

ADDITIONAL ASPECTS OF AQUEOUS EQUILIBRIA

TOPIC

17

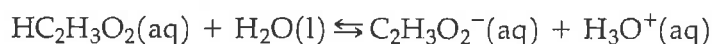
Calculations involving buffer solutions and solubility equilibria are in many ways the most important topics on the AP exam, and are also among the most difficult to master. Students must also master the quantitative relationships that govern various points during the titrations of weak acids and bases, and be able to match suitable indicators to particular titrations. Reactions involving complex ions are also included on the AP exam.

The Common Ion Effect

Section 17.1

The **common ion effect** decreases the ionization of a weak electrolyte when a common ion is added to the solution.

Consider the ionization of acetic acid in water.



Adding sodium acetate, $\text{NaC}_2\text{H}_3\text{O}_2$, to this solution will increase the concentration of acetate ion, $\text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$. The effect will be to shift the equilibrium to the left in accordance with Le Châtelier's principle, decreasing the ionization of acetic acid. The resulting solution is a buffer containing both a weak acid and a conjugate weak base.

Buffer Solutions

Section 17.2

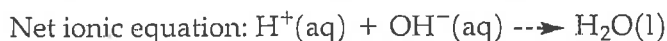
A **buffer solution** is a solution that resists a change in pH upon addition of small amounts of strong acid or base. A mixture of a weak acid and its conjugate base, both existing in significant quantities in the same solution, constitutes an effective buffer. The solution's resistance to pH change arises because the weak acid can react with small quantities of strong base, and the weak base can react with small quantities of strong acid.

Your Turn 17.1

To make a buffer solution, what weak acid must be added to an amount of sodium acetate? Write a chemical equation and its corresponding equilibrium expression. Write your answer in the space provided.

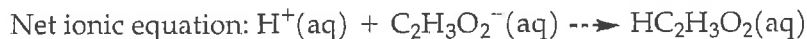
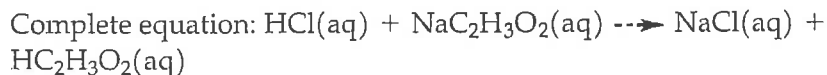
Understanding the reactions of acids with bases is the key to understanding how a buffer solution works both qualitatively and quantitatively. It is important to know how acids and bases react with each other. For example, consider the reactions of equal molar amounts of the following acids and bases.

1. A strong acid reacts completely with a strong base to yield a neutral solution.

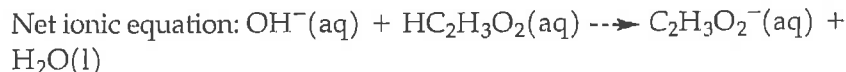
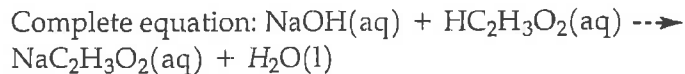


The solution is neutral because both the sodium and chloride ions are neutral ions.

2. A strong acid reacts completely with a weak base to yield a weak acid.



3. A strong base reacts completely with a weak acid to yield a weak base.



4. A weak acid does not react appreciably with a conjugate weak base.

Your Turn 17.2

Write and balance complete and net ionic equations for the reaction of aqueous ammonia solution with nitric acid. Write your answer in the space provided.

Calculating the pH of a Buffer

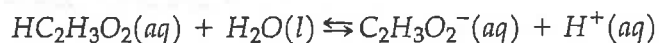
The pH of a buffer solution is calculated just like the pH of a weak acid solution.

Example:

What is the pH of an aqueous mixture containing 0.20 M acetic acid and 0.10 M sodium acetate?

Solution:

Employ an ICE table for the ionization of acetic acid and include the initial concentrations of both the weak acid and the weak base:



I	0.20	0.10	0
C	-x	+x	+x
E	0.20-x	0.10+x	x

$$K_a = [\text{C}_2\text{H}_3\text{O}_2^-][\text{H}^+]/[\text{HC}_2\text{H}_3\text{O}_2] = (0.10 + x)(x)/(0.20 - x)$$

If x is small compared to 0.10, then $0.10 + x \approx 0.10$ and $0.20 - x \approx 0.20$

$$\text{So } K_a = 0.10x/0.20$$

$$1.8 \times 10^{-5} = 0.10x/0.20$$

$$x = [\text{H}_3\text{O}^+] = 3.6 \times 10^{-5}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.6 \times 10^{-5}) = 4.44$$

Because the ICE tables for all buffer solutions are the same, the equation used in all buffer calculations can be generalized as:

$$K_a = x[\text{base}]/[\text{acid}]$$

or its logarithmic form:

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

where K_a is the ionization constant of the weak acid,
 x is the molar concentration of hydrogen ion, $[\text{H}^+]$,
 $[\text{base}]$ is the initial concentration of the weak base, and
 $[\text{acid}]$ is the initial concentration of the weak acid.



Common misconception: Although calculations involving acid-base equilibria can be reduced to a few simple equations, the key to solving acid-base equilibria problems lies in understanding the chemistry and how the equations apply to the chemical reactions involved. Although the math may seem simple, the chemistry can be complex.

Table 17.1 reviews the equations used in solving quantitative acid-base problems.

Table 17.1. Common equations useful in solving acid-base equilibria problems

Strong acid	$x = I$	$x = [\text{H}^+]$, $I =$ initial acid concentration
Strong base	$y = I$ ($y = 2I$ for dibasic)	$y = [\text{OH}^-]$, $I =$ initial base concentration
Weak acid	$K_a = x^2/I$	$K_a =$ weak acid ionization constant
Weak base	$K_b = y^2/I$	$K_b =$ weak base ionization constant
Buffer	$K_a = x[\text{base}]/[\text{acid}]$ or $\text{pH} = \text{pK}_a + \log([\text{base}]/[\text{acid}])$	$[\text{base}] =$ initial base concentration $[\text{acid}] =$ initial acid concentration $\text{pK}_a = -\log K_a$

Before the equations in Table 17.1 can be applied, the chemistry of the solution must be identified and understood. Table 17.2 summarizes what happens when an acid and base are mixed.

Table 17.2. Solutions resulting from various acid-base reactions

If the Solution Contains:	And the Base Is in Excess, the Resulting Solution Is a:	And the Acid Is in Excess, the Resulting Solution Is a:	And Neither the Acid nor the Base Is in Excess, the Resulting Solution Is a:
Strong acid + strong base	Strong base	Strong acid	Neutral solution pH = 7
Strong acid + weak base	*Buffer	Strong acid	Weak acid
Weak acid + strong base	Strong base	*Buffer	Weak base
Weak acid + weak base	*Buffer	*Buffer	*Buffer

*Whenever a buffer solution results, the volume change need not be considered when calculating pH.

Common misconception: A buffer can be prepared from more than just a weak acid and the salt of the acid or a weak base and the salt of the base. A buffer is formed whenever a limiting amount of strong base is added to an excess amount of weak acid because the strong base reacts completely, converting some, but not all of the weak acid to its conjugate base. Similarly, a limiting amount of strong acid added to an excess amount of weak base forms a buffer solution.



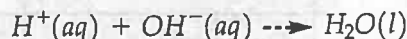
→ Your Turn 17.3

Explain how nitric acid and sodium acetate can be used to make a buffer solution. Illustrate your answer using a chemical equation. Write your answer in the space provided.

Examples:

a. What is the pH of a solution made by mixing 1.0 L of 0.10 M HCl with 2.0 L of 0.060 M NaOH?

1. Write the net ionic equation.



2. Calculate the amount of moles of acid and of base.

$$\text{mol HCl} = 1.0 \text{ L} \times 0.10 \text{ mol/L} = 0.10 \text{ mol HCl}$$

$$\text{mol NaOH} = 2.0 \text{ L} \times 0.06 \text{ mol/L} = 0.12 \text{ mol NaOH}$$

3. Subtract the limiting reactant from the excess reactant to obtain the amount of excess reactant that remains. (A strong acid and a strong base will react completely to the extent of the limiting reactant.)

$$0.12 \text{ mol NaOH} - 0.10 \text{ mol HCl} = 0.02 \text{ mol NaOH remains.}$$

4. Calculate the total volume of the solution and the concentration(s) of the acid or base in solution.

$$\text{Volume} = 1.0 \text{ L} + 2.0 \text{ L} = 3.0 \text{ L.}$$

$$[OH^-] = 0.02 \text{ mol} / 3.0 \text{ L} = 0.0067 \text{ M}$$

5. Calculate the pH.

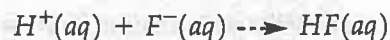
$$pOH = -\log[OH^-] = -\log(.0067) = 2.18.$$

$$pH = 14 - pOH = 14 - 2.18 = 11.82$$

6. Is the answer reasonable? Yes. This pH is consistent for a solution containing an excess of strong base.

b. What is the pH of a solution made by mixing 1.0 L of 0.11 M HCl with 3.0 L of 0.080 M NaF?

1. Write the net ionic equation.



2. Calculate the amount of moles of acid and of base.

$$\text{mol HCl} = 1.0 \text{ L} \times 0.11 \text{ mol/L} = 0.11 \text{ mol HCl}$$

$$\text{mol NaF} = 3.0 \text{ L} \times 0.080 \text{ mol/L} = 0.24 \text{ mol NaF}$$

3. All of the limiting strong acid will react with the base to form an amount of conjugate acid equal to the amount of limiting acid. Additionally, there is some weak base left over.

$$0.24 \text{ mol NaF} - 0.11 \text{ mol HCl} = 0.13 \text{ mol NaF plus } 0.11 \text{ mol HF.}$$

4. This is a buffer because it contains weak acid and weak base and the volume change is not important.

5. Calculate the pH.

$$pH = pK_a + \log [\text{base}]/[\text{acid}]$$

K_a for HF = 6.8×10^{-4} (from Table D-1 of Chemistry the Central Science)

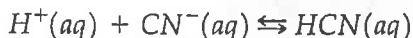
$$pK_a = -\log K_a = -\log 6.8 \times 10^{-4} = 3.17$$

$$pH = 3.17 + \log(0.13/0.11) = 3.24.$$

6. Is the answer reasonable? Yes. This pH is consistent for a buffer solution containing slightly more weak base than weak acid and whose weak acid has a $pK_a = 3.17$.

c. What is the pH of a solution made by mixing 1.0 L of 0.20 M HNO_3 and 2.0 L of 0.10 M NaCN?

1. Write the net ionic equation.



2. Calculate the amount of moles of acid and of base.

$$\text{mol HNO}_3 = 1.0 \text{ L} \times 0.20 \text{ mol/L} = 0.20 \text{ mol HNO}_3.$$

$$\text{mol NaCN} = 2.0 \text{ L} \times 0.10 \text{ mol/L} = 0.20 \text{ mol NaCN}.$$

3. Neither strong acid nor weak base is in excess. The strong acid will convert all of the weak base into 0.20 moles of HCN.

4. Calculate the total volume of the solution and the concentration(s) of the species in solution.

$$\text{Volume} = 1.0 \text{ L} + 2.0 \text{ L} = 3.0 \text{ L}.$$

$$[\text{HCN}] = 0.20 \text{ mol}/3.0 \text{ L} = 0.067 \text{ M}$$

5. Calculate the pH.

This is a 0.067 M solution of the weak acid HCN.

$$K_a = x^2/l$$

$$4.9 \times 10^{-10} = x^2/0.067$$

$$x = 5.7 \times 10^{-6} = [\text{H}^+]$$

$$pH = -\log[\text{H}^+] = -\log(5.7 \times 10^{-6}) = 5.24$$

6. Is the answer reasonable? Yes. A pH of 5.24 is consistent for a solution containing a weak acid.

d. What is the pH of a solution made by mixing 2.5 L of 0.20 M $\text{HC}_2\text{H}_3\text{O}_2$ with 1.0 L of 0.30 M $\text{KC}_2\text{H}_3\text{O}_2$?

Because this is a mixture of a weak acid and its conjugate weak base, no reaction will occur. This is a buffer solution.

1. Calculate the amount of moles of the acid and of the base.

$$\text{mol HC}_2\text{H}_3\text{O}_2 = 2.5 \text{ L} \times 0.20 \text{ mol/L} = 0.50 \text{ mol HC}_2\text{H}_3\text{O}_2.$$

$$\text{mol KC}_2\text{H}_3\text{O}_2 = 1.0 \text{ L} \times 0.30 \text{ mol/L} = 0.30 \text{ mol KC}_2\text{H}_3\text{O}_2.$$

2. Calculate the pH.

$$\text{pH} = \text{pKa} + \log[\text{base}]/[\text{acid}]$$

$$\text{pKa of HC}_2\text{H}_3\text{O}_2 = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = 4.74 + \log(0.30/0.50) = 4.74 - 0.22 = 4.52$$

3. Is the answer reasonable? Yes. A pH of 4.52 is consistent with a buffer whose weak acid has a K_a of 4.74. Because the buffer contains more weak acid than weak base, the pH is slightly lower than the pKa.

Section 17.3

Acid-Base Titrations

An **acid-base titration** is a method to determine an unknown concentration of an acid or a base. A titration determines the volume of a standard solution of base of known concentration that is required to completely react with the acid sample. Similarly, a standard solution of an acid is used to measure an unknown concentration of base.

An **acid-base indicator** changes color at the **end point** of the titration.

The indicator signals the **equivalence point**, the point at which there are equal molar amounts of acid and base.

Alternatively, a pH meter can be used to monitor a titration from start to finish.

A **titration curve** is a graph of pH vs. mL of titrant. Various acid-base titrations produce distinctive titration curves.

Figure 17.1 shows a typical titration curve for a strong acid and a strong base. A strong acid–strong base titration curve is typified by the following properties:

The pH before the titration begins is that of a strong acid.

As strong base is added, the pH rises slightly because the concentration of the strong acid decreases as it becomes neutralized by strong base.

Near the equivalence point the pH rises dramatically. The pH at the equivalence point is always 7 for a strong acid–strong base titration.

After the equivalence point the pH is that of a strong base. It rises slightly because of the increasing amount of strong base.

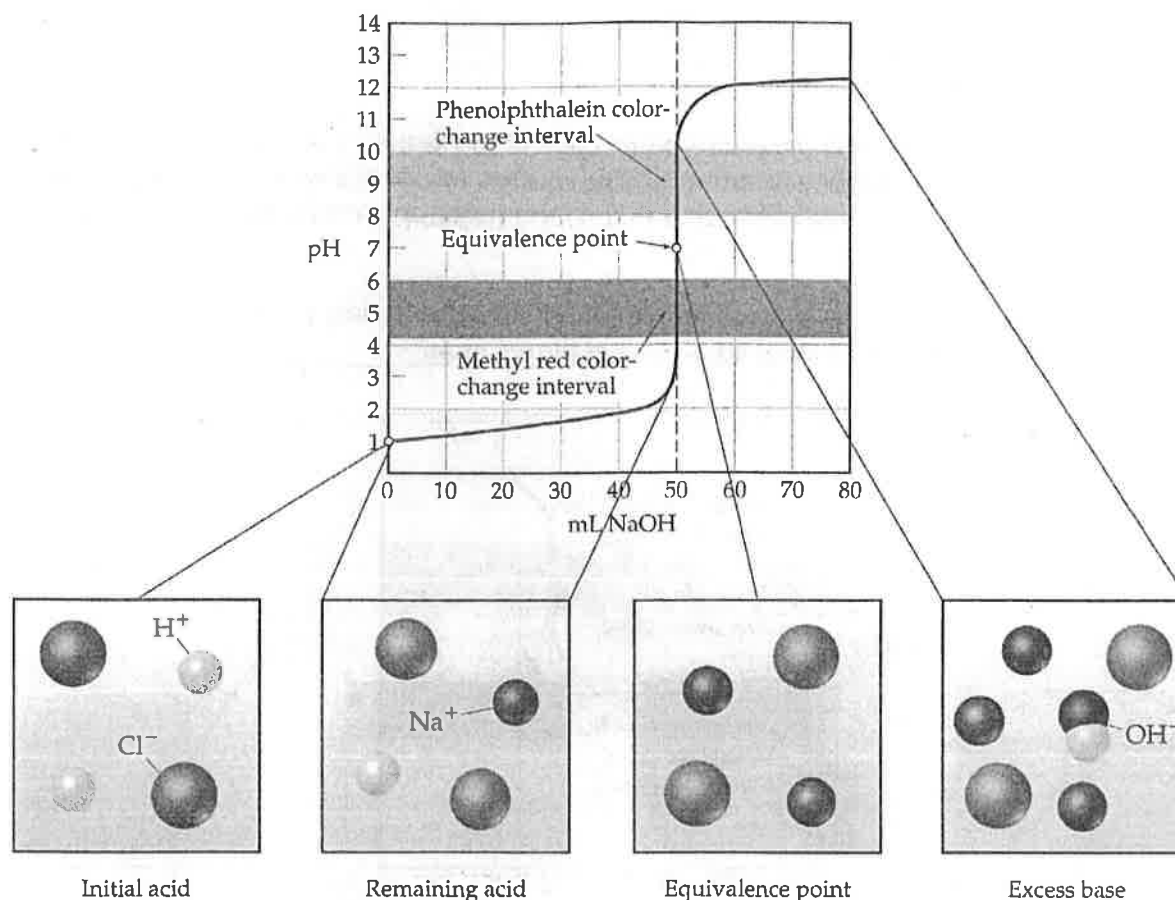
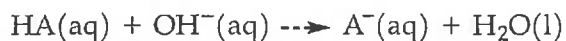


Figure 17.1. Typical acid-base titration curve for a strong acid and a strong base.

Figure 17.2 shows a titration curve of a weak acid and a strong base. Although a weak acid–strong base titration curve looks similar to a titration curve for a strong acid and strong base, there are significant differences:

The pH before the titration begins is higher because it is that of a weak acid in water.

The “buffered region” of the titration curve shows that the pH changes slightly as more and more strong base is added which replaces *some, but not all*, of the weak acid with conjugate base.



$$\text{pH} = \text{pK}_a - \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

The pH where the amount of titrant is equal to half the amount required to reach the equivalence point defines the pK_a of the weak acid because when $[\text{base}] = [\text{acid}]$ in the equation,

$$\text{pH} = \text{pK}_a - \log\left(\frac{[\text{base}]}{[\text{acid}]}\right),$$

then $\text{pH} = \text{pK}_a$.

Near the equivalence point the rise in pH is not as significant for a weak acid–strong base titration. The equivalence point of a weak acid–strong base titration always has a pH greater than 7. At this point, only conjugate weak base is in solution.

Beyond the equivalence point, only the concentration of strong base need be considered to calculate the pH of the solution.

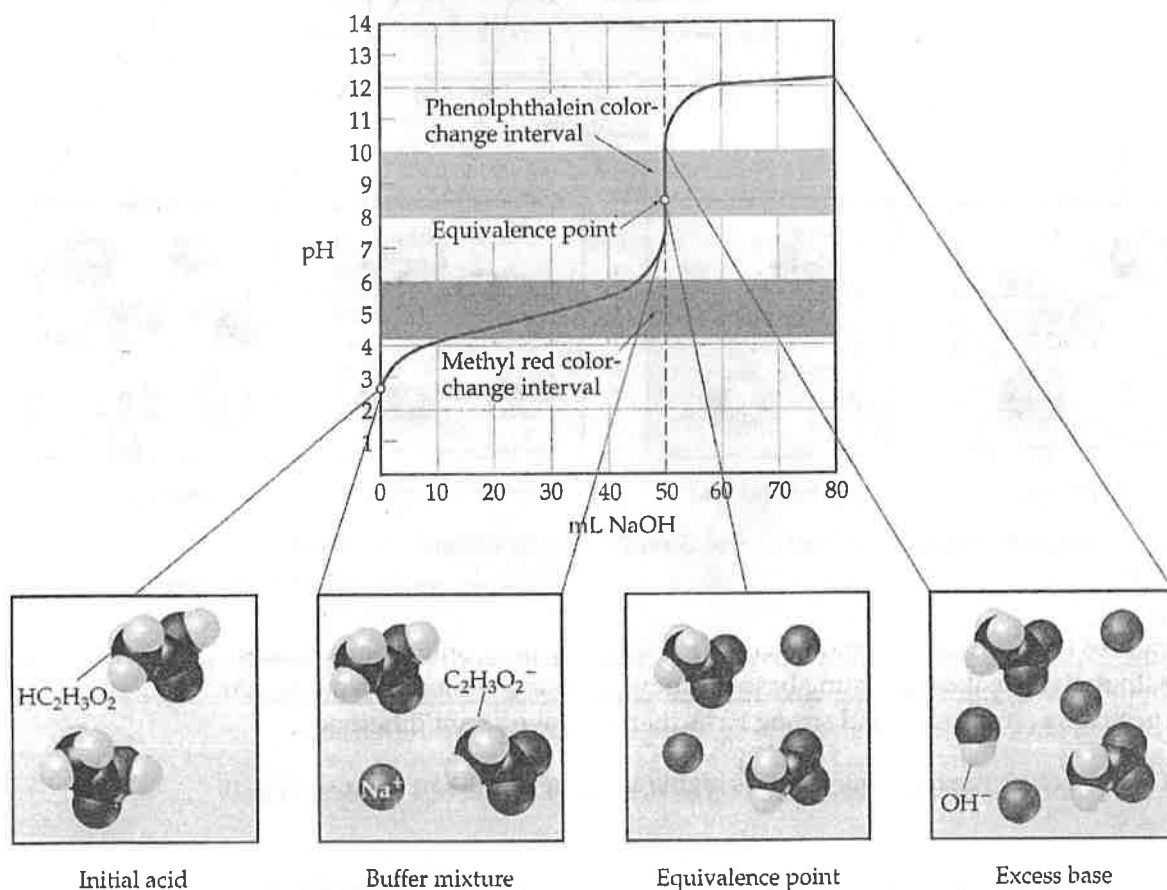


Figure 17.2. A weak acid titrated with a strong base.

In order for an indicator to accurately signal the equivalence point of a titration, the pH at which it changes color must match the pH of the equivalence point. Table 17.3 shows the pK_a's and pH range in which common indicators change color.

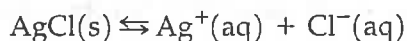
Table 17.3. Color changes of acid-base indicators and their pKa's

Indicator	Color Change	pH Range	pKa
Bromphenol blue	yellow to blue	3–4.5	4
Bromcresol green	yellow to blue	4–5	4.5
Methyl red	red to yellow	4.5–6	5
Bromthymol blue	yellow to blue	6–7.5	7
Phenol red	yellow to red	7–8	7.5
Phenolphthalein	colorless to pink	8–10	9
Alizarin yellow R	yellow to red	10–12	11

Solubility Equilibria

Section 17.4

When a precipitate forms from the mixing of two solutions, an equilibrium is established between the solid precipitate and its dissolved ions. For example, consider the slightly soluble salt, silver chloride, AgCl. In a saturated solution, one that has dissolved the maximum amount of solute, the ions are in equilibrium with the solid:



The equilibrium expression for this reaction is:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

The equilibrium constant, K_{sp} , is another special case of K_c and is called the **solubility product constant**.

For silver chloride, $K_{sp} = 1.8 \times 10^{-10}$ (From Table D-3, Appendix D in *Chemistry the Central Science*).

The ICE table is:

	AgCl(s) =	Ag ⁺ (aq) +	Cl ⁻ (aq)
I	I	0	0
C	-x	+x	+x
E	I - x	x	x

The **molar solubility** of silver chloride is the number of moles of silver chloride that dissolve in a liter of water. That is, the molar solubility = x . For every mole of AgCl that dissolves, one mole of Ag^+ and one mole of Cl^- is formed so:

$$x = [\text{Ag}^+] = [\text{Cl}^-] \quad \text{and}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

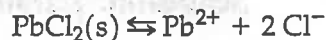
Substituting:

$$K_{\text{sp}} = x^2$$

$$1.8 \times 10^{-10} = x^2$$

$$x = 1.3 \times 10^{-5} \text{ M} = \text{the molar solubility of silver chloride.}$$

Consider the slightly soluble salt, lead(II) chloride, PbCl_2 . In a saturated solution, the ions are in equilibrium with the solid:



The equilibrium expression for this reaction is:

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

For lead(II) chloride, $K_{\text{sp}} = 1.6 \times 10^{-5}$.

For every mole of PbCl_2 that dissolves, one mole of Pb^{2+} and two moles of Cl^- are formed so:

$$x = [\text{Pb}^{2+}] \quad \text{and} \quad [\text{Cl}^-] = 2x$$

Substituting:

$$K_{\text{sp}} = (x)(2x)^2 = 4x^3$$

$$(1.6 \times 10^{-5})/4 = x^3$$

$$x = 0.016 \text{ M} = \text{the molar solubility of lead(II) chloride}$$

When a solid precipitate establishes an equilibrium with its ions in solution, the resulting K_{sp} expression, and its relationship to the molar solubility, x , is derived from the ICE table. It is dependent on the stoichiometry of the dissolution reaction. Table 17.4 shows the relationship of the K_{sp} expression and the molar solubility in water expression to various reactions.

Table 17.4. The K_{sp} expressions and molar solubility in water expressions for various solubility equilibria reactions

Dissolution Equilibrium	K_{sp} Expression	Molar Solubility, x
$\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$	$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$	$K_{sp} = (x)(x) = x^2$
$\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$	$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$	$K_{sp} = (x)(2x)^2 = 4x^3$
$\text{LaCl}_3(s) \rightleftharpoons \text{La}^{3+}(aq) + 3\text{F}^-(aq)$	$K_{sp} = [\text{La}^{3+}][\text{F}^-]^3$	$K_{sp} = (x)(3x)^3 = 27x^4$
$\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$	$K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$	$K_{sp} = (3x)^3(2x)^2 = 108x^5$

Factors that Affect Solubility Section 17.5

The molar solubility of a precipitate is always greater in pure water than it is in an aqueous solution containing a common ion.

Common misconception: The molar solubility expression in water does not apply to solutions containing common ions. For common ions the molar solubility must be derived from an ICE table.



Example:

Calculate the molar solubility of cerium fluoride, CeF_3 , in

- pure water
- a solution containing 0.2 M CeCl_3 .
- a solution containing 0.2 M NaF .

$$K_{sp} = 8 \times 10^{-16}$$

Solution:

a. The reaction is: $\text{CeF}_3(s) \rightleftharpoons \text{Ce}^{3+}(aq) + 3\text{F}^-(aq)$

The K_{sp} expression is

$$K_{sp} = [\text{Ce}^{3+}][\text{F}^-]^3$$

$$K_{sp} = (x)(3x)^3 = 27x^4$$

$$K_{sp} = 8 \times 10^{-16} = 27x^4$$

$$x = 7 \times 10^{-5} \text{ M}$$

b. The molar solubility expression in water does not apply to solutions containing common ions. It must be derived from the ICE table. Here cerium ion is the common ion. (Chloride is a soluble spectator ion.)

	$\text{CeF}_3(s) \rightleftharpoons$	$\text{Ce}^{3+}(aq) + 3\text{F}^{-}(aq)$	
I	I	0.2	0
C	-x	+x	+3x
E	I - x	0.2 + x	3x

$$K_{sp} = [\text{Ce}^{3+}][\text{F}^{-}]^3$$

$$K_{sp} = 8 \times 10^{-16} = (0.2 + x)(3x)^3$$

If $x \ll \ll \ll 0.2$ then $0.2 + x \approx 0.2$

$$8 \times 10^{-16} = (0.2)(3x)^3$$

$$x = 5 \times 10^{-6} \text{ M}$$

c. The ICE table is similar to Part b except that here, fluoride is the common ion. (Sodium ion is a soluble spectator ion.)

	$\text{CeF}_3(s) \rightleftharpoons$	$\text{Ce}^{3+}(aq) + 3\text{F}^{-}(aq)$	
I	I	0	0.2
C	-x	+x	+3x
E	I - x	x	0.2 + 3x

$$K_{sp} = [\text{Ce}^{3+}][\text{F}^{-}]^3$$

$$K_{sp} = 8 \times 10^{-16} = (x)(0.2 + 3x)^3$$

If $3x \ll \ll \ll 0.2$ then $0.2 + 3x \approx 0.2$

$$8 \times 10^{-16} = (x)(0.2)^3$$

$$x = 1 \times 10^{-13} \text{ M}$$

Notice that in both Parts b and c where a common ion is involved, the molar solubility of cerium fluoride is less than in pure water.

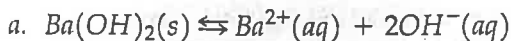
The **reaction quotient, Q**, is used to predict whether a precipitate will form under a set of given conditions.

Example:

Consider a solution made by adding 175 mL of 0.10 M BaCl_2 to 40 mL of 0.50 M NaOH . Assume the volumes are additive. K_{sp} for barium hydroxide is 5.0×10^{-3} .

- a. Write the net ionic equation for the dissolution of barium hydroxide.
- b. What is the value of Q?

- c. K_{sp} for $Ba(OH)_2$ is 5.0×10^{-3} . Will a precipitate form?
 d. What must be the concentration of OH^- for a precipitate to form in 0.10 M $BaCl_2$?

Solution:

b. $Q = [Ba^{2+}][OH^-]^2$

$$Q = (0.10 \text{ M})(175/215)[(0.50)(40/215)]^2 = 7.0 \times 10^{-4}$$

c. $K_{sp} > Q$. No precipitate will form because the concentrations of the ions are too small. Q must be at least as large as K_{sp} .

d. $K_{sp} = [Ba^{2+}][OH^-]^2$

$$5.0 \times 10^{-3} = [0.10][OH^-]^2$$

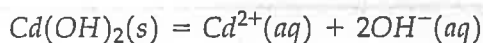
$$[OH^-] = 0.22 \text{ M}$$

The solubility of a hydroxide precipitate is affected by the pH of a solution.

Example:

Calculate the molar solubility of $Cd(OH)_2$ in a pH 9.5 buffer.

$$K_{sp} = 2.5 \times 10^{-14}$$

Solution:

$$K_{sp} = 2.5 \times 10^{-14} = [Cd^{2+}][OH^-]^2$$

When the pH = 9.5, the pOH = $14 - 9.5 = 4.5$ so $[OH^-] = 10^{-4.5}$.

$$K_{sp} = 2.5 \times 10^{-14} = [Cd^{2+}][10^{-4.5}]^2$$

$$[Cd^{2+}] = 2.5 \times 10^{-5}$$

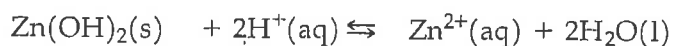
Complex Ions

A **complex ion** is a metal ion bonded to one or more Lewis bases. We have seen that a characteristic property of metal ions is their ability to act as Lewis acids by attracting nonbonding electron pairs of water molecules. Some metal ions also commonly attract the nonbonding pairs of other Lewis bases, such as ammonia molecules and hydroxide ions, to form complex ions. Table 17.5 illustrates the formation of some common complex ions. A rough rule of thumb that works about three-fourths of the time is that the number of Lewis bases (called ligands) that a given metal ion attracts is equal to double its positive charge. The common exceptions to this rule are shown in Table 17.4 with an asterisk, *.

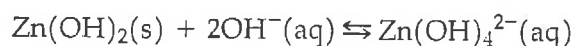
Table 17.5. The formation of some common complex ions

Complex Ion	Equilibrium Reaction
$\text{Ag}(\text{NH}_3)_2^+(\text{aq})$	$\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(\text{aq})$
$\text{Ag}(\text{CN})_2^-(\text{aq})$	$\text{Ag}^+(\text{aq}) + 2\text{CN}^-(\text{aq}) \rightleftharpoons \text{Ag}(\text{CN})_2^-(\text{aq})$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq})$	$\text{Ag}^+(\text{aq}) + 2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(\text{aq})$
$\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$	$\text{Cu}^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$
$\text{Cu}(\text{CN})_4^{2-}(\text{aq})$	$\text{Cu}^{2+}(\text{aq}) + 4\text{CN}^-(\text{aq}) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(\text{aq})$
$^*\text{Fe}(\text{CN})_6^{4-}(\text{aq})$	$\text{Fe}^{2+}(\text{aq}) + 6\text{CN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(\text{aq})$
$\text{Fe}(\text{CN})_6^{3-}(\text{aq})$	$\text{Fe}^{3+}(\text{aq}) + 6\text{CN}^-(\text{aq}) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(\text{aq})$
$^*\text{Al}(\text{OH})_4^-(\text{aq})$	$\text{Al}^{3+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightleftharpoons \text{Al}(\text{OH})_4^-(\text{aq})$
$^*\text{Cr}(\text{OH})_4^-(\text{aq})$	$\text{Cr}^{3+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightleftharpoons \text{Cr}(\text{OH})_4^-(\text{aq})$
$\text{Zn}(\text{OH})_4^{2-}(\text{aq})$	$\text{Zn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightleftharpoons \text{Zn}(\text{OH})_4^{2-}(\text{aq})$
$\text{Sn}(\text{OH})_4^{2-}(\text{aq})$	$\text{Sn}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightleftharpoons \text{Sn}(\text{OH})_4^{2-}(\text{aq})$
$\text{Pb}(\text{OH})_4^{2-}(\text{aq})$	$\text{Pb}^{2+}(\text{aq}) + 4\text{OH}^-(\text{aq}) \rightleftharpoons \text{Pb}(\text{OH})_4^{2-}(\text{aq})$

The hydroxides of the cations Al^{3+} , Cr^{3+} , Zn^{2+} , Sn^{2+} and Pb^{2+} are amphoteric because they can act as either an acid or a base. These hydroxides dissolve in both acidic and basic solutions. Zinc hydroxide acts as a base when it is neutralized by an acid.



Zinc hydroxide can act as an acid in the presence of excess hydroxide to form a complex ion.



Multiple Choice Questions

1. A solution is known to contain ions of Ag^+ , Cu^{2+} , and Pb^{2+} . What will happen when 1.0 M HCl is added to the solution?
 - A) No precipitate will form.
 - B) Only AgCl will precipitate.
 - C) Both AgCl and PbCl_2 will precipitate.
 - D) Both PbCl_2 and CuCl_2 will precipitate.
 - E) All three ions will form precipitates.
2. The K_{sp} of CaF_2 is 4.3×10^{-11} in pure water. In acidic solution the solubility of CaF_2 is expected to:
 - A) increase because Ca^{2+} ion is acidic.
 - B) decrease because Ca^{2+} ion is acidic.
 - C) increase because F^- ion is basic.
 - D) decrease because F^- ion is basic.
 - E) remain the same as in pure water.
3. Which has the greatest molar solubility in water at 25°C ?
 - A) ammonium nitrate
 - B) barium sulfate
 - C) iron(II) sulfide
 - D) lead(II) carbonate
 - E) copper(II) phosphate
4. When mixed, which pair of aqueous solutions will form a precipitate?
 - A) KNO_3 and CaBr_2
 - B) NaNO_3 and $(\text{NH}_4)_2\text{CO}_3$
 - C) CaCl_2 and K_2CO_3
 - D) K_2SO_4 and $(\text{NH}_4)_2\text{S}$
 - E) LiClO_4 and CuSO_4

5. Which of these slightly soluble salts would show an increased solubility in a 1.0 M aqueous solution of HCl?
- PbCl_2
 - CuCO_3
 - $\text{Ba}_3(\text{PO}_4)_2$
- I only
 - II only
 - I and II only
 - II and III only
 - I, II, and III
6. If equal volumes of the following pairs are mixed, which of the resulting solutions will NOT make a buffer solution?
- 0.20 M NaCN and 0.40 M HCN
 - 0.20 M HF and 0.10 M KOH
 - 0.20 M KF and 0.05 M HCl
 - 0.15 M NaCN and 0.20 M HCl
 - 0.20 M NaOH and 0.30 M HF
7. 0.10 M hydrofluoric acid ($K_a = 6.8 \times 10^{-4}$) is titrated with 0.10 M sodium hydroxide solution. Which indicator is the most appropriate for signaling the end point of the titration? The approximate pH range for the color change of each indicator is given.
- bromphenyl blue pH = 3 - 4.5
 - phenolphthalein pH = 8 - 10
 - thymol blue pH = 1.5 - 2.5
 - alizarin yellow R pH = 11 - 12
 - bromthymol blue pH = 6 - 7
8. Which acid is best when preparing a buffer of pH = 9.0?
- hydrazoic acid, $K_a = 1.9 \times 10^5$
 - hydrofluoric acid, $K_a = 6.8 \times 10^4$
 - sulfuric acid, strong acid, $K_{a2} = 1.2 \times 10^{-2}$
 - hypobromous acid, $K_a = 2.5 \times 10^{-9}$
 - carbonic acid, $K_{a1} = 4.3 \times 10^{-7}$, $K_{a2} = 5.6 \times 10^{-11}$

9. Which of the following hydroxides is not amphoteric?
- A) KOH
 - B) $\text{Al}(\text{OH})_3$
 - C) $\text{Zn}(\text{OH})_2$
 - D) $\text{Pb}(\text{OH})_2$
 - E) $\text{Sn}(\text{OH})_2$
10. When dissolved in aqueous solution which pair would behave as a buffer?
- A) HCl and NaCl
 - B) KOH and KCl
 - C) HNO_2 and NaNO_2
 - D) HNO_3 and NH_4NO_3
 - E) $\text{Ca}(\text{OH})_2$ and CaSO_4

Free Response Questions

1. Solid NaCl is added slowly to a solution containing 0.10 M AgNO_3 and 0.20 M $\text{Pb}(\text{NO}_3)_2$. K_{sp} for AgCl is 1.8×10^{-10} . K_{sp} for PbCl_2 is 1.6×10^{-5} .
- a. Write a net ionic equation and corresponding K_{sp} expression for the dissolution of solid
 - i. silver chloride
 - ii. lead(II) chloride
 - b. Calculate the $[\text{Cl}^-]$ required to form each precipitate.
 - c. Which precipitate forms first? Explain your answer.
 - d. What is the concentration of the first metal ion to precipitate when the second one just begins to precipitate?
 - e. If 100 mL of 0.05 M NaCl is added to 200 mL of solution containing 0.005 M AgNO_3 and 0.10M $\text{Pb}(\text{NO}_3)_2$, does a precipitate form? If so, which one(s) form? Explain.
2. 0.450 moles of hydrazoic acid, HN_3 , ($K_{\text{a}} = 1.9 \times 10^{-5}$) are added to enough water to make 1.55 liters of solution.
- a. Write a chemical equation for the reaction of hydrazoic acid with water and write the corresponding equilibrium expression.
 - b. Calculate the pH of the solution.

- c. Calculate the pH of the solution after 0.350 moles of sodium azide, NaN_3 , is added. Assume no volume change.
- d. Calculate the pH of the solution in Part c after 0.0150 moles of HCl are added. Assume no volume change.
- e. What is the pH of a 0.350 M solution of NaN_3 ?

Additional Practice in Chemistry the Central Science

For more practice working buffer and solubility equilibria problems in preparation for the Advanced Placement examination, try these problems in Chapter 17 of Chemistry the Central Science:

Additional Exercises: 17.77, 17.79, 17.80, 17.81, 17.82, 17.84, 17.85, 17.87, 17.91, 17.92, 17.94.

Integrated Exercises: 17.102, 17.103, 17.104, 17.105.

Multiple Choice Answers and Explanations

1. C. Chlorides are soluble except those of mercury(I), lead(II), and silver ions.
2. C. Most anions are basic. Their negative charges attract protons. The only neutral anions are those anions of strong acids. HF is a weak acid.
3. A. All common salts of ammonium, sodium, and potassium ions are soluble in water.
4. C. Most carbonates, phosphates, hydroxides, and sulfides are insoluble. The exceptions include salts of the ammonium ion and the ions of Group 1.
5. D. The anions of weak acids are basic and will show increased solubility in acids. The anions of strong acids are neutral and the solubility of neutral salts will not be affected. Sulfate ion is the anion of a strong acid and is only slightly basic.
6. D. A buffer consists of a weak acid and a conjugate weak base. It can be formed by mixing the conjugates directly, or in this case by mixing an excess of weak base with a limiting strong acid or by mixing excess weak acid by limiting strong base. Excess strong or weak acid will not result in a buffer solution.
7. B. For an indicator to correctly signal the end point of the titration, the color change must closely match the pH of the equivalence point of

the titration. A titration of a weak acid with a strong base will produce only a weak base at the equivalence point. Therefore the pH of the equivalence point will be higher than 7, but not in the strong base range ($\text{pH} > 11$).

8. D. The pH of a buffer will be close to the pKa of the weak acid from which it is made.

$$\text{pH} = \text{pKa} + \log[\text{base}]/[\text{acid}].$$

$$\begin{aligned} \text{The pKa of hydrobromous acid} &= -\log K_a \\ &= -\log(2.5 \times 10^{-9}) = 8.6 \end{aligned}$$

9. A. Amphoteric hydroxides are those that form complex ions in the presence of excess hydroxide ions. All those listed are amphoteric except KOH.
10. C. A buffer consists of a weak acid and its conjugate weak base. The only conjugate pair listed is nitrous acid and sodium nitrite.

Free Response Answers

1. a. i. $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$ $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$
 ii. $\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$ $K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$

b. $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$

$$1.8 \times 10^{-10} = (0.10)[\text{Cl}^-]$$

$$[\text{Cl}^-] = 1.8 \times 10^{-9} \text{ M required to precipitate AgCl.}$$

$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$1.6 \times 10^{-5} = [(0.20)^+][\text{Cl}^-]^2$$

$$[\text{Cl}^-] = 8.9 \times 10^{-3} \text{ M required to precipitate PbCl}_2.$$

- c. AgCl precipitates first because it requires less $[\text{Cl}^-]$ to form a precipitate.

- d. The second metal ion, Pb^{2+} , just begins to precipitate when $[\text{Cl}^-]$ reaches $8.9 \times 10^{-3} \text{ M}$. At this chloride ion concentration, the silver ion can be calculated from:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

$$1.8 \times 10^{-10} = [\text{Ag}^+](8.9 \times 10^{-3} \text{ M})$$

$$[\text{Ag}^+] = 2.0 \times 10^{-8} \text{ M.}$$

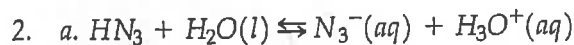
- e. Calculate Q for each equilibrium in Part a and compare each Q to the corresponding K_{sp} . In each case, if $K_{sp} < Q$, a precipitate will form.

$$Q = [Ag^+][Cl^-] = [(0.005 M)(200/300)][(0.05)(100/300)] \\ = 5.6 \times 10^{-5}$$

$K_{sp} < Q$ for $AgCl$ so a precipitate does form.

$$Q = [Pb^{2+}][Cl^-]^2$$

$$1.6 \times 10^{-5} = (0.10 M)(200/300)[(0.05)(100/300)]^2 \\ = 1.9 \times 10^{-5}. K_{sp} < Q \text{ for } PbCl_2 \text{ so a precipitate forms.}$$



$$K_a = [N_3^-][H_3O^+]/[HN_3]$$

b. $K_a = [N_3^-][H_3O^+]/[HN_3]$

$$[HN_3] = 0.450 \text{ mol}/1.55 \text{ L} = 0.290 \text{ M}$$

$$x = [N_3^-] = [H_3O^+]$$

$$1.9 \times 10^{-5} = (x)(x)/(0.290 \text{ M})$$

$$x = [H_3O^+] = 2.35 \times 10^{-3} \text{ M}$$

$$pH = -\log[H_3O^+] = -\log(2.35 \times 10^{-3}) = 2.63$$

c. $pH = pK_a + \log([N_3^-]/[HN_3])$

$$[N_3^-] = 0.350 \text{ moles}/1.55 \text{ L} = 0.226 \text{ M}$$

$$pK_a = -\log K_a = -\log(1.9 \times 10^{-5}) = 4.72$$

$$pH = 4.72 + \log(0.350/0.450) = 4.72 - 0.11 = 4.61$$

d. 0.015 mol of HCl will convert 0.0150 mol of azide to hydrazoic acid:

$$\text{moles of } N_3^- = 0.350 - 0.015 = 0.335 \text{ mol}$$

$$\text{moles of } HN_3 = 0.450 + 0.015 = 0.465 \text{ mol}$$

$$pH = 4.72 + \log(.335/.465) = 4.72 - 0.14 = 4.58$$

e. $K_b = K_w/K_a = (y)(y)/0.350$
 $= 1 \times 10^{-14}/1.9 \times 10^{-5} = y^2/0.350$

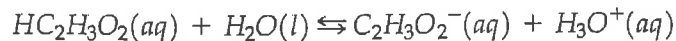
$$y = [OH^-] = 1.36 \times 10^{-5} \text{ M}$$

$$pOH = -\log(1.36 \times 10^{-5}) = 4.87$$

$$pH = 14 = pOH = 14 - 4.87 = 9.13$$

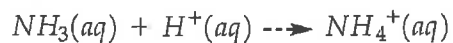
Your Turn Answers

17.1. Acetic acid added to sodium acetate will form a buffer solution.



$$K_a = [\text{C}_2\text{H}_3\text{O}_2^-][\text{H}_3\text{O}^+]/[\text{HC}_2\text{H}_3\text{O}_2]$$

17.2. $\text{NH}_3(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{NH}_4\text{NO}_3(\text{aq})$



17.3. A limiting amount of nitric acid added to an excess of sodium acetate will form a buffer because the strong acid will convert some, but not all of the weak base to acetic acid, a weak acid. The resulting solution will contain both a weak acid and its conjugate weak base.

