Ch. 17 Additional Aqueous Equilibria

- Chapter 16 situations basically only involved one solute: strong or weak acid; strong or weak base; or ionic salt
- Real solutions often have >1 solute
  - ⇒more complex equilibria, pH calculations
  - ⇒extra solute impacts degree to which first chemical dissociates

3 general multi-solute situations:

1. buffers: weak acid and weak base mixture, to which strong acid or base may be added
2. titration: mixing acid and base, at least one of which is normally strong
3. partially soluble solids: impact of pH or other salts on solubility

17.1 Buffer solutions: resist change in pH when either acid or base added

- Crucial in nature: blood pH, lake pH, etc. must be tightly controlled.
- Blood: pH ≈7.40 ± 0.05
  - o pH < 7.35 → acidosis   pH > 7.45 → alkalosis
- The body needs a system for keeping the blood at the target pH, and protecting it from the extreme pH disruption that could result from addition of acid or base
- Many cellular processes likewise depend on precise control of pH
- Buffers provide protection against the addition of H^+ or HO^-

1. Unbuffered: Find pH

   a. 1.0 L pure water

   b. 1.0 L water + 0.1 mol HCl

   c. 1.0 L water + 0.1 mol NaOH

Point: In an unbuffered, unprotected solution, a small addition of strong acid or base can cause a massive and dangerous shift in pH.

A. Reaction of strong acid with weak base. Background Facts:

•While it reacts only slightly with water, a weak acid reacts **almost completely** with strong base

•While it reacts only slightly with water, a weak base reacts **almost completely** with strong acid

WB + water:	$NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + HO^{\ominus}$	$K = 1.8 \times 10^{-5}$
WB + SA:	$NH_3 + HCl \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$	$K = 1.8 \times 10^{+9}$
WA + water:	$HF + H_2O \rightleftharpoons H_3O^{\oplus} + F^{\ominus}$	$K = 6.8 \times 10^{-4}$
WA + SB:	$HF + NaOH \rightleftharpoons H_2O + NaF$	$K = 6.8 \times 10^{+10}$

1. Key: Strong acid $H^{\oplus}$ can be consumed by weak base.
- Strong acid is replaced by weak acid   HCl (SA) in, $NH_4^{\oplus}$ (WA) out
2. Strong base $HO^{\ominus}$ can be consumed by weak acid
- The strong base is replaced by weak base   NaOH (SB) in, NaF (WB) out

B. <u>Buffer Action</u>: A buffer system contains <u>both</u> a weak acid (to neutralize any added $OH^{\ominus}$) and a weak base (to neutralize any added $H^{\oplus}$) (Fig 17.2 Buffer Action)

- normally the weak acid and weak base are conjugates
- normally they are present in approximately equal quantities, but not always

1. Since a strong acid reacts with a weak base to produce a weak acid, addition of strong acid results in a weak increase in acidity rather than a strong increase
2. Since a strong base reacts with a weak acid to produce a weak base, addition of strong base results in a weak increase in basicity rather than a strong increase

C. The pH of buffer solutions: Ka, pKa, H^+, pH

1. Formula

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus} \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

rearrange: $$\boxed{pH = pK_a + \log\frac{[\text{base}]}{[\text{acid}]}}$$ "Henderson-Hasselbalch Equation"

$pK_a = -\log K_a$
$K_a = 10^{-pKa}$

Practical note: **<u>the base/acid ratio can be entered in moles/moles</u>** or in molarity/molarity, whichever is easier and more accessible
• since the volume is common to both base and acid

2. Some Practical Simple Stuff
a. A buffer pH depends on:
    1. pK_a which depends on K_a (weak acid strength)
    2. Base/acid ratio
b. If you have a target pH that you want for a solution, choose an acid with the appropriate K_a and pK_a
c. If the base/acid ratio = 1, then $pH = pK_a$
    - This is a helpful reference: basically the $pH \approx pK_a$, adjusted to the basic or acidic side of pK_a depending on whether you have more of the base or of the acid
        a. More base than acid: → pH number is higher (more basic) than pK_a
        b. Less base than acid: → pH number is lower (more acidic) than pK_a
d. Adding base increases the weak base/weak acid ratio, and makes the pH more basic
e. Adding acid decreases the weak base/weak acid ratio, and makes the pH more acidic

C. Buffer Capacity: determined by the quantity of weak acid/base
-dictates how much strong acid/base is consumed before buffer exhausted
-if more strong acid(base) is added than there is weak base(acid), the capacity is exceeded.

Consider 1.0 L water. Determine the pH's for the following solutions.

1. A solution with 0.5 moles of HF? (K_a for HF = 6.8×10^{-4})

Scenario

2. A solution with 0.5 moles of NaF?

Scenario

3. A solution with 0.5 moles of HF and 0.5 moles of NaF? (K_a for HF = 6.8×10^{-4})

Scenario

4. A solution with 0.5 moles of HF and 0.5 moles of NaF, to which 0.1 moles of HCl is added?

Scenario

5. A solution with 0.5 moles of HF and 0.5 moles of NaF, to which 0.1 moles of NaOH is added?

Scenario

Tips:
1. Diagnose the scenario
2. For a buffer, use Henderson-Hasselbalch equation
3. When strong acid or base is added to a buffer, write out the reaction that would occur with the strong acid or base on the left side, and then work out the ICE change.

D. Creating/Recognizing a Buffer

-must end with **weak acid/weak base** pair

1. Mix some weak acid with it’s conjugate weak base

HF, NaF H_3PO_4, NaH_2PO_4 $NaHSO_4$,Na_2SO_4 CH_3COOH, CH_3COONa NH_4Cl, NH_3

2. Start with one of conjugate pair, and add less than an equivalent amount of strong acid or strong base to create the other

Begin	Add(1/2 as much)	Result
Weak Acid	Strong Base	weak acid + conj base
Weak Base	Strong Acid	weak acid + conj base

Ex:	HF	+	$NaOH$	$\rightleftharpoons$	H_2O	+	NaF
I	0.4 moles		0.20 moles				0
C							
E							

Ex:	NH_3	+	HCl	$\rightleftharpoons$	$NH_4^+Cl^-$
I	0.6 mol		0.3 mol		0
C					
E					

Note: doesn’t work if you add too much strong acid/base:

Ex:	NH_3	+	HCl	$\rightleftharpoons$	$NH_4^+Cl^-$
I	0.6 mol		0.6 mol		0
C					
E					

Buffer Recognition

1. Which combos would make a buffer solution?

a. HF, KF

b. NH_4Cl, NH_3

c. HCl (0.2 M), NaN_3 (0.4 M)

d. HCl (0.2 mol), NaN_3 (0.1 M)

e. HN_3, $NaCl^-$

f. KF, NaF

g. KF, NaOH

h. HF, HCl

i. NH_3, KF

j. HF (0.2 mol), NaOH (0.1 mol)

Key: a) two acids don't work b) two bases don't work
c) an acid and a base is required d) tricky: strong and weak mixtures react, sometimes resulting in a buffer combination (both weak acid and weak base, examples c and j), but sometimes not, depending on ratios (example d)

2. Which could be added to 0.4 mol Na^+CN^- to give a buffer?

a. HCN

b. 0.2 mol HCl

c. 0.2 mol NaOH

d. 0.5 mol HCl

3. Which could be added to 0.4 mol H_3PO_4 to give a buffer?

a. NaH_2PO_4

b. 0.2 mol NaOH

c. 0.4 mol NaOH

d. 0.2 mol HCl

e. KCl

E. Simple Buffer Calcs

a. find pH Logic: $K_a \rightarrow pK_a \rightarrow pH$

b. find K_a Logic: $pH \rightarrow pK_a \rightarrow K_a$

c. solve for quantity of acid or base needed for target pH

Logic: pH and pK_a → base/acid ratio → needed quantity to achieve that ratio

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

"Henderson-Hasselbalch Equation"

- remember: mole/mole ration works as well as molarity/molarity ratio for base/acid

1. **Finding pH**. Find pH for buffer 0.12 M HNO_2, 0.16M $NaNO_2$ $K_a(HNO_2) = 4.5 \times 10^{-4}$

2. **Finding pK_a**. [HA] = 0.11 M [NaA] = 0.13 M. What is K_a for HA if pH = 5.18?

3. **Finding quantity of acid or base**. How many grams of NaF (42 g/mol) should be added to 612 mL solution of 0.4 M HF ($K_a = 6.8 \times 10^{-4}$) to produce a buffer solution in which pH = 3.10?

Logic:

F. pH Changes after Strong Acid or Strong Base is added to a Buffer Solution

(note: the following is written in terms of adding strong acid. Use analogous strategy for addition of strong base)

1. Write out the reaction of the added strong acid with the buffer's weak base
2. Make out an ICE-type table to show how the quantities of weak base and weak acid change as a result of the reaction
   a. Remember that a strong acid basically reacts completely with the weak base
   b. It's often best to do the ICE in terms of moles rather than molarity
   c. The "E" at the end is really the "**E**nd" of the acid-base reaction. It may not represent equilibrium
3. Assess the situation at the end of the ICE analysis
   a. Are both weak acid and weak base present?
      - buffer situation → Use HH equation

$$\boxed{\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]}}$$

   b. Is only weak acid left? (the strong acid exhausted the weak base?)
      - weak acid situation → use Ch. 16 procedure.
      - Be sure your weak acid is in terms of molarity, and factors in the combined volumes

$$[\mathrm{H}^{\oplus}] = \sqrt{K_a \times [\text{weak acid}]}$$

   c. Is strong acid as well as weak acid lieft? (The strong acid exhausted the buffer's weak base, and you still have some strong acid left over?)
      - Strong acid situation
      - Be sure your strong acid is in terms of molarity, and factors in the combined volumes

$$[\mathrm{H}^{\oplus}] = [\text{strong acid}]$$

Note: Scenario "a" is when the buffer capacity is not exhausted, and you still have a buffer situation at the end. Scenario's "b" and "c" both represent cases where the buffer capacity is exhausted, and you do **not** have a buffer scenario at the end of the reaction.

Problems

Given a 1.0 L solution that is initially 0.2 M in both HF and KF, assess the situation and find the pH after the following acids or bases are added.

a. 0.1 mol HCl added Assess:

Reaction:

I

C

E

b. 0.1 mol NaOH added Assess:

Reaction:

I

C

E

c. 1.0 L of 0.20-M HCl added Assess:

Reaction:

I

C

E

E

d. 1.5 L of 0.20-M mol NaOH added Assess:

Reaction: Web answer key has error on this one, fix

I

C

E

E

17.2 Acid-Base Titration

1. An acid and a base are mixed, at least one being strong
2. "equivalence point" or "end point:" equal moles of acid/base
3. Indicator often used to turn color, or pH meter used to give "titration curve"
4. Unlike buffer, pH changes fast near endpoints

A. Endpoint Situations: Qualitative, Non-Math Version

Acid In	Base In	Conjugate Acid Out	Conjugate Base Out	Endpoint Outcome	Endpoint pH	Example
Strong Acid	Strong Base	Non-acid	Non-base	Neutral	$pH = 7.0$	1
Strong Acid	Weak Base	Weak acid	Non-base	Weakly acidic	$pH < 7.0$	2
Weak Acid	Strong Base	Non-acid	Weak base	Weakly basic	$pH > 7.0$	3

Example		Endpoint pH
1	$HCl + NaOH \rightarrow$	
2	$HCl + NaCN \rightarrow$	
3	$HF + NaCN \rightarrow$	

1. Would the pH at endpoint be acidic, basic, or neutral when titrated with NaOH?

a. HCN

b. HNO_3

c. HF

2. Would pH at endpoint be acidic, basic, or neutral when titrated with HCl?

a. NaOH

b. NaF^-

B. Calculation of pH at the **Endpoint** for a Titration

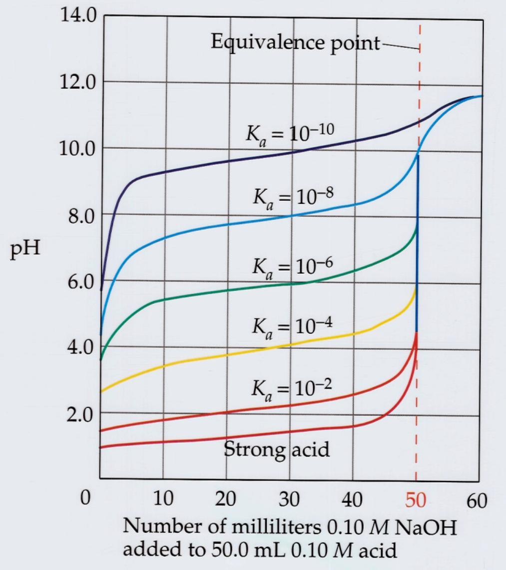
- Review: at endpoint equal moles of acid and base have been added. At least one of them was a strong acid or base, and possibly both.
- Three Possible Scenarios

Acid In	Base In	Endpoint Outcome	Endpoint pH	pH Strategy
Strong Acid	Strong Base	Neutral	pH = 7.0	None needed, pH = 7
Strong Acid	Weak Base	Weak acid	pH < 7.0	$K_a \rightarrow [H^+] \rightarrow$ pH
Weak Acid	Strong Base	Weak base	pH > 7.0	$K_a \rightarrow K_b \rightarrow [OH^-] \rightarrow$ pOH $\rightarrow$ pH

Problem: What is the pH after 40 mL of 0.10-M NaOH is added to 20 mL of 0.20-M HClO? (The K_a for HClO = 3.0×10^{-8})

C. Titration Curves: a plot of how pH changes as strong acid is added to a solution of base, or as a strong base is added to a solution of acid

T–132 Fig. 17.12 Effect of Ka on Titration Curve



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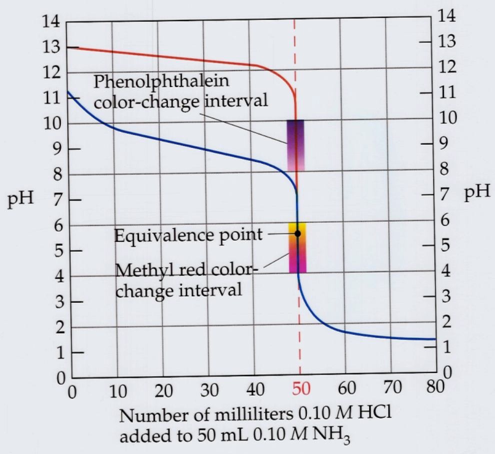
T–133 Fig. 17.13 Strong Acid-Weak Base Titration Curve



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2 Key Diagnostic features:

1. Initial pH
   - Acidic or basic? Strong or weak?
   - This reflects what you started with, before you titrate it with the strong acid or base.
2. The endpoint/equivalence point pH
   - Acidic, neutral, or basic?
   - As we saw before, this reflects what kind of acid and base were involved

Initial pH	pH < 2	2 < pH < 7	7 < pH < 12	12 < pH
Initial acid/base				

Endpoint pH	pH < 2	pH = 7	pH > 7
Acid			
Base			

Odds n ends

1. Endpoint pH is where pH changes most steeply, rapidly
2. When a weak acid is titrated by a strong base, the titration involves an extended "buffer zone" prior to the end-point, during which the pH change is rather gradual
   a. Prior to the endpoint, some of the weak acid is converted to weak base, so a conjugate weak acid/weak base buffer situation exists.
   b. The analogous situation happens when a weak base is titrated by a strong acid
3. When a weak acid "HA" is titrated by a strong base, at the half-way point (half-way to the end-point), half of the original weak acid HA is converted to its weak conjugate base A^-
   - At this point, the pH = pK_a (see HH-equation when [base]/[acid] = 1)
   - The analogous situation happens when a weak base is titrated by a strong acid

Problems

1. An initial pH = 1.3 and an equivalence point of 7 corresponds to a titration curve in which a __

__________________________ is added to a __________________________.

2. An initial pH = 9.3 and an equivalence point of 4.7 corresponds to a titration curve in which a

__________________________ is added to a __________________________.

D. Titration Calculations Involving Endpoint/Equivalence Point

Key: At equivalence point, moles acid = moles base

- know one ⇒ know other

Applications

1. Find volume required
2. Determine unknown concentrations
3. Determine unknown grams

Problems

1. What volume of 0.12 M NaOH is needed to titrate 36 mL of 0.14 M HCl to its endpoint?

2. When 42 mL of aqueous HCl is titrated by 0.10 M NaOH, it takes 25 mL of the NaOH solution to reach the endpoint. What is the [HCl] of the original solution?

3. How many grams of KOH (56 g/mol) would it take to neutralize 86 mL of 1.2 M HNO_3?

E. General pH Strategy: Finding the pH after Acid or Base is added to a solution

- Whether it be to a buffer solution, a strong acid solution, a weak acid solution, a strong base solution or a weak base solution prior to the new addition
- The strategy is similar to when we added acid or base to a buffer

1. Write out the acid-base reaction
   - It helps to recognize which species are acidic or basic or neutral, and weak or strong
2. Calculate the initial moles
   - Number of moles = molarity x volume (in Liters)
3. Use ICE to determine post-reaction ("E") moles
4. Assess the post-reaction situation, based on what's left at the end
5. Solve the pH problem from there

	<u>Post-Reaction Situation</u>		
1	Strong acid only	$[H^+] = [SA]$	
2	Strong acid plus weak acid	$[H^+] = [SA]$	Ignore WA, which makes insignificant contribution
3	Strong base only	$[HO^-] = [SB]$	
4	Strong base plus weak base	$[HO^-] = [SB]$	Ignore WB, which makes insignificant contribution
5	Weak acid only	$[H^+] = \sqrt{K_a x[WA]}$	Qual: pH < 7
6	Weak base only	$[HO^-] = \sqrt{K_b x[WB]}$	Qual: pH > 7 May need to find K_b from K_a
7	Weak acid plus weak base	$pH = pK_a + \log\frac{[base]}{[acid]}$	Buffer solution
8	No acid or base; only neutral salts	pH = 7.0	

- For many of these, it will be necessary to calculate molarities
- To do this, make sure that you factor in the total, combined volume

Key: Recognizing the Final Situation!!

Strong base added to weak acid. (Strong acid/weak base combinations would be analogous.)
What is pH after:

A. 20 mL of 0.10 M NaOH is added to 20 mL of 0.10 M HClO? ($K_a = 3.0 \times 10^{-8}$)

B. 20 mL of 0.10 M NaOH is added to 10 mL of 0.10 M HClO?

C. 20 mL of 0.10 M NaOH is added to 30 mL of 0.10 M HClO? ($K_a = 3.0 * 10^{-8}$)

F. Addition of strong acid to a weak acid solution. (Analog would be strong base to weak base)

1. A solution has 1 L of 0.40 M acetic acid ($K_a = 1.80 \times 10^{-5}$). Find the pH and [$CH_3COO^-$]

Ex: $HA \quad + \quad \rightleftharpoons \quad H^+ \quad + \quad A^-$

I

C

E

2. Suppose 0.10 moles of HCl is added to the above solution (assume no change in volume). Find the pH and [CH_3COO^-]

Ex: $HA \quad + \quad \rightleftharpoons \quad H^+ \quad + \quad A^-$

I

C

E

<u>Notice:</u>

1. The strong acid dominates the pH
2. When a weak acid is in water by itself, then [H^+] = [A^-]
3. But when strong acid was added (as an additional source of [H^+],) [H^+] >> [A^-]
4. The equilibrium constant still applies. With [H^+] up, [A^-] goes down, ala LeChatelier's principle

17.4 Solubility Equilibria for Ionic Compounds: K_{sp}

- The solubility of ionic compounds is a big deal, from kidney stones to drinking water to stalagtites and stalagmites

A. K_{sp} "Solubility Product Constant"

- In a "saturated solution," insoluble solid is in equilibrium with aqueous ions
- Easy to write K expressions

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq) \qquad K=$$

I

C

E (doesn't matter, not in K!!)

B. Various K_{sp} setups, depending on Formulas and Number of Cations/Anions Produced:

1. $AgCl(s) \rightleftharpoons$ K =

2. $Zn(OH)_2(s) \rightleftharpoons$ K =

3. $ScCl_3(s) \rightleftharpoons$ K =

4. $Al_2(SO_4)_3(s) \rightleftharpoons$ K =

<u>Points:</u>

1. Manipulating equations with x^3 or x^4 is common!
2. While the solid itself doesn't appear in the K expression, the value of "x" does tell how many moles/L of the original solid can dissolve.
    - If you know how many moles/Liter of product solute is present, you know how many moles/Liter of parent solid actually dissolves

C. Technical note: often K_{sp} problems end up with x^3 or x^4 type terms. What does this mean and how do I solve them?

- Ex 1: $x^3 = 100$ meaning: x times x times x = 100. Or, $x = 100^{1/3}$ (x = 4.64)
  - Calculator: find your calculator's $\sqrt[x]{y}$ key, enter 100 for "y" and 3 for "x"
  - In other words, solve as $x = \sqrt[3]{100}$
  - On my Texas Instruments Calculator (yours may differ):
    - enter 100 first
    - click the $\sqrt[x]{y}$ key second
    - enter 3 third

- Ex 2: $0.26^3 = x$ meaning: 0.26 times 0.26 times 0.26 = x. (x = 0.0176)
  - Calculator: find your calculator's y^x key, enter 0.26 for "y" and 3 for "x"
  - On my Texas Instruments Calculator (yours may differ, x^y for Casio?):
    - enter 0.26 first
    - click the y^x key second
    - enter 3 third

Calculator Practice

x equals

1. $x^3=125$
   - enter 125
   - click the $\sqrt[x]{y}$ key
   - enter 3
2. $x^3=200$
3. $x^4=12.7$

x equals

4. $12^3=x$
   - enter 12
   - click the y^x key
   - enter 3
5. $8^4=x$
6. $3.2^3=x$

D. Definitions
1. "Solubility": g/L of solid that dissolves
2. "Molar solubility": mol/L of solid that dissolves

E. Interconverting Solubility and K_{sp}: Calculations

1. Working from K_{sp} to solubility:

K_{sp} $\rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

2. Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

Working from K_{sp} to solubility:

K_{sp} $\rightleftharpoons$ moles/L of ions $\rightleftharpoons$ moles/L of solid $\rightleftharpoons$ (g/L) of solid

1. $PbCl_2$ (278 g/mol) $PbCl_2$ (s) $\rightleftharpoons$ K =
$K_{sp}=1.6 \times 10^{-5}$

a. Calculate $[Pb^{2+}]$ and $[Cl^-]$ for a saturated solution of $PbCl_2$.

b. Calculate molar solubility (mol/L) for $PbCl_2$

c. Calculate mass solubility (g/L) for $PbCl_2$

d. What mass of $PbCl_2$ (278 g/mol) would dissolve in 140 mL?

Working from solubility to K_{sp}:

Solubility of compound (g/L) $\rightleftharpoons$ Molar solubility of compound (mol/L) $\rightleftharpoons$ Molar concentration of ions $\rightleftharpoons$ K_{sp}

1. Find K_{sp} for CaF_2 whose molar solubility is 2.1×10^{-4} mol/L.

Molar solubility plus stoichiometry tells us what ion concentrations are, from which K can be found.

2. $BaCO_3$ (197g/mol) has a solubility of 0.014 g/L. Find K_{sp} for $BaCO_3$.

17.5 Factors that affect Solubility of Ionic Compounds (LeChatelier's Principle)

A. pH Factor: If anion is basic, solubility increases at low pH (high $[H^+]$)

1. Via selective removal of anion (product side)
2. Many basic anions: OH^-, F^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-} etc.
3. Few non-basic anions: Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, HSO_4^-

Example 1: $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$

Add acid:

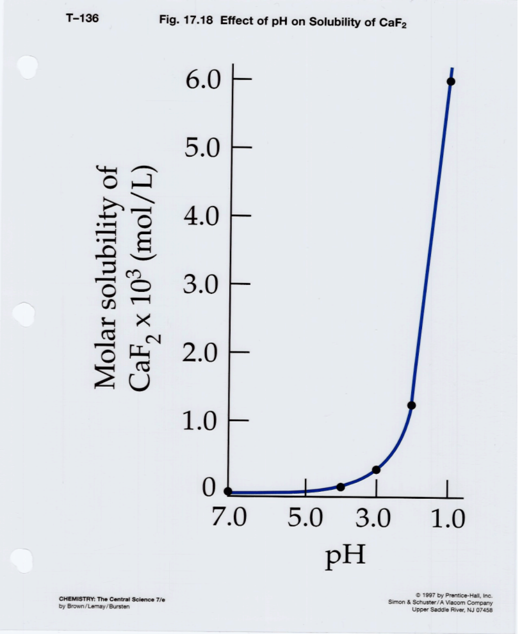
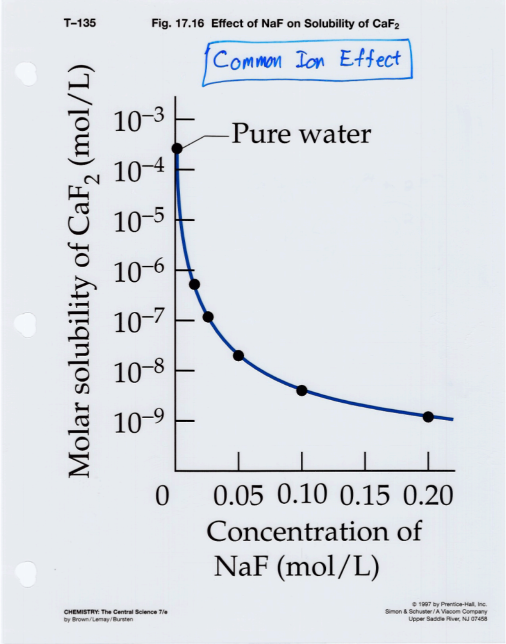
By selective removal of $[OH^-]$,
$Q < K$, so ala LeChatelier,
solid $Cu(OH)_2$ keeps dissolving,
and $[Cu^{2+}]$ keeps rising

Example 2: $PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^-(aq)$ $K=[Pb^{2+}][F^-]^2$

Add acid:

Example 3: $PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$ $K=[Pb^{2+}][Br^-]^2$

Add acid:

pH Effect on CaF$_2$ (fluoride is a basic anion)	**Common Ion Effect** (fluoride from NaF is the "common ion")
	

B. Common Ion Effect: A "common ion" decreases solubility

Example: $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

Additive	Equilibrium Shift	Impact on:	Ratio of $[Ba^{2+}]$ to $[SO_4^{2-}]$		Impact on Moles of $BaSO_4$	Impact on Solubility of $BaSO_4$
1 Add $Ba^{2+}(aq)$ (for example, $Ba(NO_3)_2$)		$[SO_4^{2-}]$	$[Ba^{2+}]$	$[SO_4^{2-}]$		
2 Add SO_4^{2-} (aq) (for example, Na_2SO_4)		$[Ba^{2+}]$	$[Ba^{2+}]$	$[SO_4^{2-}]$		

Notes:

1. If Ba^{2+} or SO_4^{2-} is added as a common ion from a different source, that pushes the equilibrium to left, so solubility decreases
2. Case 1, where $Ba(NO_3)_2$ was added:
   a. The barium ion concentration $[Ba^{2+}]$ is dominated by the fully soluble $[Ba(NO_3)_2]$ source
   b. Simplifying assumption allows the contribution "x" from $BaSO_4$ to be ignored
   c. As a result, solving for $[SO_4^{2-}]$ and thus the molar solubility of $BaSO_4$ under these conditions becomes easy.

Point: When a known concentration of a common ion is present, you can easily:

1. Calculate molar concentrations of ions
2. Calculate molar solubility of the solid

Problem:

1. What is the molar solubility of $BaSO_4$ when added to regular water?

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$

2. What is the molar solubility of $BaSO_4$ in the presence of 0.10-M $Ba(NO_3)_2$?

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$

3. What is the molar solubility of $BaSO_4$ in the presence of 0.50-M Na_2SO_4?

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq) \qquad K = 1.1 \times 10^{-10}$

How would the solubility of the salts be affected?

Q's: 1. Is there a common ion? 2. Is there a basic anion that might be impacted by pH?

	Added $Ca(NO_3)_2$	Added NaF	Added HNO_3	More soluble at Low or High pH?
1. CaF_2				
2. $CaCO_3$				
3. $Ca(OH)_2$				
4. ZnF_2				
5. $PbCl_2$				
6. AgI				
7. $ZnSO_4$				

8. What is molar solubility of AgBr ($K_{sp}=3.3x10^{-13}$) in a solution with 0.20 M NaBr (which of course dissolves fully)?

9. What would AgBr solubility be without NaBr present?

10. Determine molar solubility for $Mg(OH)_2$ ($K_{sp}=1.5 \text{ x } 10^{-11}$) at the following pH's:

Equation:

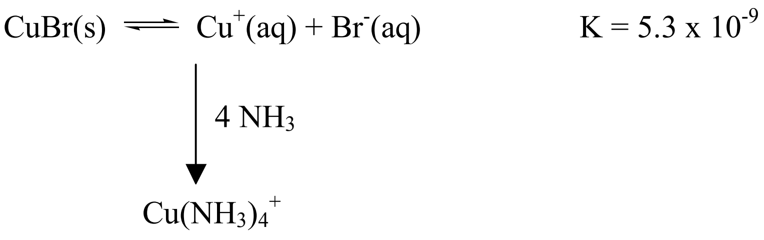
a. pH=12.00

b. pH=6.00

pH often can define the concentrion of hydroxide (or other basic anions whose K_a is known)

C. Complex Ion Formation (not for test, but lab relevant)

- many Lewis bases can <u>increase</u> the solubility of a solid by <u>irreversible removal</u> of a product cation
- NH_3, ^-CN common



$$CuBr(s) \rightleftharpoons Cu^+(aq) + Br^-(aq) \qquad K = 5.3 \text{ x } 10^{-9}$$

$$Cu^+ \xrightarrow{4\ NH_3} Cu(NH_3)_4^+$$

- Selective, irreversible removal of the copper ion via ammonia complexation drives the equilibrium in the right direction.
    - Thus, the solubility of the original solid increases.

General pH Strategy: Finding the pH after Acid or Base is added to a solution

- Whether it be to a buffer solution, a strong acid solution, a weak acid solution, a strong base solution or a weak base solution prior to the new addition
- The strategy is similar to when we added acid or base to a buffer

6. Write out the acid-base reaction
   - It helps to recognize which species are acidic or basic or neutral, and weak or strong
7. Calculate the initial moles
   - Number of moles = molarity x volume (in Liters)
8. Use ICE to determine post-reaction ("E") moles
9. Assess the post-reaction situation, based on what's left at the end
10. Solve the pH problem from there

	Post-Reaction Situation		
1	Strong acid only	$[H^+] = [SA]$	
2	Strong acid plus weak acid	$[H^+] = [SA]$	Ignore WA, which makes insignificant contribution
3	Strong base only	$[HO^-] = [SB]$	
4	Strong base plus weak base	$[HO^-] = [SB]$	Ignore WB, which makes insignificant contribution
5	Weak acid only	$[H^+] = \sqrt{K_a x [WA]}$	Qual: pH < 7
6	Weak base only	$[HO^-] = \sqrt{K_b x [WB]}$	Qual: pH > 7 May need to find K_b from K_a
7	Weak acid plus weak base	$pH = pK_a + \log \frac{[base]}{[acid]}$	Buffer solution
8	No acid or base; only neutral salts	pH = 7.0	

- For many of these, it will be necessary to calculate molarities
- To do this, make sure that you factor in the total, combined volume

Key: Recognizing the Final Situation!!

APPENDIX
Table of Solubility Product C) Constants (K_{sp} at 25^o C) (OWL)

Bromides	$PbBr_2$	6.3 x 10^{-6}		Iodides	PbI_2	8.7 x 10^{-9}
	AgBr	3.3 x 10^{-13}			AgI	1.5 x 10^{-16}
Carbonates	$BaCO_3$	8.1 x 10^{-9}		Oxalates	BaC_2O_4	1.1 x 10^{-7}
	$CaCO_3$	3.8 x 10^{-9}			CaC_2O_4	2.3 x 10^{-9}
	$CoCO_3$	8.0 x 10^{-13}			MgC_2O_4	8.6 x 10^{-5}
	$CuCO_3$	2.5 x 10^{-10}		Phosphates	$AlP0_4$	1.3 x 10^{-20}
	$FeCO_3$	3.5 x 10^{-11}			$Ba_3(P0_4)_2$	1.3 x 10^{-29}
	$PbCO_3$	1.5 x 10^{-13}			$Ca_3(P0_4)_2$	1.0 x 10^{-25}
	$MgCO_3$	4.0 x 10^{-5}			$CrP0_4$	2.4 x 10^{-23}
	$MnCO_3$	1.8 x 10^{-11}			$Pb_3(P0_4)_2$	3.0 x 10^{-44}
	$NiCO_3$	6.6 x 10^{-9}			Ag_3P0_4	1.3 x 10^{-20}
	Ag_2CO_3	8.1 x 10^{-12}			$Zn_3(P0_4)_2$	9.1 x 10^{-33}
	$ZnCO_3$	1.5 x 10^{-11}		Sulfates	$BaS0_4$	1.1 x 10^{-10}
Chlorides	$PbCl_2$	1.7 x 10^{-5}			$CaS0_4$	2.4 x 10^{-5}
	AgCl	1.8 x 10^{-10}			$PbS0_4$	1.8 x 10^{-8}
Chromates	$BaCrO_4$	2.0 x 10^{-10}			Ag_2S0_4	1.7 x 10^{-5}
	$CaCrO_4$	7.1 x 10^{-4}		Sulfides	CaS	8 x 10^{-6}
	$PbCrO_4$	1.8 x 10^{-14}			CoS	5.9 x 10^{-21}
	Ag_2CrO_4	9.0 x 10^{-12}			CuS	7.9 x 10^{-37}
Cyanides	$Ni(CN)_2$	3.0 x 10^{-23}			FeS	4.9 x 10^{-18}
	AgCN	1.2 x 10^{-16}			Fe_2S_3	1.4 x 10^{-88}
	$Zn(CN)_2$	8.0 x 10^{-12}			PbS	3.2 x 10^{-28}
Fluorides	BaF_2	1.7 x 10^{-6}			MnS	5.1 x 10^{-15}
	CaF_2	3.9 x 10^{-11}			NiS	3.0 x 10^{-21}
	PbF_2	3.7 x 10^{-8}			Ag_2S	1.0 x 10^{-49}
	MgF_2	6.4 x 10^{-9}			ZnS	2.0 x 10^{-25}
Hydroxides	AgOH	2.0 x 10^{-8}		Sulfites	$BaS0_3$	8.0 x 10^{-7}
	$Al(OH)_3$	1.9 x 10^{-33}			$CaS0_3$	1.3 x 10^{-8}
	$Ca(OH)_2$	7.9 x 10^{-6}			Ag_2S0_3	1.5 x 10^{-14}
	$Cr(OH)_3$	6.7 x 10^{-31}				
	$Co(OH)_2$	2.5 x 10^{-16}				
	$Cu(OH)_2$	1.6 x 10^{-19}				
	$Fe(OH)_2$	7.9 x 10^{-15}				
	$Fe(OH)_3$	6.3 x 10^{-38}				
	$Pb(OH)_2$	2.8 x 10^{-16}				
	$Mg(OH)_2$	1.5 x 10^{-11}				
	$Mn(OH)_2$	4.6 x 10^{-14}				
	$Ni(OH)_2$	2.8 x 10^{-16}				
	$Zn(OH)_2$	4.5 x 10^{-17}				