

## Chapter 15 - Applications of Aqueous Equilibria

GCC CHM152

### 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.

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### Common Ion Concept Problem

Given this reaction:



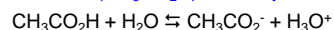
What happens to the pH of the acetic acid solution if we add  $\text{NaCH}_3\text{CO}_2$ ?

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### Common Ion Effect

What is the pH of 0.100 M  $\text{CH}_3\text{CO}_2\text{H}$  solution?  $K_a = 1.8 \times 10^{-5}$   
 $\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}_3\text{O}^+$

- pH = 2.87 for WA (without a common ion)
- What is the pH of 0.100 M  $\text{CH}_3\text{CO}_2\text{H}$  if we add 0.050 M  $\text{NaCH}_3\text{CO}_2$ ? Have WA ( $\text{CH}_3\text{CO}_2\text{H}$ ) and conj base ( $\text{CH}_3\text{CO}_2^-$ )



I, M				
C, M				
E, M				

- pH = 4.44 for WA w/ common ion (CB); pH ↑ as predicted

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### Common Ion Problem

*\*See worksheet key for complete solution*

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

HF = WA: write WA rxn, set up ICE, solve  $K_a$  for x

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

WA = HF, conj base =  $\text{F}^-$

WA eq rxn, have both HA & A<sup>-</sup>! Solve  $K_a$  for x

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### 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.  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$

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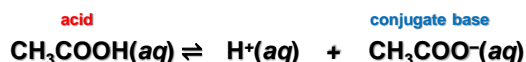
## Which are buffer solutions?

Identify the solutions below that would make good buffer solutions :

- ♦ HF and NaF
- ♦ NH<sub>3</sub> and NH<sub>4</sub>Cl
- ♦ KOH and KF
- ♦ CH<sub>3</sub>COOH and LiCH<sub>3</sub>COO
- ♦ NaNO<sub>3</sub> and HNO<sub>3</sub>
- ♦ NaOH and NaCl

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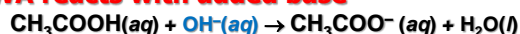
## How Buffer Solution works



reacts with  
added base

reacts with  
added acid

**WA reacts with added base**



**WB reacts with added acid**



## Buffer Capacity

**Buffer capacity** is the amount of acid or base the buffer can neutralize before there is a significant change in pH.

**Buffers work best when [HA] and [A<sup>-</sup>] are equal.**

⇒ For buffers to be effective, the ratio of Base:Acid should be within a factor of 10.

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

- **Buffer capacity is also greater when larger amounts of HA and A<sup>-</sup> are present.**

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## Buffer Range

**Buffers only work within a narrow range:**

$$\text{pH} = \text{pK}_a \pm 1$$

- To make a buffer, select an acid (and salt containing its CB) with a pK<sub>a</sub> close to the pH you want (pK<sub>a</sub> ± 1), and adjust the [base]/[acid] ratio to obtain the desired pH.
- How would you make a buffer solution with pH = 4.10? What could you use to make this?

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## Henderson-Hasselbalch Equation

- pH of a buffer solution can be calculated from the Henderson Hasselbalch Equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

- ♦ Only use this for buffers where you have a conjugate acid/base pair!
- ♦ Can use moles or M – depending on given info ⇒ V units cancel since it's a ratio of [base]/[acid]!

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## ICE vs Change Tables

	ICE table	Change Table
<b>When to use</b>	Weak acid or base in water	SA or SB is one of the reactants
<b>Units</b>	molarity	moles
<b>Labels</b>	Initial, Change, Equilibrium	Initial, Change, Final
<b>Arrows</b>	⇌	→
<b>How to find x</b>	Solve for x at equilibrium	x = L.R. = smallest # of initial moles

## pH of Buffer Solution

What is the pH of 500.0 mL of 0.10 M  $\text{HCO}_2\text{H}$  combined with 400.0 mL of 0.20 M  $\text{NaHCO}_2$ ? For  $\text{HCO}_2\text{H}$ ,  $K_a = 1.8 \times 10^{-4}$   
See worksheet key for more detail!

- If given V's for each substance  $\Rightarrow$  calc moles (or diluted M)
- Write WA hydrolysis reaction ( $\text{HA} = \text{HCO}_2\text{H}$ )
- Plug amounts into HH equation or  $K_a$  expression

Initial mol  $\text{HCO}_2\text{H} =$   
Initial mol  $\text{HCO}_2^- =$

WA rxn:

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]}\right)$$

pH =

Note: Don't use original M's if V's of each solution are given! 13

## Buffer + HCl

B) What is pH after 20.0 mL of 0.50 M HCl is added to buffer?

- Write AB neut:  $\text{H}_3\text{O}^+$  reacts with  $\text{A}^-$  to form HA so  $\text{A}^- \downarrow$  and  $\text{HA} \uparrow$
- calc moles, set up change table, plug final moles into HH!

Initial mol HCl = (0.0200 L) (0.50 M) = 0.010 mol = LR



Initial moles				
Change in moles				
Final moles				

$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]}\right)$  (initially pH = 3.95 for part A)

pH =

- pH  $\downarrow$  slightly when SA added to buffer
  - If same amount of SA was added to water, pH would drop from 7 to 2!

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## Buffer Solutions + NaOH

C) What is pH after 20.0 mL of 0.50 M NaOH is added to buffer?

- Write AB rxn:  $\text{OH}^-$  reacts with HA to form  $\text{A}^-$  so  $\text{HA} \downarrow$  and  $\text{A}^- \uparrow$
- calc moles, set up change table, plug final moles into HH!

Initial mol  $\text{OH}^- = (0.0200 \text{ L}) (0.50 \text{ M}) = 0.010 \text{ mol } \text{OH}^- = \text{LR}$



Initial moles				
Change in moles				
Final moles				

$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]}\right)$  (initially pH = 3.95 for part A)

pH =

- pH  $\uparrow$  slightly when SB added to buffer
  - If same amount of SB was added to water, pH would rise from 7 to 12!

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## Group Quiz 13

Consider a buffer solution prepared from HOCl and NaOCl.

A) Write the net ionic equation for the neutralization reaction that occurs when NaOH is added to this buffer.

B) Will the pH stay the same, increase or decrease when NaOH is added?

C) Write the net ionic equation for the neutralization reaction that occurs when HI(aq) is added to this buffer.

D) Will the [HOCl] increase, decrease or stay the same when HI(aq) is added?

E) Will the [OCl<sup>-</sup>] increase, decrease or stay the same when HI(aq) is added?

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## pH Titration Curves

4 key regions on a titration curve

- Initial solution (before titrant is added)
- Before the equivalence point
- At the equivalence point
- After the equivalence point

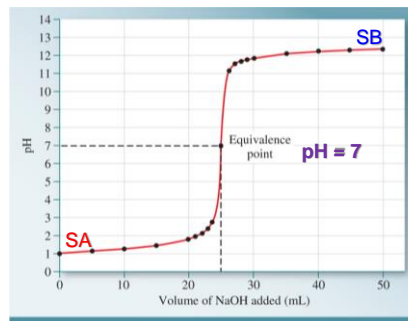
For Titration problems may use mmol :

1 mole = 1000 mmoles

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

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## Strong Acid- Strong Base Titration



## Strong Acid-Strong Base

Draw 4 beakers.

- 1) Draw 2 moles HCl. (How do we draw SA?)
- 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.

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## SA-SB Titration Problem

pH's for titration of 20.00 mL of 0.200 M HCl by 0.100 M NaOH.  
SA SB

**AB neut reaction:**  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

a) 0 mL NaOH, **just have SA solution**

For SA:  $[\text{H}_3\text{O}^+] = [\text{HCl}] = 0.200 \text{ M}$

•  $\text{pH} = -\log(0.200) = 0.700$  initial pH of SA

b) 5.00 mL NaOH, **Before eq. pt so have excess SA**

• Calculate initial moles of acid & base,

• Subtract LR to find final moles of excess acid

•  $[\text{SA}] = [\text{H}_3\text{O}^+] = \text{final moles SA}/\text{total volume}$

•  $[\text{H}_3\text{O}^+] = 3.50 \text{ mmol H}_3\text{O}^+ / 25.00 \text{ mL} = 0.140 \text{ M}$

•  $\text{pH} = -\log(0.140) = 0.854$  (low pH due to excess SA)

See worksheet key for more detail!

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## SA-SB Titration problem

pH's for 20.00 mL of 0.200 M HCl titrated by 0.100 M NaOH.

**AB neut reaction:**  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

3) 40.00 mL NaOH, at equivalence point

• mol acid = mol base = 4.00 mmol

•  $\text{pH} = 7$  (neutral pH, just have neutral salt and water left)

• pH is always 7 at eq pt for strong acid-strong base!

4) 50.00 mL NaOH, **After eq. pt so have excess SB!**

• Calculate moles of acid and base

• subtract LR to find final moles of excess base

•  $[\text{SB}] = [\text{OH}^-] = \text{final moles of base}/\text{total volume}$

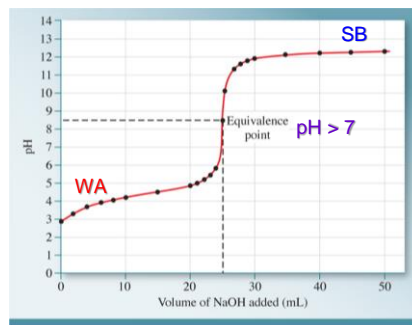
•  $[\text{OH}^-] = 1.00 \text{ mmol OH}^- / 70.00 \text{ mL} = 0.01429 \text{ M}$

•  $\text{pOH} = -\log(0.01429) = 1.845$

•  $\text{pH} = 12.155$  (high pH due to excess SB)

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## Weak Acid- Strong Base Titration



## Weak Acid-Strong Base

Draw 4 beakers.

- 1) Draw 2 moles weak acid. (Assume WA is not dissociated!)
- 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.

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## WA-SB Titration Problem

50.00 mL of 0.100 M acetic acid titrated by 0.150 M KOH.  
 $K_a = 1.8 \times 10^{-5}$  WA SB

A) 0 mL of base; **initial pH of WA = WA problem!**

• Must set up ICE and  $K_a$ ,  $x = [\text{H}_3\text{O}^+]$



I, M	0.100		0	0
C, M	-x		+x	+x
E, M	0.100 - x		x	x

$$K_a = \frac{x^2}{[\text{HA}]}$$

$$x = [\text{H}_3\text{O}^+] = \sqrt{0.100 \times 1.8 \times 10^{-5}} = 1.34 \times 10^{-3} \text{ M}$$

$\text{pH} = 2.87$  (initial pH for WA solution)

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## WA-SB Titration before Eq Pt

50.00 mL of 0.100 M acetic acid titrated by 0.150 M KOH.  
 $K_a = 1.8 \times 10^{-5}$

General steps:

- Write Neut rxn:  $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{COO}^-$
- Calc moles and use change table to determine what remains after neutralization!

- B) 10.00 mL KOH (pH before eq pt = buffer problem)
- Both HA and  $\text{A}^-$  are present  $\Rightarrow$  **buffer region**
  - Final moles HA = initial moles HA - moles base added
  - Final moles  $\text{A}^-$  formed = moles base added
  - Plug final moles (or final M's) into HH equation
  - **DO NOT USE HH EQUATION FOR ANY OTHER REGION OF WA-SB TITRATION CURVE!**

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## WA-SB Titration at Eq Pt

50.00 mL of 0.100 M acetic acid titrated by 0.150 M KOH

- V of KOH at eq pt = 33.33 mL

- C) at the eq. pt.; basic salt is present = WB problem!
- At the eq pt all of the SB and WA have reacted to produce a basic salt. (Remember the anion for a WA is not neutral – its basic!)
  - Calculate  $[\text{A}^-]$  = moles conj base/ total volume
  - Conj Base ( $\text{A}^-$ ) reacts with water:  $\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$
  - Set up ICE table
  - find  $K_b = K_w / K_a$  ;
  - Solve  $K_b = x^2/[\text{A}^-]$  for x, where  $x = [\text{OH}^-]$
  - calculate pOH and convert to pH

pH = 8.76

\*See titration worksheet key for complete solution!

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## WA-SB Titration after Eq Pt

50.00 mL of 0.100 M acetic acid titrated by 0.150 M KOH.

d) 50.00 mL KOH (After eq pt: excess  $\text{OH}^-$  from SB)

- pH is determined primarily from excess SB.
  - We can neglect the hydrolysis of conjugate base since it would contribute a lot less  $\text{OH}^-$  compared to the SB.
- pH calc after eq pt is same for SA-SB and WA-SB!
- $[\text{OH}^-]$  = final moles  $\text{OH}^-$  / total volume  
 mmol  $\text{OH}^-$  = 7.50 mmol – 5.00 mmol = 2.50 mmol  $\text{OH}^-$   
 total mL = 50.00 + 50.00 = 100.00 mL  
 $[\text{OH}^-]$  = 2.50 mmol/100.00 mL = 0.0250 M  $\text{OH}^-$   
 pOH =  $-\log(0.0250 \text{ M}) = 1.602$   
 pH =  $14 - 1.602 = 12.398$

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## Half Equivalence Point

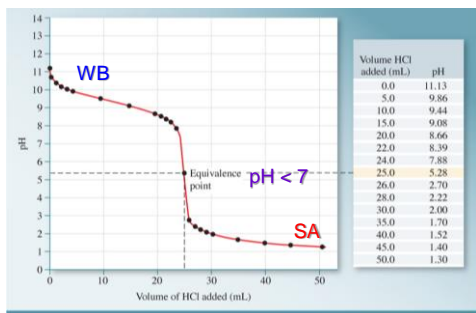
- Special Region exists when Acid is half neutralized:
- Half of the acid remains and the other half has been converted into its conjugate base
- At the  $\frac{1}{2}$  eq pt, moles HA remaining = moles  $\text{A}^-$  formed
- Thus,  $[\text{HA}] = [\text{A}^-]$

$$\text{pH} = \text{p}K_a + \log \left( \frac{[\text{A}^-]}{[\text{HA}]} \right)$$

at  $\frac{1}{2}$  eq pt:  $\text{pH} = \text{p}K_a$

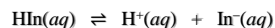
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## Strong Acid-Weak Base Titrations

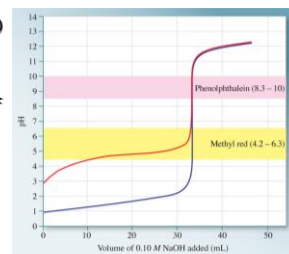


## End Point for Acid-Base Titrations

The endpoint in a titration can be visualized with the use of an **acid-base indicator**. (The acid and conjugate base forms of the indicator have different colors)



The **endpoint** of a titration is the point at which the color of the indicator changes.



## Indicators for Acid-Base Reactions

TABLE 17.3 Some Common Acid-Base Indicators

Indicator	Color		pH range
	In acid	In base	
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

## Solubility Equilibria

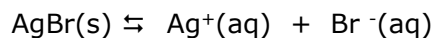
- Some combinations of ions form solid precipitates in aqueous solutions. (Refer to Solubility rules)
- These “insoluble” salts dissolve to a small extent and form a saturated solution.
- The undissolved solid and the dissociated ions in solution establish an equilibrium reaction.
- $K_{sp}$  is the equilibrium constant for the dissociation of an insoluble salt.

important biological examples:

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

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## Example. The dissolution of AgBr



$$K_{sp} = [\text{Ag}^+][\text{Br}^-]$$

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

- It is a measure of how soluble a salt is in  $\text{H}_2\text{O}$
- $\Rightarrow$  For salts with the same # of ions, the smaller the  $K_{sp}$ , the less soluble the salt.

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TABLE 17.4 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	Dissolution equilibrium	$K_{sp}$
Aluminum hydroxide	$\text{Al}(\text{OH})_3(s) \rightleftharpoons \text{Al}^3+(aq) + 3\text{OH}^-(aq)$	$1.8 \times 10^{-33}$
Barium carbonate	$\text{BaCO}_3(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{CO}_3^{2-}(aq)$	$8.1 \times 10^{-9}$
Barium fluoride	$\text{BaF}_2(s) \rightleftharpoons \text{Ba}^{2+}(aq) + 2\text{F}^-(aq)$	$1.7 \times 10^{-8}$
Barium sulfate	$\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$	$1.1 \times 10^{-10}$
Bismuth sulfide	$\text{Bi}_2\text{S}_3(s) \rightleftharpoons 2\text{Bi}^{3+}(aq) + 3\text{S}^{2-}(aq)$	$1.6 \times 10^{-72}$
Cadmium sulfide	$\text{CdS}(s) \rightleftharpoons \text{Cd}^{2+}(aq) + \text{S}^{2-}(aq)$	$8.0 \times 10^{-28}$
Calcium carbonate	$\text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq)$	$8.7 \times 10^{-9}$
Calcium fluoride	$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$	$4.0 \times 10^{-11}$
Calcium hydroxide	$\text{Ca}(\text{OH})_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)$	$8.0 \times 10^{-6}$
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2(s) \rightleftharpoons 3\text{Ca}^{2+}(aq) + 2\text{PO}_4^{3-}(aq)$	$1.2 \times 10^{-28}$
Calcium sulfate	$\text{CaSO}_4(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{SO}_4^{2-}(aq)$	$2.4 \times 10^{-5}$
Chromium(III) hydroxide	$\text{Cr}(\text{OH})_3(s) \rightleftharpoons \text{Cr}^{3+}(aq) + 3\text{OH}^-(aq)$	$3.0 \times 10^{-38}$
Cobalt(II) sulfide	$\text{CoS}(s) \rightleftharpoons \text{Co}^{2+}(aq) + \text{S}^{2-}(aq)$	$4.0 \times 10^{-21}$
Copper(I) bromide	$\text{CuBr}(s) \rightleftharpoons \text{Cu}^+(aq) + \text{Br}^-(aq)$	$4.2 \times 10^{-8}$
Copper(I) iodide	$\text{CuI}(s) \rightleftharpoons \text{Cu}^+(aq) + \text{I}^-(aq)$	$5.1 \times 10^{-12}$
Copper(II) hydroxide	$\text{Cu}(\text{OH})_2(s) \rightleftharpoons \text{Cu}^{2+}(aq) + 2\text{OH}^-(aq)$	$2.2 \times 10^{-20}$
Copper(II) sulfide	$\text{CuS}(s) \rightleftharpoons \text{Cu}^{2+}(aq) + \text{S}^{2-}(aq)$	$6.0 \times 10^{-36}$
Iron(II) hydroxide	$\text{Fe}(\text{OH})_2(s) \rightleftharpoons \text{Fe}^{2+}(aq) + 2\text{OH}^-(aq)$	$1.6 \times 10^{-14}$
Iron(II) hydroxide	$\text{Fe}(\text{OH})_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{OH}^-(aq)$	$1.1 \times 10^{-38}$
Iron(III) phosphate	$\text{FePO}_4(s) \rightleftharpoons \text{Fe}^{3+}(aq) + \text{PO}_4^{3-}(aq)$	$1.3 \times 10^{-25}$
Iron(II) sulfide	$\text{FeS}(s) \rightleftharpoons \text{Fe}^{2+}(aq) + \text{S}^{2-}(aq)$	$6.0 \times 10^{-19}$
Lead(II) bromide	$\text{PbBr}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Br}^-(aq)$	$6.6 \times 10^{-6}$
Lead(II) carbonate	$\text{PbCO}_3(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{CO}_3^{2-}(aq)$	$3.3 \times 10^{-14}$
Lead(II) chloride	$\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{Cl}^-(aq)$	$2.4 \times 10^{-4}$
Lead(II) chromate	$\text{PbCrO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{CrO}_4^{2-}(aq)$	$2.0 \times 10^{-14}$
Lead(II) fluoride	$\text{PbF}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{F}^-(aq)$	$4.0 \times 10^{-8}$
Lead(II) iodide	$\text{PbI}_2(s) \rightleftharpoons \text{Pb}^{2+}(aq) + 2\text{I}^-(aq)$	$1.4 \times 10^{-8}$
Lead(II) sulfate	$\text{PbSO}_4(s) \rightleftharpoons \text{Pb}^{2+}(aq) + \text{SO}_4^{2-}(aq)$	$1.8 \times 10^{-8}$

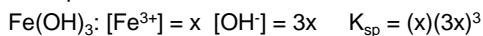
Write the solubility equilibrium reactions and  $K_{sp}$  expressions for  $\text{Sr}_3(\text{PO}_4)_2$ .

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## Solubility

- $K_{sp}$  can be used to calculate the solubility
- 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

Example:



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## Solubility/ $K_{sp}$ Practice

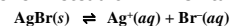
- $K_{sp}$  for AgBr is  $7.7 \times 10^{-13}$ . Calculate the molar and gram solubility.
- If a saturated solution prepared by dissolving  $\text{CaF}_2$  in water has  $[\text{Ca}^{2+}] = 3.3 \times 10^{-4} \text{ M}$ , what is the value of  $K_{sp}$ ?
- $K_{sp}$  for  $\text{Al}(\text{OH})_3$  is  $1.9 \times 10^{-33}$ . Calculate the molar solubility.
- The solubility of  $\text{Ca}(\text{OH})_2$  is 0.233 g/L. Calculate  $K_{sp}$ .

Refer to solubility worksheet key!

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## Calculate solubility from $K_{sp}$

The  $K_{sp}$  of silver bromide is  $7.7 \times 10^{-13}$ . Calculate the molar solubility. (Note: book uses "s" instead of x in ICE table.)



I (M)		0	0
(M)		+x	+x
E (M)		x	x

$$K_{sp} = [\text{Ag}^+][\text{Br}^-] = 7.7 \times 10^{-13}$$

$$7.7 \times 10^{-13} = (x)(x)$$

$$x = 8.8 \times 10^{-7} \text{ M}$$

$$\frac{8.8 \times 10^{-7} \text{ mol AgBr}}{1 \text{ L}} \times \frac{187.8 \text{ g}}{1 \text{ mol AgBr}} = 1.7 \times 10^{-4} \text{ g/L}$$

## Does a precipitate form?

We can calculate the reaction quotient Q to predict if precipitation will occur

$Q > K_{sp}$ , eq shifts ← (toward s) ppt forms

- There are excess ions in solution that will precipitate out to form a solid

$Q = K_{sp}$ , Saturated solution, no ppt

- solution holds maximum amount of dissolved salt

$Q < K_{sp}$ , no ppt; eq shifts → (towards ions)

- Unsaturated solution, the ion [ ]'s are not high enough to form a solid

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## Precipitation of Ionic Cmpds

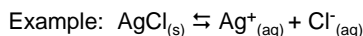
Will a precipitate form when 0.150 L of 0.10 M lead (II) nitrate and 0.100 L of 0.20 M sodium chloride are mixed? For  $\text{PbCl}_2$ ,  $K_{sp} = 1.2 \times 10^{-5}$

\* see worksheet key

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## Common Ion Effect

- Solubility is decreased when a common ion is added to a solution containing an insoluble salt!



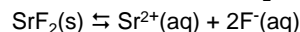
If we add NaCl to a AgCl solution,  $[\text{Cl}^-] \uparrow$ , eq shifts left  
As eq shifts left, some AgCl precipitates out of solution,

**Thus, adding a common ion decreases the solubility!**

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## Common Ion Effect

What will happen if solid NaF is added to a solution of saturated  $\text{SrF}_2$ ?



- Calculate the molar solubility of  $\text{SrF}_2$  in pure water ( $K_{sp} = 4.3 \times 10^{-9}$ ).
- Calculate the molar solubility of  $\text{SrF}_2$  in 0.010 M NaF.

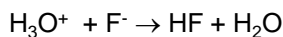
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## Effect of pH on Solubility

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



Add strong acid (e.g. HCl) provides  $\text{H}_3\text{O}^+$  ions:



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

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## pH and solubility

E.g. For the following salts, predict whether the salt will dissolve in an acidic solution.

A. AgBr \_\_\_\_\_

B.  $\text{CaCO}_3$  \_\_\_\_\_

C.  $\text{PbCl}_2$  \_\_\_\_\_

D. BaS \_\_\_\_\_

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## Complex Ions

A **complex ion** contains a metal cation bonded to one or more molecules or ions called ligands.

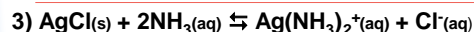
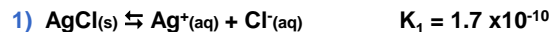
- The ligands act as Lewis bases. (e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ )
- $K_f$  is the equilibrium constant for the formation of a complex ion.
- Table 17.5 lists  $K_f$  values

A solution of  $\text{CoCl}_2$  is pink because of the presence of  $\text{Co}(\text{H}_2\text{O})_6^{2+}$  ions:  
 $\text{Co}^{2+} + 6 \text{H}_2\text{O} \rightleftharpoons \text{Co}(\text{H}_2\text{O})_6^{2+}$



## Effect of Complex Ion on Solubility

**Formation of complex ions can increase solubility of an insoluble salt**



$$K_3 = K_1 \times K_2 = 2.7 \times 10^{-3}$$

• In qual lab, ammonia is added to dissolve our AgCl precipitate so it can be separated from Hg.

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## Qualitative Analysis

- Skipping Selective Precipitation
- 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.