



Ch 14.6 to 15 - Applications of Aqueous Equilibria

GCC CHM152

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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 NaCH_3CO_2 ?

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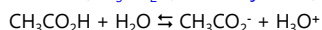
Common Ion Effect

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



- $x = [\text{H}_3\text{O}^+] =$
- $\text{pH} =$ _____ 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 NaCH_3CO_2 ? Have WA ($\text{CH}_3\text{CO}_2\text{H}$) and conj base (CH_3CO_2^-)



I, M	0.100		0.050	0
C, M	-x		+x	+x
E, M	0.100 - x		0.050+x	x

$K_a =$

$x =$

- $\text{pH} =$

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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. NH_3 and NH_4Cl

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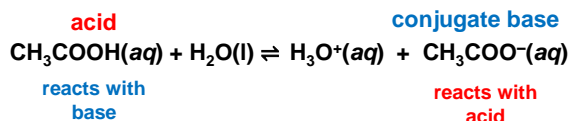
Which are buffer solutions?

Identify the solutions below that would make good buffer solutions :

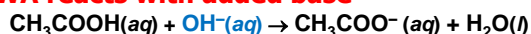
- ♦ HF and NaF
- ♦ NH₃ and NH₄Cl
- ♦ KOH and KF
- ♦ CH₃COOH and LiCH₃COO
- ♦ NaNO₃ and HNO₃
- ♦ NaOH and NaCl

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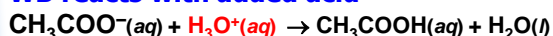
How Buffer Solution works



WA reacts with added base



WB reacts with added acid



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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⁻] 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⁻ 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_a close to the pH you want (pK_a ± 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?

Look at K_a table in last chapter for pK_a close to 4.10

- Benzoic acid, C₆H₅COOH K_a = 6.5 × 10⁻⁵ so pK_a = 4.19
- Use mix of C₆H₅COOH and salt (NaC₆H₅COO)

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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
When to use	Weak acid or base in water	Neutralization Reaction
Units	molarity	moles
Labels	Initial, Change, Equilibrium	Initial, Change, Final
Arrows	⇌	→
How to find x	Solve for x at equilibrium	x = L.R. = smallest # of initial moles

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pH of Buffer Solution

What is the pH of 500.0 mL of 0.10 M HCO_2H combined with 400.0 mL of 0.20 M NaHCO_2 ? For HCO_2H , $K_a = 1.8 \times 10^{-4}$

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: $\text{HCO}_2\text{H}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HCO}_2^-(\text{aq})$

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

pH =

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

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Buffer + HCl

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

- Write AB neut: H_3O^+ reacts with 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 = = LR



Initial moles				
Change in moles				
Final moles				

pH = (initially 3.95)

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

Initial mol $\text{OH}^- =$ = LR



Initial moles				
Change in moles				
Final moles				

pH = (initially 3.95)

- **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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Example. HOCl/NaOCl Buffer

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⁻] 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

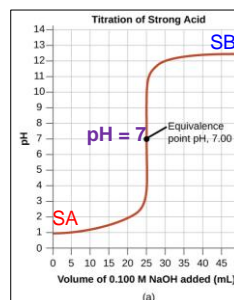
For Titration problems may use mmol :

1 mole = 1000 mmoles

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

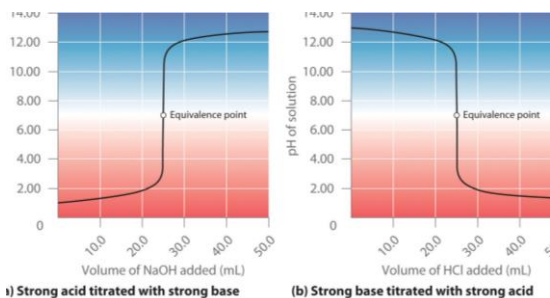
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Strong Acid- Strong Base Titration



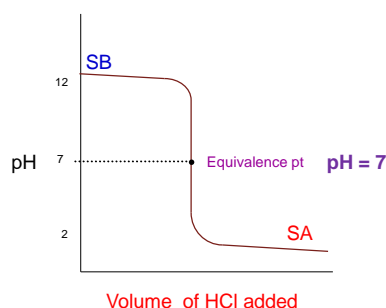
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SA-SB and SB-SA Titrations



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Strong Base titrated by a Strong Acid



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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; initial pH of SA

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

♦ $\text{pH} = -\log [\text{H}_3\text{O}^+] =$

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

♦ Excess moles SA =

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

♦ $[\text{H}_3\text{O}^+] =$

♦ $\text{pH} =$

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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

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

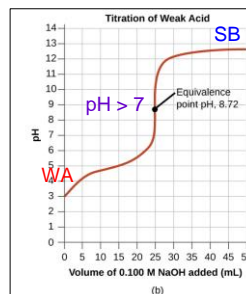
♦ $[\text{OH}^-] =$

♦ $\text{pOH} = -\log ([\text{OH}^-]) =$

♦ $\text{pH} = 14 - \text{pOH} =$

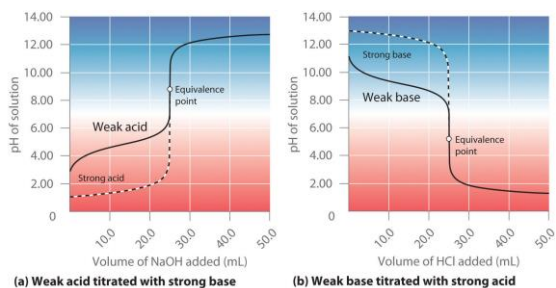
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Weak Acid- Strong Base Titration



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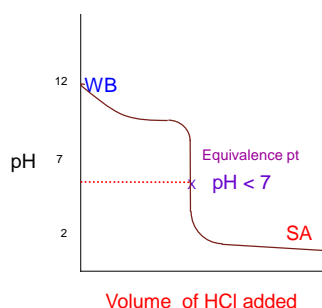
WA-SB and WB-SA Titrations



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Weak Base Titrated by Strong Acid



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Weak Acid-Strong Base

Draw 4 bakers.

- 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.

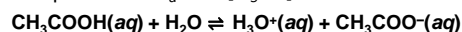
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WA-SB Titration Problem

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 , $x = [H_3O^+]$



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

$$K_a = \frac{x^2}{[HA]} \quad x = [H_3O^+] = \sqrt{0.100 \times 1.8 \times 10^{-5}} = 1.34 \times 10^{-3} M$$

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: $HA + OH^- \rightarrow H_2O + A^-$

- Write Neut rxn: $CH_3COOH + OH^- \rightarrow H_2O + CH_3COO^-$
- 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 A^- are present \Rightarrow **buffer region**
- Final moles HA = initial moles HA - moles base added
- Final moles 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 $[A^-]$ = moles conj base/ total volume
- Conj Base (A^-) reacts with water: $A^- + H_2O \rightleftharpoons HA + OH^-$
- Set up ICE table
- find $K_b = K_w / K_a$;
- Solve $K_b = x^2/[A^-]$ for x, where $x = [OH^-]$
- calculate pOH and convert to pH

pH = 8.76 (see worksheet key for work)

*Note = pH must be > 7 for WA-SB at eq pt

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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 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 OH⁻ compared to the SB.
- pH calc after eq pt is same for SA-SB and WA-SB!
- [OH⁻] = final moles OH⁻/ total volume**

$$\text{mmol OH}^- =$$

$$\text{total mL} =$$

$$[\text{OH}^-] =$$

$$\text{pOH} = -\log [\text{OH}^-] =$$

$$\text{pH} = 14 - \text{pOH} =$$

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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 1/2 eq pt, moles HA remaining = moles A⁻ formed
- Thus, [HA] = [A⁻]

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

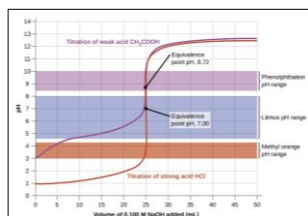
$$\text{at } \frac{1}{2} \text{ eq pt: } \text{pH} = \text{pK}_a$$

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End Point for Acid-Base Titrations

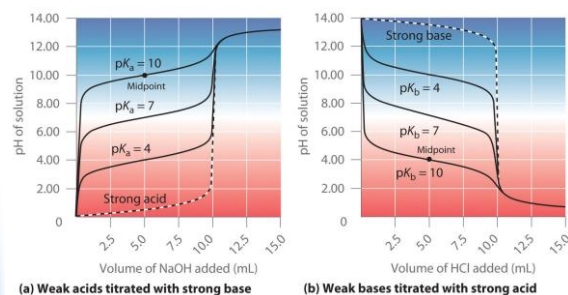
The endpoint in a titration can be visualized with the use of an **acid-base indicator**. (The acid and conjugate base forms of the indicator have different colors)

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



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Acid-Base Titrations – Comparing Curves

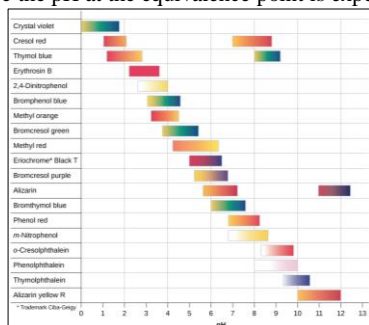


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Acid-Base Titration Indicators

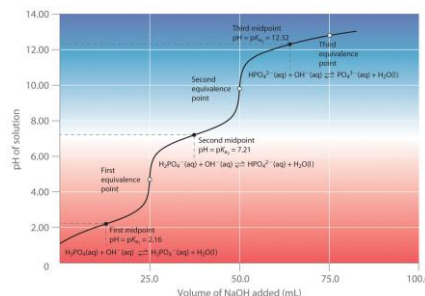
Figure 14.22: Different indicators can be used depending on where the pH at the equivalence point is expected to be.



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Polyprotic Acid Titration: H₃PO₄ with NaOH

- One eq. pt. for each proton.
- 3 eq. pts. and 3 half eq. pts.



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Solubility Equilibria

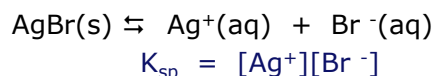
- ❖ Some combinations of ions form solid precipitates in aqueous solutions. (Refer to Solubility rules in Ch 9)
- ❖ These “insoluble” salts dissolve to a small extent and form a saturated solution.
- ❖ The undissolved solid and the dissociated ions in solution establish an equilibrium reaction.
- ❖ K_{sp} 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} is the solubility product constant - its the equilibrium constant for insoluble salts

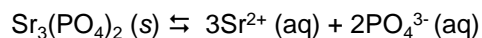
- It is a measure of how soluble a salt is in H_2O
- ⇒ For salts with the same # of ions, the smaller the K_{sp} , the less soluble the salt.
- ⇒ Table on next slide shows some K_{sp} values

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Substance	Ppt color	K_{sp} value
AgCl	white	1.6×10^{-10}
AgBr	off-white	5.0×10^{-13}
AgI	yellow	1.5×10^{-16}
PbS	black	7×10^{-29}
PbCl ₂	white	1.6×10^{-5}
Fe(OH) ₃	rust red	4×10^{-38}
CaCO ₃	white	8.7×10^{-9}
BaSO ₄	white	2.3×10^{-8}

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

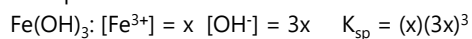


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Solubility

- 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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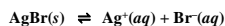
Solubility/ K_{sp} Practice

1. K_{sp} for AgBr is 7.7×10^{-13} . Calculate the molar and gram solubility.
2. 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} ?
3. K_{sp} for $\text{Al}(\text{OH})_3$ is 1.9×10^{-33} . Calculate the molar solubility.
4. 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 7.7×10^{-13} . Calculate the molar solubility.



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

- Include Ion Charges!
- Assume salt added to H₂O so initial ion []'s = 0
- x = molar solubility of salt

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

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

$$\text{molar solubility} = x =$$

gram solubility =

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Solubility/K_{sp} Practice

Remember:

- Molar solubility = x in ICE table!
- K_{sp} = eq constant for dissolution of salt!
- Refer to solubility worksheet key!

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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

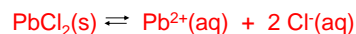
$Q < K_{sp}$, no ppt; eq shifts → (towards ions)

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

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Precipitation of Ionic Compds

Does a precipitate form in a solution that contains 0.010 M $\text{Pb}(\text{NO}_3)_2$ and 0.020 M NaCl? K_{sp} for $\text{PbCl}_2 = 1.6 \times 10^{-5}$



$$[\text{Pb}^{2+}] = [\text{Pb}(\text{NO}_3)_2] = 0.010 \text{ M} \quad [\text{Cl}^-] = [\text{NaCl}] = 0.020 \text{ M}$$

Calculate Q and compare Q to K!

$$Q = [\text{Pb}^{2+}][\text{Cl}^-]^2$$

$$Q =$$

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Common Ion Effect

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

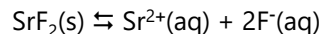
Example: $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$

- 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 SrF_2 ?



- Calculate the molar solubility of SrF_2 in pure water ($K_{sp} = 4.3 \times 10^{-9}$).
- Calculate the molar solubility of SrF_2 in 0.010 M NaF.

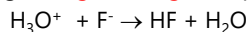
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Effect of pH on Solubility

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

E.g. $\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$

Adding **strong acid (e.g. HCl)** provides H_3O^{+} ions:



- Adding H^{+} causes $[\text{F}^{-}]$ ____, equilibrium shifts ____ to form more ____ & solubility of CaF_2 ____.

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pH and solubility

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

- NH_4Br
- CaCO_3
- RbCl
- 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. H_2O , NH_3)
- K_f is the equilibrium constant for the formation of a complex ion.
- Table 15.2 lists K_f values

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Formation Constant (K_f) values

Table 15.2: Common Complex Ions and Their Formation Constants

Substance	K_f at 25°C
$[\text{Cd}(\text{CN})_4]^{2-}$	1.3×10^7
$\text{Ag}(\text{NH}_3)_2^{+}$	1.7×10^7
$[\text{AlF}_6]^{3-}$	7.0×10^{19}

The larger the formation constant, the more stable the complex ion is. More values can be found in **Appendix K**.

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Effect of Complex Ion on Solubility

Formation of complex ions can increase solubility of an insoluble salt

- 1) $\text{AgCl}(\text{s}) \rightleftharpoons \text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \quad K_1 = 1.7 \times 10^{-10}$
- 2) $\text{Ag}^{+}(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^{+}(\text{aq}) \quad K_2 = 1.6 \times 10^7$
- 3) $\text{AgCl}(\text{s}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$
 $K_3 = K_1 \times K_2 = 2.7 \times 10^{-3}$

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

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Selective Precipitation

Some compounds can be separated based on **selective precipitation**. This is the separation of precipitates based on different K_{sp} values. For example, AgCl ($K_{sp} = 1.6 \times 10^{-10}$), AgBr ($K_{sp} = 7.7 \times 10^{-13}$), and AgI ($K_{sp} = 8.3 \times 10^{-17}$) all precipitate.

Because silver iodide's K_{sp} value is so low (it is less soluble than the other salts), it would precipitate before the other two. Almost all of the AgI would precipitate before AgCl and AgBr would.

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