

Chapter 17. Additional Aspects of Aqueous Equilibria

Common Student Misconceptions

- Students often believe that the pH at the equivalence point for any titration is 7.00; in other words, students often think that neutralization always results in the formation of a *neutral* solution.
- Students often think that titration is a new type of a reaction, rather than an experimental technique.
- Students tend to find buffers particularly difficult to understand.
- Students often forget to consider volume changes that occur when two solutions are mixed (this will have an effect on the concentration of the species present).
- The approximate nature of the Henderson-Hasselbalch equation in a majority of applications is often lost on students.
- Students tend to confuse K_{sp} and solubility.
- Students often struggle with the concept of competing or subsequent equilibria when considering factors affecting solubility of ionic compounds.
- Students often confuse amphiprotic and amphoteric substances.

Teaching Tips

- Students should review Le Châtelier's principle, pH of salts, and solubility rules prior to starting this chapter.
- The common ion effect can be introduced as an example of how Le Châtelier's principle works.
- In terms of problem-solving skills, this is probably the most difficult chapter for most students.
- The latter sections of this chapter offer an opportunity for a review of inorganic nomenclature.

Lecture Outline

17.1 The Common Ion Effect^{1,2,3,4,5}

- 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.

$$\text{HC}_2\text{H}_3\text{O}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_2\text{H}_3\text{O}_2^-(\text{aq})$$
 - If we add additional $\text{C}_2\text{H}_3\text{O}_2^-$ ions, from 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 the 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**.
 - 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.
- 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.

¹ "The Common-Ion Effect: Second Demonstration" from Live Demonstrations

² "Common-Ion Effect" Animation from Instructor's Resource CD/DVD

³ "Effect of Acetate Ion on the Acidity of Acetic Acid: The Common-Ion Effect" from Live Demonstrations

⁴ "The Common-Ion Effect: Ammonium Hydroxide and Ammonium Acetate" from Live Demonstrations

⁵ "Acetic Acid" 3-D Model from Instructor's Resource CD/DVD

17.2 Buffered Solutions

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

Composition and Action of Buffered Solutions^{6,7,8,9,10,11}

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

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

Calculating the pH of a Buffer^{12,13,14,15}

- The pH of the buffer is related to K_a and to the relative concentrations of the acid and base.
- We can derive an equation that shows the relationship between conjugate acid-base concentrations, pH and K_a .
- By definition:

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

- Rearranging, we get:

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

- If we take the negative natural logarithm of each side of the equation, we get:

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

- By definition:

$$\text{pH} = \text{p}K_a - \log \frac{[\text{HX}]}{[\text{X}^-]}$$

⁶ “A Good Idea Leads to a Better Buffer” from Further Readings

⁷ “Phosphate Buffers and Telephone Poles—A Useful Analogy with Limitations” from Further Readings

⁸ “Buffering Action and Capacity” from Live Demonstrations

⁹ “Buffering Action of Alka-Seltzer” from Live Demonstrations

¹⁰ Figure 17.2 from Transparency Pack

¹¹ “Equilibrium: The Dissociation of Acetic Acid” from Live Demonstrations

¹² “The Henderson-Hasselbalch Equation: Its History and Limitations” from Further Readings

¹³ “Calculating pH Using Henderson-Hasselbalch Equation” Activity from Instructor’s Resource CD/DVD

¹⁴ “One-Hundred Years of pH” from Further Readings

¹⁵ “Buffer pH” Activity from Instructor’s Resource CD/DVD

- An alternate form of this equation is:

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

- 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 the 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.

Buffer Capacity and pH Range¹⁶

- **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.
- The **pH range** of a buffer is the pH range over which it is an effective buffer.
 - The pH range of a buffer is generally within one pH unit of the $\text{p}K_a$ of the buffering agent.

Addition of Strong Acids or Bases to Buffers^{17,18,19}

- Keep in mind that reactions between strong acids and weak bases proceed essentially to completion.
- The same is true for reactions between strong bases and weak acids.
 - If we do not exceed the buffering capacity of the buffer, then the added strong acid or base is completely consumed by reaction with the buffer.
- We can break the calculation into two parts.
 - A *stoichiometric* calculation.
 - The addition of a strong acid or base results in a neutralization reaction:

$$\text{X}^- + \text{H}_3\text{O}^+ \rightarrow \text{HX} + \text{H}_2\text{O}$$

$$\text{HX} + \text{OH}^- \rightarrow \text{X}^- + \text{H}_2\text{O}$$
 - By knowing how much H_3O^+ or OH^- was added, we know how much HX or X^- was formed.
 - An *equilibrium* calculation.
 - With the concentrations of HX and X^- (taking into account the change in volume of the solution) we can calculate the pH from the Henderson-Hasselbalch equation:

17.3 Acid-Base Titrations^{20,21}

- In an acid-base titration:
 - a solution of base of known concentration is added to an acid (or an acid of known concentration is added to a base).
 - acid-base indicators, or pH meters, are used to signal the equivalence point.
 - The *equivalence point* is the point at which stoichiometrically equivalent quantities of acid and base have been added.
 - The plot of pH versus volume during a titration is called a **pH titration curve**.

¹⁶ “Determination of the Neutralizing Capacity of Antacids” from Live Demonstrations

¹⁷ “Buffer pH Calculation” Activity from Instructor’s Resource CD/DVD

¹⁸ Figure 17.3 from Transparency Pack

¹⁹ “Blood-Chemistry Tutorials: Teaching Biological Applications of General Chemistry Material” from Further Readings

²⁰ “Acid-Base Titration” Animation from Instructor’s Resource CD/DVD

²¹ “Hydroxide Ion” 3-D Model from Instructor’s Resource CD/DVD

Strong Acid–Strong Base Titrations^{22,23,24,25,26,27}

- 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.
 - The cation of a strong base and the anion of a strong acid do not undergo hydrolysis.
 - Therefore, $\text{pH} = 7.00$.
 - 4. *After the equivalence point*.
 - The pH is determined by the excess base in the solution.
 - Therefore, $\text{pH} > 7$.
- 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^{28,29,30,31}

- Consider the titration of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, with 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:

$$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{OH}^-(aq) \rightarrow \text{C}_2\text{H}_3\text{O}_2^-(aq) + \text{H}_2\text{O}(l)$$
 - 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.

²² “Acid-Base Indicators: A New Look at an Old Topic” from Further Readings²³ “Teas as Natural Indicators” from Live Demonstrations²⁴ “Acid-Base Titration” Activity from Instructor’s Resource CD/DVD²⁵ “Edible Acid-Base Indicators” from Further Readings²⁶ “Predicting Acid-Base Titration Curves without Calculations” from Further Readings²⁷ Figure 17.7 from Transparency Pack²⁸ Figure 17.8 from Transparency Pack²⁹ “Titration Calculation” Activity from Instructor’s Resource CD/DVD³⁰ Figure 17.10 from Transparency Pack³¹ Figure 17.11 from Transparency Pack

- 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 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 is NOT equal to 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 steeper than in the strong acid-strong base case.
 - However, then there is a leveling off due to buffer effects.
 - The middle section of the titration curve 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 due to the formation of a neutral salt.
 - The pH is > 7.00 for the weak acid-strong base equivalence point due to the formation of a basic salt.

Titration of Polyprotic Acids^{32,33}

- 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 H_3PO_4 with NaOH there are three equivalence points:
 - one for the formation of H_2PO_4^- ,
 - one for the formation of HPO_4^{2-} , and
 - one for the formation of PO_4^{3-} .

Titration with an Acid-Base Indicator³⁴

- How can we analyze the titration (i.e., how will we know when we are at the equivalence point)?
 - We often use a pH indicator.
 - The indicator chosen should begin and end its color change anywhere on the rapid-rise portion of the titration curve.
 - The *end point* in a titration is the point where the indicator changes color.
 - It represents a close approximation of the equivalence point.
 - Consider adding a strong base (e.g., NaOH) to a solution of a strong acid (e.g., HCl).
 - We know the pH at the equivalence point is 7.00.

³² Figure 17.12 from Transparency Pack

³³ “Phosphorous Acid” 3-D Model from Instructor’s Resource CD/DVD

³⁴ Figure 17.15 from Transparency Pack

- The pH changes rapidly only over the pH range from about pH 11 to 3.
- To detect the equivalence point, we use an indicator that changes color somewhere close to the pH at the equivalence point.
- Usually, we use phenolphthalein, which changes color between pH 8.3 and 10.0.
 - Methyl red is a poor choice as it changes color between pH 4.2 and 6.0, before the equivalence point is reached.
- In acid, phenolphthalein is colorless.
- As NaOH is added, there is a slight pink color at the addition point.
- When the flask is swirled and the reagents mixed, the pink color disappears.
- At the end point, the solution is light pink.
- If more base is added, the solution turns darker pink.
- The equivalence point in a titration is the point at which the acid and base are present in stoichiometrically equivalent quantities.
- Consider adding a strong acid (e.g., HCl) to a solution of a weak base (e.g., NH₃).
 - We know the pH at the equivalence point is 5.28.
 - Here methyl red is a good choice while phenolphthalein would be a poor choice for indicator.

FORWARD REFERENCES

- Redox titrations will be briefly mentioned in Chapter 20 (section 20.2).
- Oxyacids of phosphorus will be discussed in more detail in Chapter 22 (section 22.8).

17.4 Solubility Equilibria^{35,36,37}

The Solubility-Product Constant, K_{sp} ^{38,39,40,41,42,43}

- Consider a saturated solution of BaSO₄ in contact with solid BaSO₄.
 - We can write an equilibrium expression for the dissolving of the slightly soluble solid.

$$\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$$
 - Because BaSO₄(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 BaSO₄ is:

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$
- 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} ⁴⁴

- *Solubility* is the amount of substance that dissolves to form a saturated solution.
 - This is often expressed as *grams of solute* that will dissolve *per liter of solution*.
- *Molar solubility* is the *number of moles of solute* that dissolve to form a *liter of saturated solution*.

³⁵ “Solubility of Some Silver Compounds” from Live Demonstrations

³⁶ “Red and White Precipitates in Sodium Silicate” from Live Demonstrations

³⁷ “The Murky Pool” from Further Readings

³⁸ “The K_{sp} -Solubility Conundrum” from Further Readings

³⁹ “Silver Ion Solubilities: Red and White Precipitates” from Live Demonstrations

⁴⁰ “The Useless Tea Kettle” from Further Readings

⁴¹ “Assessing Students’ Conceptual Understanding of Solubility Equilibrium” from Further Readings

⁴² “Solubility Product Constant” Activity from Instructor’s Resource CD/DVD

⁴³ “What Should We Teach Beginners about Solubility and Solubility Products?” from Further Readings

⁴⁴ Figure 17.16 from Transparency Pack

- We can use the solubility to find K_{sp} and vice versa.
 - To convert solubility to K_{sp} :
 - Convert solubility into molar solubility (via molar mass).
 - Convert molar solubility into the molar concentration of ions at equilibrium (equilibrium calculation).
 - Use the equilibrium concentration of ions in the K_{sp} expression.
 - To convert K_{sp} to solubility:
 - Write the K_{sp} expression.
 - Let x = the molar solubility of the salt.
 - Use the stoichiometry of the reaction to express the concentration of each species in terms of x .
 - Substitute these concentrations into the equilibrium expression and solve for x .
 - This calculation works best for salts whose ions have low charges.

FORWARD REFERENCES

- The role of acid-base and solubility reactions in tying the ocean to the atmosphere and the global climate will be discussed in Chapter 18 (sections 18.3 and 18.4).
- Water softening to remove hardness ions will be discussed in Chapter 18 (section 18.4).
- Calculations involving K_{sp} versus ΔG_{rxn}° will be performed in Chapter 19 (section 19.7).

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, and
 - The presence of complexing agents.
 - Amphoterism* is related to the effects of both pH and complexing agents.

Common-Ion Effect

- The solubility of a slightly soluble salt is decreased when a common ion is added.
 - This is an application of Le Châtelier's principle.
- Consider the solubility of CaF_2 :

$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^{-}(aq)$$
 - If more F^{-} is added (i.e., by the addition of NaF), the equilibrium shifts to the left to offset the increase.
 - Therefore, $\text{CaF}_2(s)$ is formed and precipitation occurs.
 - As NaF is added to the system, the solubility of CaF_2 decreases.
- In general, the solubility of a slightly soluble salt is decreased by the presence of a second salt that produces a common ion.

Solubility and pH^{45,46,47}

- Again, we apply Le Châtelier's principle:

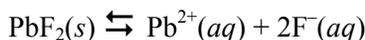
$$\text{Mg}(\text{OH})_2(s) \rightleftharpoons \text{Mg}^{2+}(aq) + 2\text{OH}^{-}(aq)$$
 - If OH^{-} is removed, then the equilibrium shifts toward the right and $\text{Mg}(\text{OH})_2$ dissolves.
 - OH^{-} can be removed by adding a strong acid:

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

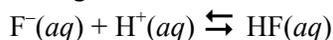
⁴⁵ "Dissolution of $\text{Mg}(\text{OH})_2$ by Acid" Animation from Instructor's Resource CD/DVD

⁴⁶ "Fizzing and Foaming: Reactions of Acids with Carbonates" from Live Demonstrations

⁴⁷ "Milk of Magnesia versus Acid" from Live Demonstrations



- If the F^{-} is removed, then the equilibrium shifts towards the right and PbF_2 dissolves.
- F^{-} can be removed by adding a strong acid:

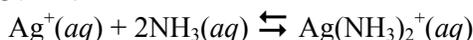


- As pH decreases, $[\text{H}^{+}]$ increases and solubility of PbF_2 increases.
- The effect of pH on solubility can be dramatic.
- The effect is most significant if one or both ions involved are at least somewhat acidic or basic.
- In general:
 - The solubility of slightly soluble salts containing basic ions increases as pH decreases.
 - The more basic the anion is, the greater the effect.

Formation of Complex Ions^{48,49,50,51,52,53,54,55,56}

- 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.
 - For example, AgCl has a very low solubility.
 - K_{sp} for $\text{AgCl} = 1.8 \times 10^{-10}$
 - However, the solubility is greatly increased if ammonia is added.
 - Why?

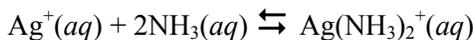
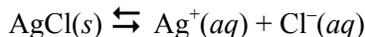
- Consider the formation of $\text{Ag}(\text{NH}_3)_2^{+}$:



- The $\text{Ag}(\text{NH}_3)_2^{+}$ is called a **complex ion**.
- NH_3 (the attached Lewis base) is called a *ligand*.
- The equilibrium constant for the reaction is called the **formation constant**, K_{f} :

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

- Consider the addition of ammonia to AgCl (white salt):



- The overall reaction is:



- Effectively, the $\text{Ag}^{+}(aq)$ has been removed from solution.
- By Le Châtelier's principle, the forward reaction (the dissolving of AgCl) is favored.

⁴⁸ "Chemical Aspects of Dentistry" from Further Readings

⁴⁹ "Dentifrice Fluoride" from Further Readings

⁵⁰ "Fluorine Compounds and Dental Health: Applications of General Chemistry Topics" from Further Readings

⁵¹ "Colorful Complex Ions in Ammonia" from Live Demonstrations

⁵² "Green and Blue Copper Complexes" from Live Demonstrations

⁵³ "Complexometric Titrations: Competition of Complexing Agents in the Determination of Water Hardness with EDTA" from Further Readings

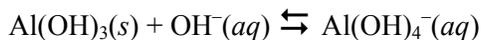
⁵⁴ "Ammonia" 3-D Model from Instructor's Resource CD/DVD

⁵⁵ "Diamminsilver Cation" 3-D Model from Instructor's Resource CD/DVD

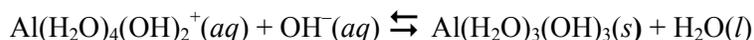
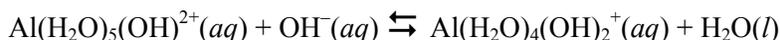
⁵⁶ "Hydrated Aluminum Cation" 3-D Model from Instructor's Resource CD/DVD

Amphoterism^{57,58,59}

- Substances that are capable of acting either as an acid or a base are **amphoteric**.
 - The term is similar to one discussed earlier: *amphiprotic*, which relates more generally to any species that can either gain or lose a proton.
- **Amphoteric metal oxides and hydroxides** will dissolve in either a strong acid or a strong base.
 - Examples are hydroxides and oxides of Al^{3+} , Cr^{3+} , Zn^{2+} , and Sn^{2+} .
 - The hydroxides generally form complex ions with several hydroxide ligands attached to the metal:



- Hydrated metal ions act as weak acids.
 - As strong base is added, protons are removed:



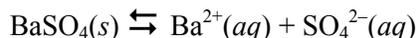
- The addition of an acid reverses these reactions.

FORWARD REFERENCES

- Chelating agents will be further mentioned in Chapters 23 (section 23.3, respectively).
- Amphoteric oxides of transition metals will be mentioned in Chapter 22 (section 22.5).
- The formation of stable cyanide complexes with transition metals will be brought up in Chapter 22 (section 22.10).
- Chemistry of coordination compounds, including hemoglobin and chlorophyll, will be discussed detail throughout Chapter 23.

17.6 Precipitation and Separation of Ions

- Consider the following:



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

Selective Precipitation of Ions⁶⁰

- Ions can be separated from each other based on the solubilities of their salts.
 - Example: If HCl is added to a solution containing Ag^+ and Cu^{2+} , the silver precipitates (K_{sp} for AgCl is 1.8×10^{-10}) while the Cu^{2+} remains in solution.
 - Removal of one metal ion from a solution is called *selective precipitation*.
- The sulfide ion is often used to separate metal ions.
 - Example: Consider a mixture of $\text{Zn}^{2+}(aq)$ and $\text{Cu}^{2+}(aq)$.
 - CuS ($K_{\text{sp}} = 6 \times 10^{-37}$) is less soluble than ZnS ($K_{\text{sp}} = 2 \times 10^{-25}$).
 - Thus, CuS will be removed from solution before ZnS .
 - As H_2S is bubbled through the acidified green solution, black CuS forms.
 - When the precipitate is removed, a colorless solution containing $\text{Zn}^{2+}(aq)$ remains.

⁵⁷ “Precipitation Reactions” Movie from Instructor’s Resource CD/DVD

⁵⁸ “Acid-Base Chemistry of the Aluminum Ion in Aqueous Solution” from Further Readings

⁵⁹ “Acidic and Basic Properties of Oxides” from Live Demonstrations

⁶⁰ “Selective Precipitation of Ions” Activity from Instructor’s Resource CD/DVD

- When more H_2S is added to the solution, a second precipitate of white ZnS forms.

17.7 Qualitative Analysis for Metallic Elements^{61,62,63,64,65}

- **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. separation of individual ions within each group by selectively dissolving members of the group.
 3. specific tests to determine whether a particular ion is present or absent.

⁶¹ “Major Sources of Difficulty in Students’ Understanding of Basic Inorganic Qualitative Analysis” from Further Readings

⁶² Figure 17.23 from Transparency Pack

⁶³ “Qualitative Analysis” Activity from Instructor’s Resource CD/DVD

⁶⁴ “Swimming Pools, Hot Rods, and Qualitative Analysis” from Further Readings

⁶⁵ “Flame Tests for Metals” Movie from Instructor’s Resource CD/DVD

Further Readings:

1. Charles L. Bering, "A Good Idea Leads to a Better Buffer," *J. Chem. Educ.*, Vol. 64, **1987**, 803–805.
2. Edwin S. Gould, "Phosphate Buffers and Telephone Poles—A Useful Analogy with Limitations," *J. Chem. Educ.*, Vol. 76, **1999**, 1511.
3. Henry N. Po and N. M. Senozan, "The Henderson-Hasselbalch Equation: Its History and Limitations," *J. Chem. Educ.*, Vol. 78, **2001**, 1499–1503.
4. Rollie J. Myers, "One-Hundred Years of pH," *J. Chem. Educ.*, Vol. 87, **2010**, 30–32.
5. Rachel E. Casidey, Dewey Holten, Richard Krathen, and Regina F. Frey, "Blood-Chemistry Tutorials: Teaching Biological Applications of General Chemistry Material," *J. Chem. Educ.*, Vol. 78, **2001**, 1210–1214. The relationship between oxygen transport, iron transport, blood buffering, kidney dialysis, and general topics is discussed.
6. Ara S. Kooser, Judith L. Jenkins, and Lawrence E. Welch, "Acid-Base Indicators: A New Look at an Old Topic," *J. Chem. Educ.*, Vol. 78, **2001**, 1504–1506.
7. Robert C. Mebane and Thomas R. Rybolt, "Edible Acid-Base Indicators," *J. Chem. Educ.*, Vol. 62, **1985**, 285.
8. Dennis Barnum, "Predicting Acid-Base Titration Curves without Calculations," *J. Chem. Educ.*, Vol. 76, **1999**, 938–942.
9. Robert Perkins, "The Useless Tea Kettle," *J. Chem. Educ.*, Vol. 61, **1984**, 383.
10. Roy W. Clark and Judith M. Bonicamp, "The K_{sp} -Solubility Conundrum," *J. Chem. Educ.*, Vol. 75, **1998**, 1182–1185.
11. Robert Perkins, "The Murky Pool," *J. Chem. Educ.*, Vol. 61, **1984**, 383–384.
12. Andres Raviolo, "Assessing Students' Conceptual Understanding of Solubility Equilibrium," *J. Chem. Educ.*, Vol. 78, **2001**, 629–631.
13. Stephen J. Hawkes, "What Should We Teach Beginners about Solubility and Solubility Products?" *J. Chem. Educ.*, Vol. 75, **1998**, 1179–1181.
14. Murry Helfman, "Chemical Aspects of Dentistry," *J. Chem. Educ.*, Vol. 59, **1982**, 666–668.
15. Philip E. Rakita, "Dentifrice Fluoride," *J. Chem. Educ.*, Vol. 81, **2004**, 677–680.
16. Gabriel Pinto, "Fluorine Compounds and Dental Health: Applications of General Chemistry Topics," *J. Chem. Educ.*, Vol. 86, **2009**, 185–187.
17. Edward Koubek, Cole McWherter, and George L. Gilbert, "Acid-Base Chemistry of the Aluminum Ion in Aqueous Solution," *J. Chem. Educ.*, Vol. 75, **1998**, 60.

18. Kim Chwee, Daniel Tan, Ngoh Khang Goh, Lian Sai Chai, and David F. Teagust, "Major Sources of Difficulty in Students' Understanding of Basic Inorganic Qualitative Analysis," *J. Chem. Educ.*, Vol. 81, **2004**, 725–732.
19. M. Cecilia Yappert and Donald B. DuPre, "Complexometric Titrations: Competition of Complexing Agents in the Determination of Water Hardness with EDTA," *J. Chem. Educ.*, Vol. 74, **1997**, 1422–1423.
20. Dale D. Clyde, "Swimming Pools, Hot Rods, and Qualitative Analysis," *J. Chem. Educ.*, Vol. 65, **1988**, 911–913.

Live Demonstrations:

1. Lee. R. Summerlin, and James. L. Ealy, Jr., "The Common Ion Effect: Second Demonstration," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 1* (Washington: American Chemical Society, **1988**), pp. 93–94. The reaction of calcium carbonate and acetic acid is used to demonstrate the common ion effect.
2. Bassam Z. Shakhashiri, "Effect of Acetate Ion on the Acidity of Acetic Acid: The Common Ion Effect," *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 3* (Madison: The University of Wisconsin Press, **1989**), pp. 155–157.
3. Lee. R. Summerlin, and James. L. Ealy, Jr., "The Common Ion-Effect: Ammonium Hydroxide and Ammonium Acetate," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 1* (Washington: American Chemical Society, **1988**), p. 95.
4. Bassam Z. Shakhashiri, "Buffering Action and Capacity," *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 3* (Madison: The University of Wisconsin Press, **1989**), pp. 173–185.
5. Bassam Z. Shakhashiri, "Buffering Action of Alka-Seltzer," *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 3* (Madison: The University of Wisconsin Press, **1989**), pp. 186–187.
6. Lee. R. Summerlin, Christie L. Borgford, and Julie B. Ealy, "Equilibrium: The Dissociation of Acetic Acid," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society, **1988**), pp.160–161. Changes in indicator color upon addition of base or acetate to acetic acid are explored.
7. Bassam Z. Shakhashiri, "Determination of Neutralizing Capacity of Antacids," *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 3* (Madison: The University of Wisconsin Press, **1989**), pp. 162–166.
8. Dianne N. Epp, "Teas as Natural Indicators," *J. Chem. Educ.*, Vol. 70, **1993**, 326. The use of teas as natural acid-base indicators is demonstrated.
9. Lee. R. Summerlin, Christie L. Borgford, and Julie B. Ealy, "Solubility of Some Silver Compounds," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society, **1988**), pp. 83–85. The solubility of a series of silver salts and complexes is explored in this colorful demonstration.

10. Lee R. Summerlin, Christie L. Borgford, and Julie B. Ealy, "Silver Ion Solubilities: Red and White Precipitates," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society, **1988**), pp. 124–125. This is an effective introduction to equilibrium; the relative solubilities of silver chromate and silver chloride are investigated.
11. Bassam Z. Shakhshiri, "Fizzing and Foaming: Reactions of Acids with Carbonates," *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 3* (Madison: The University of Wisconsin Press, **1989**), pp. 96–99.
12. Lee. R. Summerlin, Christie L. Borgford, and Julie B. Ealy, "Milk of Magnesia versus Acid," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society, **1988**), p. 173. An antacid, milk of magnesia, is mixed with acid in this demonstration.
13. Lee. R. Summerlin, Christie L. Borgford, and Julie B. Ealy, "Colorful Complex Ions in Ammonia," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society, **1988**), pp. 75–76. Ammine complexes of copper and cobalt are prepared in this demonstration.
14. Lee. R. Summerlin, Christie L. Borgford, and Julie B. Ealy, "Green and Blue Copper Complexes," *Chemical Demonstrations, A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society, **1988**), pp.71–72. Three copper complexes are prepared in this demonstration.
15. Bassam Z. Shakhshiri, "Acidic and Basic Properties of Oxides," *Chemical Demonstrations: A Handbook for Teachers of Chemistry, Volume 3* (Madison: The University of Wisconsin Press, **1989**), pp. 109–113.
16. Lee R. Summerlin, Christie L. Borgford, and Julie B. Ealy, "Red and White Precipitates in Sodium Silicate," *Chemical Demonstrations: A Sourcebook for Teachers, Volume 2* (Washington: American Chemical Society **1988**), p. 131.