization using  $K_a = 6.25 \times 10^{-5}$ .



-  $K_a = 6.25 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{Bnz}^-]}{[\text{HBnz}]} = \frac{x^2}{(0.0153 - x)} = \frac{x^2}{0.0153} = \frac{x^2}{1.53 \times 10^{-2}}$

-  $x^2 = 9.56 \times 10^{-7} \quad [\text{H}_3\text{O}^+] = x = 9.77 \times 10^{-4} \text{ M} \quad \text{pH} = -\log(9.77 \times 10^{-4}) = 3.01$

- Degree of Ionization =  $[\text{Bnz}^-]_{\text{eqm}} \div [\text{HBnz}]_0 = x \div 0.0153 = 0.0639 \text{ (or 6.39 \%)}$

Note that Degree of Ionization depends on both  $K_a$  and  $[\text{HA}]$ .

Ex 16.03 Determine pH of 2.05 g Salicylic Acid (HSal) in 0.500 L solution if  $K_a = 1.05 \times 10^{-3}$ .

- Moles HSal =  $\frac{2.05 \text{ g}}{138.12 \frac{\text{g}}{\text{mol}}} = 0.0148 \text{ mol}$        $[\text{HSal}]_0 = \frac{0.0148 \text{ mol}}{0.500 \text{ L}} = 0.0296 \text{ M}$
- $\text{HSal} + \text{H}_2\text{O} \rightleftharpoons \text{Sal}^{-1} + \text{H}_3\text{O}^{+1}$   

0.0296	0	0
$\frac{-x}{0.0296 - x}$	$\frac{+x}{x}$	$\frac{+x}{x}$
- $K_a = 1.05 \times 10^{-3} = \frac{[\text{H}_3\text{O}^{+1}][\text{Sal}^{-1}]}{[\text{HSal}]} = \frac{x^2}{(0.0296 - x)}$
- We cannot neglect x in this problem because  $[\text{HSal}]_0 / K_a = 28.2$ , which is less than 100.
- First, rearrange the equation to a single line:  $x^2 = (1.05 \times 10^{-3})(0.0296 - x)$
- Then, rearrange to set equation equal to zero:  $x^2 + (1.05 \times 10^{-3})(x) - (3.11 \times 10^{-5}) = 0$
- The solution to this quadratic equation is:  $x = (1/2) \times [-K_a + \sqrt{K_a^2 + 4[\text{HSal}]_0 K_a}]$
- Substituting with the values above, we get:  $x = (1/2) \times [-(1.05 \times 10^{-3}) + (1.12 \times 10^{-2})]$
- The final result is:  $x = 5.08 \times 10^{-3} \text{ M} = [\text{Sal}^{-1}] = [\text{H}_3\text{O}^{+1}]$
- Ionization =  $\frac{x}{[\text{HSal}]_0} = \frac{5.08 \times 10^{-3}}{0.0296} = 0.172$        $\text{pH} = -\log(5.08 \times 10^{-3}) = 2.29$

Polyprotic Acids (Formula has more than one  $\text{H}^{+1}$ )

- $\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \rightarrow \text{HSO}_4^{-1} + \text{H}_3\text{O}^{+1}$        $K_{a1} > 10^{+6}$  (strong acid)
  - $\text{HSO}_4^{-1} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{-2} + \text{H}_3\text{O}^{+1}$        $K_{a2} = 1.1 \times 10^{-2}$  (weak acid)
  - $\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{HCO}_3^{-1} + \text{H}_3\text{O}^{+1}$        $K_{a1} = 4.3 \times 10^{-7}$
  - $\text{HCO}_3^{-1} + \text{H}_2\text{O} \rightarrow \text{CO}_3^{-2} + \text{H}_3\text{O}^{+1}$        $K_{a2} = 4.8 \times 10^{-11}$
  - $K_{a1} > K_{a2} > K_{a3}$  (for example  $\text{H}_3\text{PO}_4 > \text{H}_2\text{PO}_4^{-1} > \text{HPO}_4^{-2}$ )
- The increasing negative charges on the subsequent acids decrease the acidity.

Ex 16.04 Determine pH and Ion Concentrations for a 0.100 M Adipic Acid ( $\text{H}_2\text{Adi}$ ) solution.

- Adipic acid is diprotic with  $K_{a1} = 3.82 \times 10^{-5}$  and  $K_{a2} = 3.87 \times 10^{-6}$ .
- $\text{H}_2\text{Adi} + \text{H}_2\text{O} \rightleftharpoons \text{HAdi}^{-1} + \text{H}_3\text{O}^{+1}$   

0.100	0	0
$\frac{-x}{0.100 - x}$	$\frac{+x}{x}$	$\frac{+x}{x}$
- $K_{a1} = 3.82 \times 10^{-5} = \frac{[\text{H}_3\text{O}^{+1}][\text{HAdi}^{-1}]}{[\text{H}_2\text{Adi}]} = \frac{x^2}{(0.100 - x)} = \frac{x^2}{0.100}$
- $x^2 = K_{a1}[\text{H}_2\text{A}]_0 = 3.82 \times 10^{-6}$       and       $x = \sqrt{K_{a1}[\text{H}_2\text{A}]_0} = 1.95 \times 10^{-3} \text{ M}$
- Ignore the change in  $[\text{H}_3\text{O}^{+1}]$  due to the second reaction.  
 The second acid ( $\text{HAdi}^{-1}$ ) is much weaker than first acid ( $\text{H}_2\text{Adi}$ ).
- So:       $[\text{H}_3\text{O}^{+1}] = [\text{HAdi}^{-1}] = x = 1.95 \times 10^{-3} \text{ M}$
- And:       $\text{pH} = -\log(1.95 \times 10^{-3}) = 2.71$
- Use x for the starting concentrations of both  $\text{H}_3\text{O}^{+1}$  and  $\text{HAdi}^{-1}$  in the 2<sup>nd</sup> table (next page).

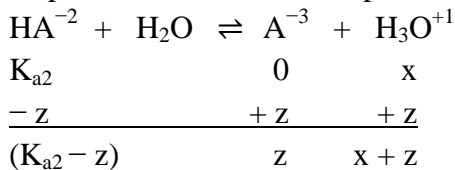
- $\text{HAdi}^{-1} + \text{H}_2\text{O} \rightleftharpoons \text{Adi}^{-2} + \text{H}_3\text{O}^{+1}$   

$$\frac{1.95 \times 10^{-3} \quad 0 \quad 1.95 \times 10^{-3}}{-y \quad +y \quad +y}$$

$$\frac{(1.95 \times 10^{-3}) - y}{y} = \frac{(1.95 \times 10^{-3}) + y}{y}$$
- $K_{a2} = 3.87 \times 10^{-6} = \frac{[\text{H}_3\text{O}^{+1}][\text{Adi}^{-2}]}{[\text{HAdi}^{-1}]} = \frac{[(1.95 \times 10^{-3}) + y][y]}{[(1.95 \times 10^{-3}) - y]} = \frac{[1.95 \times 10^{-3}][y]}{[1.95 \times 10^{-3}]} = y$
- $y \ll 1.95 \times 10^{-3}$  so  $[(1.95 \times 10^{-3}) + y] = [(1.95 \times 10^{-3}) - y] = 1.95 \times 10^{-3} \text{ M}$
- This makes both of those terms cancel and  $K_{A2} = 3.87 \times 10^{-6} \text{ M} = y = [\text{Adi}^{-2}]$
- In general  $[\text{A}^{-2}] = K_{a2}$  for a diprotic (or triprotic) acid

Triprotic Acid (has a third equilibrium table)

- The first equilibrium table results in  $[\text{H}_3\text{O}^{+1}] = [\text{H}_2\text{A}^{-1}] = x = \sqrt{K_{a1}[\text{H}_3\text{A}]_0}$
- The second equilibrium table results in  $[\text{HA}^{-2}] = y = K_{a2}$
- Triprotic acids have a third proton and a third equilibrium table.



- $K_{a3} = \frac{(z)(x + z)}{(K_{a2} - z)} = \frac{zx}{K_{a2}}$  and  $[\text{A}^{-3}] = z = \frac{K_{a2}K_{a3}}{x} = \frac{K_{a2}K_{a3}}{\sqrt{K_{a1}[\text{H}_3\text{A}]_0}}$

Base Ionization [Constants](#) and Equilibria

- $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^{+1} + \text{OH}^{-1}$
- $K_b = \frac{[\text{NH}_4^{+1}][\text{OH}^{-1}]}{[\text{NH}_3]} = 1.76 \times 10^{-5}$
- $\text{p}K_b = -\log_{10}(K_b) = 4.75$
- $K_b = 10^{-\text{p}K_b} = 10^{-4.75} = 1.76 \times 10^{-5}$

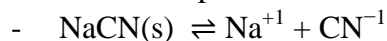
Ex 16.05 Determine pH for a Basic Solution of 0.015 M Trimethylamine ( $K_b = 6.3 \times 10^{-5}$ )

- $\text{N}(\text{CH}_3)_3 + \text{H}_2\text{O} \rightleftharpoons \text{HN}(\text{CH}_3)_3^{+1} + \text{OH}^{-1}$   

$$\frac{0.015 \quad 0 \quad 0}{-x \quad +x \quad +x}$$

$$\frac{(0.015 - x)}{x} = \frac{x}{x}$$
- $K_b = \frac{[\text{HN}(\text{CH}_3)_3^{+1}][\text{OH}^{-1}]}{[\text{N}(\text{CH}_3)_3]} = \frac{x^2}{(0.015 - x)} = \frac{x^2}{(0.015)} = 6.3 \times 10^{-5}$
- $x^2 = K_b \times [\text{Base}]_0 = (6.3 \times 10^{-5}) \times (0.015) = 9.45 \times 10^{-7}$
- $[\text{OH}^{-1}] = [\text{HN}(\text{CH}_3)_3^{+1}] = x = \sqrt{K_b[\text{Base}]_0} = 9.72 \times 10^{-4} \text{ M}$
- $\text{pOH} = -\log(x) = 3.01$
- $\text{pH} = 14.00 - 3.01 = 10.99 = 11.0$

Acid-Base Properties of salt solutions: Salts can be acidic, basic, or neutral

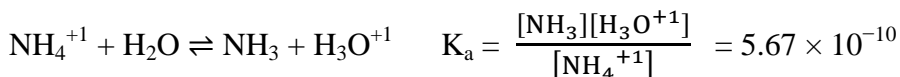


$\text{Na}^{+1}$  is not reactive with  $\text{H}_2\text{O}$ , but  $\text{CN}^{-1}$  is a weak base and has a  $K_b$  expression.



- Reaction of an acid or a base with water is called a hydrolysis (acid/base can be ion as well)

- For example,  $\text{NH}_4^{+1}$  is an acid with a hydrolysis, and its reaction has a  $K_a$  expression.



### Ex 16.06 Acidity and Basicity of Ionic Salts

- Conjugate ions of strong acids/bases, such as of  $\text{HCl}$  and  $\text{LiOH}$ , do not hydrolyze.

So, salts containing both conjugates together, such as  $\text{LiCl}$ , are **neutral**.

- Salts with the conjugates of a strong base and a weak acid, such as  $\text{KF}$ , are **basic**.

$\text{F}^{-1}$  is the conjugate of the weak acid  $\text{HF}$ . It will hydrolyze and it is a base.

- Salts with the conjugates of a weak base and a strong acid, such as  $\text{Pb}(\text{NO}_3)_2$ , are **acidic**.

$\text{Pb}^{+2}$  is the conjugate of the weak base  $\text{Pb}(\text{OH})_2$ . It will hydrolyze and it is an acid.

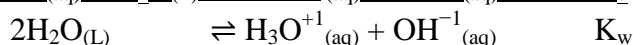
- Salts with the conjugates of both a weak base and a weak acid, such as  $\text{NH}_4\text{ClO}$ , have two ions that hydrolyze.

So, they can be **basic or acidic** depending on the components.

$K_a$  for  $\text{NH}_4^{+1}$  is  $5.67 \times 10^{-10}$ , and  $K_b$  for  $\text{ClO}^{-1}$  is  $3.5 \times 10^{-7}$ .

The  $K_b$  is larger than the  $K_a$ , so  $\text{NH}_4\text{ClO}$  is basic.

### Ionization Constants ( $K_a$ and $K_b$ ) for a Pair of Conjugates



- For a pair of conjugates  $K_a \times K_b = K_w = 1.00 \times 10^{-14}$

- Also,  $\mathbf{pK_a + pK_b = pK_w = 14.00}$

Ex 16.07 a. Find  $K_b$  for  $\text{ClO}^{-1}$  if  $K_a$  for  $\text{HClO}$  is  $2.9 \times 10^{-8}$

$$K_b = K_w \div K_a = (1.0 \times 10^{-14}) \div (2.9 \times 10^{-8}) = 3.5 \times 10^{-7}$$

b. Find  $K_a$  for  $\text{NH}_4^{+1}$  if  $K_b$  for  $\text{NH}_3$  =  $1.76 \times 10^{-5}$

$$K_a = K_w \div K_b = (1.0 \times 10^{-14}) \div (1.76 \times 10^{-5}) = 5.68 \times 10^{-10}$$

Ex 16.08 Determine the pH of a Sodium Benzoate Salt Solution (0.100 M  $\text{NaBnz}$ )



0.100                      0                      0                       $K_b = (1.00 \times 10^{-14}) \div (6.25 \times 10^{-5}) = 1.60 \times 10^{-10}$

$\frac{-x}{0.100 - x} \quad \frac{+x}{x} \quad \frac{+x}{x} \quad K_b = \frac{(x)(x)}{(0.100 - x)} = \frac{x^2}{0.100} = 1.60 \times 10^{-10}$

0.100 - x                      x                      x                       $[\text{OH}^{-1}] = x = \sqrt{0.100 \times K_b} = \sqrt{16.0 \times 10^{-12}} = 4.00 \times 10^{-6}$

$\text{pOH} = -\log[\text{OH}^{-1}] = 5.40 \text{ and } \text{pH} = 14.00 - 5.40 = 8.60$

### Common Ion Effect

- The common ion effect is a shift in equilibrium (usually to left) that is caused by adding a second solute which possesses an ion in the reaction.
- For acetic acid, below, we can add HCl, which provides  $\text{H}_3\text{O}^{+1}$ .  

$$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^{-1} + \text{H}_3\text{O}^{+1}$$
- $\text{H}_3\text{O}^{+1}$  is on the product side, so the equilibrium shifts to the left.  
 Less acetic acid is dissociated, so this decreases the degree of ionization.
- Adding  $\text{OH}^{-1}$  would remove  $\text{H}_3\text{O}^{+1}$ , which would create the opposite effect.  
 The equilibrium would shift to the right, and more acetic acid would be dissociated.

Common Ion Effect is similar for a weakly-soluble base:  $\text{Ca}(\text{OH})_{2(s)} \rightleftharpoons \text{Ca}^{+2}_{(aq)} + 2\text{OH}^{-1}_{(aq)}$

- **Solubility Product:**  $K_{sp} = [\text{Ca}^{+2}_{(aq)}][\text{OH}^{-1}_{(aq)}]^2$
- The solid is not included in the  $K_{sp}$ ! Pure solids are excluded from equilibrium constants.
- **Molar solubility (molsol)** is the effective mol/L of the dissolved solid.
- Without a common ion, molsol =  $[\text{Ca}^{+2}] = (1/2)[\text{OH}^{-1}]$ .
- If another source of  $\text{Ca}^{+2}$  (such as  $\text{CaCl}_2$ ) is added, then eqm shifts to left as product is added.
- Also, molsol no longer equals  $[\text{Ca}^{+2}]$ . Molsol will be decreased as eqm shifts to left.  
 That is, less of the solid reactant dissolves because of the additional  $\text{Ca}^{+2}$ .
- But molsol still equals  $(1/2)[\text{OH}^{-1}]$ , and can be calculated by titrating with an acid.  
 At the stoichiometric point: mol  $\text{H}^{+}$  added = mol  $\text{OH}^{-1}$  in sample
- For any slightly soluble salt, addition of a second salt containing one of the ions involved will shift the equilibrium to the left and decrease the molsol.
- Note that  $K_{sp}$  is a constant and does not change.

Ex 16.09 Degree of Ionization for 0.200 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.75 \times 10^{-5}$ ) with 0.0100 M HCl

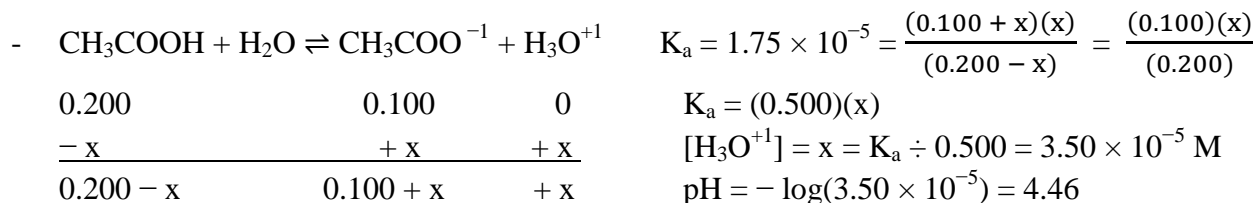
- $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^{-1} + \text{H}_3\text{O}^{+1}$   

0.200	0	0.0100
$-x$	$+x$	$+x$
0.200 - x	+ x	0.0100 + x
- $K_a = 1.75 \times 10^{-5} = \frac{(0.0100 + x)(x)}{(0.200 - x)} = \frac{(0.0100)(x)}{(0.200)} = (0.0500)(x)$
- $[\text{CH}_3\text{COO}^{-1}] = x = \frac{(1.75 \times 10^{-5})}{(0.0500)} = 3.50 \times 10^{-4} \text{ M}$
- Degree of Ionization =  $\frac{(3.50 \times 10^{-4})}{(0.200)} = 1.75 \times 10^{-3} = 0.175 \%$
- The degree of ionization for 0.20 M  $\text{CH}_3\text{COOH}$  without HCl is 0.94 %, which can be determined using the same equation as in Examples 16.01 and 16.02.
- The degree of ionization is much smaller with HCl present because the added  $\text{H}_3\text{O}^{+1}$  shifts the equilibrium back to the left.

Buffers – A solution which resists changes in pH when small amounts of acid or base are added.

- A buffer contains either a weak acid or base, along with the conjugate ion.  
So, the buffer solution possesses both an acid component and a base component.
- Two important characteristics: capacity and pH.
- Capacity is the amount of acid or base needed to create a large pH change, which depends on the amount of each conjugate that is in solution.
- The pH is determined by the  $K_a$  and by the ratio of the two conjugates' concentrations.

Ex 16.10 Determine pH for Solution of 0.200 M  $\text{CH}_3\text{COOH}$  and 0.100 M  $\text{CH}_3\text{COONa}$



Ex 16.11 Determine the pH of 40 mL of 0.100 M  $\text{NH}_3$  mixed with 60 mL of 0.100 M  $\text{NH}_4^{+1}$

- $[\text{NH}_3] = (0.100 \text{ M})(0.0400 \text{ L}) / (0.100 \text{ L}) = 0.0400 \text{ M}$  ( $M_2 = M_1 V_1 / V_2$  and  $V_2 = 0.100 \text{ L}$ )
- $[\text{NH}_4^{+1}] = (0.100 \text{ M})(0.0600 \text{ L}) / (0.100 \text{ L}) = 0.0600 \text{ M}$
- $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^{+1} + \text{OH}^{-1}$   

$$\begin{array}{ccc}
 0.0400 & 0.0600 & 0 \\
 -x & +x & +x \\
 \hline
 0.0400 - x & 0.0600 + x & +x
 \end{array}$$
- $K_b = 1.76 \times 10^{-5} = \frac{(0.0600 + x)(x)}{(0.0400 - x)} = \frac{(0.0600)(x)}{(0.0400)} = 1.50(x)$
- $x = K_b \div 1.50 = 1.17 \times 10^{-5} \text{ M} = [\text{OH}^{-1}]$
- $\text{pOH} = -\log(1.17 \times 10^{-5}) = 4.93$  and  $\text{pH} = 14.00 - 4.93 = 9.07$

Ex 16.12 75.0 ml with both 0.200 M  $\text{CH}_3\text{COOH}$  ( $K_a = 1.7 \times 10^{-5}$ ) and 0.100 M  $\text{CH}_3\text{COONa}$  is mixed with 10.0 ml of 0.100 M HCl. Determine the pH after mixing.

- mol  $\text{H}_3\text{O}^{+1} = (0.0100 \text{ L})(0.100 \text{ M}) = 0.00100 \text{ mol } \text{H}_3\text{O}^{+1}$
- $\text{H}_3\text{O}^{+1}$  will convert  $\text{CH}_3\text{COO}^{-1}$  into  $\text{CH}_3\text{COOH}$
- mol  $\text{CH}_3\text{COOH} = (0.0750 \text{ L})(0.200 \text{ M}) + 0.00100$   
 $= 0.0150 \text{ mol} + 0.00100 \text{ mol} = 0.0160 \text{ mol } \text{CH}_3\text{COOH}$
- $[\text{CH}_3\text{COOH}] = (0.0160 \text{ mol}) \div (0.0850 \text{ L}) = 0.188 \text{ M}$
- mol  $\text{CH}_3\text{COO}^{-1} = (0.0750 \text{ L})(0.100 \text{ M}) - 0.00100 \text{ mol}$   
 $= 0.00750 \text{ mol} - 0.00100 \text{ mol} = 0.00650 \text{ mol } \text{CH}_3\text{COO}^{-1}$
- $[\text{CH}_3\text{COO}^{-1}] = (0.00650 \text{ mol}) \div (0.0850 \text{ L}) = 0.0765 \text{ M}$
- $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^{-1} + \text{H}_3\text{O}^{+1} \quad K_a = 1.75 \times 10^{-5} = \frac{(0.0765 + x)(x)}{(0.188 - x)} = \frac{(0.0765)(x)}{(0.188)}$   

$$\begin{array}{ccc}
 0.188 & 0.0765 & 0 \\
 -x & +x & +x \\
 \hline
 0.188 - x & 0.0765 + x & +x
 \end{array} \quad \begin{array}{l}
 K_a = (0.407)(x) \\
 [\text{H}_3\text{O}^{+1}] = x = K_a \div 0.407 = 4.30 \times 10^{-5} \text{ M} \\
 \text{pH} = -\log(4.30 \times 10^{-5}) = 4.37
 \end{array}$$

### Henderson-Hasselbalch Equation

- Rearrange the  $K_a$  equation and take the  $-\log$ :  $-\log[\text{H}_3\text{O}^{+1}] = -\log\left[\frac{(K_a)[\text{HA}]}{[\text{A}^{-1}]}\right]$
- This is the result for a weak acid buffer:  $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^{-1}]}{[\text{HA}]}\right)$
- This is the result for a weak base buffer:  $\text{pH} = (\text{p}K_w - \text{p}K_b) + \log\left(\frac{[\text{B}]}{[\text{HB}^{+1}]}\right)$

Apply the Henderson-Hasselbalch equation to Example 16.10

- $\text{p}K_a = -\log(1.75 \times 10^{-5}) = 4.76$
- $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{A}^{-1}]}{[\text{HA}]}\right) = 4.76 + \log\left(\frac{0.100}{0.200}\right) = 4.76 + \log(1/2) = 4.76 - 0.301 = 4.46$

Apply the Henderson-Hasselbalch equation to Example 16.11

- $\text{p}K_b$  of  $\text{NH}_3 = -\log(1.76 \times 10^{-5}) = 4.75$   $\text{p}K_a$  of  $\text{NH}_4^{+1} = \text{p}K_w - \text{p}K_b = 14.00 - 4.75 = 9.25$
- $\text{pH} = \text{p}K_a + \log\left(\frac{[\text{B}]}{[\text{HB}^{+1}]}\right) = 9.25 + \log\left(\frac{0.0400}{0.0600}\right) = 9.25 - 0.18 = 9.07$

Acid-Base Titration Curves: Plotting pH vs. Volume of Titrant

- [Equivalence Point](#) is the point in a titration where stoichiometric amount of titrant is added. At this point, the solution is neutralized precisely so that:  $\text{mol OH}^{-1} = \text{mol H}_3\text{O}^{+1}$
- $\text{pH} = 7$  at the equivalence point if both strong acid and strong base are used.
- Weak acids/bases have conjugates that hydrolyze, so the pH is not 7 at their equiv point.
- Titration of a weak acid yields a basic conjugate, so  $\text{pH} > 7$  at its equivalence point.
- Conversely, a weak base has an acidic conjugate and  $\text{pH} < 7$  at its equivalence point.
- If the equivalence point is unknown, then the [indicator selection](#) is difficult.

Ex 16.14 0.0250 L of 0.100 M HBnz is titrated to its equivalence point with 0.100 M NaOH

- Find the equivalence point pH if  $K_a = 6.24 \times 10^{-5}$
  - $\text{mol OH}^{-1}$  added =  $\text{mol HBnz}$  in sample =  $(0.0250 \text{ L})(0.100 \text{ M}) = 0.00250 \text{ mol}$
  - All of the 0.00250 moles of HBnz are converted to  $\text{Bnz}^{-1}$  at the equivalence point.
  - Total  $V = 0.0250 \text{ L} + 0.0250 \text{ L} = 0.0500 \text{ L}$
  - At the equivalence point, we have  $[\text{Bnz}^{-1}] = \text{moles} / V = 0.00250 \text{ mol} / 0.0500 \text{ L} = 0.0500 \text{ M}$
  - Use this value as the initial concentration for the  $\text{Bnz}^{-1}$  hydrolysis reaction seen in Example 16.08. Solve the table to find the equivalence point pH.
  - $\text{Bnz}^{-1} + \text{H}_2\text{O} \rightleftharpoons \text{HBnz} + \text{OH}^{-1}$
- |            |          |          |
|------------|----------|----------|
| 0.0500     | 0        | 0        |
| <u>- x</u> | <u>x</u> | <u>x</u> |
| 0.0500 - x | x        | x        |
- $K_a = 6.24 \times 10^{-5}$   $K_b = \frac{K_w}{K_a} = 1.60 \times 10^{-10} = \frac{[\text{OH}^{-1}][\text{HBnz}]}{[\text{Bnz}^{-1}]} = \frac{x^2}{0.0500 - x} = \frac{x^2}{0.0500}$
  - $x = \sqrt{8.00 \times 10^{-12}} = 2.83 \times 10^{-6} = [\text{OH}^{-1}]$   $\text{pOH} = 5.55$   $\text{pH} = 14.00 - 5.55 = 8.45$