

Chapter 15 - Applications of Aqueous Equilibria

GCC CHM152

Neutralization: Strong Acid-Strong Base

Molecular: $\text{HCl}_{(\text{aq})} + \text{NaOH}_{(\text{aq})} \rightarrow \text{NaCl}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$

- ♦ SA-SB rxn goes to completion (one-way \rightarrow)

• Write ionic and net ionic rxns

$\text{H}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})} + \text{Na}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{Na}^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

• Net: $\text{H}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})}$

- ♦ After neutralization, what's in solution?
- ♦ Do either of the salt ions react with water?
- ♦ What is pH of the salt solution?

Neutralization: Weak Acid-Strong Base

$\text{HF}_{(\text{aq})} + \text{KOH}_{(\text{aq})} \rightarrow \text{KF}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$

- ♦ Rxn goes to completion due to SB

Write ionic and net rxns:

$\text{HF}_{(\text{aq})} + \text{K}^+_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{K}^+_{(\text{aq})} + \text{F}^-_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})}$

Net: $\text{HF}_{(\text{aq})} + \text{OH}^-_{(\text{aq})} \rightarrow \text{H}_2\text{O}_{(\text{l})} + \text{F}^-_{(\text{aq})}$

- ♦ After neutralization, what's in solution?
- ♦ Do either of the salt ions react with water?
- ♦ What will the pH of the solution be, roughly?

Neutralization: Strong Acid-Weak Base

$\text{HCl}_{(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightarrow \text{NH}_4^+_{(\text{aq})} + \text{Cl}^-_{(\text{aq})}$

- ♦ Rxn goes to completion because of strong acid

Write ionic and net rxns:

$\text{H}^+_{(\text{aq})} + \text{Br}^-_{(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightarrow \text{NH}_4^+_{(\text{aq})} + \text{Br}^-_{(\text{aq})}$

Net Ionic: $\text{H}^+_{(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightarrow \text{NH}_4^+_{(\text{aq})}$

- ♦ After neutralization, what's in solution?
- ♦ Do either of the salt ions react with water?
- ♦ What will the pH of the solution be, roughly?

Neutralization: Weak Acid-Weak Base

$\text{CH}_3\text{COOH}_{(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightleftharpoons \text{NH}_4\text{CH}_3\text{COO}_{(\text{aq})}$

- ♦ Reaction does not go to completion since no reactant is completely ionized.

Ionic: $\text{CH}_3\text{COOH}_{(\text{aq})} + \text{NH}_3_{(\text{aq})} \rightleftharpoons \text{NH}_4^+_{(\text{aq})} + \text{CH}_3\text{COO}^-_{(\text{aq})}$

Net: same

The salt remaining after neutralization contains an acidic and a basic ion, so pH depends on their relative K_a and K_b values.

Neutralization Reactions

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

Common Ion effect

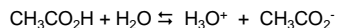
The shift in equilibrium caused by the addition of a substance having an ion in common with the equilibrium mixture.

- ♦ Adding a common ion suppresses the ionization of a weak acid or a weak base.

The source of the common ion is typically provided by adding a strong acid, a strong base or a soluble salt to the equilibrium reaction mixture.

Common Ion Concept Problem

Given this reaction:



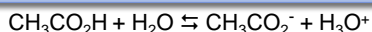
What happens to the pH of the acetic acid solution if we add NaCH_3CO_2 ?

$[\text{CH}_3\text{CO}_2^-] \uparrow$

Eq shifts \leftarrow

$[\text{H}_3\text{O}^+] \downarrow$, thus pH \uparrow

Common Ion Effect



0.100 M $\text{CH}_3\text{CO}_2\text{H}$, $K_a = 1.8 \times 10^{-5}$

- WA soln: pH = 2.87

Add common ion CH_3CO_2^- , pH \uparrow

0.100 M $\text{CH}_3\text{CO}_2\text{H}$, add 0.050 M NaCH_3CO_2

- Mix of WA and conj base: pH = 4.44

Common Ion Problem

- What is the pH of 1.00 M HF solution?
 $K_a = 7.0 \times 10^{-4}$
- What is the pH of 1.00 M HF solution after adding 0.500 M NaF? $K_a = 7.0 \times 10^{-4}$

16.3 Buffer Solution

A solution that resists changes in pH when a small amount of acid or base is added.

- Buffers are used to control pH
e.g. biological buffers maintain the pH of all body fluids

Best buffer systems consist of either

- a weak acid and its conjugate base
e.g. $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$
- a weak base and its conjugate acid
e.g. NH_3 and NH_4Cl

Which are buffer solutions?

- Identify the solutions below that would make good buffer solutions (what criteria need to be met?):
 - ♦ 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 :

$$\text{pH} = \text{p}K_a \pm 1$$

Thus $0.1 < [\text{HA}]/[\text{A}^-] < 10$

- 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.
- Also the [acid]:[base] ratio must be less than 10:1 (or 1:10)
- Optimum buffer has same amount of HA & A⁻.

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 $\text{p}K_a$, and select an appropriate combination.
- How would you make a buffer solution with $\text{pH} = 4.10$? What could you use to make this?

Table of K_a values

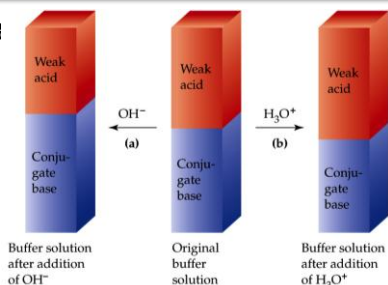
Acid	K_a
HF	3.5×10^{-4}
HNO ₂	4.5×10^{-4}
C ₉ H ₈ O ₄ (aspirin)	3.0×10^{-4}
HCO ₂ H (formic)	1.7×10^{-4}
C ₆ H ₈ O ₆ (ascorbic)	8.0×10^{-5}
C ₆ H ₅ CO ₂ H (benzoic)	6.5×10^{-5}
CH ₃ CO ₂ H (acetic)	1.8×10^{-5}
HCN	4.9×10^{-10}
C ₆ H ₅ OH (phenol)	1.3×10^{-10}

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, which component of the buffer soln will HCl react with (acid or base)?
 - H⁺ will react with F⁻ (conj. base)
- Add NaOH, which component of the buffer soln will NaOH react with (acid or base)?
 - OH⁻ will react with HF (weak acid)
- There will be a pH change in each case, but not as much as if the HCl (or NaOH) were added to **water**.

Buffer Solutions

- Figure 15.3



[Buffers shockwave animation](#)

Henderson-Hasselbalch Equation

- When solving for $[\text{H}_3\text{O}^+]$ at equilibrium and assuming $x \ll [\text{HA}]$ & $[\text{A}^-]$ for good buffer action, the equilibrium expression $K_a = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}]$ can be rearranged to give a simplified calculation:
- $\text{pH} = \text{p}K_a + \log ([\text{A}^-] / [\text{HA}])$
 - Can use moles or M – depending on given info
 - V units cancel since it's a ratio of [base]/[acid]

Buffer Solutions + HCl

- 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? $K_a = 1.8 \times 10^{-4}$
- $\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) = 4.04$
- Now add 10.0 mL of 0.50 M HCl
 - ♦ calculate moles of substances, then calculate changes
 - ♦ Use a CHANGE Table (initial, change, final)

Buffer Solutions + HCl

- To find the new pH, first assume that all the added strong acid reacts with A^- to form HA .
 - ♦ $\text{H}_3\text{O}^+ + \text{A}^- \rightarrow \text{H}_2\text{O} + \text{HA}$
 - ♦ How many moles of HA, A^- , and H_3O^+ are in solution?
- Initial mol HA = (0.10 M) (0.5000 L) = 0.050 mol
- Initial mol A^- = (0.20 M) (0.5000 L) = 0.10 mol
- mol HCl = (0.0100 L) (0.50 M) = 0.0050 mol
- Final mol A^- = 0.10 mol - 0.0050 mol = **0.095 mol A^-**
- Final mol HA = 0.050 mol + 0.0050 mol = **0.055 mol HA**
- ❖ Can use final moles in H-H equation. Why?
- $\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) = 3.98$ (initially 4.04 w/o acid)
- **pH ↓ slightly when SA added to buffer**

Buffer +NaOH

- What will happen when we add a strong base to a buffer system?
 - ♦ Added base reacts with HA to form A^- :
 - ♦ $\text{HA} \downarrow$ and $\text{A}^- \uparrow$
 - ♦ $\text{HA} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{A}^-$
- Add 10.0 mL of 0.500 M NaOH to the formic acid/sodium formate buffer. What is the new pH?

Buffer Solutions + NaOH

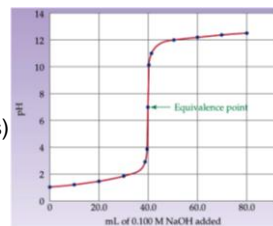
- First assume that all OH^- reacts with HCO_2H :
- $\text{HCO}_2\text{H} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCO}_2^-$
- How many moles of base were added?
- mol OH^- = (0.500 M) (0.0100 L) = 0.00500 mol OH^-
- final mol HA = 0.050 mol - 0.00500 mol = **0.045 mol**
- final mol A^- = 0.10 mol + 0.00500 mol = **0.105 mol**
- $\text{pH} = \text{p}K_a + \log \left(\frac{[\text{A}^-]}{[\text{HA}]} \right) = 4.11$ (initially 4.04 w/o SB)
- **pH ↑ slightly when SB added**
- In water, pH would change from 7 to 13 if same amount of **SB** was added.

Practice Ex. Try after class

- 1) Calculate the pH of a 1.25 L buffer solution made up of 0.50 M acetic acid and 0.50 M sodium acetate. $K_a = 1.8 \times 10^{-5}$
- 2) What is the pH of the solution when 25.00 mL of 0.40 M NaOH is added to the buffer?

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 0.100 M NaOH. Find equiv. pt. first!

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

Strong Acid-Strong Base

- Draw 4 beakers.
- 1) Draw 2 moles HCl.
- 2) Draw what happens when 1 mole NaOH is added.
- 3) Draw what happens when 2 moles NaOH are added.
- 4) Draw what happens when 3 moles NaOH are added.

HCl + NaOH Titration

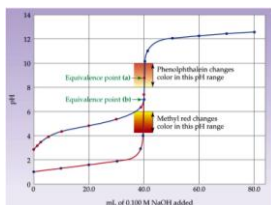
- 1) 0 mL NaOH, pH is calculated from strong acid. $[\text{H}_3\text{O}^+] = 0.200 \text{ M}$
 - ♦ $\text{pH} = -\log(0.200) = 0.700$ initial pH of SA
- 2) 5.00 mL NaOH, acid is still in excess; but by how much?
 - ♦ mmol acid – mmol base
 - ♦ $(0.200 \text{ M})(20.00 \text{ mL}) - (0.100 \text{ M})(5.00 \text{ mL})$
 - ♦ $[\text{H}_3\text{O}^+] = \text{mmol} / \text{total solution volume}$
 - ♦ $[\text{H}_3\text{O}^+] = 3.50 \text{ mmol} / 25.00 \text{ mL} = 0.140 \text{ M}$
 - ♦ $\text{pH} = -\log(0.140) = 0.854$ excess SA so pH still quite low!

HCl + NaOH Titration

- 3) 40.00 mL NaOH added; at the equivalence point, neutral salt and water in solution.
 - ♦ mmol acid = mmol base = 4.00 mmol
 - ♦ $\text{pH} = 7$ (always 7 for strong acid-strong base!)
- 4) 50.00 mL NaOH added, base in excess. Calc moles (or mmol) of excess base remaining
 - ♦ mmol base – mmol acid
 - ♦ $(0.100 \text{ M})(50.00 \text{ mL}) - (0.200 \text{ M})(20.00 \text{ mL})$
 - ♦ 1.00 mmol base excess / 70.00 mL = 0.01429 M NaOH
 - ♦ $\text{pOH} = -\log(0.01429) = 1.845$, $\text{pH} = 12.155$ excess SB
- Problems 15.13, 15.14

Weak Acid-Strong Base

- Acetic acid in flask, KOH 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 acetic w/ 0.150 M KOH.
 - ♦ Find eq. pt., K_a , $\text{p}K_a$, and mmols of acid first



Weak Acid-Strong Base

- Draw 4 beakers.
- 1) Draw 2 moles acetic acid.
- 2) Draw what happens when 1 mole KOH is added.
- 3) Draw what happens when 2 moles KOH are added.
- 4) Draw what happens when 3 moles KOH are added.

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: ???? mL base
- After equivalence point: 50.00 mL base

*See titration worksheet key for complete solution to this problem!

Weak Acid-Strong Base

- Initial pH before adding base. This is a weak acid. How do we find the pH of a weak acid?

$K_a =$	HA	$H_2O \rightleftharpoons$	H_3O^+	A^-
Initial	0.100 M	-	0	0
Change	-x	-	+x	+x
Equilibrium	0.100 - x	-	x	x

$$x = [H_3O^+] = \sqrt{[HA] \times K_a} = \sqrt{0.100 \times 1.8 \times 10^{-5}} = 1.34 \times 10^{-3} \text{ M}$$

0.100 M acetic acid, pH = 2.87

Weak Acid-Strong Base

- Before equiv. pt.: **this is the buffer zone (both weak acid and its conjugate base are present)**.
 - ♦ Use change table to find mmoles excess acid and mmoles cong. base produced. All strong base is converted to conjugate acid (strong base is completely consumed).
 - ♦ $[HA] = (\text{mmoles acid} - \text{mmoles base}) / \text{total volume}$
 - ♦ $[A^-] = \text{mmoles base} / \text{total volume}$
 - ♦ $pH = pK_a + \log ([A^-] / [HA])$

Weak Acid-Strong Base

- At equivalence point: **Find pH of basic salt**
 - ♦ 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.
 - ♦ Since all the weak acid has been consumed and converted to its conjugate base at the equivalence point, the mmoles of A^- are now known.
 - ♦ $\text{mmoles } A^- / \text{total mL} = [A^-]$
 - ♦ Where total mL = mL acid + mL base
 - ♦ Conjugate base reacts with water ($A^- + H_2O \rightleftharpoons HA + OH^-$).
 - ♦ Set up ICE table (using K_b) and solve for $[OH^-]$ and pH.

Weak Acid-Strong Base

- **At equivalence point:**
 - ♦ 5.00 mmol HA and 5.00 mmol SB have reacted
 - ♦ 5.00 mmol conj. base (A^-) have been formed
 - ♦ Total V = 50.00 mL + 33.33 mL = 83.33 mL
 - ♦ $[A^-] = 5.00 \text{ mmol} / 83.33 \text{ mL} = 0.0600 \text{ M } A^-$
 - ♦ WB hydrolysis: $A^- + H_2O \rightleftharpoons HA + OH^-$
 - ♦ $K_b = K_w / K_a$
 - ♦ Set up ICE table!
 - ♦ $K_b = (x^2 / (0.0600 - x))$
 - ♦ $x = [OH^-]$; then find pH
 - ♦ **pH = 8.76 (see worksheet key!)**

Weak Acid-Strong Base

- After the equivalence point: **Excess OH^- ions**
 - ♦ 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 $[OH^-]$.
 - ♦ $[A^-]$ is a minor contributor and doesn't need to be calculated.
 - ♦ **$[OH^-] = (\text{mmoles base} - \text{mmoles acid}) / \text{total volume}$**

Weak Acid-Strong Base

- After the equivalence point:
 - ♦ 50.00 mL of 0.100 M acid (5.00 mmol) and 50.00 mL of 0.150 M base (7.50 mmol)
 - ♦ 7.50 mmol OH⁻ added – 5.00 mmol acid present = 2.50 mmol OH⁻ remaining
 - ♦ total mL = 50.00 + 50.00 = 100.00 mL
 - ♦ [OH⁻] = 2.5 mmol/100.00 mL = 0.0250 M OH⁻
 - ♦ pOH = -log (0.0250 M) = 1.602
 - ♦ pH = 14 – 1.602 = **12.398**

Group Quiz #14

- Exactly 50.00 mL of 0.20 M hydrazoic acid ($K_a = 1.9 \times 10^{-5}$) are titrated with a 0.15 M KOH solution. Calculate the pH when 66.67 mL of base have been added:

Animations:

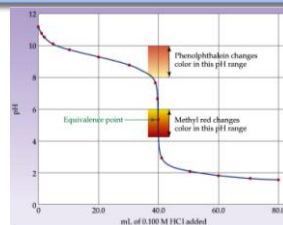
<http://www.chembio.uoguelph.ca/educmat/chem19104/chemtoons/chemtoons.htm>

Half Equivalence Point

- 33.34 mL base added (half the volume needed to get to eq pt for quiz #14 problem)
- At this point half the acid has been neutralized
mmol substances at half eq pt:
mmol HA = (10.00 mmol – 5.00 mmol) = 5.00 mmol
- mmol A⁻ = 5.00 mmol
- Thus, [HA] = [A⁻]
- pH = pK_a + log ([A⁻]/[HA]) = pK_a

Weak Base-Strong Acid

- Figure 15.10



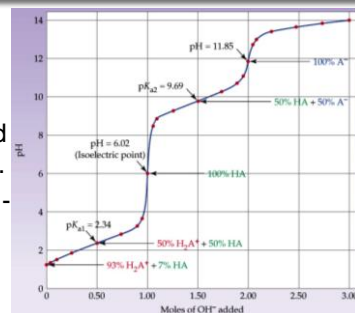
- Calculations are similar to weak acid/strong base; opposite values; extra steps to find pH values. See pages 613 - 615 for outline.

Acid-Base Indicators

Indicator	pH	0	1	2	3	4	5	6	7	8	9	10	11	12	
Methyl violet	Yellow	Violet													
Thymol blue	Red	Yellow (acid range)			Blue (base range)										
Methyl orange	Red	Yellow-orange			Blue										
Broncesol green	Yellow	Blue													
Methyl red	Red	Yellow													
Chlorophenol red	Yellow	Red			Red										
Bromthymol blue	Yellow	Blue			Blue										
Phenol red	Yellow	Red			Red										
Phenolphthalein	Colorless	Red													
Thymolphthalein	Colorless	Blue													
Alizarin yellow	Yellow	Violet													

Polyprotic Acid Titrations

- One eq. pt. for each proton
- 2 eq. pts. and 2 half eq. pts.
- Figure 15.11 - Alanine with NaOH



Solubility equilibria

Dissolution of slightly soluble salts in water

important biological examples:

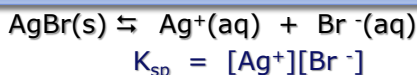
- tooth decay - tooth enamel dissolves in acidic soln
- formation of kidney stones - salts precipitate in kidney

15.10 Solubility Equilibria

- ❖ Many ions combine to form solid precipitates in aqueous solutions. (Solubility rules)
- ❖ These “insoluble” salts dissolve to a small extent and form a saturated solution.
- ❖ The undissolved solid and the dissociated ions in solution establish an equilibrium system that is characterized by the solubility product constant, K_{sp} .



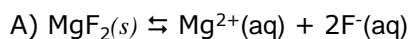
Example. The dissolution of AgBr



K_{sp} is the solubility product constant - the equilibrium constant for insoluble salts

- It is a measure of how soluble a salt is in H_2O
- ⇒ For salts with the same # of ions, the smaller the K_{sp} , the less soluble the salt.
- ⇒ Table 15.2 shows some K_{sp} values

Write the solubility equilibrium reactions and K_{sp} expressions for a) MgF_2 b) $\text{Ca}_3(\text{PO}_4)_2$.



$$K_{sp} = [\text{Mg}^{2+}][\text{F}^-]^2$$



$$K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

Solubility

- K_{sp} can be used to calculate the **solubility**, which can be compared for different salts.
- **Solubility (molar solubility)** = molar concentration of dissolved salt; ion concentrations are related to this by their coefficients.
- Solubility can also be expressed in g/L
- Examples:
 - AgCl: $[\text{Ag}^+] = x$ $[\text{Cl}^-] = x$ $K_{sp} = (x)(x)$
 - Ag_2S : $[\text{Ag}^+] = 2x$ $[\text{S}^{2-}] = x$ $K_{sp} = (2x)^2(x)$
 - $\text{Fe}(\text{OH})_3$: $[\text{Fe}^{3+}] = x$ $[\text{OH}^-] = 3x$ $K_{sp} = (x)(3x)^3$

Solubility/ K_{sp} Practice

- K_{sp} for AgBr is 7.7×10^{-13} . Calculate the molar and gram solubility (solve for x).
- If a saturated solution prepared by dissolving CaF_2 in water has $[\text{Ca}^{2+}] = 3.3 \times 10^{-4} \text{ M}$, what is the value of K_{sp} ?
- K_{sp} for Cu_2O is 2.0×10^{-15} . Calculate the molar solubility.
- The solubility of $\text{Ca}(\text{OH})_2$ is 0.233 g/L. Calculate K_{sp} .
- **Worked example 15.8 – 15.10, Problems 15.21 – 15.24**

Solubility/ K_{sp} Practice

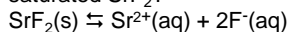
- Solubility = x in ICE table!
- K_{sp} = eq constant for dissolution of salt!
- AgBr: $x = 8.8 \times 10^{-7}$ M; $x = 1.6 \times 10^{-4}$ g/L
- CaF_2 : $K_{sp} = 1.4 \times 10^{-10}$
- Cu_2O : $x = 7.9 \times 10^{-6}$ M
- $\text{Ca}(\text{OH})_2$: $K_{sp} = 1.24 \times 10^{-7}$

Common Ion Effect

- Solubility is decreased when a common ion is added
 $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$
- Common ion effect: add more Cl^- to precipitate Ag^+ from solution.
- Saturated solution of AgCl: Find (x)
 - $K_{sp} = 1.70 \times 10^{-10}$
- Add 0.100 M Cl^-
 - $0.100 \gg 1.30 \times 10^{-5}$, so $[\text{Cl}^-] = 0.100$ M
- What is the new $[\text{Ag}^+]$? Note this is x in ICE!

Common Ion Effect

What will happen if I add solid NaF to a solution of saturated SrF_2 ?



a) Calculate the molar solubility of SrF_2 in pure water ($K_{sp} = 4.3 \times 10^{-9}$).

b) Calculate the molar solubility of SrF_2 in 0.010 M NaF.

Common Ion Effect

- $\text{SrF}_2(s) \rightleftharpoons \text{Sr}^{2+}(aq) + 2\text{F}^-(aq)$ (in water)
- Equil: $x \quad 2x$
- $K_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2 = 4.3 \times 10^{-9}$
- $x = 1.0 \times 10^{-3}$ M
- $\text{SrF}_2(s) \rightleftharpoons \text{Sr}^{2+}(aq) + 2\text{F}^-(aq)$ (in NaF)
- Initial: $0 \quad 0.010$
- Equil: $x \quad 0.010 + 2x$
- $K_{sp} = [\text{Sr}^{2+}][\text{F}^-]^2 = 4.3 \times 10^{-9}$
- $x = 4.3 \times 10^{-5}$ M



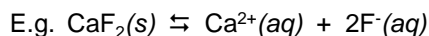
Worked ex 15.11, Problem 15.25

Group Quiz #15

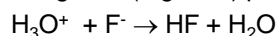
- Calculate the molar solubility of $\text{Cu}(\text{OH})_2$.
 $K_{sp} = 1.6 \times 10^{-19}$
- Calculate the molar solubility of $\text{Cu}(\text{OH})_2$ when 0.10 M $\text{Cu}(\text{NO}_3)_2$ is added.

Effect of pH on Solubility

Addition of an acid can increase the solubility of an insoluble basic salt.



Add strong acid (e.g. HCl) provides H_3O^+ ions:



- Adding H^+ causes $[\text{F}^-] \downarrow$, equilibrium shifts right to form more F^- & solubility of $\text{CaF}_2 \uparrow$.

pH and solubility

- E.g. For the following salts, predict whether the salt will dissolve in an acidic solution.
- A. AgBr _____
- B. CdCO₃ _____
- C. PbCl₂ _____
- D. BaS _____

Precipitation of Ionic Compds

- Note: book refers to IP, same idea as Q (value of concentration ratios NOT necessarily at equilibrium)
- Compare Q and K. System will shift until $Q_{sp} = K_{sp}$ (a saturated solution)
- Example: We want to know if precipitate will form when 0.150 L of 0.10 M lead (II) nitrate and 0.100 L of 0.20 M sodium chloride are mixed?
- Find Q_{sp} and relate it to K_{sp} .

Precipitation of Ionic Compds

- **Worked Example 15.14:** Will a precipitate form when 0.150 L of 0.10 M lead (II) nitrate and 0.100 L of 0.20 M sodium chloride are mixed?
- What is the precipitate that will form? What are K_{sp} and the equilibrium expression?
- Find total concentration of each ion once mixed.
- **Problem 15.29**

Precipitation

- $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$
- Calculate moles of each ion.
- Convert moles to concentration using total volume.
- Plug concentrations into Q_{sp} equation.
- If $Q_{sp} > K_{sp}$, rxn shifts left (toward solid) and precipitate will form.
- If $Q_{sp} < K_{sp}$, rxn shifts right (toward ions) and precipitate will not form.

Precipitation of Ionic Compds

- $Q > K_{sp}$ Supersaturated; **ppt forms**
- $Q = K_{sp}$ Saturated
- $Q < K_{sp}$ Unsaturated; **no ppt forms**
- 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} .

Group quiz 16

Will a solution containing 4.0×10^{-5} M Cl⁻ and 2.0×10^{-4} M Ag⁺ form a precipitate of AgCl? $K_{sp} = 1.70 \times 10^{-10}$
(Hint: think Q)

Complex Ion Equilibria

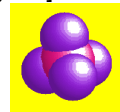
Formation of complex ions can increase solubility of an insoluble salt

Complex ion: ion containing a metal cation bonded to one or more molecules or ions which are called ligands. The ligands act as Lewis bases (e.g. NH_3 , H_2O , OH^-)

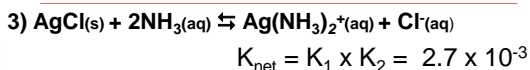
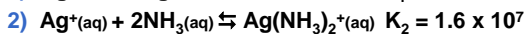
- E.g. $\text{Al}(\text{H}_2\text{O})_6^{3+}$, CuBr_4^-

Complex Ion Equilibria

- Lewis acid-base reactions also reach a state of equilibrium
- Metal ion + ligand \rightleftharpoons complex ion
- $K_f = \frac{[\text{complex ion}]}{[\text{metal ion}][\text{ligand}]}$
- K_f = formation constant
- $\text{Hg}^{2+} + 4\text{I}^- \rightleftharpoons \text{HgI}_4^{2-}$
- $K_f = \frac{[\text{HgI}_4^{2-}]}{[\text{Hg}^{2+}][\text{I}^-]^4}$
- K_f values are usually pretty large



Adding NH_3 to AgCl solution increases the solubility of AgCl :



- In qual lab we add ammonia to dissolve our AgCl precipitate so it can be separated from Hg .

Qualitative Analysis

- Skipping section 15.14: Selective Precipitation
- 15.15 Qualitative analysis is used to identify unknown ions in a solution.
 - 152LL should read this section before qual lab!
- Each ion can be precipitated out by addition of selective reagents.
- Purely qualitative research, like solving a puzzle.