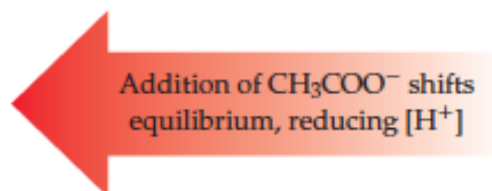
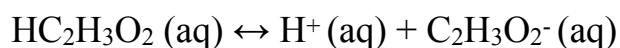


## Chapter 17. Additional Aspects of Aqueous Equilibria

### 17.1 The Common Ion Effect

- The dissociation of a weak electrolyte is decreased by the addition of a strong electrolyte that has an ion in common with the weak electrolyte.
- For example, consider the ionization of a weak acid, acetic acid.



- ♣ If we add additional  $\text{C}_2\text{H}_3\text{O}_2^-$  ions by the addition of a strong electrolyte, (e.g.,  $\text{NaC}_2\text{H}_3\text{O}_2^-$ ) the equilibrium is shifted to the left.
- ♣ This causes a reduction in the  $[\text{H}^+]$  and a decrease in the percent ionization of the acetic acid.
- ♣ By adding sodium acetate, we have disturbed the acetic acid equilibrium.
- ♣ In effect, we have added a product of this equilibrium (i.e., the acetate ion).
  - This phenomenon is called the **common-ion effect**.
- Common ion equilibrium problems are solved following the same pattern as other equilibrium problems.
  - ♣ However, the initial concentration of the common ion (from the salt) must be considered

What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

$$\text{CH}_3\text{COOH}(aq) \rightleftharpoons \text{H}^+(aq) + \text{CH}_3\text{COO}^-(aq)$$

Initial	0.30 M	0	0.30 M
Change	-x M	+x M	+x M
Equilibrium	(0.30 - x) M	x M	(0.30 + x) M

$$K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30 + x)}{0.30 - x}$$

$$K_a = 1.8 \times 10^{-5} = \frac{x(0.30)}{0.30}$$

$$x = 1.8 \times 10^{-5} \text{ M} = [\text{H}^+]$$

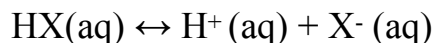
$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

## 17.2 Buffered Solutions

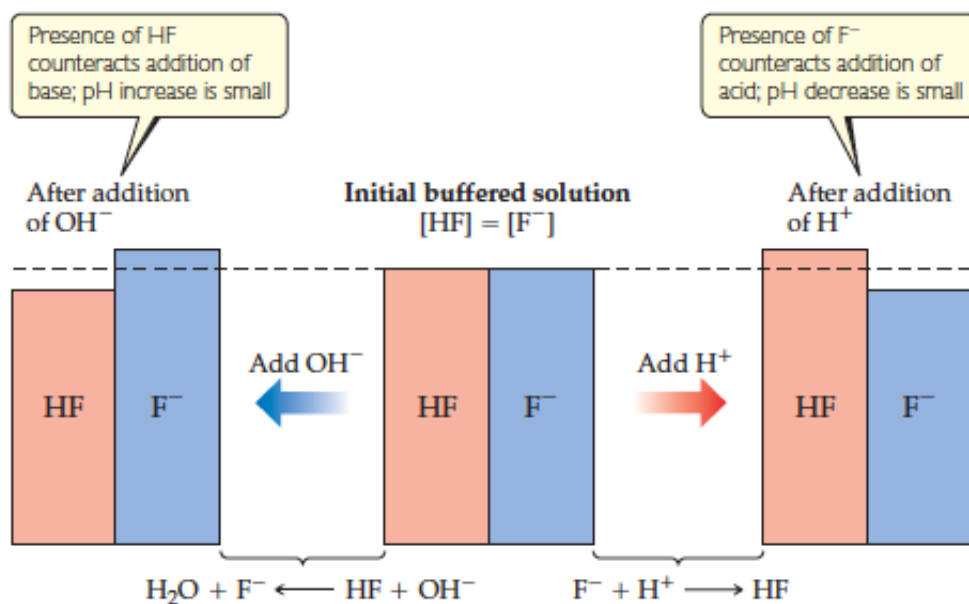
- A buffered solution or buffer is a solution that resists a change in pH upon addition of small amounts of strong acid or strong base.

### Composition and Action of Buffered Solutions

- A buffer consists of a mixture of a weak acid (HX) and its conjugate base ( $X^-$ )



- Thus a buffer contains both:
  - ♣ An acidic species (to neutralize  $\text{OH}^-$ ) and
  - ♣ A basic species (to neutralize  $\text{H}^+$ ).
- When a small amount of  $\text{OH}^-$  is added to the buffer, the  $\text{OH}^-$  reacts with HX to produce  $X^-$  and water.
  - ♣ But the  $[\text{HX}]/[\text{X}^-]$  ratio remains more or less constant, so the pH is not significantly changed.
- When a small amount of  $\text{H}^+$  is added to the buffer,  $X^-$  is consumed to produce HX.
  - ♣ Once again, the  $[\text{HX}]/[\text{X}^-]$  ratio is more or less constant, so the pH does not change significantly.



## Buffer Capacity and pH

- **Buffer capacity** is the amount of acid or base that can be neutralized by the buffer before there is a significant change in pH.
- Buffer capacity depends on the concentrations of the components of the buffer.
- ♣ The greater the concentrations of the conjugate acid-base pair, the greater the buffer capacity.

- By definition:

$$K_a = \frac{[H^+][X^-]}{[HX]}$$

- Rearranging, we get:
- $$[H^+] = K_a \times \frac{[HX]}{[X^-]}$$

- If we take the negative log of each side of the equation we get:

- $-\log[H^+] = -\log K_a - \log \frac{[HX]}{[X^-]}$

- By definition:

$$pH = pK_a - \log \frac{[HX]}{[X^-]}$$

- An alternate form of this equation is:

$$pH = pK_a + \log \frac{[X^-]}{[HX]} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

- The above equation is the **Henderson-Hasselbalch equation**

- ♣ Note that this equation uses the equilibrium concentrations of the acid and conjugate base.
- ♣ However, if  $K_a$  is sufficiently small (i.e. if the equilibrium concentration of undissociated acid is close to the initial concentration), then we can use the initial values of the acid and base concentrations in order to get a good estimate of the pH.

### Example:

What is the pH of a buffer that is 0.12 M in lactic acid [ $\text{CH}_3\text{CH}(\text{OH})\text{COOH}$ , or  $\text{HC}_3\text{H}_5\text{O}_3$ ] and 0.10 M in sodium lactate [ $\text{CH}_3\text{CH}(\text{OH})\text{COONa}$ , or  $\text{NaC}_3\text{H}_5\text{O}_3$ ]? For lactic acid,  $K_a = 1.4 \times 10^{-4}$

	$\text{HC}_3\text{H}_5\text{O}_3(aq)$	$\rightleftharpoons$	$\text{H}^+(aq)$	+	$\text{C}_3\text{H}_5\text{O}_3^-(aq)$
Initial	0.12 M		0		0.10 M
Change	-x M		+x M		+x M
Equilibrium	(0.12 - x) M		x M		(0.10 + x) M

$$K_a = 1.4 \times 10^{-4} = \frac{[\text{H}^+][\text{C}_3\text{H}_5\text{O}_3^-]}{[\text{HC}_3\text{H}_5\text{O}_3]} = \frac{x(0.10 + x)}{(0.12 - x)}$$

$$K_a = 1.4 \times 10^{-4} = \frac{x(0.10)}{0.12}$$

$$[\text{H}^+] = x = \left(\frac{0.12}{0.10}\right)(1.4 \times 10^{-4}) = 1.7 \times 10^{-4} \text{ M}$$

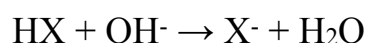
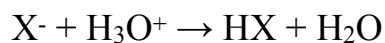
$$\text{pH} = -\log(1.7 \times 10^{-4}) = 3.77$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 3.85 + \log \left(\frac{0.10}{0.12}\right)$$

$$= 3.85 + (-0.08) = 3.77$$

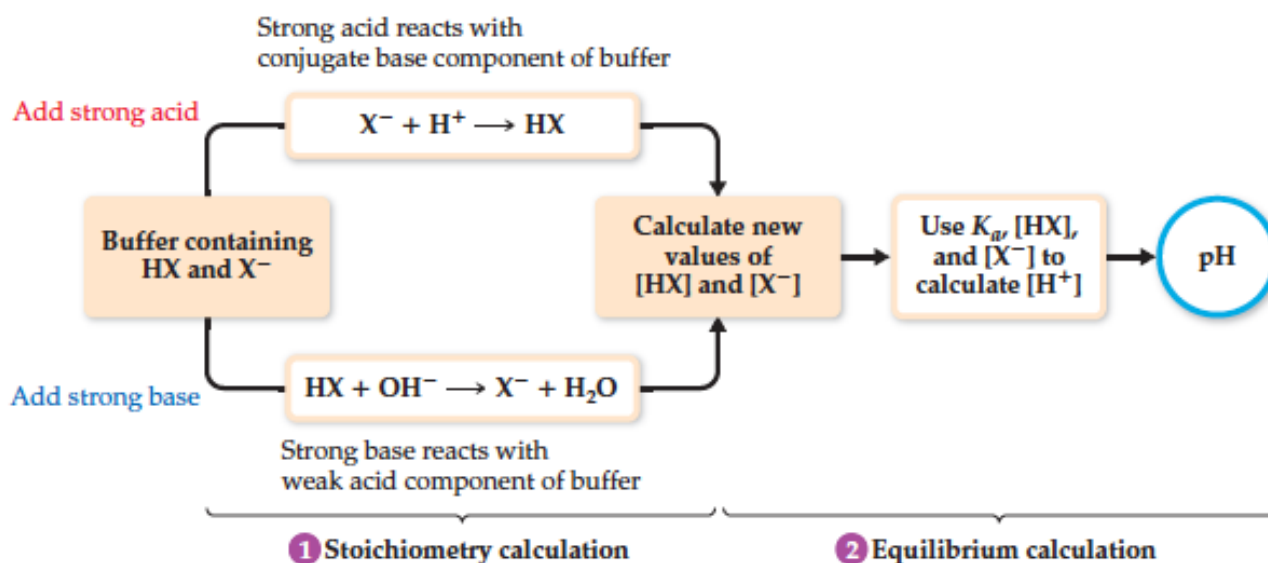
## Addition of Strong Acids or Bases to Buffers

- We break the calculation into two parts.
  - ♣ A stoichiometric calculation.
  - ♣ An equilibrium calculation.
- The addition of strong acid or base results in a neutralization reaction:



- By knowing how much  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  was added we know how much HX or  $\text{X}^-$  is formed.
  - ♣ This is the stoichiometric calculation.
- With the concentrations of HX and  $\text{X}^-$  (note the change in volume of solution) we can calculate the pH from the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$



### 17.3 Acid-Base Titrations

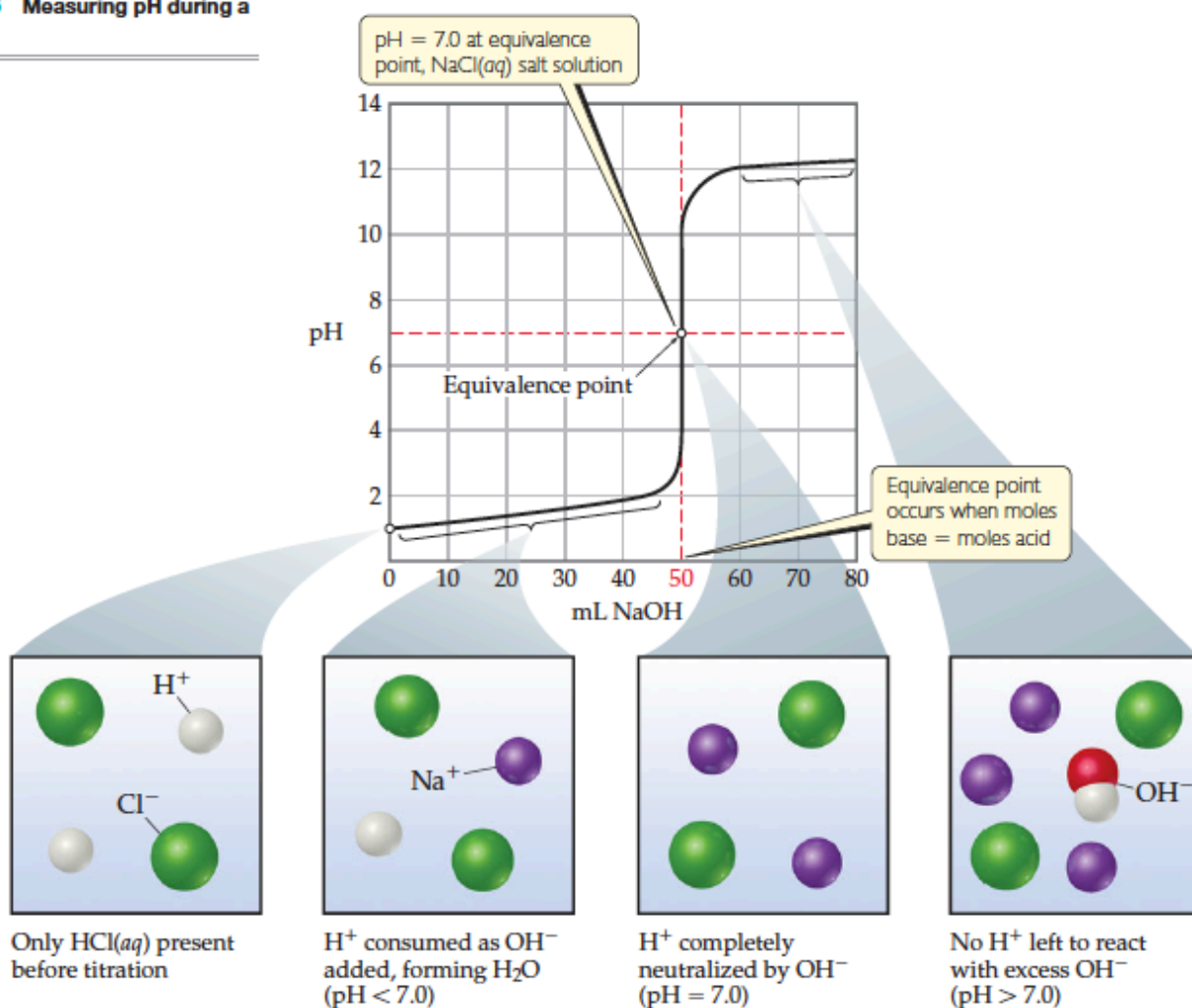
- In an acid-base titration:
  - ♣ A solution of base (or acid) of known concentration is added to an acid.
  - ♣ Acid-base indicators or a pH meter are used to signal the equivalence point.
  - ♣ The plot of pH versus volume during a titration is called a pH titration curve.

#### Strong Acid-Strong Base Titrations

- Consider adding a strong base (e.g., NaOH) to a solution of a strong acid (e.g., HCl).
- We can divide the titration curve into four regions.
  - ♣ 1. Initial pH (before any base is added).
    - The pH is given by the strong acid solution.
    - Therefore,  $\text{pH} < 7$ .
  - ♣ 2. Between the initial pH and the equivalence point.
    - When base is added before the equivalence point the pH is given by the amount of strong acid in excess.
    - Therefore,  $\text{pH} < 7$ .
  - ♣ 3. At the equivalence point.
    - The amount of base added is stoichiometrically equivalent to the amount of acid originally present.
    - Therefore, the pH is determined by the hydrolysis of the salt in solution.
    - Therefore,  $\text{pH} = 7$ .
  - ♣ 4. After the equivalence point.
    - The pH is determined by the excess base in the solution
    - Therefore,  $\text{pH} > 7$ .

- Usually, we use phenolphthalein which changes color between pH 8.3 to 10.0.
  - ♣ In acid, phenolphthalein is colorless
  - ♣ At the end point, the solution is light pink
  - ♣ The equivalence point in a titration is the point at which the acid and base are present in stoichiometrically equivalent quantities.

▲ FIGURE 17.6 Measuring pH during a titration.



▲ FIGURE 17.7 Titration of a strong acid with a strong base. The pH curve for titration of 50.0 mL of a 0.100 M solution of hydrochloric acid with a 0.100 M solution of NaOH(aq). For clarity, water molecules have been omitted from the molecular art.



Calculate the pH when (a) 49.0 mL and (b) 51.0 mL of 0.100 M NaOH solution have been added to 50.0 mL of 0.100 M HCl solution.

$$(0.0500 \text{ L soln}) \left( \frac{0.100 \text{ mol H}^+}{1 \text{ L soln}} \right) = 5.00 \times 10^{-3} \text{ mol H}^+$$

$$(0.0490 \text{ L soln}) \left( \frac{0.100 \text{ mol OH}^-}{1 \text{ L soln}} \right) = 4.90 \times 10^{-3} \text{ mol OH}^-$$

	$\text{H}^+(aq)$	+	$\text{OH}^-(aq)$	$\longrightarrow$	$\text{H}_2\text{O}(l)$
Before addition	$5.00 \times 10^{-3} \text{ mol}$		0		—
Addition			$4.90 \times 10^{-3} \text{ mol}$		
After addition	$0.10 \times 10^{-3} \text{ mol}$		0		—

$$50.0 \text{ mL} + 49.0 \text{ mL} = 99.0 \text{ mL} = 0.0990 \text{ L}$$

$$[\text{H}^+] = \frac{\text{moles H}^+(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3} \text{ mol}}{0.09900 \text{ L}} = 1.0 \times 10^{-3} \text{ M}$$

$$-\log(1.0 \times 10^{-3}) = 3.00$$

	$\text{H}^+(aq)$	+	$\text{OH}^-(aq)$	$\longrightarrow$	$\text{H}_2\text{O}(l)$
Before addition	$5.00 \times 10^{-3} \text{ mol}$		0		—
Addition			$5.10 \times 10^{-3} \text{ mol}$		
After addition	0		$0.10 \times 10^{-3} \text{ mol}$		—

$$50.0 \text{ mL} + 51.0 \text{ mL} = 101.0 \text{ mL} = 0.1010 \text{ L}$$

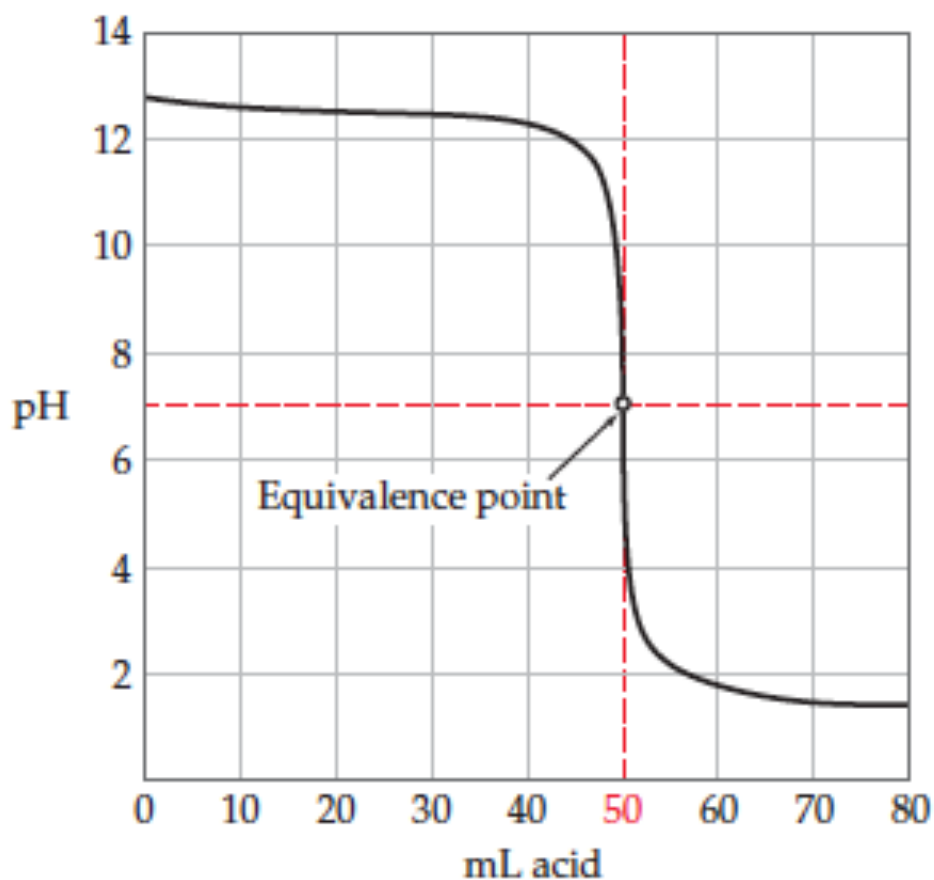
$$[\text{OH}^-] = \frac{\text{moles OH}^-(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3} \text{ mol}}{0.1010 \text{ L}} = 1.0 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log(1.0 \times 10^{-3}) = 3.00$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 3.00 = 11.00$$

### Strong Base-Strong Acid Titrations

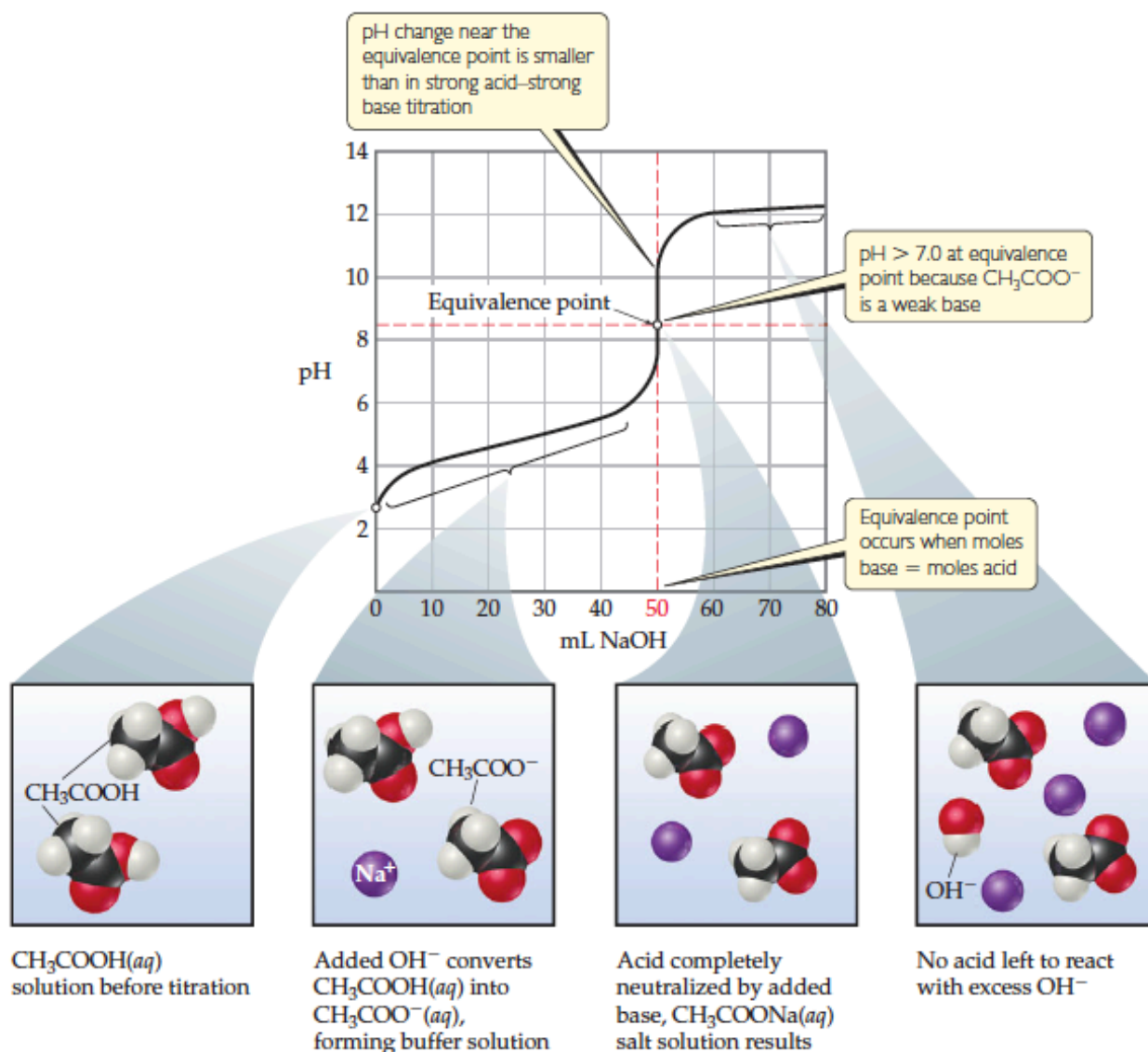
- The shape of a strong base-strong acid titration curve is very similar to a strong acid-strong base titration curve.
  - ♣ Initially, the strong base is in excess, so the  $\text{pH} > 7$ .
  - ♣ As acid is added, the pH decreases but is still greater than 7.
  - ♣ At the equivalence point, the pH is given by the salt solution (i.e.,  $\text{pH} = 7$ ).
  - ♣ After the equivalence point, the pH is given by the strong acid in excess, so pH is less than 7.



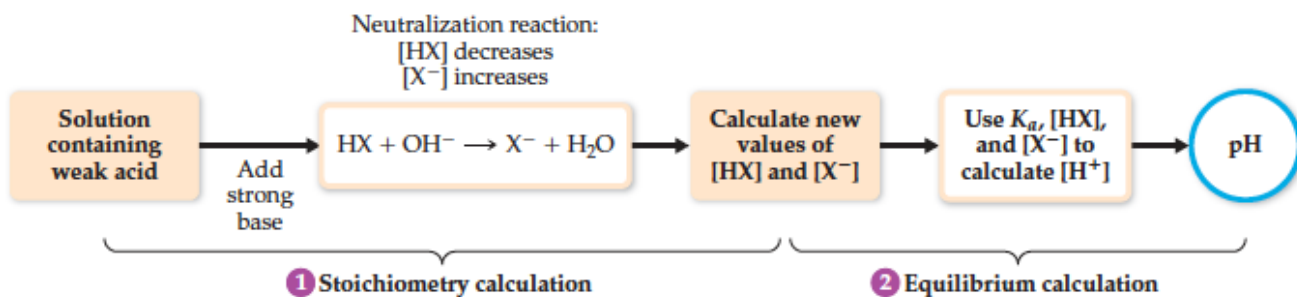
## Weak Acid-Strong Base Titration

- Consider the titration of acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$  with  $\text{NaOH}$ .
- Again, we divide the titration into four general regions:
  - ♣ 1. Before any base is added:
    - The solution contains only weak acid.
    - Therefore, pH is given by the equilibrium calculation.
  - ♣ 2. Between the initial pH and the equivalence point.
    - As strong base is added it consumes a stoichiometric quantity of weak acid:
 
$$\text{HC}_2\text{H}_3\text{O}_2 (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{C}_2\text{H}_3\text{O}_2^- (\text{aq}) + \text{H}_2\text{O} (\text{l})$$
    - However, there is an excess of acetic acid.
    - Therefore, we have a mixture of weak acid and its conjugate base.
      - ♣ Thus the composition of the mixture is that of a buffer.
      - ♣ The pH is given by the buffer calculation.
        - First the amount of  $\text{C}_2\text{H}_3\text{O}_2^-$  generated is calculated, as well as the amount of  $\text{HC}_2\text{H}_3\text{O}_2$  consumed. (Stoichiometry.)
        - Then the pH is calculated using equilibrium conditions. (Henderson-Hasselbalch equation.)
  - ♣ 3. At the equivalence point, all the acetic acid has been consumed and all the  $\text{NaOH}$  has been consumed.
    - However,  $\text{C}_2\text{H}_3\text{O}_2^-$  has been generated.
    - Therefore, the pH depends on the  $\text{C}_2\text{H}_3\text{O}_2^-$  concentration.
    - The  $\text{pH} > 7$  at the equivalence point.
    - More importantly, the pH of the equivalence point  $\neq 7$  for a weak acid-strong base titration.
  - ♣ 4. After the equivalence point:
    - The pH is given by the concentration of the excess strong base.

- The pH curve for a weak acid-strong base titration differs significantly from that of a strong acid-strong base titration.
  - For a strong acid-strong base titration:
    - ♣ The pH begins at less than 7 and gradually increases as base is added.
    - ♣ Near the equivalence point, the pH increases dramatically.
  - For a weak acid-strong base titration:
    - ♣ The initial pH rise is more steep than the strong acid-strong base case.
    - ♣ However, then there is a leveling off due to buffer effects.
    - ♣ The inflection point is not as steep for a weak acid-strong base titration.
  - The shape of the two curves after the equivalence point is the same because pH is determined by the strong base in excess.
  - The pH at the equivalence point differs also:
    - ♣ The pH is 7.00 for the strong acid-strong base equivalence point.
    - ♣ The pH is  $> 7.00$  for the weak acid-strong base equivalence point.



▲ **FIGURE 17.9** Titration of a weak acid with a strong base. The pH curve for titration of 50.0 mL of a 0.100 M solution of acetic acid with a 0.100 M solution of NaOH(aq). For clarity, water molecules have been omitted from the molecular art.



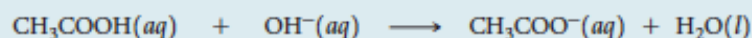
Calculate the pH of the solution formed when 45.0 mL of 0.100 M NaOH is added to 50.0 mL of 0.100 M CH<sub>3</sub>COOH

**Solve Stoichiometry Calculation:** The product of the volume and concentration of each solution gives the number of moles of each reactant present before the neutralization:

$$(0.0500 \text{ L soln}) \left( \frac{0.100 \text{ mol CH}_3\text{COOH}}{1 \text{ L soln}} \right) = 5.00 \times 10^{-3} \text{ mol CH}_3\text{COOH}$$

$$(0.0450 \text{ L soln}) \left( \frac{0.100 \text{ mol NaOH}}{1 \text{ L soln}} \right) = 4.50 \times 10^{-3} \text{ mol NaOH}$$

The  $4.50 \times 10^{-3}$  of NaOH consumes  $4.50 \times 10^{-3}$  of CH<sub>3</sub>COOH:



Before addition	$5.00 \times 10^{-3} \text{ mol}$	0	0	—
Addition		$4.50 \times 10^{-3} \text{ mol}$		
After addition	$0.50 \times 10^{-3} \text{ mol}$	0	$4.50 \times 10^{-3} \text{ mol}$	—

The total volume of the solution is

$$45.0 \text{ mL} + 50.0 \text{ mL} = 95.0 \text{ mL} = 0.0950 \text{ L}$$

The resulting molarities of CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>-</sup> after the reaction are therefore

$$[\text{CH}_3\text{COOH}] = \frac{0.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0053 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = \frac{4.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0474 \text{ M}$$

**Equilibrium Calculation:** The equilibrium between CH<sub>3</sub>COOH and CH<sub>3</sub>COO<sup>-</sup> must obey the equilibrium-constant expression for CH<sub>3</sub>COOH:

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

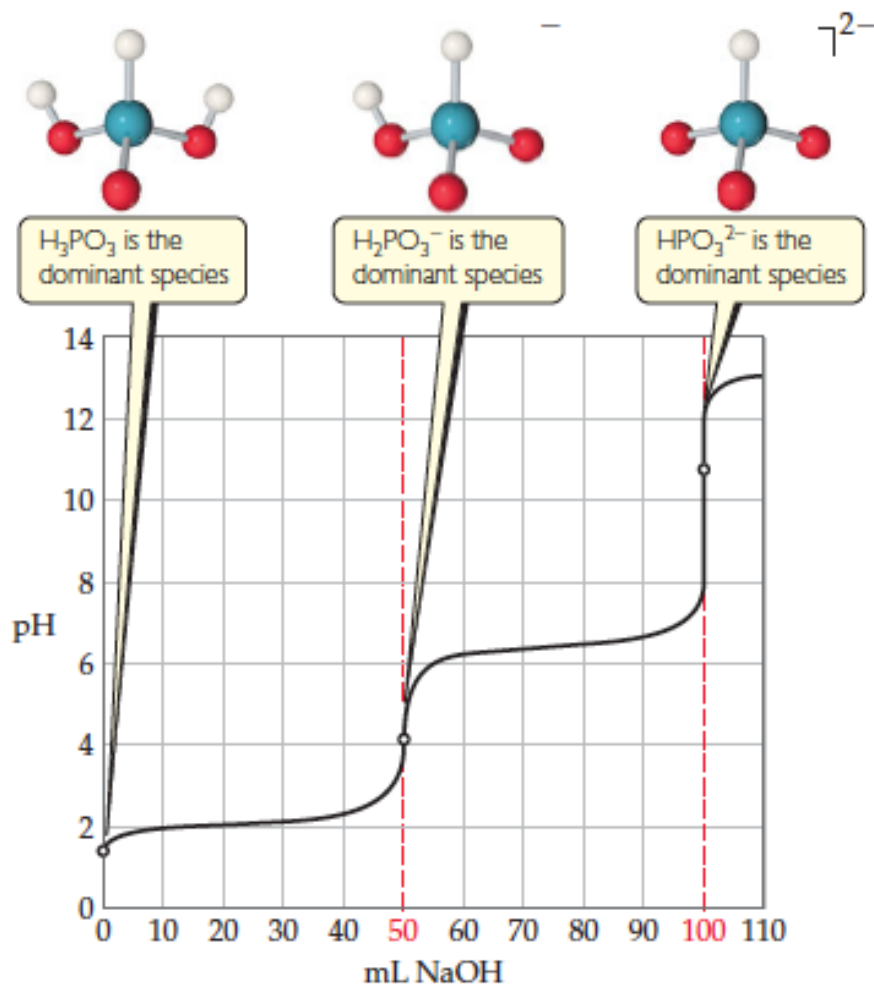
Solving for [H<sup>+</sup>] gives

$$[\text{H}^+] = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = (1.8 \times 10^{-5}) \times \left( \frac{0.0053}{0.0474} \right) = 2.0 \times 10^{-6} \text{ M}$$

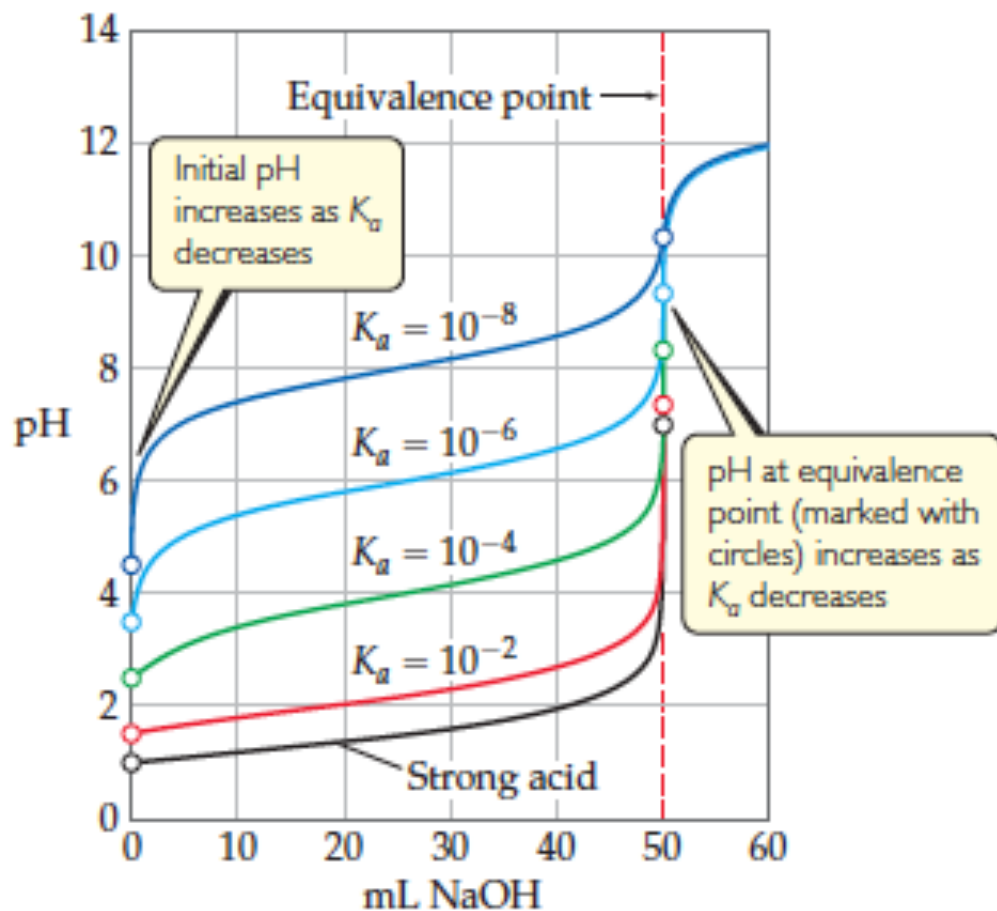
$$\text{pH} = -\log(2.0 \times 10^{-6}) = 5.70$$

## Titration of Polyprotic Acids

- In polyprotic acids, the ionizable protons dissociate in a series of steps.
  - Therefore, in a titration there are  $n$  equivalence points corresponding to each ionizable proton.
- In the titration of  $\text{H}_3\text{PO}_3$  with  $\text{NaOH}$  there are two equivalence points:
  - One for the formation of  $\text{H}_2\text{PO}_3^-$
  - One for the formation of  $\text{HPO}_3^{2-}$



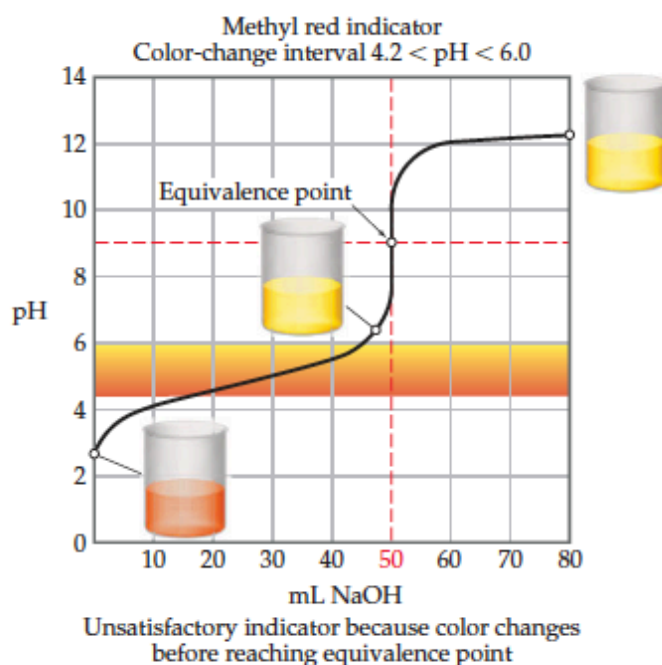
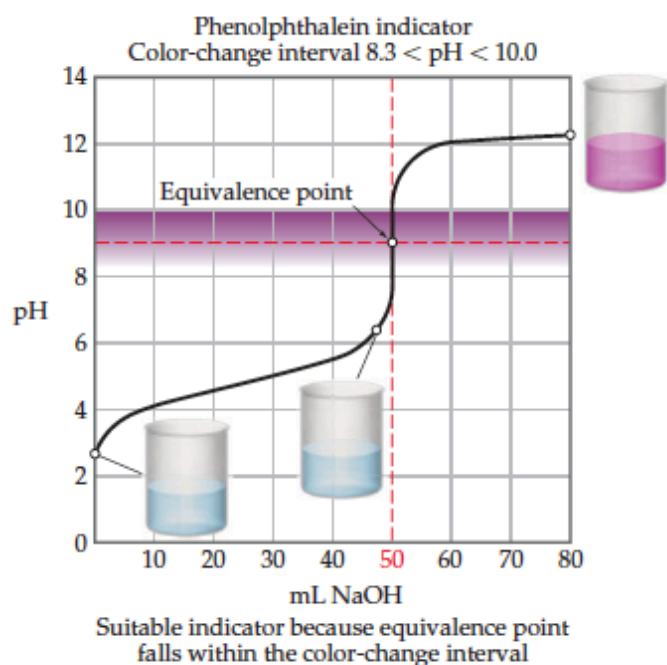
A set of curves showing the effect of acid strength on the characteristics of the titration curve when a weak acid is titrated by a strong base. Each curve represents titration of 50.0 mL of 0.10 M acid with 0.10 M NaOH. 17.4 Solubility Equilibria



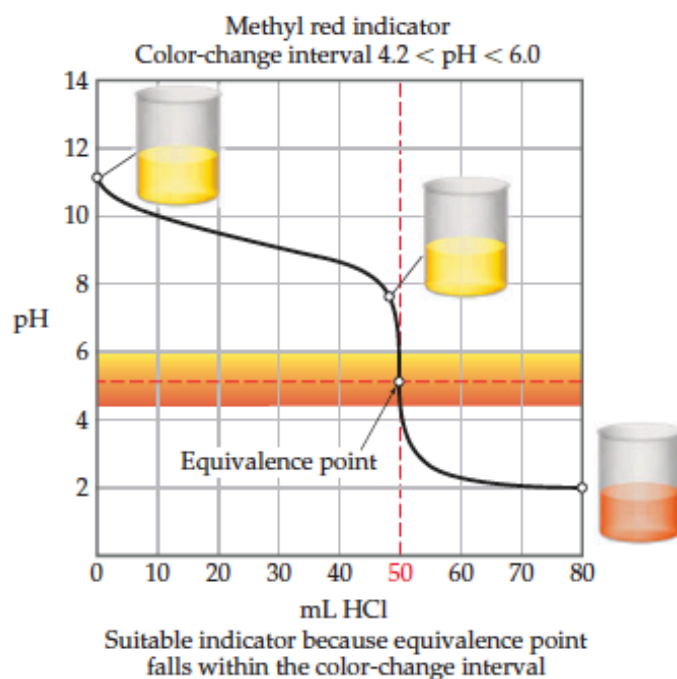
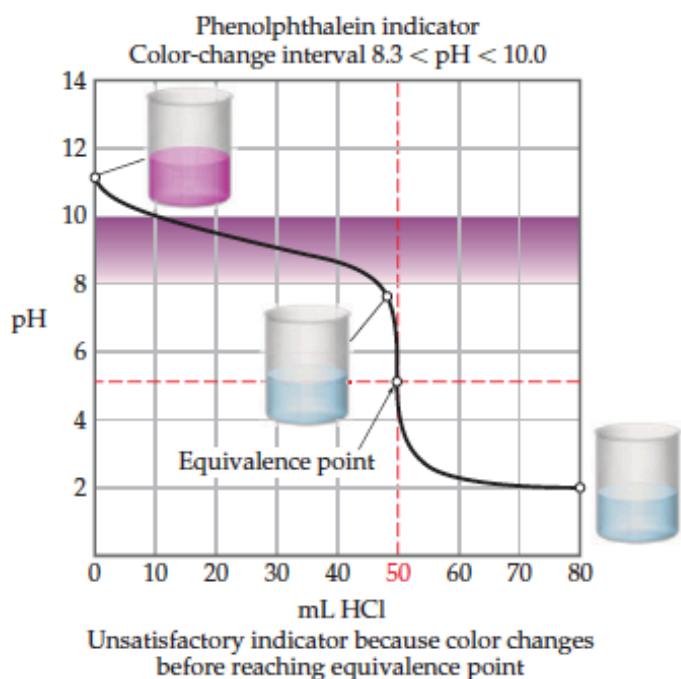
Notice that as the acid becomes weaker (that is, as  $K_a$  becomes smaller), the initial pH increases and the pH change near the equivalence point becomes less marked. Furthermore, the pH at the equivalence point steadily increases as  $K_a$  decreases, because the strength of the conjugate base of the weak acid increases.



## Titrating with an Acid–Base Indicator



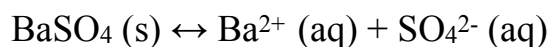
▲ FIGURE 17.14 Good and poor indicators for titration of a weak acid with a strong base.



▲ FIGURE 17.15 Good and poor indicators for titration of a weak base with a strong acid.

### Solubility-Product Constant, $K_{sp}$

- Consider a saturated solution of  $BaSO_4$  in contact with solid  $BaSO_4$ .
  - We can write an equilibrium expression for the dissolving of the slightly soluble solid.



- Because  $BaSO_4 (s)$  is a pure solid, the equilibrium expression depends only on the concentration of the ions.
- $K_{sp}$  is the equilibrium constant for the equilibrium between an ionic solid solute and its saturated aqueous solution.

♣  $K_{sp}$  is called the **solubility-product constant** or the **solubility product**.

♣  $K_{sp}$  for  $BaSO_4$  is:

$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

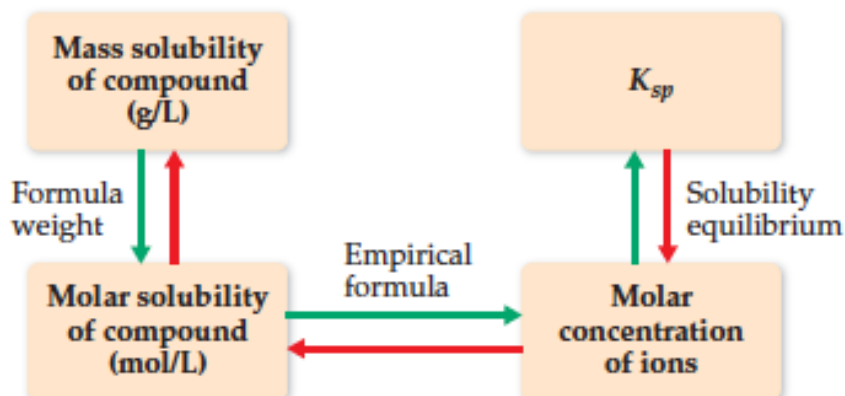
- In general: the solubility product is equal to the product of the molar concentration of ions raised to powers corresponding to their stoichiometric coefficients.

### Solubility and $K_{sp}$

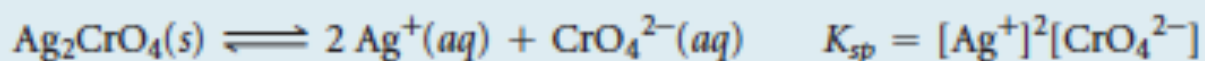
- Solubility is the amount of substance that dissolves to form a saturated solution.
- Molar solubility is the number of moles of solute that dissolve to form a liter of saturated solution.
- We can use the solubility to find  $K_{sp}$  and vice versa.

### Molar solubility

Molar solubility is the number of moles of solute that dissolve in forming 1 L of saturated solution of the solute (mole/L)



Analysis of the equilibrated solution of solid silver chromate  $\text{Ag}_2\text{CrO}_4(\text{s})$  and pure water shows that its silver ion concentration is  $1.3 \times 10^{-4} \text{ M}$ . Assuming that  $\text{Ag}_2\text{CrO}_4$  dissociates completely in water. Calculate  $K_{sp}$  for this compound.



$$[\text{CrO}_4^{2-}] = \left( \frac{1.3 \times 10^{-4} \text{ mol Ag}^+}{\text{L}} \right) \left( \frac{1 \text{ mol CrO}_4^{2-}}{2 \text{ mol Ag}^+} \right) = 6.5 \times 10^{-5} \text{ M}$$

and  $K_{sp}$  is

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (1.3 \times 10^{-4})^2(6.5 \times 10^{-5}) = 1.1 \times 10^{-12}$$

Calculating solubility from  $K_{sp}$

The  $K_{sp}$  for  $\text{CaF}_2$  is  $3.9 \times 10^{-11}$  at  $25^\circ\text{C}$ . Assuming that  $\text{CaF}_2$  dissociates completely upon dissolving and that there are no other important equilibria affecting its solubility, calculate the solubility of  $\text{CaF}_2$  in grams per liter.

Initial	—	0	0
Change	—	$+x M$	$+2x M$
Equilibrium	—	$x M$	$2x M$

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3 = 3.9 \times 10^{-11}$$

$$x = \sqrt[3]{\frac{3.9 \times 10^{-11}}{4}} = 2.1 \times 10^{-4}$$

$$\left(\frac{2.1 \times 10^{-4} \text{ mol CaF}_2}{1 \text{ L soln}}\right)\left(\frac{78.1 \text{ g CaF}_2}{1 \text{ mol CaF}_2}\right) = 1.6 \times 10^{-2} \text{ g CaF}_2/\text{L soln}$$

## Calculating the Effect of a Common Ion on Solubility

Calculate the molar solubility of  $\text{CaF}_2$  at  $25^\circ\text{C}$  in a solution that is (a)  $0.010\text{ M}$  in  $\text{Ca}(\text{NO}_3)_2$ , (b)  $0.010\text{ M}$  in  $\text{NaF}$ .

Initial	—	$0.010\text{ M}$	0
Change	—	$+x\text{ M}$	$+2x\text{ M}$
Equilibrium	—	$(0.010 + x)\text{ M}$	$2x\text{ M}$

$$K_{\text{sp}} = 3.9 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^-]^2 = (0.010 + x)(2x)^2$$

$$3.9 \times 10^{-11} = (0.010)(2x)^2$$

$$x^2 = \frac{3.9 \times 10^{-11}}{4(0.010)} = 9.8 \times 10^{-10}$$

$$x = \sqrt{9.8 \times 10^{-10}} = 3.1 \times 10^{-5}\text{ M}$$

$$[\text{Ca}^{2+}] = x \quad \text{and} \quad [\text{F}^-] = 0.010 + 2x$$

$$3.9 \times 10^{-11} = (x)(0.010 + 2x)^2 \simeq x(0.010)^2$$

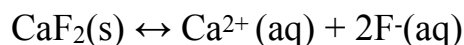
$$x = \frac{3.9 \times 10^{-11}}{(0.010)^2} = 3.9 \times 10^{-7}\text{ M}$$

## 17.5 Factors That Affect Solubility

- Three factors that have a significant impact on solubility are:
  - The presence of a common ion.
  - The pH of the solution.
  - The presence or absence of complexing agents.

### Common-Ion Effect

- Solubility is decreased when a common ion is added
  - This is an application of Le Chatelier's principle:
- Consider the solubility of  $\text{CaF}_2$ :

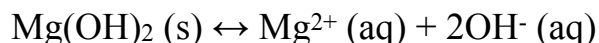


- If more  $\text{F}^{-}$  is added (i.e., by the addition of  $\text{NaF}$ ), the equilibrium shifts to offset the increase.
- Therefore,  $\text{CaF}_2(\text{s})$  is formed and precipitation occurs.

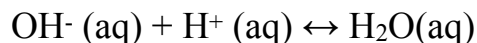
♣ As  $\text{NaF}$  is added to the system, the solubility of  $\text{CaF}_2$  decreases.

### Solubility and pH

- Again we apply Le Chatelier's principle:

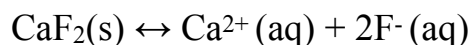


- If  $\text{OH}^{-}$  is removed, then the equilibrium shifts toward the right and  $\text{Mg}(\text{OH})_2$  dissolves.
- $\text{OH}^{-}$  can be removed by adding a strong acid:

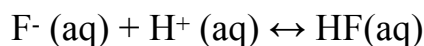


- As pH decreases,  $[\text{H}^{+}]$  increases and the solubility of  $\text{Mg}(\text{OH})_2$  increases.

- Another example:



- If the  $\text{F}^{-}$  is removed, then the equilibrium shifts towards the right and  $\text{CaF}_2$  dissolves.
- $\text{F}^{-}$  can be removed by adding a strong acid:



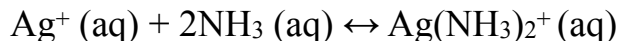
- As pH decreases,  $[\text{H}^{+}]$  increases and solubility of  $\text{CaF}_2$  increases.
- In general:
  - ♣ The solubility of slightly soluble salts containing basic ions increases as pH decreases.
  - ♣ The more basic the anion, the greater the effect.

### Formation of Complex Ions

- Recall that metal ions may act as Lewis acids in aqueous solution (water may act as the Lewis base).
  - Such an interaction may have a significant impact on metal salt solubility
- The  $\text{Ag}(\text{NH}_3)_2^{+}$  is called a **complex ion**.
- $\text{NH}_3$  (the attached Lewis base) is called a ligand.
- The equilibrium constant for the reaction is called the **formation constant**,  $K_f$

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^{+}]}{[\text{Ag}^{+}][\text{NH}_3]^2} = 1.7 \times 10^7$$

- Consider the addition of ammonia to  $\text{AgCl}$  (white salt):



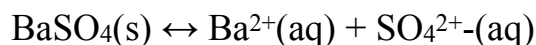
- The overall reaction is:  

$$\text{AgCl (s)} + 2\text{NH}_3 \text{ (aq)} \leftrightarrow \text{Ag(NH}_3)_2^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$
- Effectively, the  $\text{Ag}^+$  (aq) has been removed from solution.

By Le Chatelier's principle, the forward reaction (the dissolving of AgCl) is favored.

## 17.6 Precipitation and Separation of Ions

- Consider the following:



- At any instant in time,  $Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ 
  - ♣ If  $Q > K_{sp}$ , precipitation occurs until  $Q = K_{sp}$
  - ♣ If  $Q = K_{sp}$  equilibrium exists (saturated solution).
  - ♣ If  $Q < K_{sp}$ , solid dissolves until  $Q = K_{sp}$ .

Does a precipitate form when 0.10 L of  $8.0 \times 10^{-3} \text{ M Pb(NO}_3)_2$  is added to 0.40 L of  $5.0 \times 10^{-3} \text{ M Na}_2\text{SO}_4$ ?

$$(0.10 \text{ L}) \left( \frac{8.0 \times 10^{-3} \text{ mol}}{\text{L}} \right) = 8.0 \times 10^{-4} \text{ mol}$$

$$[\text{Pb}^{2+}] = \frac{8.0 \times 10^{-4} \text{ mol}}{0.50 \text{ L}} = 1.6 \times 10^{-3} \text{ M}$$

$$(0.40 \text{ L}) \left( \frac{5.0 \times 10^{-3} \text{ mol}}{\text{L}} \right) = 2.0 \times 10^{-3} \text{ mol}$$

$$[\text{SO}_4^{2-}] = \frac{2.0 \times 10^{-3} \text{ mol}}{0.50 \text{ L}} = 4.0 \times 10^{-3} \text{ M}$$

$$Q = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1.6 \times 10^{-3})(4.0 \times 10^{-3}) = 6.4 \times 10^{-6}$$

Because  $Q > K_{sp}$ ,  $\text{PbSO}_4$  precipitates.



## Selective Precipitation of Ions

- Ions can be separated from each other based on the solubilities of their salts.
  - Example: If HCl is added to a solution containing  $\text{Ag}^+$  and  $\text{Cu}^{2+}$ , the silver precipitates ( $K_{\text{sp}}$  for AgCl is  $1.8 \times 10^{-10}$ ) while the  $\text{Cu}^{2+}$  remains in solution.
    - ♣ Removal of one metal ion from a solution is called selective precipitation.
- Sulfide ion is often used to separate metal ions.
  - Example: Consider a mixture of  $\text{Zn}^{2+}$  (aq) and  $\text{Cu}^{2+}$  (aq).
    - ♣  $\text{CuS}$  ( $K_{\text{sp}} = 6 \times 10^{-37}$ ) is less soluble than  $\text{ZnS}$  ( $K_{\text{sp}} = 2 \times 10^{-25}$ )
    - ♣ Thus,  $\text{CuS}$  will be removed from solution before  $\text{ZnS}$ .

As  $\text{H}_2\text{S}$  is bubbled through the acidified green solution

### 17.7 Qualitative Analysis for Metallic Elements

- **Quantitative analysis** is designed to determine how much metal ion is present.
- **Qualitative analysis** is designed to detect the presence of metal ions.
  - Typical qualitative analysis of a metal ion mixture involves:
    - ♣ 1. Separation of ions into five major groups on the basis of their differential solubilities.
      - Insoluble chlorides.
      - Acid-insoluble sulfides.
      - Base-insoluble sulfides and hydroxides.
      - Insoluble phosphates.
      - Alkali metals and ammonium ion.
    - ♣ 2. Individual ions within each group are separated by selectively dissolving members of the group.

- ♣ 3. Specific tests are used to determine whether a particular ion is present or absent.

