


**Chapter 15 -
Applications of
Aqueous Equilibria**



Red Blood Cells: Human blood is a buffer solution - the pH is maintained at a value very close to 7.4. We'll explore buffers in this chapter.

Neutralization Reactions

- Acids and bases react to neutralize each other, but these reactions don't always go to completion.
- Strong acid-strong base (always goes to completion)
 - $\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$
 - Write Molecular, Ionic, and Net Ionic equations.
 - What's in solution? What is the pH of the salt solution?
 - $K_a = 1 / [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{14}$

Neutralization Reactions

- Weak acid-strong base
 - Molecular: $\text{HF(aq)} + \text{KOH(aq)} \rightleftharpoons \text{KF(aq)} + \text{H}_2\text{O(l)}$
 - Reaction goes essentially to completion (~100%) because of strong base.
 - Ionic: $\text{HF(aq)} + \text{K}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightleftharpoons \text{K}^+(\text{aq}) + \text{F}^-(\text{aq}) + \text{H}_2\text{O(l)}$
 - Why does HF stay together???
 - Net Ionic: $\text{HF(aq)} + \text{OH}^-(\text{aq}) \rightleftharpoons \text{H}_2\text{O(l)} + \text{F}^-(\text{aq})$
 - What's in solution?
 - What is the pH of the salt produced?
 - What will the pH of the solution be, roughly?

Neutralization Reactions

- Strong acid-weak base
 - Molecular: $\text{HBr(aq)} + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4\text{Br(aq)}$
 - Reaction goes essentially to completion because of strong acid.
 - Ionic: $\text{H}^+(\text{aq}) + \text{Br}^-(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{Br}^-(\text{aq})$
 - Net Ionic: $\text{H}^+(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq})$
 - What's in solution?
 - What is the pH of the salt produced?
 - What will the pH of the solution be, roughly?

Neutralization Reactions

- Weak acid-weak base
 - Molecular: $\text{CH}_3\text{COOH(aq)} + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4\text{CH}_3\text{COO(aq)}$
 - Ionic: $\text{CH}_3\text{COOH(aq)} + \text{NH}_3(\text{aq}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{CH}_3\text{COO}^-(\text{aq})$
 - Net Ionic: None, nothing cancels!
 - What will pH of solution be?
 - Reaction does not proceed as far toward completion as previous 3 reactions.
 - Worked Example 15.1; Problems 15.1, 15.2

Neutralization Reactions

- Predict whether the pH after neutralization will be greater than, less than, or equal to 7 for the following combinations:
 - HCl and LiOH
 - HNO_2 and KOH
 - HBr and NH_3

The Common Ion Effect

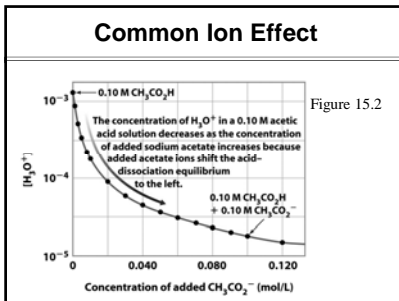
- Write the equation for the dissociation of HF in water.
- What will happen to this equilibrium if I add NaF?
 - Hint: What does NaF do in water?
- Metal ions or salts containing a conjugate weak acid or base can shift the pH of a solution.
- This is the mechanism that controls the pH of your blood and other biological systems.
 - $\text{H}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^{2-} + \text{H}_3\text{O}^+$

The Common Ion Effect

- If we add a conjugate acid (base) to a solution of a weak base (acid), the pH will shift. This is called the **common ion effect**.
 - NaCH_3CO_2 added to a solution of $\text{CH}_3\text{CO}_2\text{H}$ will make the solution more basic. Why?
- A common ion will shift a chemical equilibrium in such a direction as to get rid of some of the added (common) ion.

Common Ion Effect

- Calculate pH of solution made by adding 0.20 moles HF to 2.00 L water. (Remember: ICE tables use MOLARITY - not moles.)
- What will happen if 0.20 moles of NaF are then added? In which direction will equilibrium shift? What will happen to pH?
- How can we calculate the new pH? Hint: What will change in the ICE table?



Common Ion Effect

- $\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}_3\text{O}^+$
- Adding more CH_3CO_2^- to the solution shifts the equilibrium to the left, making the solution less acidic (H_3O^+ is consumed, pH is higher).
- 0.100 M $\text{CH}_3\text{CO}_2\text{H}$ pH = 2.879
- 0.100 M $\text{CH}_3\text{CO}_2\text{H} + 0.050$ M NaCH_3CO pH = 4.456
- CH_3CO_2^- is an ion common to $\text{CH}_3\text{CO}_2\text{H}$ and NaCH_3CO_2 solutions, consistent with LeChatelier's Principle

Common Ion Effect

- What is the pH of 20.05 g of HF added to 1.00 L of water? $K_a = 7.0 \times 10^{-4}$
- | | | | | | |
|---------|----------------------------------|----------------------|------------------------|---|--------------|
| | $\text{HF} + \text{H}_2\text{O}$ | \rightleftharpoons | H_3O^+ | + | F^- |
| Initial | — | | 0 | | 0 |
| Change | -x | | +x | | +x |
| Equil. | — - x | | x | | x |
- Assume $x \ll [\text{HF}]$
- $x = 2.7 \times 10^{-2}$, so the assumption was okay
- pH = $-\log(2.7 \times 10^{-2}) = 1.58$

Common Ion Effect

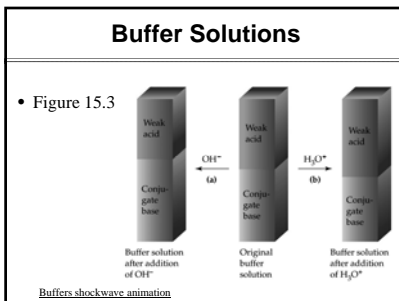
- What is the pH of 20.05 g of HF in 1.00 L of water if 21.00 g of NaF are added? $K_a = 7.0 \times 10^{-4}$
- First, predict what will happen to pH.
- $\text{NaF} + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Na}^+(\text{aq}) + \text{F}^-(\text{aq}) + \text{H}_2\text{O}(\text{l})$
- $[\text{NaF}] = [\text{F}^-]$
- ICE Table!
 - $x = 1.4 \times 10^{-3}$, so the assumption was okay
 - pH = $-\log(1.4 \times 10^{-3}) = 2.85$
- Worked Example 15.2, Problems 15.3, 15.4

Buffer Solutions

- Solution of a **weak acid and its conjugate base** (and vice versa) in approximately equal concentrations
 - i.e., Common ion solutions!!!! $\text{HF} + \text{NaF}$; $\text{NH}_3 + \text{NH}_4\text{Br}$
- Used to control pH
 - Ex: blood – buffered to maintain consistent pH; pH of all body fluids is controlled in this way. In blood, phosphate, carbonate, and hemoglobin all act as buffers.
 - Contact solution – buffered so it doesn't burn your eyes!!
- Addition of a strong acid or base to a buffer solution shifts the pH only slightly; unlike a non-buffered solution (like water).

Buffer Solutions

- $\text{HF}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{F}^-(\text{aq})$
- Add HCl, what happens to equilibrium? Which component of the common ion equilibrium will HCl react with (acid or base)?
- Add NaOH, what happens to equilibrium? Which component of the common ion equilibrium will NaOH react with (acid or base)?
- There will be a pH change in each case, but not as much as if the HCl (or NaOH) were added to water.



Group Work

- Identify the solutions below that would make good buffer solutions:
 - HF and NaF
 - NH_3 and NH_4Cl
 - KOH and KF
 - CH_3COOH and LiCH_3COO
 - NaNO_3 and HNO_3
 - NaOH and NaCl
 - HCl and NaCH_3COO

Buffer Capacity

- Buffers only work within a pH range set by the value of K_a :

$$\text{pH} = \text{p}K_a \pm 1$$
- Outside this range, we see little buffering effect.
- If you know the desired pH of a buffer solution, you can choose an acid with a $\text{p}K_a$ near the pH.

Buffer Range

- Select an appropriate acid-base pair to get within the range of the desired pH.
- Look at table of K_a values (some are shown on the next screen), calculate pK_a , and select an appropriate combination.
- How would you make a buffer solution with $pH = 4.10$? What two solutions could you use?

Table of K_a values

| Acid | K_a |
|---|-----------------------|
| HF | 7.0×10^{-4} |
| HNO ₂ | 4.5×10^{-4} |
| C ₉ H ₈ O ₄ (aspirin) | 3.0×10^{-4} |
| HCO ₂ H (formic) | 1.7×10^{-4} |
| C ₆ H ₈ O ₆ (ascorbic) | 8.0×10^{-5} |
| C ₆ H ₅ CO ₂ H (benzoic) | 6.5×10^{-5} |
| CH ₃ CO ₂ H (acetic) | 1.8×10^{-5} |
| HCN | 4.9×10^{-10} |
| C ₆ H ₅ OH (phenol) | 1.3×10^{-10} |

Henderson-Hasselbalch Equation

- Assuming that $x \ll [HA]$ and $x \ll [A^-]$ for good buffer action, the equilibrium constant expression $K_a = [H_3O^+][A^-] / [HA]$ can be rearranged to give a simplified calculation:
- $pH = pK_a + \log ([A^-] / [HA])$
- Consider 1.00 M HF, 0.500 M NaF
 $K_a = 7.0 \times 10^{-4}$, $pK_a = 3.15$
 $\log ([F^-]/[HF]) = \log (0.500/1.00) = -0.301$
 $pH = 3.15 - 0.301 = 2.85$ (same result as before - Magic!!!)

Buffer Solutions

- What is the pH of 500.0 mL of 0.10 M formic acid combined with 500.0 mL of 0.20 M sodium formate? $K_a = 1.8 \times 10^{-4}$
- $pH = pK_a + \log ([A^-]/[HA]) = 4.05$
 - Only need concentrations, not volumes
- Now add 10.0 mL of 0.50 M HCl
 - Now we need to know moles of substances to calculate new concentrations (mol/L)
 - Use a CHANGE (initial, change, final) Table

Buffer Solutions

- To find the new pH, first assume that all the added strong acid reacts to change the A^- and HA concentrations.
 - How many moles of weak acid, conj. base, and strong acid are in solution?
 - What increases, what decreases?
- HA = (0.10 M) (0.5000 L) = 0.050 mol
- A^- = (0.20 M) (0.5000 L) = 0.10 mol
- HCl = (0.0100 L) (0.50 M) = 0.0050 mol
- But volume has changed!
 - Total volume = 500.0 + 500.0 + 10.0 mL = 1010.0 mL

Buffer Solutions

- Now calculate new concentrations after reaction with acid.
- $[HA] = 0.055 \text{ mol} / 1.010 \text{ L} = 0.05446 \text{ M}$
- $[A^-] = 0.095 \text{ mol} / 1.010 \text{ L} = 0.0941 \text{ M}$
- $pH = pK_a + \log ([A^-]/[HA]) = 3.98$
- Only need to calculate new concentrations if volumes are given.

Buffer Solutions

- Water
 - Pure water: $pH = 7$
 - Add 0.100 M HCl: $pH = 1.0$
- Buffer:
 - Buffer system: $pH = 4.05$
 - Buffer with strong acid: $pH = 3.98$
- What will happen when we add a strong base to a buffer system?

Buffer Solutions

- If base is added, reduce the concentration of HA and increase the concentration of A^- by the number of moles of added base. Find new concentrations, then solve the weak acid/conjugate base system.
- Add 10.0 mL of 0.500 M NaOH to the formic acid/sodium formate buffer. What is the new pH?

Buffer Solutions

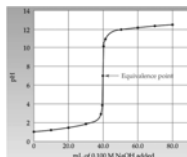
- First assume that all OH⁻ reacts with HF:
- How many moles of base were added? (0.500 M) (0.0100 L) = 0.005 mol
- HA = 0.050 mol - 0.0050 mol = 0.045 mol
- A^- = 0.10 mol + 0.0050 mol = 0.105 mol
- But volume has changed!
 - Total volume = 500.0 + 500.0 + 10.0 mL = 1010.0 mL
- Now solve for conc. $[HA] = 0.0446 \text{ M}$, $[A^-] = 0.104 \text{ M}$
- $pH = pK_a + \log ([A^-]/[HA]) = 4.11$ (started at 4.05)
- In water, pH would change from 7 to 13.

Henderson-Hasselbalch

- What is the pH of a 1.00 L solution that is 0.75 M NH_3 and 0.25 M NH_4Cl ? $K_b = 1.8 \times 10^{-5}$
- What is the pH of this solution after 0.01 mol HBr is added to it?
- Always check that your answers make sense when using the H-H equation!!
- Worked Examples 15.4, 15.5; Problems 15.9 - 15.11

pH Titration Curves

- Strong Acid-Strong Base Titrations:
- The equivalence point is the point at which equimolar amounts of acid and base have reacted (review 1st semester notes on calcs).
- Graph generated with pH probe →
- Figure 15.6



pH Titration Curves

- 4 key points on a titration curve
 - At the beginning (before titrant is added)
 - Before the equivalence point
 - At the equivalence point
 - After the equivalence point
- Consider titrating 20.00 mL of 0.200 M HCl with 0.200 M NaOH. Find equiv. pt. first!

$$M = \frac{\text{mol}}{\text{L}} = \frac{1000 \text{ mmol}}{1000 \text{ mL}} = \frac{\text{mmol}}{\text{mL}}$$

HCl + NaOH Titration

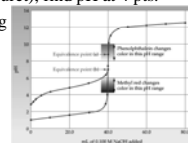
- A) 0 mL NaOH, pH is calculated from strong acid. $[\text{H}_3\text{O}^+] = 0.200 \text{ M}$
- B) 5.00 mL NaOH, acid is still in excess; but by how much?
 - mmol acid – mmol base

HCl + NaOH Titration

- C) 20.00 mL NaOH added; at the equivalence point, neutral salt and water in solution.
- D) 25.00 mL NaOH added, base in excess. By how much?
 - mmol base – mmol acid
- Problems 15.13, 15.14

Weak Acid-Strong Base

- Weak acid (pick one) in flask, strong base (pick one) is titrant (in buret); find pH at 4 pts.
- Figure 15.8 shows strong **and** weak acids.
- Titrate 50.00 mL of 0.100 M acid with 0.100 M base.
 - Find equiv. pt., K_a , pK_a , and mmoles of acid first



Example

Weak Acid-Strong Base

- 4 regions in titration curve
- Before adding base: 0.00 mL base
- Before equivalence point: 10.00 mL base
- At equivalence point: 50.00 mL base
- After equivalence point: 60.00 mL base
- Half equivalence point: 25.00 mL base

Weak Acid-Strong Base

| $K_a =$ | HA | $\text{H}_2\text{O} \rightleftharpoons$ | H_3O^+ | A^- |
|-------------|-----------|---|------------------------|--------------|
| Initial | 0.100 M | - | 0 | 0 |
| Change | -x | - | +x | +x |
| Equilibrium | 0.100 - x | - | x | x |

Weak Acid-Strong Base

- Before equiv. pt.: this is the **buffer zone** (both weak acid and its conjugate base are present).
 - pH can be found from the H-H equation but first $[\text{A}^-]$ is calculated.
 - Each drop of strong base added has reacted completely with the weak acid in the flask.
 - Calculate mmoles of strong base added. This also tells us the number of mmol of acid that have reacted.
 - mmoles acid – mmoles base = mmoles of unreacted acid left in the flask.
 - $[\text{A}^-] = \text{mmoles left} / \text{total volume}$
 - Use the Henderson-Hasselbalch equation for the pH.
 - $\text{pH} = \text{p}K_a + \log ([\text{A}^-] / [\text{HA}])$

Weak Acid-Strong Base

- Before equiv. pt.: 10.00 mL base
 - 50.0 mL of 0.100 M HA (5.00 mmol) and 10.0 mL of 0.100 M base (1.00 mmol). Use Change table to find final mmoles of each.
 - 5.00 mmol - 1.00 mmol = 4.00 mmol excess acid
 - $\text{HA} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{A}^-$
 - 5.00 mmol 1.00 mmol 0.00 mmol
 - -1.00 -1.00 +1.00
 - 4.00 mmol 0.00 mmol 1.00 mmol
 - divide by total volume = 60.0 mL
 - $[\text{HA}] = 0.0667 \text{ M}$; $[\text{A}^-] = 0.0167 \text{ M}$
 - $\text{pH} = \text{pK}_a + \log(\text{base/acid}) = \text{pK}_a + \log(0.0167/0.0667)$

Weak Acid-Strong Base

- At equivalence point:
 - We have seen that the product of a weak acid and a strong base is a basic salt and water.
 - We can expect the pH to be greater than 7.
 - Now calculate the mmoles of acid that are in the flask.
 - Since all the weak acid has been consumed and converted to its conjugate base at the equivalence point, the moles of A^- are now known.
 - mmoles $\text{A}^- / \text{total volume} = [\text{A}^-]$
 - Conjugate base reacts with water ($\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$).
 - Set up ICE table (using K_b) and solve for $[\text{OH}^-]$ and pH.

Weak Acid-Strong Base

- At equivalence point:
 - 50.0 mL of 0.100 M acid (5.00 mmol) and 50.0 mL of 0.100 M base (5.00 mmol)
 - So 5.00 mmol conj. base (A^-) in flask with 100.0 mL total volume = 0.0500 M A^-
 - ICE table $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$ $K_b = K_w / K_a$
 - $K_b = (x^2/0.050)$
 - $x = [\text{OH}^-]$

Weak Acid-Strong Base

- After the equivalence point:
 - More than enough base is added to react with all the acid in the flask. No HA remains, it is all converted to A^- .
 - pH is determined primarily from excess $[\text{OH}^-]$. $[\text{A}^-]$ is a minor contributor and doesn't need to be calculated.
 - To find $[\text{OH}^-]$, mmoles of base - mmoles of acid; then divide by the total volume of the resulting solution.

Weak Acid-Strong Base

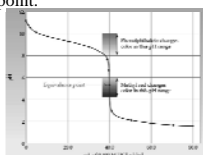
- After the equivalence point:
 - 50.00 mL of 0.100 M acid (5.00 mmol) and 60.0 mL of 0.100 M base (6.00 mmol)
 - 6.00 mmol OH^- added - 5.00 mmol acid present = 1.00 mmol remaining OH^-
 - divide by 110.00 mL = 0.009091 M OH^-
 - $\text{pOH} = -\log(0.009091 \text{ M}) = 2.04$
 - $\text{pH} = 14 - 2.04 = 11.96$

Half Equivalence Point

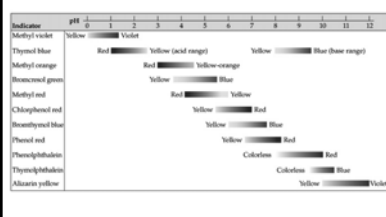
- 25.00 mL base added (half the volume needed to get to equivalence point):
 - $[\text{HA}] = (5.00 \text{ mmol} - 2.50 \text{ mmol}) / 75.00 \text{ mL}$
 - $[\text{A}^-] = 2.50 \text{ mmol} / 75.00 \text{ mL}$
 - $[\text{HA}] = [\text{A}^-]$
 - $\text{pH} = \text{pK}_a + \log([\text{A}^-]/[\text{HA}]) = \text{pK}_a$
 - Key Concept Problem 15.15; Problems 15.16, 15.17

Strong Acid-Weak Base

- Indicators can be used when pH meters are not available. Look for indicator in the right range of equivalence point.
- Figure 15.10

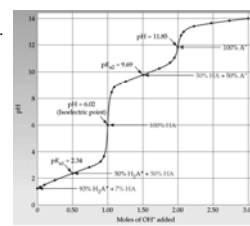


Acid-Base Indicators



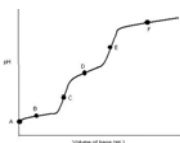
Polyprotic Acid Titrations

- One equiv. pt. for each proton
- 2 half equiv. pts.



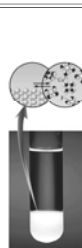
Diprotic Acid Titration

- A: acid in water
- B: pK_{a1} ; 1st H removed; 50% H₂A, 50% HA
- C: 1st equiv. pt. (HA)
- D: pK_{a2} ; 2nd H removed; 50% HA, 50% A⁻
- E: 2nd equiv. pt. (A²⁻), all acid reacted
- F: only excess base



Solubility Equilibria

- Some combinations of ions in solution form insoluble salts. Recall the solubility rules from Chapter 4.
- Even insoluble salts dissolve to a small extent.
- Extent of dissolution (solubility of solid) is determined by equilibrium! Of course!
- Solubility of insoluble salts is defined by the solubility product constant, K_{sp}
- Unsaturated, saturated, supersaturated



Solubility Product Constant

- $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$
- Write equilibrium expression (K_{sp}).



- Write an equation for the dissolution of silver sulfide. Now write the K_{sp} expression.
- What does a large K_{sp} value tell you? A small value?
- Worked example 15.7, Problem 15.20

Calculating K_{sp}

- Values for K_{sp} 's are measured by experiment. Some values for various insoluble salts are found in Table 15.2.
- K_{sp} for calcium fluoride can be calculated by adding an excess of solid salt to water to get a saturated solution, then measuring concentration of each ion.
- $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$ $K_{sp} = ?$
- $[Ca^{2+}] = 3.3 \times 10^{-4} M$; What is $[F^-]$?
- Write the K_{sp} expression. Now calculate K_{sp} (Hint: Think ICE tables....)

Solubility

- Given K_{sp} , we can also calculate solubilities of ions.
 - Solubility (or molar solubility) = moles / L
 - Gram solubility = grams / L (use molar mass to convert)
- Calculate solubility of calcium fluoride. $K_{sp} = 1.5 \times 10^{-10}$
- Write equation for solubility equilibrium. Solve for x.

Solubility/ K_{sp} Practice

- K_{sp} for silver bromide is 7.7×10^{-13} . Calculate the molar and gram solubility (solve for x).
- The solubility of calcium sulfate is found experimentally to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate.
- K_{sp} for copper (I) oxide is found to be 2.0×10^{-15} . Calculate the molar and gram solubility.
- The solubility of calcium hydroxide is 0.233 g/L. Calculate K_{sp} .
- Worked example 15.8 – 15.10, Problems 15.21 – 15.24

Common Ion Effect

- What will happen if I add solid NaF to a solution of saturated CaF₂?
- $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$
- Common ion effect:** add more F⁻ to precipitate more Ca²⁺ from solution.
- How does a common ion affect the solubility of the solid?
- Problem 15.101: Calculate the molar solubility of strontium fluoride in pure water ($K_{sp} = 4.3 \times 10^{-9}$). Calculate the molar solubility of strontium fluoride in 0.010 M sodium fluoride.

Common Ion Effect

- $SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$
- Equil: x 2x
- $K_{sp} = (x)(2x)^2 = 4.3 \times 10^{-9}$
- x = $1.0 \times 10^{-3} M$
- $SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2F^-(aq)$
- Initial: 0 0.010
- Equil: x 0.010 + 2x
- $K_{sp} = (x)(0.010 + 2x)^2 = 4.3 \times 10^{-9}$
- x = $4.3 \times 10^{-5} M$



Common Ions and Solubilities

- Calculate molar solubility of AgBr in 0.10 NaBr. $K_{sp} = 7.7 \times 10^{-13}$
 - Set up ICE table to calculate molar solubilities of Ag⁺ and Br⁻.
- | K_{sp} | AgBr(s) | \rightleftharpoons | Ag ⁺ (aq) | Br ⁻ (aq) |
|----------|---------|----------------------|----------------------|---------------------------|
| I | --- | | 0 | 1.08×10^{-4} |
| C | -x | | +x | +x |
| E | --- | | x | $x + 1.08 \times 10^{-4}$ |
- $K_{sp} = (x)(x + 1.08 \times 10^{-4}) = 7.7 \times 10^{-13}$
 - Worked example 15.11, Problem 15.25

Precipitation of Ionic Cmpds

- What are the silver and bromide ion concentrations if 0.0244 g of AgBr and 0.0111 g of NaBr are put into 1.00 L of water? **Will AgBr dissolve completely?**
- Write solubility equilibrium expressions for AgBr and NaBr.
- Calculate Q_{sp} . $Q_{sp} = [Ag^+][Br^-]$
 - $[Ag^+] = 1.30 \times 10^{-4} M$, $[Br^-] = 1.30 \times 10^{-4} + 1.08 \times 10^{-4} M$
 - $K_{sp} = 7.7 \times 10^{-13}$
- $Q_{sp} > K_{sp}$ what does this mean?
 - Not all of the AgBr can dissolve
- Worked example 15.14, Problems 15.29

Precipitation of Ionic Cmpds

- Note: book refers to IP, same idea as Q (value of concentration ratios NOT at equilibrium)
- Example: We want to know if CaF_2 will precipitate when we combine $CaCl_2$ and NaF. Have to calculate Q_{sp} and relate it to K_{sp} .
- System will shift until $Q_{sp} = K_{sp}$ (a saturated solution)

Precipitation of Ionic Cmpds

- $Q > K_{sp}$ Supersaturated; precipitate forms
- $Q = K_{sp}$ Saturated
- $Q < K_{sp}$ Unsaturated
- 2.45 mg of magnesium carbonate is placed in 1.00 L of water. Will it all dissolve? $K_{sp} = 4.0 \times 10^{-5}$
- Find molarity of solid. Write equilibrium expression for solubility. Calculate Q_{sp} .

pH and Solubilities

- Weak base metal hydroxides
 - Ex: $Mg(OH)_2$; NOT strong base (doesn't dissolve 100%)
- $Mg(OH)_2$, $K_{sp} = 1.2 \times 10^{-11}$
- Write equilibrium expression for solubility.
- What happens to equilibrium as pH increases (basic solution)?
 - Shifts left, less soluble
- What happens to equilibrium as pH decreases (acidic solution)?
 - Shifts right, more soluble
- Problem 15.26

Complex Ions

- Transition metal with anions/molecules (called ligands) bonded to it
- Complex has an overall charge
 - $Cu(H_2O)_6^{2+}$, $CoCl_4^{2-}$, $Cu(NH_3)_4^{2+}$
 - Equilibrium between complex ions and metal ion/bonded species
 - $Cu^{2+}(aq) + 6H_2O(l) \rightleftharpoons Cu(H_2O)_6^{2+}(aq)$
 - K_f is typically very large ($\sim 10^{30}$) – very stable ions
- No K_f calculations, skip amphoterism section

Qualitative Analysis

- Skipping section 15.14: Selective Precipitation
- Qualitative analysis is used to identify unknown ions in a solution.
- Each ion can be precipitated out by addition of selective reagents.
- Purely qualitative research, like solving a puzzle.