GENERAL CHEMISTRY

Chapter 17

Additional Aspects of Aqueous Equilibria

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17-1 The Common-Ion Effect

- Consider a solution of acetic acid:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

- If acetate ion (CH_3COO^-) is added to the solution, Le Châtelier says the equilibrium will shift to the left.

- The equilibrium constant itself does not change; it is the relative concentrations of products and reactants in the equilibrium expression that change

The Common-Ion Effect

“The extent of ionization of a weak electrolyte is decreased by adding to the solution a strong electrolyte that has an ion in common with the weak electrolyte.”

EXAMPLE

Calculate the fluoride ion concentration and pH of a solution that is 0.20 M in HF and 0.10 M in HCl. K_a for HF is 6.8×10^{-4}.

$$\mathrm{HF}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{F^-}(aq)$$

$$K_a = \frac{[\mathrm{H_3O^+}]\,[\mathrm{F^-}]}{[\mathrm{HF}]} = 6.8 \times 10^{-4}$$

Because HCl, a strong acid, is also present, the initial $[H_3O^+]$ is not 0, but rather 0.10 M.

	[HF], M	$[H_3O^+]$, M	$[F^-]$, M
Initially	0.20	0.10	0
Change			
At Equilibrium			

$$6.8 \times 10^{-4} = \frac{(0.10)\,(x)}{(0.20)}$$

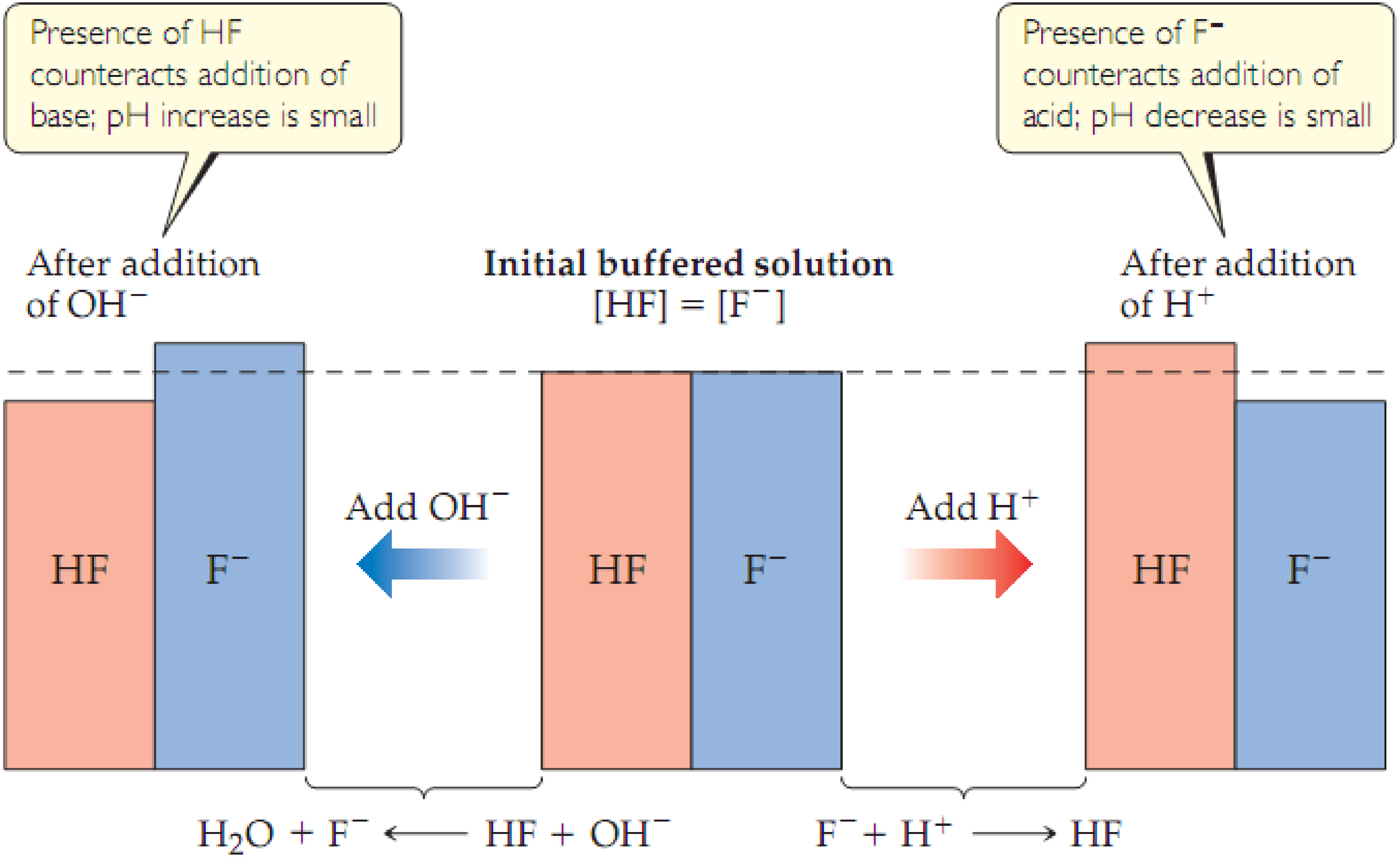
$x = 1.4 \times 10^{-3} = [H_3O^+]$

$\mathrm{pH} = -\log(0.10) = 1.00$

17-2 Buffers

- Buffers are solutions of a weak conjugate acid-base pair.
- They are particularly resistant to pH changes, even when strong acid or base is added.

Action of Buffers



Presence of HF counteracts addition of base; pH increase is small

Presence of F^- counteracts addition of acid; pH decrease is small

After addition of OH^-

Initial buffered solution

$[HF] = [F^-]$

After addition of H^+

$H_2O + F^- \longleftarrow HF + OH^-$

$F^- + H^+ \longrightarrow HF$

Buffer Calculations

Consider the equilibrium constant expression for the dissociation of a generic acid, HA:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} = [H_3O^+]\frac{[A^-]}{[HA]}$$

Taking the negative log of both side, we get

$$\underbrace{-\log K_a}_{\text{p}K_a} = \underbrace{-\log [H_3O^+]}_{\text{pH}} + -\log \frac{\overbrace{[A^-]}^{\text{base}}}{\underbrace{[HA]}_{\text{acid}}}$$

$$\text{p}K_a = \text{pH} - \log\frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}$$

Henderson–Hasselbalch equation

EXAMPLE

What is the pH of a buffer that is 0.12 *M* in lactic acid, $CH_3CH(OH)COOH$, and 0.10 *M* in sodium lactate? K_a for lactic acid is 1.4×10^{-4}.

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

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

$$= 3.77$$

EXAMPLE

How many moles of NH_4Cl must be added to 2.0 L of 0.10 M NH_3 to form a buffer whose pH is 9.00? (Assume that the addition of NH_4Cl does not change the volume of the solution.)

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \qquad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

$$pOH = 14.00 - pH = 14.00 - 9.00 = 5.00$$

$$[OH^-] = 1.0 \times 10^{-5}\ M$$

$$[NH_3] = 0.10\ M$$

$$[NH_4^+] = K_b \frac{[NH_3]}{[OH^-]} = (1.8 \times 10^{-5}) \frac{(0.10\ M)}{(1.0 \times 10^{-5}\ M)} = 0.18\ M$$

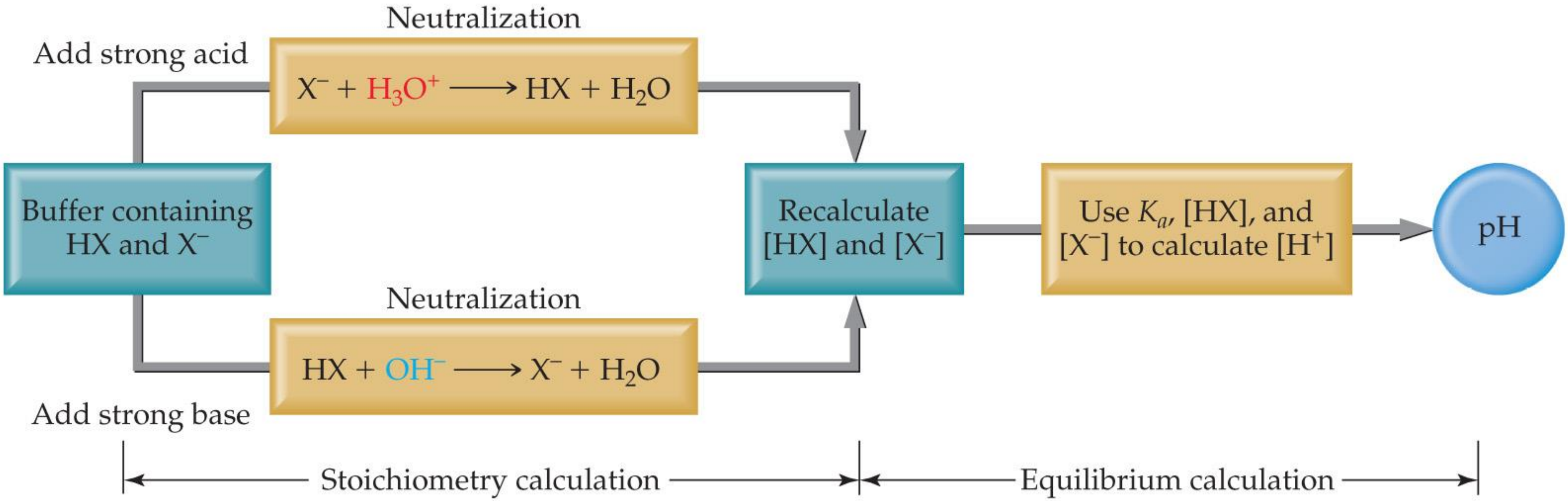
$$(2.0\ L)(0.18\ mol\ NH_4Cl/L) = 0.36\ mol\ NH_4Cl$$

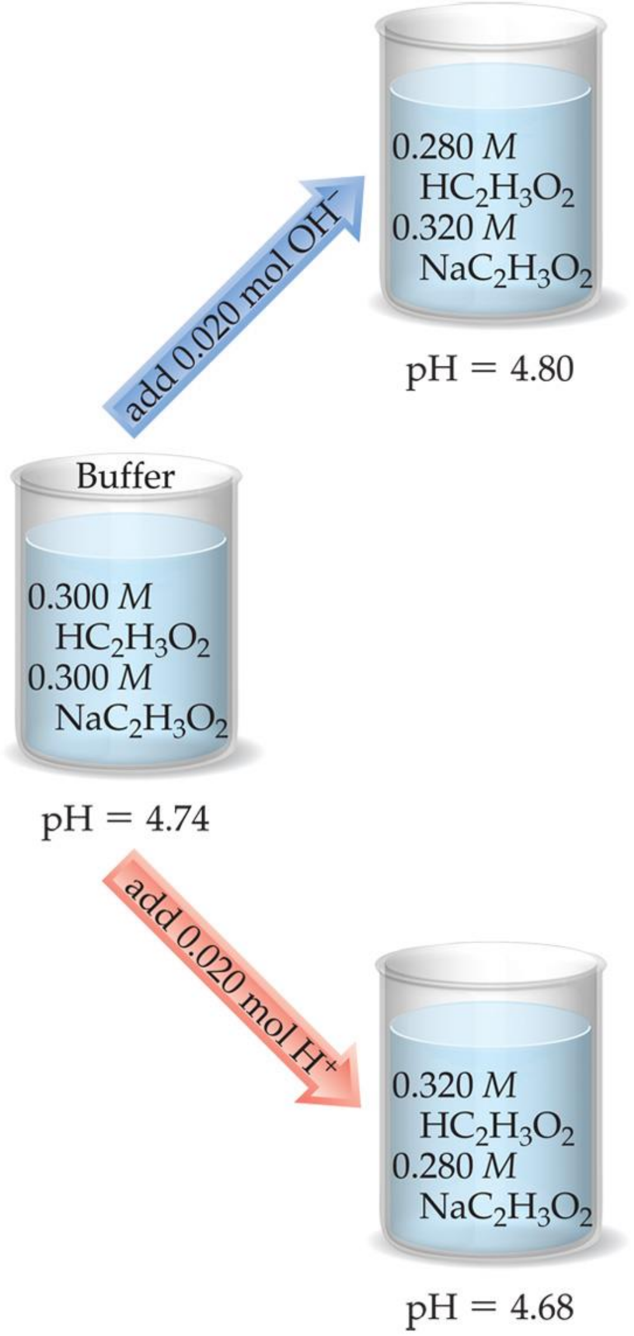
Buffer Capacity and pH Range

- The pH range is the range of pH values over which a buffer system works effectively.
- It is best to choose an acid with a pK_a close to the desired pH.
- Because log 10 = 1, buffers usually have a usable range within ±1 pH unit of pKa (that is, a range of pH = pKa ±1)

Addition of Strong Acids or Bases to Buffers

…it is safe to assume that all of the strong acid or base is consumed in the reaction.





1. Determine how the neutralization reaction affects the amounts of the weak acid and its conjugate base in solution.
2. Use the Henderson–Hasselbalch equation to determine the new pH of the solution.

EXAMPLE

A buffer is made by adding 0.300 mol $HC_2H_3O_2$ and 0.300 mol $NaC_2H_3O_2$ to enough water to make 1.00 L of solution. The pH of the buffer is 4.74. Calculate the pH of this solution after 0.020 mol of NaOH is added. $K_a=1.8\times10^{-5}$

Before the reaction, since mol $HC_2H_3O_2$ = mol $C_2H_3O_2^-$

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

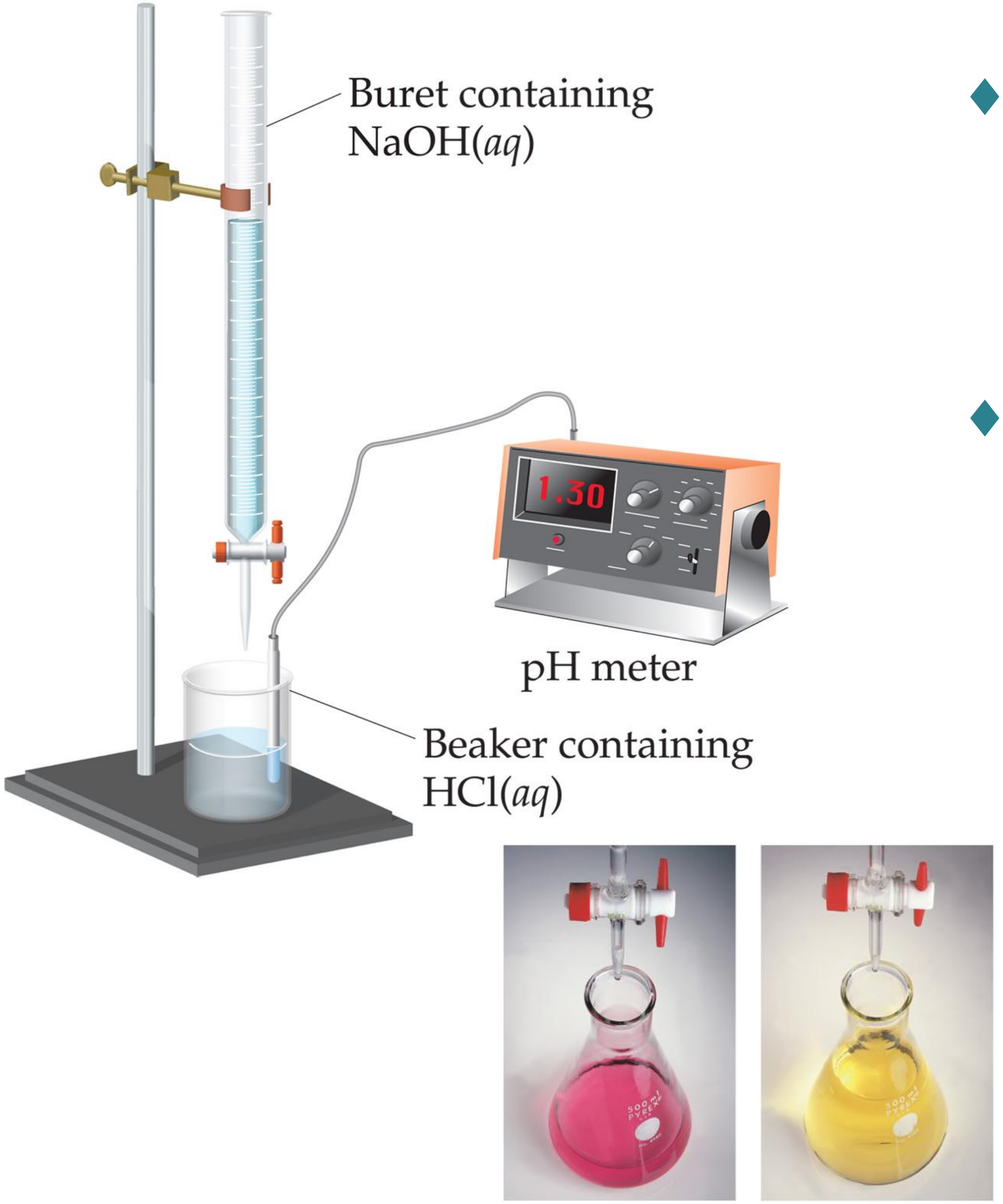
The 0.020 mol NaOH will react with 0.020 mol of the acetic acid:

$$HC_2H_3O_2(aq) + OH^-(aq) \longrightarrow C_2H_3O_2^-(aq) + H_2O(l)$$

	$HC_2H_3O_2$	$C_2H_3O_2^-$	OH^-
Before reaction	0.300 mol	0.300 mol	0.020 mol
After reaction			

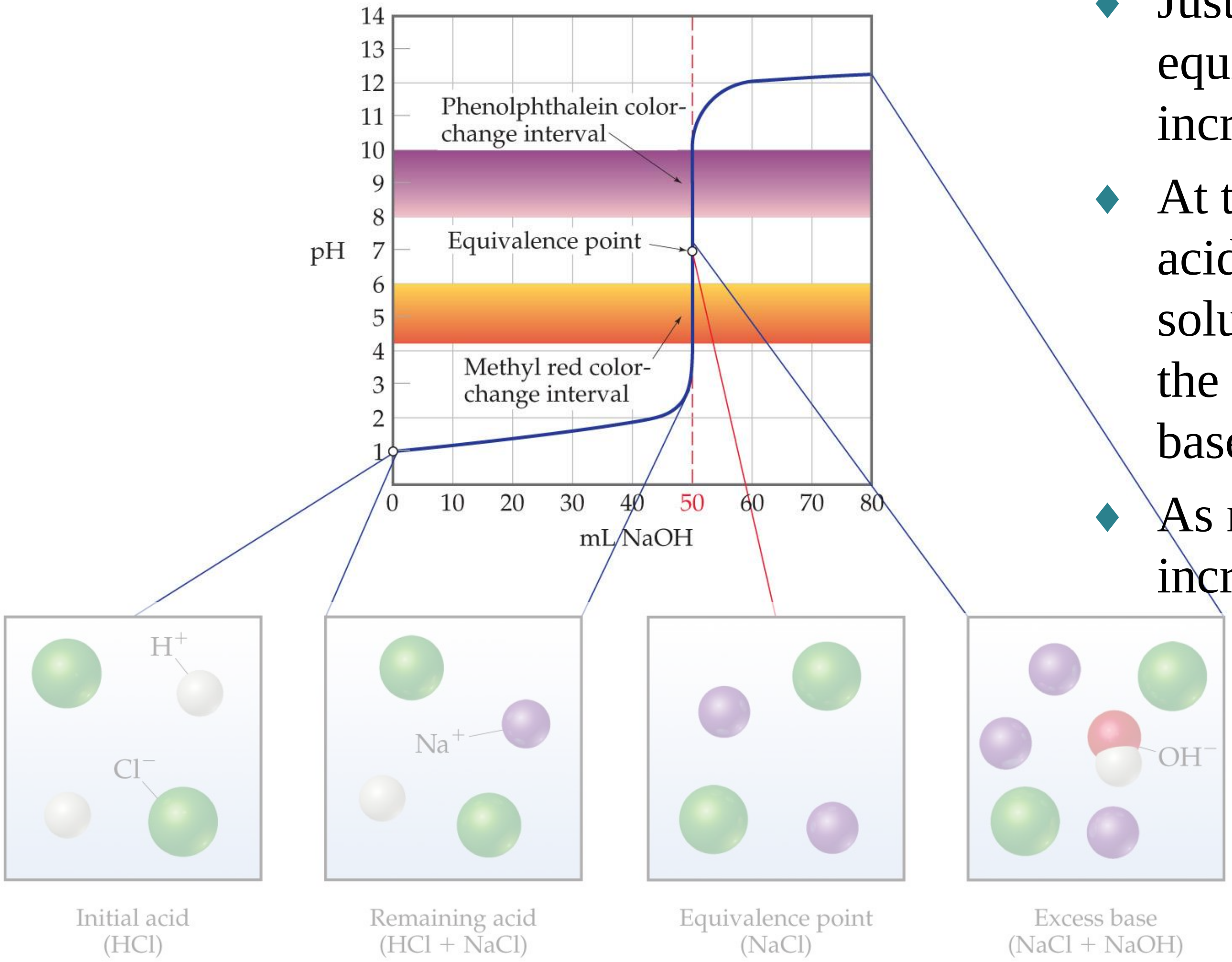
$$\mathrm{pH} = 4.74 + \log\frac{(0.320)}{(0.200)} = 4.80$$

17-3 Acid–Base Titrations



- In this technique a known concentration of base (or acid) is slowly added to a solution of acid (or base).
- A pH meter or indicators are used to determine when the solution has reached the equivalence point, at which the stoichiometric amount of acid equals that of base.

Titration of a Strong Acid with a Strong Base



- From the start of the titration to near the equivalence point, the pH goes up slowly.
- Just before (and after) the equivalence point, the pH increases rapidly.
- At the equivalence point, moles acid = moles base, and the solution contains only water and the salt from the cation of the base and the anion of the acid.
- As more base is added, the increase in pH again levels off.

EXAMPLE

Calculate the pH when the following quantities of 0.100 *M* NaOH solution have been added to 50.0 mL of 0.100 *M* HCl solution: **(a)** 49.0 mL, **(b)** 51.0 mL.

(a)

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

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

	$H^+(aq)$ +	$OH^-(aq)$ $\longrightarrow$	$H_2O(l)$
Before addition	5.00×10^{-3} mol	0	—
Addition		4.90×10^{-3} mol	
After addition	0.10×10^{-3} mol	0	—

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

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

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

EXAMPLE

Calculate the pH when the following quantities of 0.100 *M* NaOH solution have been added to 50.0 mL of 0.100 *M* HCl solution: **(a)** 49.0 mL, **(b)** 51.0 mL.

(b)

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

	$H^+(aq)$	$OH^-(aq)$	$H_2O(l)$
Before addition	5.00×10^{-3} mol	0	—
Addition		5.10×10^{-3} mol	
After addition	0	0.10×10^{-3} mol	—

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

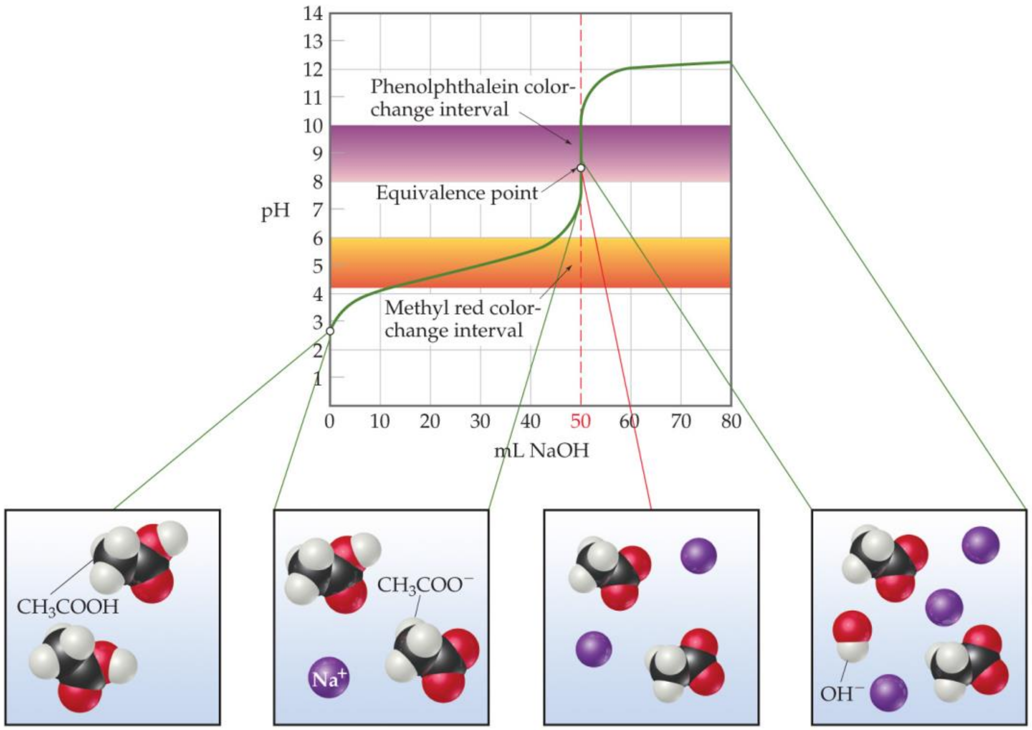
$$[OH^-] = \frac{\text{moles } OH^-(aq)}{\text{liters soln}} = \frac{0.10 \times 10^{-3}\ \text{mol}}{0.1010\ \text{L}} = 1.0 \times 10^{-3}\ M$$

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

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

Titration of a Weak Acid with a Strong Base

- Unlike in the previous case, the conjugate base of the acid affects the pH when it is formed.
- At the equivalence point the pH is >7.
- Phenolphthalein is commonly used as an indicator in these titrations.



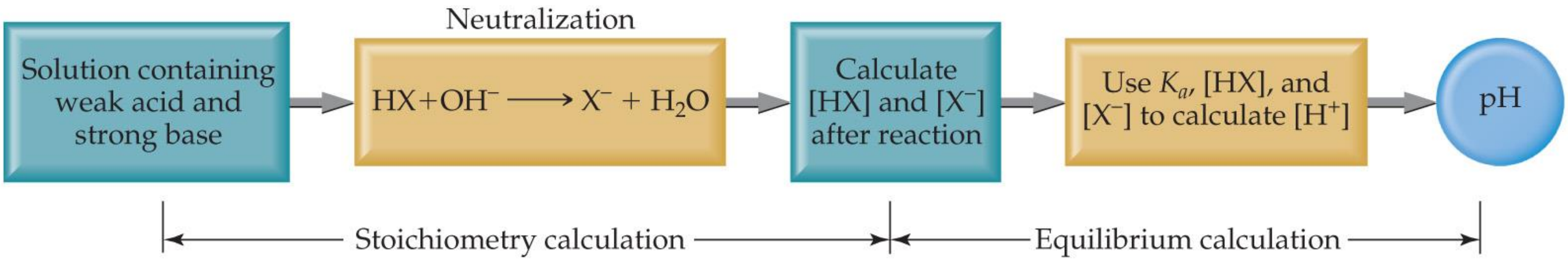
Initial acid
(CH_3COOH)

Buffer mixture
($CH_3COOH + CH_3COO^-$)

Equivalence point
(CH_3COO^-)

Excess base
($CH_3COO^- + OH^-$)

Titration of a Weak Acid with a Strong Base



Solution containing weak acid and strong base

Neutralization

$HX + OH^- \longrightarrow X^- + H_2O$

Calculate [HX] and $[X^-]$ after reaction

Use K_a, [HX], and $[X^-]$ to calculate $[H^+]$

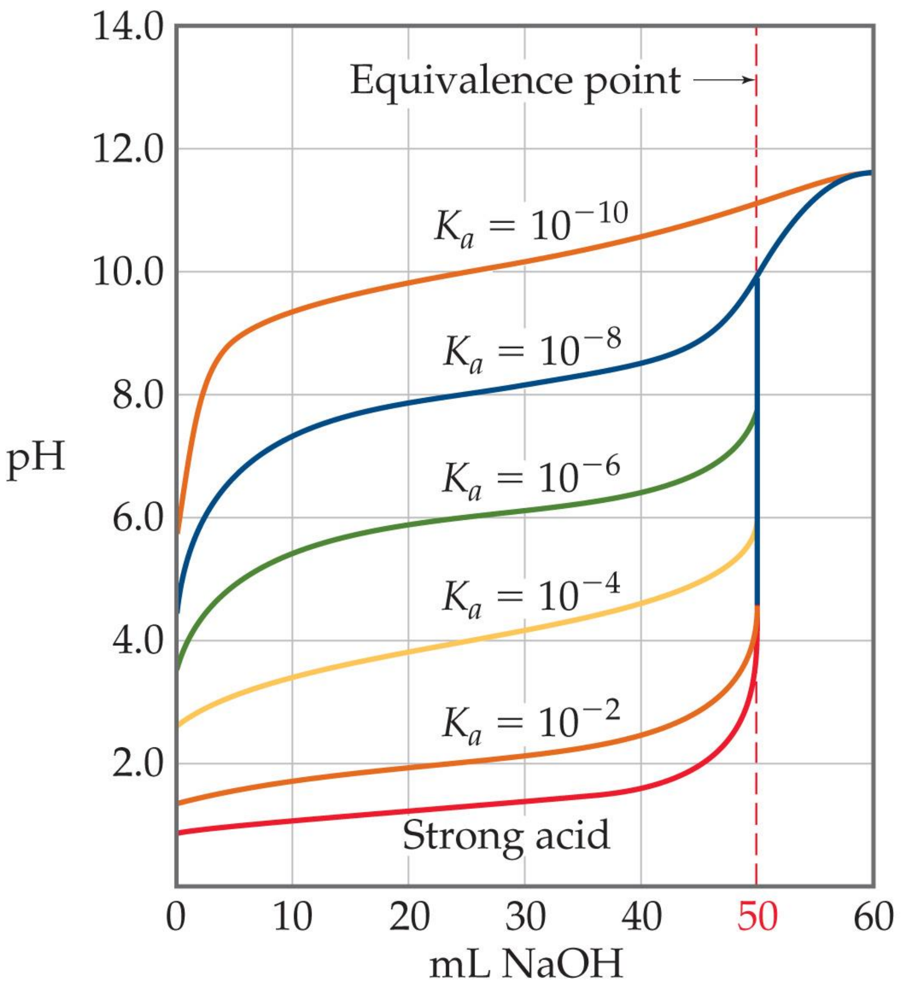
pH

Stoichiometry calculation

Equilibrium calculation

At each point below the equivalence point, the pH of the solution during titration is determined from the amounts of the acid and its conjugate base present at that particular time.

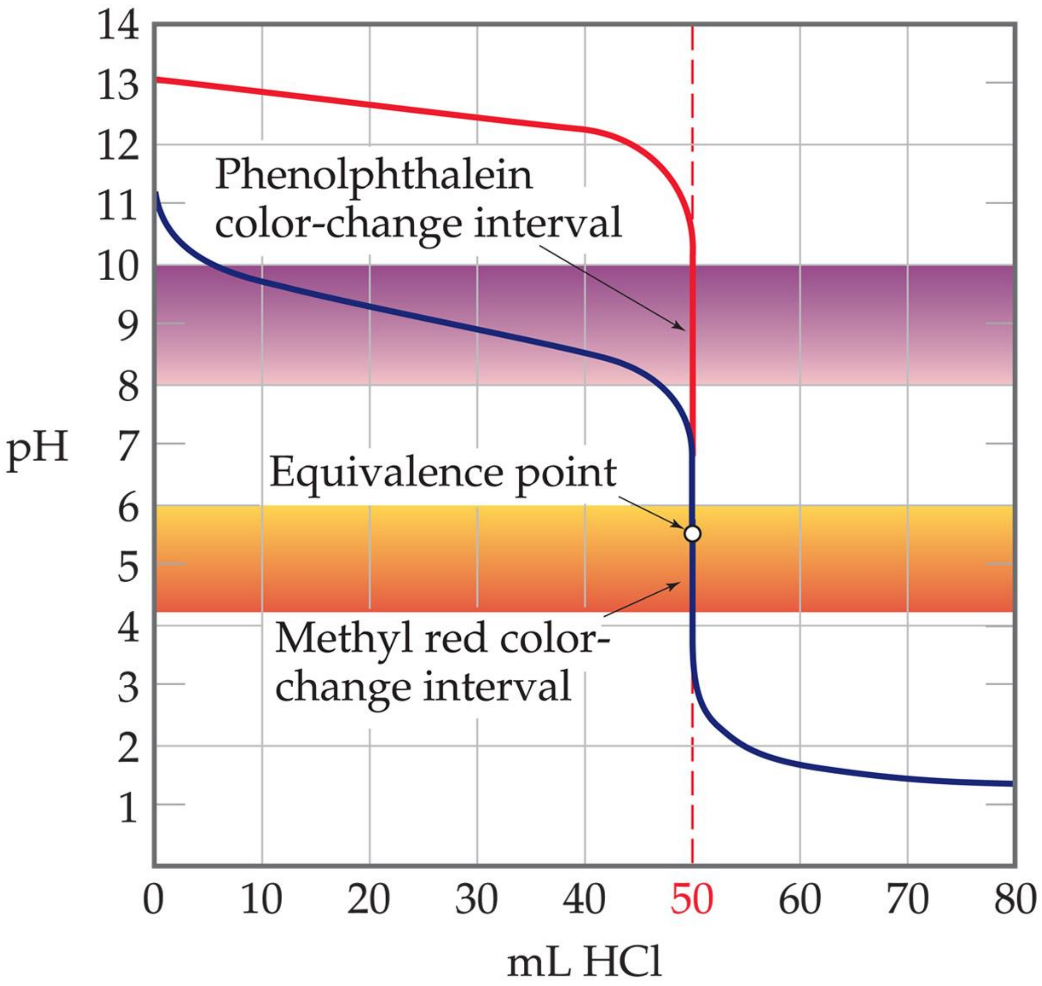
Titration of a Weak Acid with a Strong Base



With weaker acids, the initial pH is higher and pH changes near the equivalence point are more subtle.

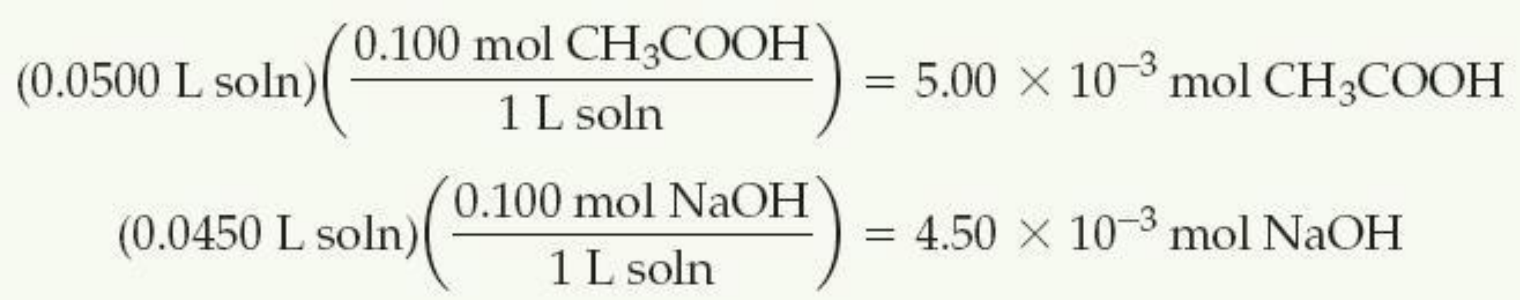
Titration of a Weak Base with a Strong Acid

- The pH at the equivalence point in these titrations is < 7.
- Methyl red is the indicator of choice.



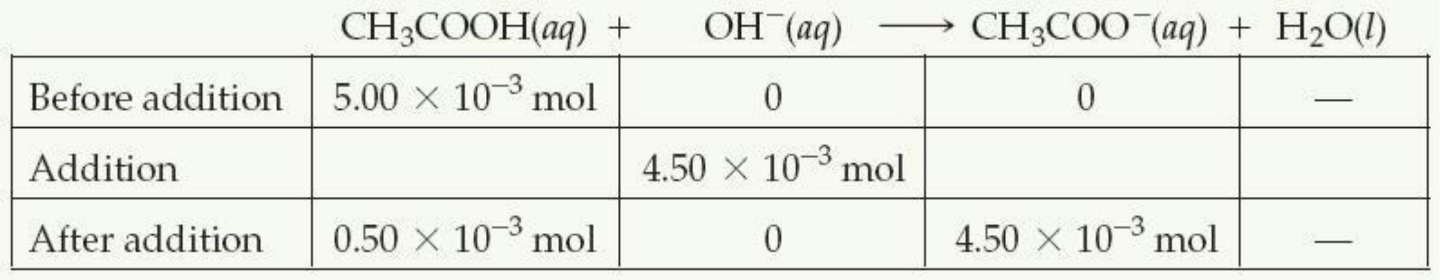
EXAMPLE

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_3COOH ($K_a = 1.8 \times 10^{-5}$).

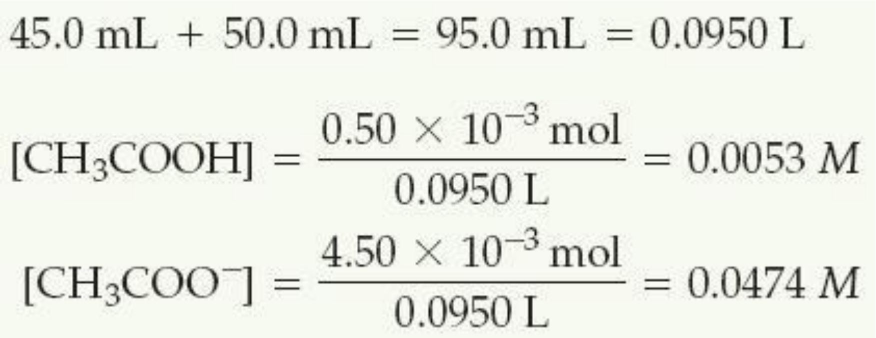


$$(0.0500 \text{ L soln})\left(\frac{0.100 \text{ mol } CH_3COOH}{1 \text{ L soln}}\right) = 5.00 \times 10^{-3} \text{ mol } CH_3COOH$$

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



	$CH_3COOH(aq)$ +	$OH^-(aq)$ $\longrightarrow$	$CH_3COO^-(aq)$ +	$H_2O(l)$
Before addition	5.00×10^{-3} mol	0	0	—
Addition		4.50×10^{-3} mol		
After addition	0.50×10^{-3} mol	0	4.50×10^{-3} mol	—



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

$$[CH_3COOH] = \frac{0.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0053\ M$$

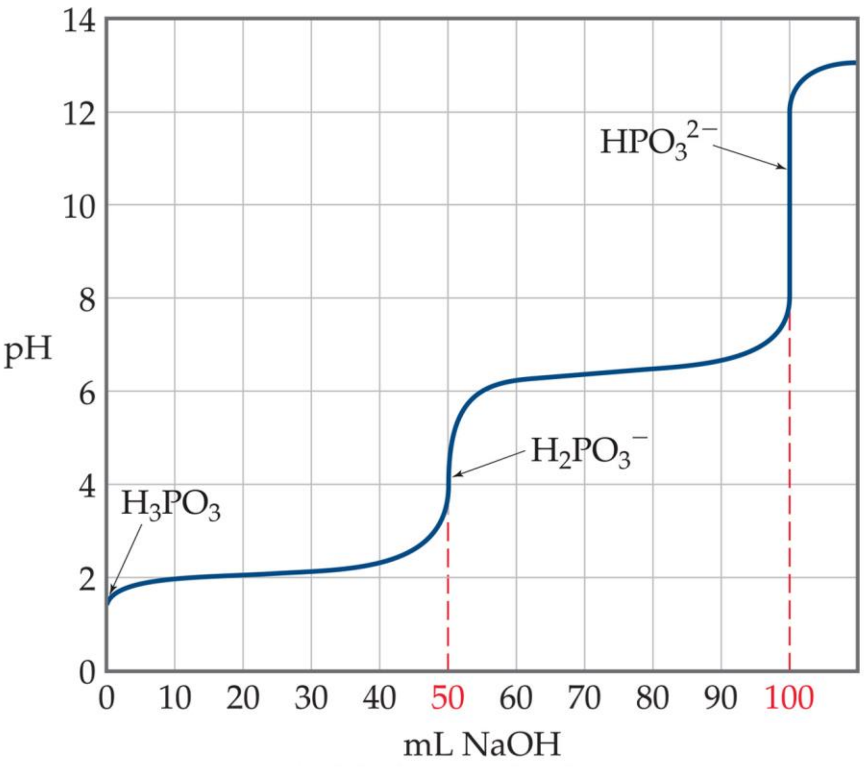
$$[CH_3COO^-] = \frac{4.50 \times 10^{-3} \text{ mol}}{0.0950 \text{ L}} = 0.0474\ M$$

$$K_a = \frac{[\mathrm{H^+}][\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]} = 1.8 \times 10^{-5}$$

$$[\mathrm{H^+}] = K_a \times \frac{[\mathrm{CH_3COOH}]}{[\mathrm{CH_3COO^-}]} = (1.8 \times 10^{-5}) \times \left(\frac{0.0053}{0.0474}\right) = 2.0 \times 10^{-6}\ M$$

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

Titrations of Polyprotic Acids



When one titrates a polyprotic acid with a base there is an equivalence point for each dissociation.

17- 4 Solubility Equilibria

Consider the equilibrium that exists in a saturated solution of $BaSO_4$ in water:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

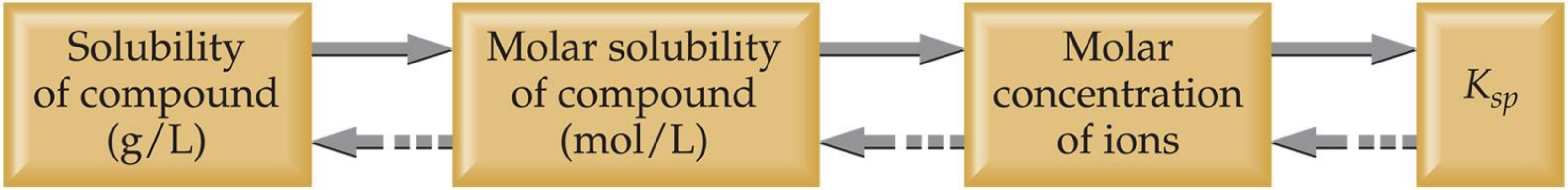
The equilibrium constant expression for this equilibrium is

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

where the equilibrium constant, K_{sp}, is called the **solubility product** (or **solubility product constant**).

Solubility Products

- K_{sp} is *not* the same as solubility.
- Solubility is generally expressed as the mass of solute dissolved in 1 L (g/L) or 100 mL (g/mL) of solution, or in mol/L (*M*).



Solubility of compound (g/L)

Molar solubility of compound (mol/L)

Molar concentration of ions

K_{sp}

EXAMPLE

Solid silver chromate is added to pure water at 25 °C. Some of the solid remains undissolved at the bottom of the flask. The mixture is stirred for several days to ensure that equilibrium is achieved between the undissolved $Ag_2CrO_4(s)$ and the solution. Analysis of the equilibrated solution shows that its **silver ion concentration is 1.3 × 10^{-4} M**. Assuming that Ag_2CrO_4 dissociates completely in water and that there are no other important equilibria involving the Ag^+ or $CrO4^{2-}$ ions in the solution, **calculate K_{sp}** for this compound.

$$Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[CrO_4^{2-}]$$

$$[CrO_4^{2-}] = \left(\frac{1.3 \times 10^{-4}\ \text{mol Ag}^+}{\text{L}}\right)\left(\frac{1\ \text{mol CrO}_4^{2-}}{2\ \text{mol Ag}^+}\right) = 6.5 \times 10^{-5}\ M$$

$$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (1.3 \times 10^{-4})^2(6.5 \times 10^{-5}) = 1.1 \times 10^{-12}$$

17-5 Factors That Affect Solubility

- The Common-Ion Effect
  - If one of the ions in a solution equilibrium is already dissolved in the solution, the equilibrium will shift to the left and the solubility of the salt will decrease.

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

EXAMPLE

Calculate the molar solubility of CaF_2 at 25 °C in a solution that is **(a)** 0.010 *M* in $Ca(NO_3)_2$, **(b)** 0.010 *M* in NaF. K_{sp} of CaF_2 is $3.9x10^{-11}$

$$K_{sp} = [Ca^{2+}][F^-]^2 = 3.9 \times 10^{-11}$$

(a)

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\,F^-(aq)$$

	$CaF_2(s)$	$Ca^{2+}(aq)$	$2\,F^-(aq)$
Initial	—	0.010 *M*	0
Change	—	$+x\ M$	$+2x\ M$
Equilibrium	—	$(0.010 + x)\ M$	$2x\ M$

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

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

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

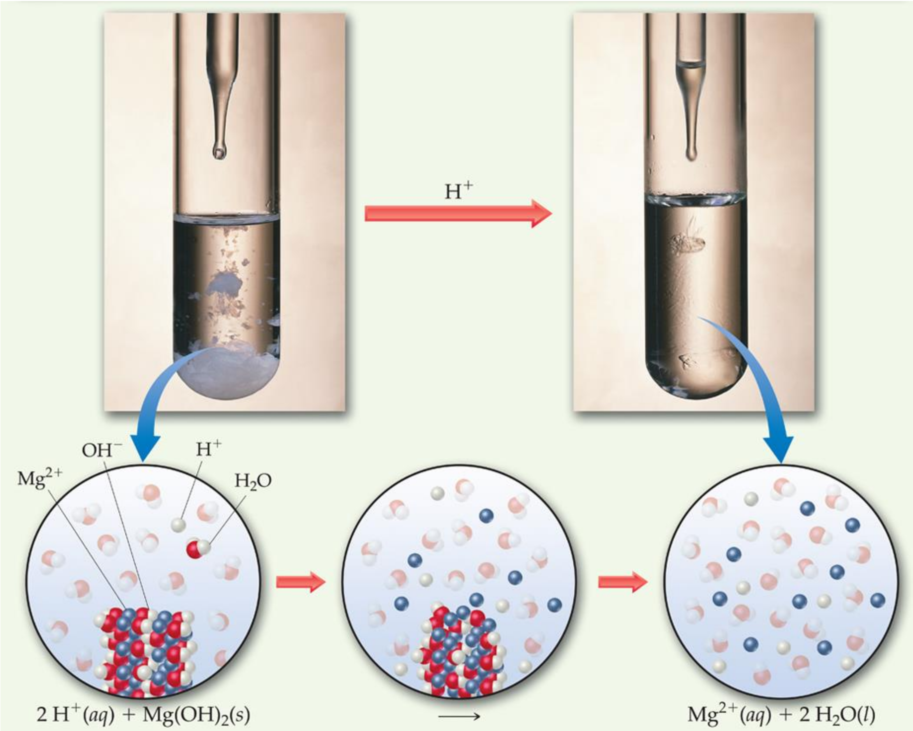
(b)

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

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

$$x = 3.9 \times 10^{-7}\ M$$

Solubility and pH



- pH
  - If a substance has a basic anion, it will be more soluble in an acidic solution.
  - Substances with acidic cations are more soluble in basic solutions.

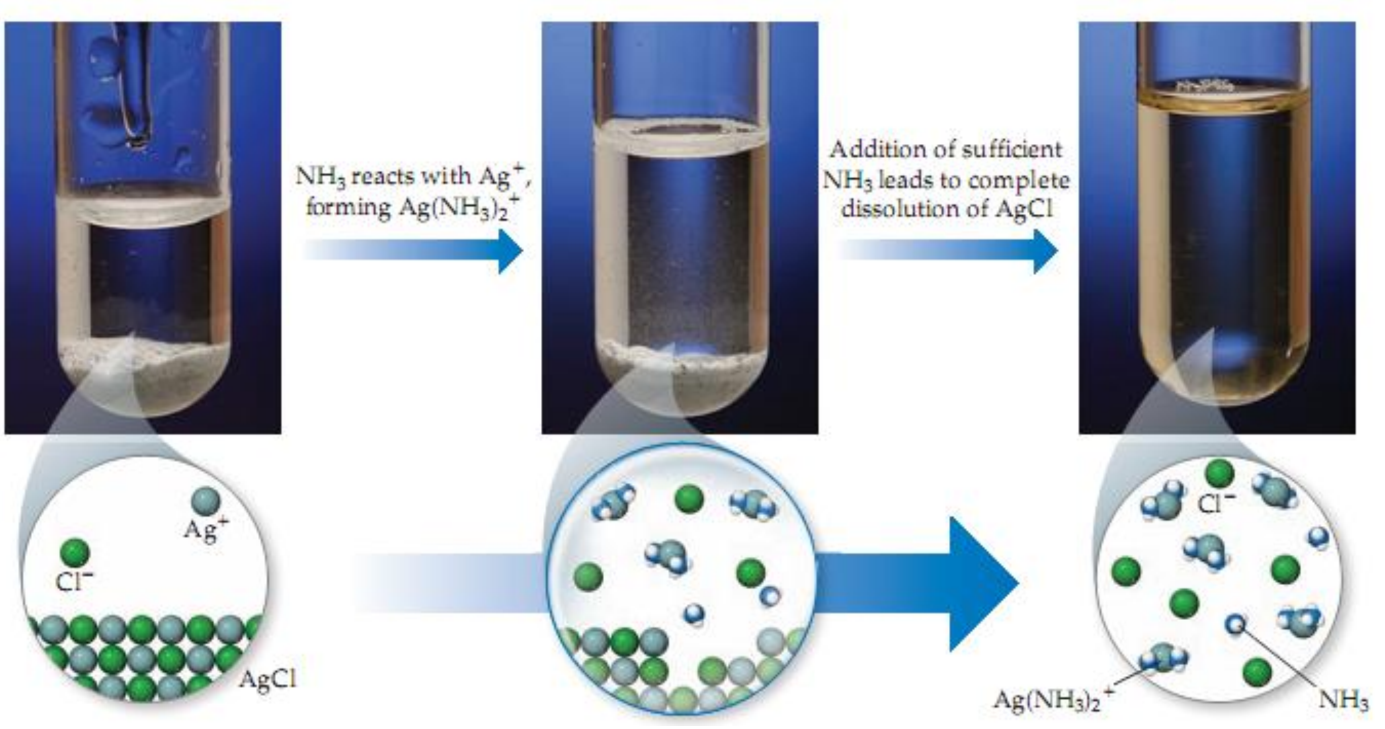
EXAMPLE

Which of the following substances will be more soluble in acidic solution than inbasic solution:

(a) $Ni(OH)_2(s)$, **(b)** $CaCO_3(s)$, **(c)** BaF2(s), **(d)** AgCl(s)?

Complex Ions

- Metal ions can act as Lewis acids and form complex ions with Lewis bases in the solvent.



- The formation of these complex ions increases the solubility of these salts.

$$\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq)$$

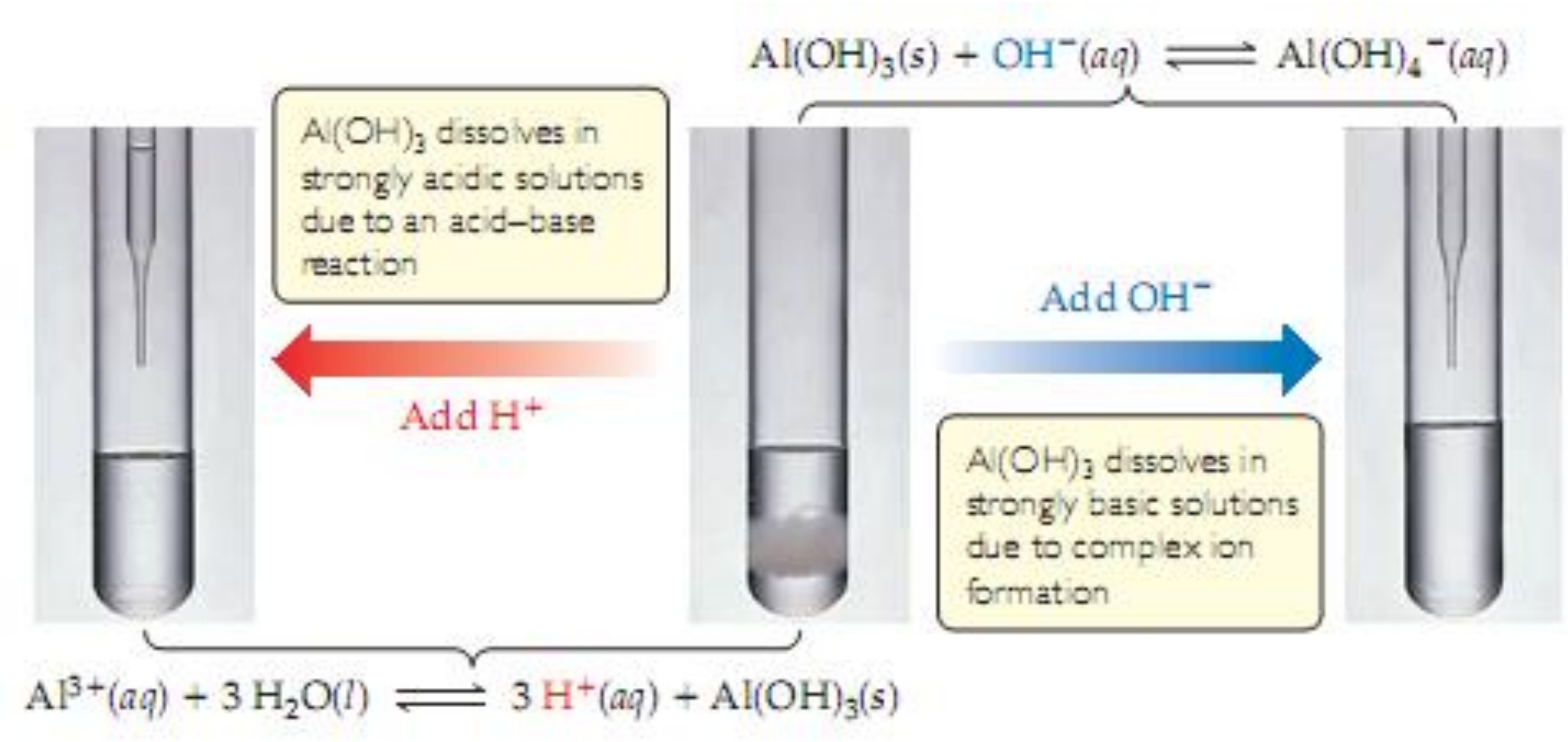
$$\mathrm{Ag}^+(aq) + 2\,\mathrm{NH}_3(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2}^+(aq)$$

$$\text{Overall:}\quad \mathrm{AgCl}(s) + 2\,\mathrm{NH}_3(aq) \rightleftharpoons \mathrm{Ag(NH_3)_2}^+(aq) + \mathrm{Cl}^-(aq)$$

EXAMPLE

Calculate the concentration of Ag^+ present in solution at equilibrium when concentrated ammonia is added to a 0.010 *M* solution of $AgNO_3$ to give an equilibrium concentration of $[NH_3] = 0.20$ *M*. Neglect the small volume change that occurs when NH_3 is added.

Amphoterism



$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$

$Al(OH)_3$ dissolves in strongly acidic solutions due to an acid–base reaction

$Al(OH)_3$ dissolves in strongly basic solutions due to complex ion formation

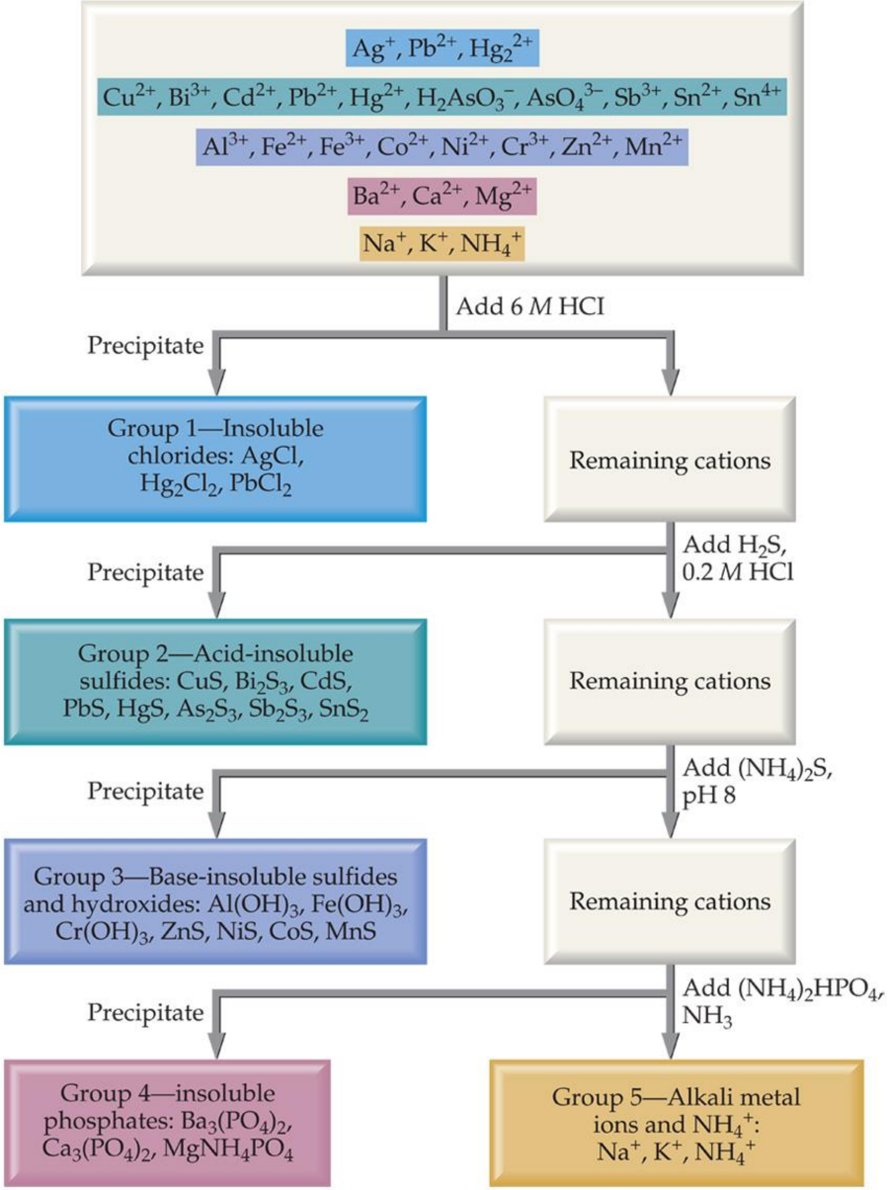
$Al^{3+}(aq) + 3\,H_2O(l) \rightleftharpoons 3\,H^+(aq) + Al(OH)_3(s)$

- Amphoteric metal oxides and hydroxides are soluble in strong acid or base, because they can act either as acids or bases.
- Examples of such cations are Al^{3+}, Zn^{2+}, and Sn^{2+}.

17-6 Precipitation and separationof Ions

- In a solution,
  - If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.
  - If $Q < K_{sp}$, more solid can dissolve until $Q = K_{sp}$.
  - If $Q > K_{sp}$, the salt will precipitate until $Q = K_{sp}$.

Selective Precipitation of Ions



One can use differences in solubilities of salts to separate ions in a mixture.

EXAMPLE

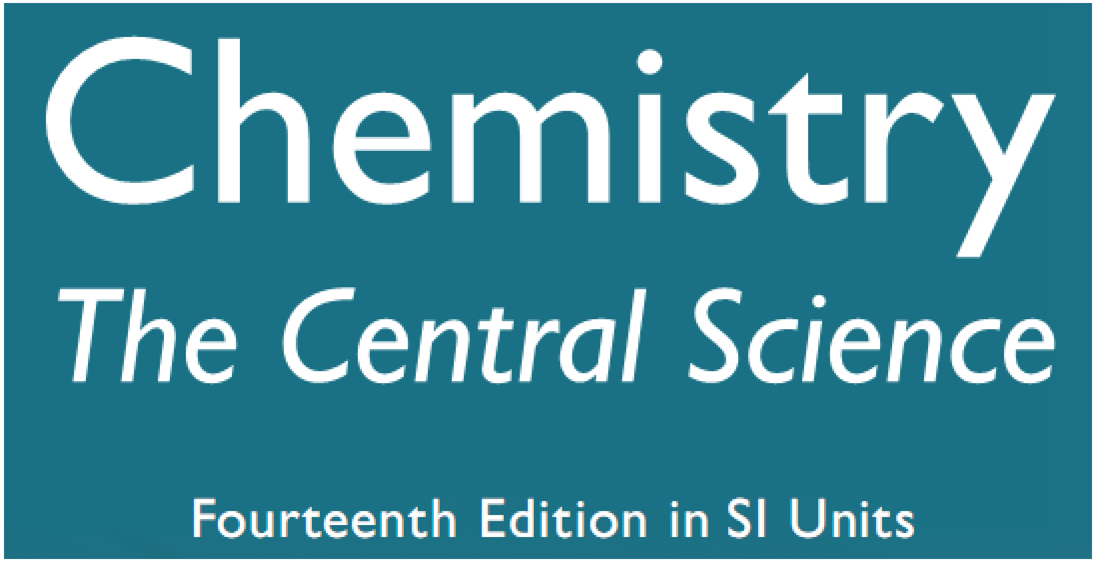
Will a precipitate form when 0.10 L of 8.0×10^{-3} *M* $Pb(NO_3)_2$ is added to 0.40 L of 5.0×10^{-3} *M* Na_2SO_4?

Homeworks

17.111

17.119

Due: August 28th 2019



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