Chapter 17: Additional Aspects of Aqueous Equilibria

Problems: 1-58, 61-70

17.1 THE COMMON ION EFFECT

common-ion effect: The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances

Le Chatelier's Principle

– If a system at equilibrium is disturbed by a change in concentration, pressure, or temperature, the system will shift to partially counteract the change.

How does this apply to acid-base equilibrium systems?

– Addition of the conjugate base or the conjugate acid of a dissolved substance will change the concentration of the dissolved substance.

Example: For each of the following descriptions, write the relevant acid-base equilibrium equation, and predict if pH increases or decreases with each change:

a. A 0.5 M $NaC_2H_3O_2$ solution is added to a 0.5 M $HC_2H_3O_2$ solution

b. A 0.5 M KF solution is added to a 0.5 M KF solution

c. A 0.5 M NH_4Cl solution is added to a 0.5 M NH_3 solution

Example: a. Calculate the pH of a 0.25 M $HC_2H_3O_2$ (K_a=1.8 x 10^{-5}) solution.

b. Calculate the pH of a solution that's 0.25 M $HC_2H_3O_2$ (K_a=1.8 x 10^{-5}) and 0.25 M $NaC_2H_3O_2$.

17.2 BUFFERED SOLUTIONS

Buffered solutions (or **buffers**) resist changes in pH when small amounts of either acids (H^+) or bases (OH^-) are added

Composition and Action of Buffered Solutions

Types of buffers:

- a weak acid and its conjugate base (e.g. HF and F^-)
- a weak base and its conjugate acid (e.g. NH_3 and NH_4^+)

Example of a buffer:

- Human blood can absorb acids and bases produced by biological reactions without a change in pH

Buffer Capacity and pH

- the amount of acid or base a buffer can neutralize before the pH begins to change appreciably

Determination of [H+] and pH in a Buffer System

For the following general reaction: $\mathbf{HX\,(aq) \rightleftharpoons H^+\,(aq) + X^-\,(aq)}$

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

so we can solve for $[H^+]$ using $\mathbf{[H^+] = K_a \times \frac{[HX]}{[X^-]}}$ and $\mathbf{pH = -\log [H^+]}$

Combining the last two equations:

$$\mathbf{pH = -\log [H^+] = -\log\left(K_a \frac{[HX]}{[X^-]}\right) = -\log K_a - \log\frac{[HX]}{[X^-]}}$$

Since $\mathbf{pK_a = -\log K_a}$, we can take the inverse of the second term and change the sign to + instead of –. This gives the **Henderson-Hasselbach** equation for finding the pH of any buffer:

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

Example: A buffer solution contain 0.50 M $HC_2H_3O_2$ (K_a=1.8 x 10^{-5}) and 0.50 M $NaC_2H_3O_2$. Calculate the pH of the solution.

1. First, write the equilibrium expression for $HC_2H_3O_2$.

2. Set up your equilibrium table.

3. Solve for pH.

Thus, for buffers where **$[HX] \approx [X^-]$** ⇒ **$[H^+] \approx K_a$** ⇒ **$pH \approx pK_a$**.

Addition of Strong Acids (H^+) and Bases (OH^-) to Buffers

– The pH of a buffer changes only slightly when moderate amounts of a strong acid or a strong base are added
  - All **H^+** ions react with **X^-** to form **HX**: $H^+ (aq) + X^- (aq) \Rightarrow HX (aq)$
  - All **OH^-** ions react with **HX** to form **X^-**: $OH^- (aq) + HX (aq) \Rightarrow X^- (aq)$

Example: Calculate the change in pH that occurs when 0.010 mol of NaOH is added to a 1.0 L buffer containing 0.50 M $HC_2H_3O_2$ (K_a=1.8 x 10^{-5}) and 0.50 M $NaC_2H_3O_2$. (Use the original pH calculated in the previous problem.)

1. First, solve the stoichiometry problem.
   - Since the NaOH completely dissociates, all the resulting OH^- completely reacts with $HC_2H_3O_2$.
   - Use this information to find initial concentrations.

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

mol before reaction

Δ in # mol

mol after reaction

2. Next, solve the equilibrium problem.
   - Set up the equilibrium table.
   - Solve for pH.
   - Indicate the change in pH for the original buffer.

Example: Compare the pH change for the previous problem with the change in pH that occurs when 0.010 mol of solid NaOH is added to 1.0 L of water.

Note how well a buffer resists a pH change much better than an unbuffered solution or a pure solvent.

Choosing a Buffer System

- Buffers are **most effective when [HX] ≈ [X⁻]**, for which **pH ≈ pK_a**.
  - If we want to maintain a buffer that maintains a given pH, choose a weak acid that has a pK_a closest to that pH and prepare a buffer using that weak acid and its conjugate base.

Example: A scientist wants to prepare a solution buffered at pH=4.30 using one of the following acids. Which would be the best choice?

a. chloroacetic acid (K_a=1.35 x 10^{-3})
b. propanoic acid (K_a=1.3 x 10^{-5})
c. benzoic acid (K_a=6.4 x10^{-5})
d. hypochlorous acid (K_a=3.5 x 10^{-8})

Explain how you would prepare a buffer solution.

Acid-Base Indicators

– Weak acid and its conjugate base that exhibit different colors

An acid-base indicator is derivated from a weak acid, HIn (aq):

$$\text{HIn (aq)} \rightleftharpoons \text{H}^{+}\text{ (aq)} + \text{In}^{-}\text{ (aq)}$$

$$\text{where} \qquad K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$$

The color observed for the indicator depends on the ratio: $\frac{[\text{HIn}]}{[\text{In}^-]}$

Three distinct cases exist:

1. If $\frac{[\text{HIn}]}{[\text{In}^-]} \geq 10$ Mostly HIn exists, so you see the "acid" color.
2. If $\frac{[\text{HIn}]}{[\text{In}^-]} \leq 0.1$ Mostly In^- exists, so you see the "base" color.
3. If $\frac{[\text{HIn}]}{[\text{In}^-]} \approx 1$ The color is between the "acid" and "base" colors.

– In the titration of an acid with a base (i.e. starting at a low pH), we assume the ***color change*** becomes apparent at a ***1 pH unit below the pK$_a$*** of the acid.

– In the titration of a base with an acid (i.e. starting at a high pH), we assume the ***color change*** becomes apparent at a ***1 pH unit above the pK$_a$*** of the acid.

Example: Bromthymol blue (K_a=1.0 x 10^{-7}) is yellow in its HIn form and blue in its In^- form. Suppose we put a few drops of this indicator in a strongly acidic solution. If the solution is then titrated with NaOH, at what pH will the indicator change color?

We consider the range of indicators to be limited: **pH range = pK_a of HIn ± 1**

Ex. 1: What is the useful pH range for bromthymol blue (K_a=1.0 x 10^{-7})?

Ex. 2: What is the useful pH range for phenolphthalein (K_a=1.0 x 10^{-9})?

Ex. 3: What is the useful pH range for methyl red (K_a=1.0 x 10^{-5})?

These indicators are useful for monitoring acid-base titrations with the following endpoints:

Indicator	pH at End Point
Methyl red	5
Bromthymol blue	7
Phenolphthalein	9

17.3 Acid-Base Titrations

In an acid-base titration, the **equivalence point** is when the reaction between the acid and base are complete—i.e. when equal amounts of H^+ and OH^- are present.

The indicator is used to monitor the reaction. Since the **endpoint** is when the indicator changes color, ***ideally the endpoint should correspond to the equivalence point***.

Strong Acid-Strong Base Titrations

- The net ionic equation for a strong acid reacting with a strong base is given as:

$$H^+ (aq) + OH^- (aq) \Rightarrow H_2O (l) \qquad K=1.0 \times 10^{14}$$

- One can monitor the progress of an acid-base titration by plotting the pH of the solution being analyzed as a function of the amount of titrant added.
  - This plot is called a **pH titration curve**.

Consider the pH curve for the titration of HCl with NaOH (Fig 17.6, p. 653)

- With less than a drop, the pH can jump from about 3.6 to about 10
  - ⇒ This means any indicator within that range will be suitable for monitoring an acid-base titration between a strong acid and a strong base
    - ⇒ Why we can use phenolphthalein, bromthymol blue, methyl red, etc.
  - ⇒ Also, we can get the pH at the equivalence point (when an equal amount of acid or base has been added)
    - For ***titrations between strong acids and strong bases***, ***pH=7*** at the ***equivalence point*****.**

Example: A 25.00 mL sample of 1.00 M HCl is titrated with 1.00 M NaOH

a. Write the chemical equation for the reaction between HCl (aq) and NaOH (aq).

b. Determine the excess HCl present (in mL) when 24.49 mL of NaOH has been added, then calculate the pH of the solution when 24.49 mL of NaOH has been added.

c. Determine the excess NaOH present (in mL) when 25.01 mL of NaOH has been added, then calculate the pH of the solution when 25.01 mL of NaOH has been added.

Weak Acid-Strong Base Titrations

- When dealing with a weak acid, the weak acid dissociation equilibrium will complicate calculations of pH—i.e. because the acid does not completely dissociate like a strong acid, the pH calculation is not as straightforward.

  Consider the pH curve for the titration of acetic acid, $HC_2H_3O_2$, with NaOH (Fig. 17.9, p. 655)

  - Neutralization of the $HC_2H_3O_2$ with NaOH produces $C_2H_3O_2^-$, which acts as a weak base
    - In the region centered at the halfway point of the titration, the solution contains equal amounts of the weak acid ($HC_2H_3O_2$) and conjugate base ($C_2H_3O_2^-$), which act as a buffer. In this region, the pH changes slowly.

Example: a. Write the chemical equation for the reaction between acetic acid and sodium hydroxide:

b. Write the expression for K_a:

c. Recognize that when **$[HC_2H_3O_2] = [C_2H_3O_2^-]$** (which occurs half-way to the equivalence point)**, $[H^+] = K_a$, so pH = p K_a.**

Thus, ***at the halfway point of the titration*** when $[HC_2H_3O_2] = [C_2H_3O_2^-]$, **pH = p$K_a$.**

- Again, the equivalence point is when equal amount of acid or base is added.
  - At the equivalence point, the presence of $C_2H_3O_2^-$ (a weak base)makes the **pH>7**
  - ⇒ For this reaction, only phenolphthalein is a suitable indicator. Methyl red changes color before the equivalence point.
    - ⇒ **In the titration of a weak acid with a strong base, the pH at the equivalence point will be greater than 7.**

Example: 25.00 mL of 1.00 M $HC_2H_3O_2$ (K_a=1.8×10^{-5}) is titrated with 1.00 M NaOH

a. Calculate the pH of the solution before NaOH has been added.

b. Calculate the pH of the solution when 12.50 mL of NaOH has been added. This is halfway to the equivalence point, so equal amounts of the weak acid ($HC_2H_3O_2$) and conjugate base ($C_2H_3O_2^-$) exist, and system acts like a buffer. Solve for pH using pK_a of $HC_2H_3O_2$.

c. Calculate the pH of the solution when 25.00 mL of NaOH has been added.

This is the equivalence point. All of the $HC_2H_3O_2$ has been converted to $C_2H_3O_2^-$, but the volume of the solution has doubled (from the NaOH), so the concentration of $C_2H_3O_2^-$ must be half the original $[HC_2H_3O_2]$.

Set up your equilibrium table, then solve for the pH.

Strong Acid-Weak Base

- Because the titration of a weak base results in the formation of a weak acid, the pH calculation is not as straightforward.

  Consider the pH curve for the titration of NH_3 with HCl (Fig. 14.8, p. 414)
  - Again, the equivalence point is when equal amount of acid or base is added.
    - ⇒ For this reaction, only methyl red is a suitable indicator. Bromthymol blue and phenolphthalein change color too early.
  - In the region centered at the halfway point of the titration, the solution contains equal amounts of the weak base (NH_3) and conjugate acid (NH_4^+), which act as a buffer. In this region, the pH changes slowly.
    - ⇒ **Also, remember when $[NH_3] = [NH_4^+]$, $pH = pK_a$.**
    - Neutralization of the NH_3 with HCl produces NH_4^+, which acts as a weak acid, lowering the pH, so **pH<7**
      - ⇒ **In the titration of a weak base with a strong base, the pH at the equivalence point will be less than 7.**

Titrations of Polyprotic Acids

- Some weak acids are polyprotic—i.e. they have more than one ionizable H atom.

In the titration of a polyprotic weak acid, the protons are titrated in succession.

- The titration curve shows two equivalence points (see Fig. 17.13 on p. 659) and the pK_{a1} and pK_{a2} can be determined experimentally from the equivalence points.
- The anion formed in one step is then ionized in the next step.
- With each successive step, the ionization constant becomes smaller, usually by several orders of magnitude.
  - Should be more difficult to remove a proton from a positively charged ion and even more difficult from a highly charged ion.

    ⇒ **For the polyprotic acid, H_2X: $[H_2X] >> [HX^-] >> [X^{2-}]$**

17.4 Solubility Equilibria

In CHM 151, we learned that two solution can mix to form a precipitate, depending on the Solubility Rules.

For example: $AgNO_3\,(aq) + NaCl\,(aq) \Rightarrow AgCl\,(s) + NaNO_3\,(aq)$

The net ionic equation is: $Ag^+\,(aq) + Cl^-\,(aq) \Rightarrow AgCl\,(s)$

For a saturated solution, the equilibrium is established between the solid and the ions in solution, and the solubility equilibrium can be expressed as:

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$$

The Solubility-Product Constant (K_{sp})

We can write the equilibrium expression for the dissolving of AgCl (s):

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

where **K_{sp}** is the **solubility-product constant** (or simply **solubility product**), which indicates the solubility of the product for a given temperature (usually at 25°C)

- the smaller the K_{sp}, the less soluble the compound
- Note: The equilibrium expression only contains the ions since solids are never included in the expression.

Example: Write the K_{sp} expressions for the following compounds:

a. $Cr(OH)_3$

b. Ag_2SO_4

c. $Ca_3(PO_4)_2$

K_{sp} and the Equilibrium Concentrations of Ions

Example: Solve for the solubility product (K_{sp}) given the concentration of one of the ions in solution.

a. A sample of $PbCl_2$ at equilibrium has a lead (II) ion concentration of 3.9×10^{-2} M. Calculate the solubility product for $PbCl_2$.

b. A sample of $Al(OH)_3$ at equilibrium has an aluminum ion concentration of 2.86×10^{-9} M. Calculate the solubility product for $Al(OH)_3$.

K_{sp} and Water Solubility

- Since water is often the solvent, solubility is also called water solubility

molar solubility: amount of solute in moles per liter of a saturated solution

solubility: amount of solute in grams per liter of a saturated solution (g/L)

Example: Calculate the molar solubility and the solubility (in g/L) of lead (II) iodide (K_{sp}=8.4 x 10^{-9}).

a. Write the solubility product for PbI_2.

b. Set up an equilibrium table.

c. Solve for the unknown, x, which gives the molar solubility (i.e. the amount of the solute that remains in solution).

d. Convert the molar solubility to solubility (in g/L).

17.6 Precipitation and Separation of Ions (Part 1)

Previously, we used the Solubility Rules to predicts which precipitates will form when two solutions are mixed.

- In general, the **Solubility Rules are only valid for ion concentrations greater than or equal to 0.1 M.**
  - For concentrations lower than 0.1 M, precipitates may not form even if they are listed as "insoluble" in the Solubility Rules

    ⇒ **K_{sp}'s can be used to predict precipitate formation regardless of ion concentration**

The ion product, Q, is taken at a given instant

- just like the reaction quotient, Q, for gases

Three cases exist:

$Q > K_{sp}$: The solution contains higher concentrations of ions than it can hold at equilibrium. The **solution is supersaturated**, so **precipitate forms** to reduce the concentration of ions until the ion product is equal to **K_{sp}**, and equilibrium is established.

$Q < K_{sp}$: The solution contains lower concentrations of ions than the solution can hold at equilibrium. The **solution is unsaturated**, so **no precipitate forms**; equilibrium cannot be established.

$Q = K_{sp}$: The solution contains exactly the right concentrations of ions that the solution can hold at equilibrium. **The solution is saturated** and is at the point of precipitation.

Example: In an experiment, 200.0 mL of 0.0040 M $BaCl_2$ are added to 600.0 mL of 0.0080 M K_2SO_4. Will a precipitate form? ($K_{sp} = 1.1 \times 10^{-10}$ for $BaSO_4$)

a. Solve for $[BaCl_2]$ and $[K_2SO_4]$ using the dilution equation ($M_1V_1=M_2V_2$).

b. Write the expression for P then solve for the numerical value for P. Finally, compare it with K_{sp}.

17.5 Factors that Affect Solubility

Common Ion Effect

- **Adding a common ion** (same cation or anion in the compound) **decreases the solubility of the compound**
  - Le Chatelier's principle applies, so the system shifts to consume added reactants or products
    - ⇒ Increasing the ion concentration causes a shift to the left to precipitate out excess ions until ion product is re-established.

Example: Calculate the molar solubility of AgCl (K_{sp}=1.8 x 10^{-10}) in a 6.5 x 10^{-3} M $AgNO_3$ solution.

a. Show the dissociation of $AgNO_3$.

b. Write the solubility product for AgCl.

c. Set up an equilibrium table.

d. Solve for the unknown, x, to get the molar solubility.

Dissolving Precipitates

We can dissolve some precipitates using strong acids and what we know about complex ions.

pH and Solubility

Strong Acids can be used to dissolve:

1. Insoluble metal hydroxides
2. Insoluble salts where the anion is a weak base

Metal Hydroxides

– Metal hydroxides react with H^+ ions to produce H_2O, leaving the metal ion in solution

Consider the reaction: $Zn(OH)_2\ (s) \rightleftharpoons Zn^{2+}\ (aq) + 2\ OH^-\ (aq)$

If we add HCl (aq), the resulting H^+ ions react with the OH^- because K_w=1.00 x 10^{14} for the formation of water: $H^+\ (aq) + OH^-\ (aq) \Rightarrow H_2O\ (l)$

Balancing and adding these two reactions together:

$$\begin{array}{lllll} 1. & Zn(OH)_2\ (s) & \rightleftharpoons & Zn^{2+}\ (aq) & + \ 2\ \cancel{OH^-}\ (aq) \\ 2. & 2\ H^+\ (aq) + 2\ \cancel{OH^-}\ (aq) & \Rightarrow & 2\ H_2O\ (l) & \\ \hline & Zn(OH)_2\ (s) + H^+\ (aq) & \rightleftharpoons & Zn^{2+}\ (aq) & + \ H_2O\ (l) \end{array}$$

Thus, adding a strong acid to a metal hydroxide increases the solubility of the metal hydroxide—i.e. causes it to dissolve in conditions where it normally wouldn't.

Anion is a Weak Base

–Formation of a weak acid from the anion allows metal ion to remain in solution

a. Adding a strong acid to a metal carbonate results in the formation of the weak acid, H_2CO_3 (aq):

$$ZnCO_3\,(s) + H^+\,(aq) \rightleftharpoons Zn^{2+}\,(aq) + H_2CO_3\,(aq)$$

b. Adding a strong acid to a metal sulfide results in the formation of the weak acid, H_2S (aq):

$$ZnS\,(s) + 2\,H^+\,(aq) \rightleftharpoons Zn^{2+}\,(aq) + H_2S\,(aq)$$

Example: Write a net ionic equation to explain why each of the following precipitates dissolves in a strong acid.

a. $Fe(OH)_3$

b. BaF_2

Thus, decreasing the pH (or adding H^+ ions) increases the solubility of metal hydroxides and weakly basic salts (whose anions are weak bases).

Formation of Complex Ions

– NH_3 and OH^- can be used to dissolves precipitates that containing cations that form stable complex ions with NH_3 or OH^-

For example, adding NH_3 to AgCl (s):

$$AgCl\,(s) + 2\,NH_3\,(aq) \rightleftharpoons Ag(NH_3)_2^+\,(aq) + Cl^-\,(aq)$$

Example: Using Table 17.1, identify the precipitates below which can be dissolved with either NH_3 or OH^-. Explain why.

a. AgCl

b. $Ca_3(PO_4)_2$

c. $Al(OH)_3$

d. $CuCrO_4$

17.6 Precipitation and Separation of Ions (part 2)

Selective Precipitation (or **Fractional Precipitation) of Ions**

– The removal of one type of ion from solution by precipitation while leaving other ions in solution.

To separate a mixture, we take the solubilities of each ion into account.

– For example, if we want to remove Ag^+ ions from a mixture containing both K^+ and Ag^+ ions, we can add NaCl (aq) since Ag^+ will react with Cl^- to form AgCl (s).

– We can also separate ions that are both insoluble since each precipitate has varying solubilities (different K_{sp}'s)

Example: $AgNO_3$ is slowly added to a solution that is 0.020 M Cl^- and 0.020 M Br^-.

a. Calculate the concentration of Ag^+ needed to initiate precipitation of AgBr (K_{sp}=5.0 x 10^{-13}).

b. Calculate the concentration of Ag^+ needed to initiate precipitation of AgCl (K_{sp}=1.8 x 10^{-10}).

c. What is the concentration of Br^- ions remaining in solution just before AgCl begins to precipitate? Use the [Ag^+] when AgCl is precipitating to get [Br^-].

d. What is the percentage of Br^- ions remaining in solution right before AgCl precipitates?

From this last calculation, we can see that most of the Br^- ions have already precipitated before AgCl precipitates. Thus, Br^- ions can be quantitatively separated from Cl^- ions by fractional precipitation.

17.7 Qualitative Analysis for Metallic Elements

- the determination of ions present in a solution

In general, about 20 ions cations can be analyzed readily in aqueous solution.

- Since an unknown solution can contain one or all twenty ions, a systematic analysis must be carried out to find out what ions are present.
  - During each step, some ions are precipitated out of solution while others remain dissolved. Between each step, the precipitate is separated from the solution using filtration.

General Steps:

1. Precipitate out some ions with HCl (aq).
2. Precipitate out some of the remaining ions in solution with H_2S (aq) at a pH=5.
3. Precipitate out some of the remaining ions in solution by adding NaOH (or another base) to raise the pH to 9.
4. Precipitate out some of the remaining ions by adding $(NH_4)_2HPO_4$ (aq).
5. The ions remaining in solution can be separated using flame tests, reaction with NaOH and litmus test

We divide these ions into 5 groups:

Group I: Ag^+, Hg_2^{2+}, Pb^{2+}

- When **HCl (aq)** is added, only these precipitate as insoluble chlorides; all others dissolve.
- To separate the three precipitates from each other:
  1. $PbCl_2$ is dissolved in hot water.
  2. AgCl can be dissolved with NH_3 to form $Ag(NH_3)_2^+$.

Group II: Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sn^{4+}, Sb^{3+}

- At a pH=5, only the very insoluble sulfides (i.e. with very low K_{sp}) will precipitate
- Those sulfides with higher solubilities with remain in solution.

Group III: Co^{2+}, Zn^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}

- At a pH=9, even the sulfides with higher solubilities will precipitate, some as insoluble hydroxides (e.g. **$Al(OH)_3$, $Fe(OH)_3$, $Cr(OH)_3$**)

Group IV: Mg^+, Ca^{2+}, Ba^{2+}, Sr^{2+}

- When **$(NH_4)_2HPO_4$ (aq)** is added, of the remaining ions, only these precipitate; all others dissolve.

Group V: Na^+, K^+, NH_4^+

- Flame tests are used to identify Na^+ (yellow flame) and K^+ (violet-blue flame)
- NaOH is added to NH_4^+ to produce NH_3—turns red litmus blue.