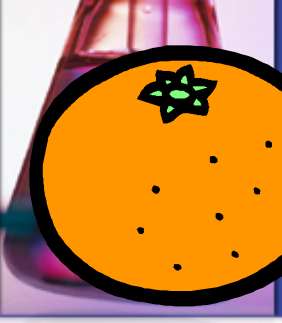
Chapter 15

Application of Aqueous Equilibria

Chapter 15 Preview

App. Aqueous Equilibria

- Acid-bases Equilibria
  - Acid-base, Common ion, Equilibria calculation
  - Buffer solution, Buffer capacity
  - Titration and pH curve, strong A-Strong B, Weak A-Strong B, Strong A-Weak B, Acid-Base indicators
- Solubility Equilibria
  - Solubility product, Relative solubilities, Common ion effect, pH and solubility
  - Precipitation and qualitative analysis
- Complex Ion Equilibria
  - Complex ions and solubilities



Introduction

All the chemistry of the natural world occurs in aqueous solution, three equilibria will be cover:

- More application of Acid-Base chemistry
- Solubility of salts and their equilibria
- Formation of complex ions and their equilibria

15.1 Solutions of Acid or Bases Containing a Common Ion

Consider mixture of CH_3COONa (strong electrolyte) and CH_3COOH (weak acid).

$$CH_3COONa\ (s) \longrightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$$

common ion

The presence of a common ion **suppresses** the ionization of a weak acid or a weak base.

The ***common ion effect*** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

Equilibrium Calculations

Consider mixture of salt NaA and weak acid HA.

$$NaA\ (s) \longrightarrow Na^+\ (aq) + A^-\ (aq)$$

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = \frac{K_a\,[HA]}{[A^-]}$$

Henderson-Hasselbalch equation

$$-\log [H^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

$$-\log [H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$$

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

$$pH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a$$

What is the pH of a solution containing 0.30 *M* HCOOH and 0.52 *M* HCOOK?

Mixture of weak acid and conjugate base!

$$HCOOH\ (aq) \rightleftharpoons H^+\ (aq) + HCOO^-\ (aq)$$

	HCOOH	H^+	$HCOO^-$
Initial (*M*)	0.30	0.00	0.52
Change (*M*)	-*x*	+*x*	+*x*
Equilibrium (*M*)	0.30 - *x*	*x*	0.52 + *x*

Common ion effect

$0.30 - x \approx 0.30$

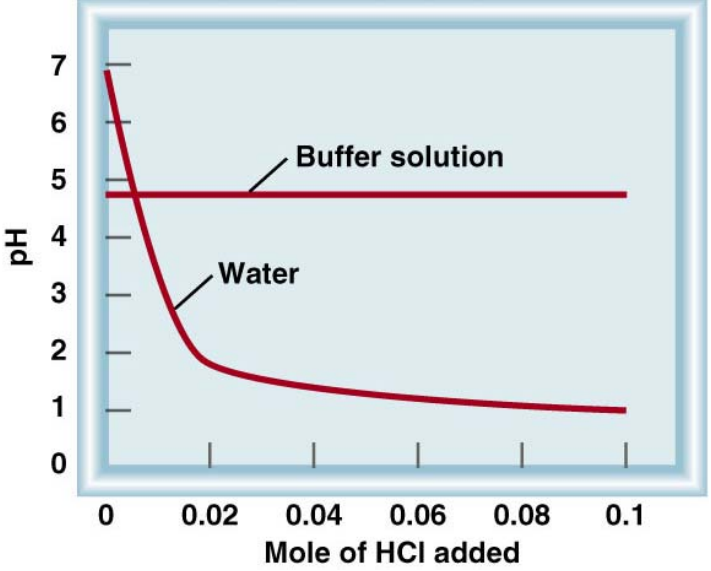
$0.52 + x \approx 0.52$

HCOOH $pK_a = 3.77$

$$pH = pK_a + \log \frac{[HCOO^-]}{[HCOOH]}$$

$$pH = 3.77 + \log \frac{[0.52]}{[0.30]} = 4.01$$

15.2 Buffered Solutions



A ***buffer solution*** is a solution of:

1. A weak acid or a weak base **and**
2. The salt of the weak acid or weak base

Both must be present!

A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base.

Consider an equal molar mixture of CH_3COOH and CH_3COONa

Add strong acid

$$H^+ (aq) + CH_3COO^- (aq) \longrightarrow CH_3COOH (aq)$$

Add strong base

$$OH^- (aq) + CH_3COOH (aq) \longrightarrow CH_3COO^- (aq) + H_2O (l)$$

15.2 Buffered Solutions

Which of the following are buffer systems? (a) KF/HF (b) KBr/HBr, (c) Na_2CO_3/$NaHCO_3$

(a) KF is a weak acid and F^- is its conjugate base

buffer solution

(b) HBr is a strong acid

not a buffer solution

(c) CO_3^{2-} is a weak base and HCO_3^- is it conjugate acid

buffer solution

QUESTION

The dissociation constant of propanoic acid ($HC_3H_5O_2$) is 1.3×10^{-5}. What is the pH of a buffer made with 0.50 M propanoic acid and 0.25 M $NaC_3H_5O_2$ (the sodium salt of propanoic acid)?

1. 4.59
2. 5.19
3. 7.00
4. I'm not getting any of these answers.

Choice 1 is the correct pH of the buffer. There is an assumption being made here about the concentration of the salt to be only from the salt added. This ignores the small amount of propionate [$C_3H_5O_2^-$] that may be produced from the acid dissociation.

Calculate the pH of the 0.30 *M* NH_3/0.36 *M* NH_4Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 *M* NaOH to 80.0 mL of the buffer solution?

$$NH_4^+ (aq) \rightleftharpoons H^+ (aq) + NH_3 (aq)$$

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]} \qquad pK_a = 9.25 \qquad pH = 9.25 + \log \frac{[0.30]}{[0.36]} = 9.17$$

	$NH_4^+ (aq)$	+ $OH^- (aq)$	⟶	$H_2O (l)$ +	$NH_3 (aq)$
start (moles)	0.029	0.001			0.024
end (moles)	0.028	0.0			0.025

final volume = 80.0 mL + 20.0 mL = 100 mL

$$[NH_4^+] = \frac{0.028}{0.10} \qquad [NH_3] = \frac{0.025}{0.10} \qquad pH = 9.25 + \log \frac{[0.25]}{[0.28]} = 9.20$$

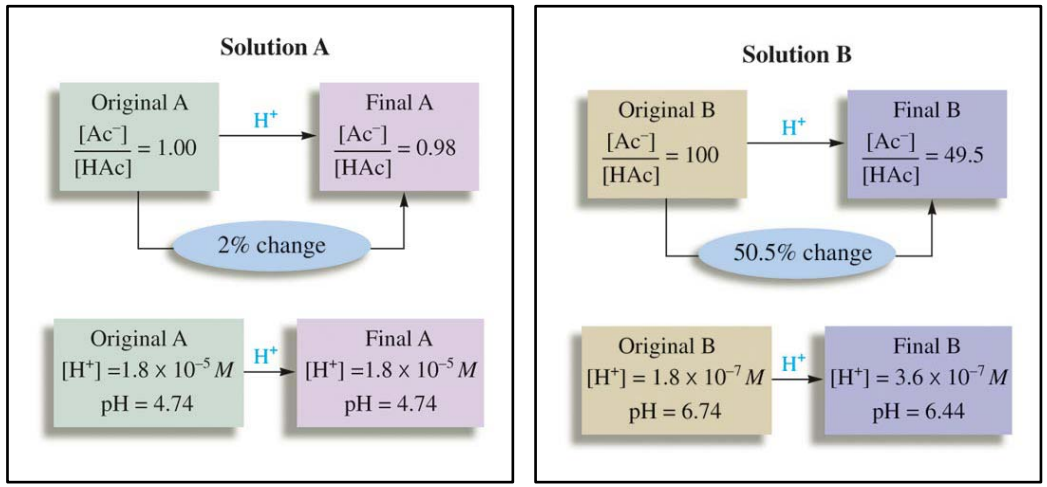
15.3 Buffered Capacity

The ability of buffers to absorb amount of H^+ or OH^- without a significant change in pH. It is determined by the ratio $[A^-]/[HA]$.

Adding 0.010 mol gaseous HCl to 1L of the following solutions:

A- 1.0 M HAc & 1.0 M NaAc
(before): pH = 4.74
(after): pH = 4.74 - 0.0088 = 4.73
0.2 % change

B- 0.010 M HAc & 1.0 M NaAc
(before): pH = 4.74 + 2.00 = 6.74
(after): pH = 4.74 + 1.69 = 6.43
4.5 % change



The best buffer is the one has ratio closest to 1 or its equilibrium constant is of value close to the desired pH.

QUESTION

To culture a certain bacteria a microbiologist would like to buffer the media at a pH of 3.75. To maximize the efficiency of the system a 1:1 ratio of acid to salt will be used. Which of the following acids would make the best choice for the buffer?

1. Acetic acid; $K_a = 1.8 \times 10^{-5}$
2. Propanoic acid; $K_a = 1.3 \times 10^{-5}$
3. Formic acid; $K_a = 1.8 \times 10^{-4}$
4. Nitrous acid; $K_a = 4.0 \times 10^{-4}$

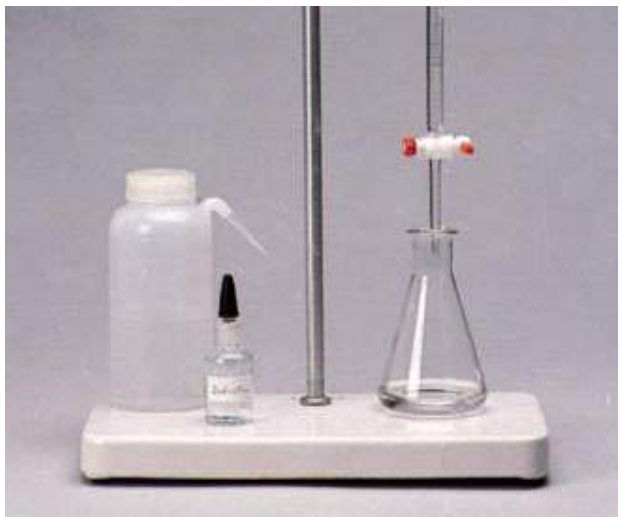
Choice 3 represents the best selection for this buffer. If the acid:salt ratio is to be 1:1, the pH will equal K_a. At a pH of 3.75 the closest pK_a would be from formic acid: 1.3×10^{-4}.

15.4 Titrations and pH Curves

In a ***titration*** a solution of accurately known concentration is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Equivalence point – the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point …**End Point**



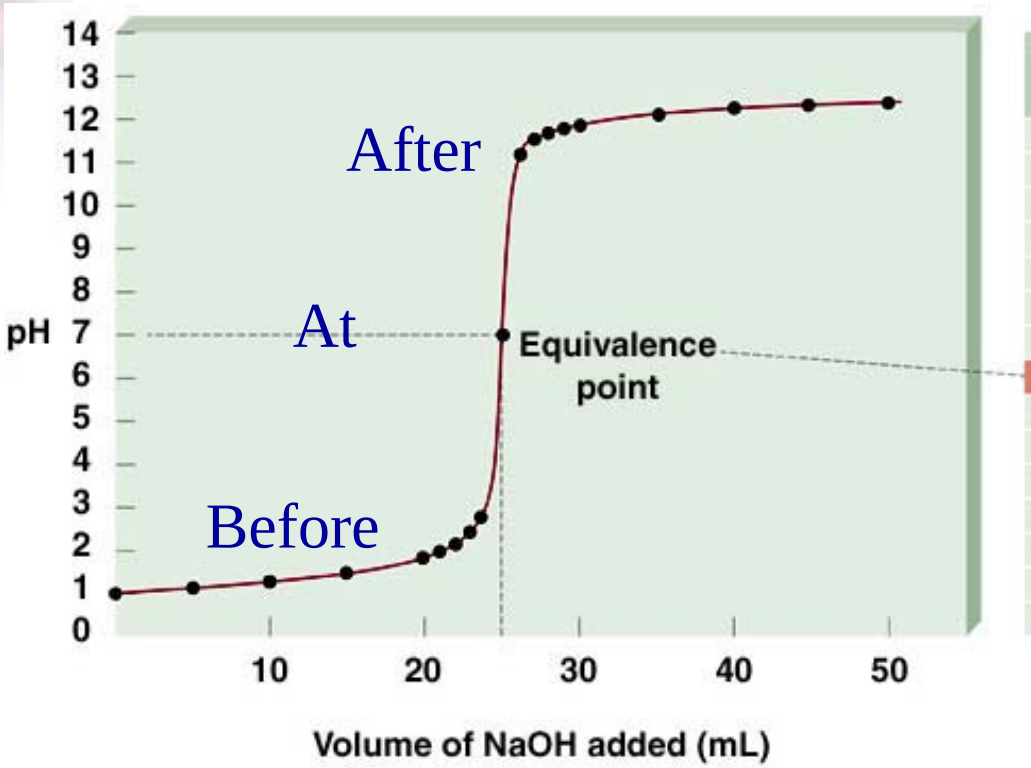
Slowly add base to unknown acid UNTIL

The indicator changes color (pink)

Strong Acid-Strong Base Titrations

$NaOH\ (aq) + HCl\ (aq) \longrightarrow H_2O\ (l) + NaCl\ (aq)$

$OH^-\ (aq) + H^+\ (aq) \longrightarrow H_2O\ (l)$



Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Before: $[H^+]$ = Left moles (Acid-Added Base)/Total volume

At: $[H^+]$ = Water

After: $[OH^-]$ = Left moles (Added Base-Acid)/Total volume

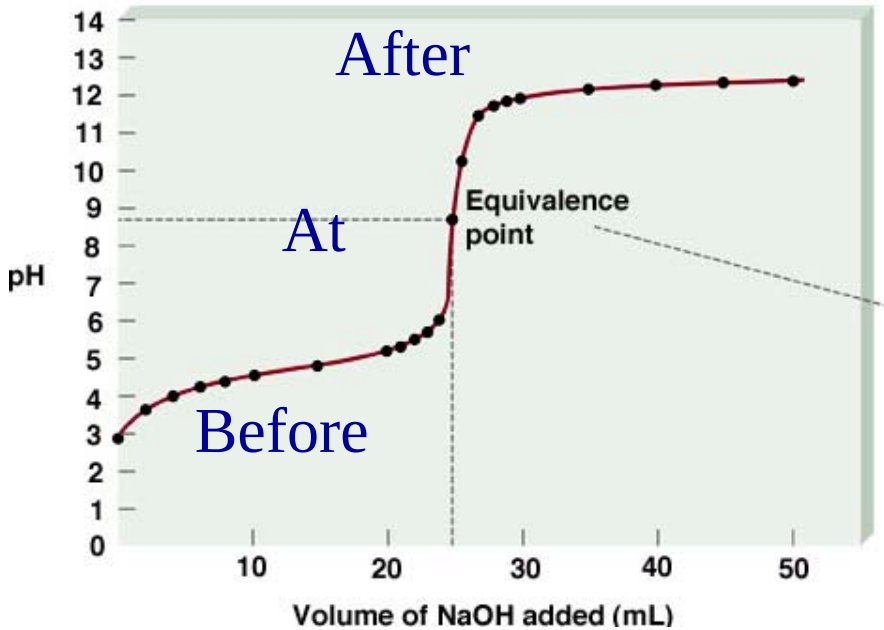
Weak Acid-Strong Base Titrations

$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (l)$

$CH_3COOH\ (aq) + OH^-\ (aq) \longrightarrow CH_3COO^-\ (aq) + H_2O\ (l)$

At equivalence point (pH > 7):

$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + CH_3COOH\ (aq)$



Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Before: $[H^+]$ = Left moles (Acid-Added Base)/Total volume then use ICE

At: $[H^+]$ = Use ICE for Salt of weak acid and strong base

After: $[OH^-]$ = Left moles (Added Base-Acid)/Total volume

Exactly 100 mL of 0.10 *M* HNO_2 are titrated with a 0.10 *M* NaOH solution. What is the pH at the equivalence point ?

start (moles) 0.01 0.01

$$HNO_2\ (aq) + OH^-\ (aq) \longrightarrow NO_2^-\ (aq) + H_2O\ (l)$$

end (moles) 0.0 0.0 0.01

Final volume = 200 mL $\quad [NO_2^-] = \frac{0.01}{0.200} = 0.05\ M$

$$NO_2^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + HNO_2\ (aq)$$

	NO_2^-	OH^-	HNO_2
Initial (*M*)	0.05	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.05 - x$	x	x

$$K_b = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{x^2}{0.05-x} = 2.2 \times 10^{-11}$$

pOH = 5.98

$0.05 - x \approx 0.05 \quad x \approx 1.05 \times 10^{-6} = [OH^-]$

pH = 14 – pOH = 8.02

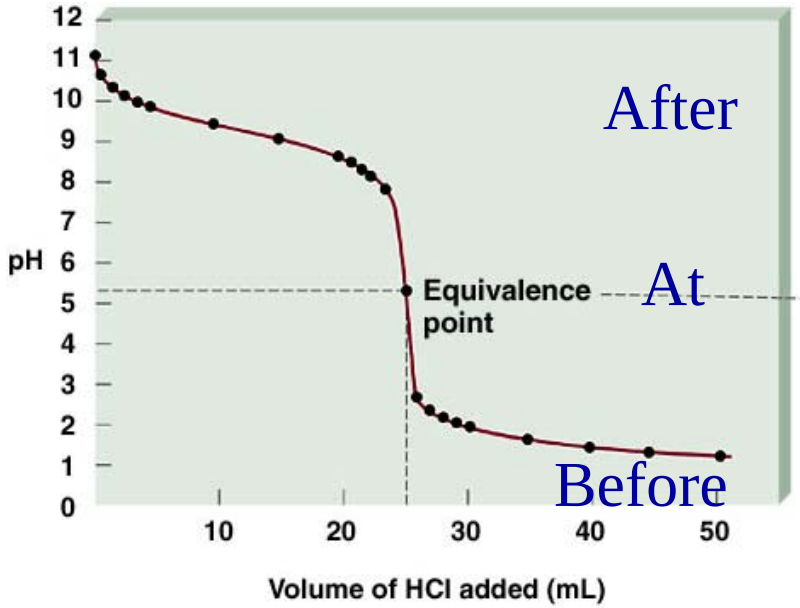
Strong Acid-Weak Base Titrations

$HCl\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$

$H^+\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$

At equivalence point (pH < 7):

$NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_3\ (aq) + H^+\ (aq)$



Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

Before: $[OH^-]$ = Left moles (Base-Added Acid)/Total volume then use ICE

At: $[H^+]$ = Use ICE for Salt of strong acid and weak base

After: $[H^+]$ = Left moles (Added Acid-Base)/Total volume

15.5 Acid-Base Indicators

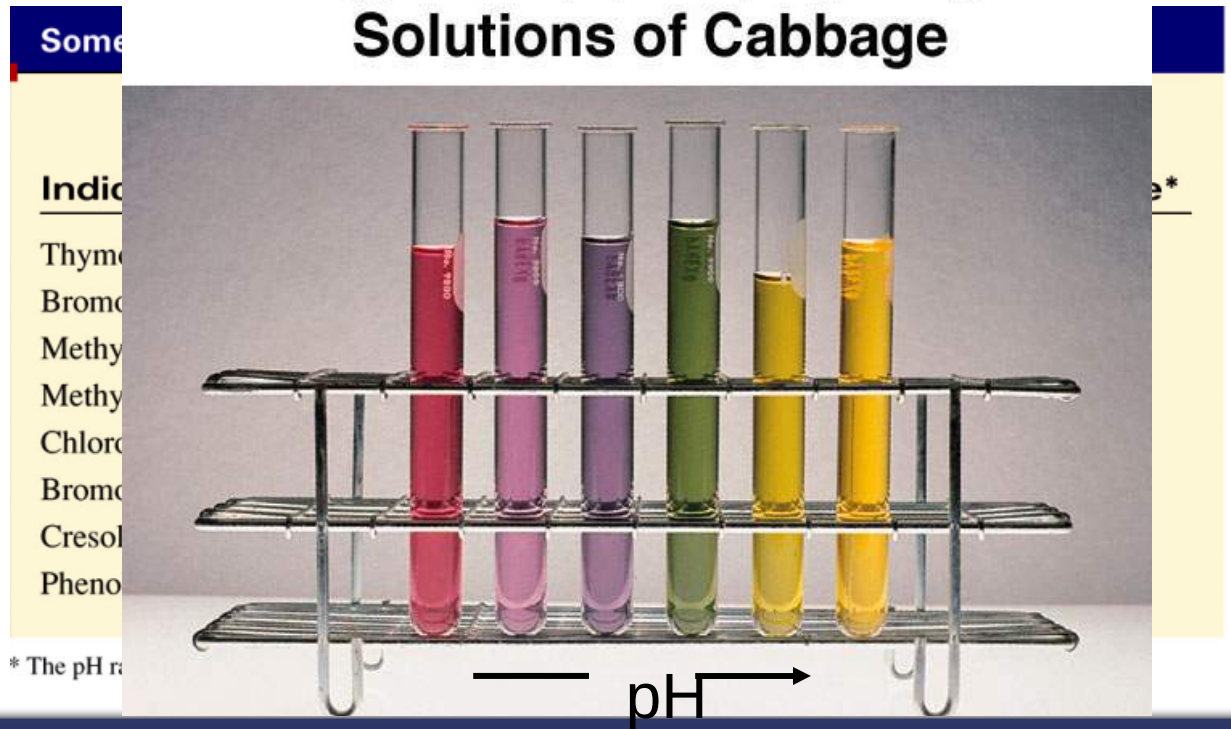
$$HIn\ (aq) \rightleftharpoons H^+\ (aq) + In^-\ (aq)$$

$\frac{[HIn]}{[In^-]} \geq 10$ Color of acid (HIn) predominates

$\frac{[HIn]}{[In^-]} \leq 10$ Color of conjugate base (In^-) predominates

The useful range for any indicator is given by

$$pKa \pm 1$$



Which indicator(s) would you use for a titration of HNO_2 with KOH ?

Weak acid titrated with strong base.

At equivalence point, will have conjugate base of weak acid.

At equivalence point, pH > 7

Use cresol red or phenolphthalein

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

15.6 Solubility Equilibria and Solubility Product

$$AgCl\,(s) \rightleftharpoons Ag^{+}\,(aq) + Cl^{-}\,(aq)$$

$K_{sp} = [Ag^+][Cl^-]$ **K_{sp}** is the ***solubility product constant***

$MgF_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2F^{-}\,(aq)$ $K_{sp} = [Mg^{2+}][F^-]^2$

$Ag_2CO_3\,(s) \rightleftharpoons 2Ag^{+}\,(aq) + CO_3^{2-}\,(aq)$ $K_{sp} = [Ag^+]^2[CO_3^{2-}]$

$Ca_3(PO_4)_2\,(s) \rightleftharpoons 3Ca^{2+}\,(aq) + 2PO_4^{3-}\,(aq)$ $K_{sp} = [Ca^{2+}]^3[PO_3^{3-}]^2$

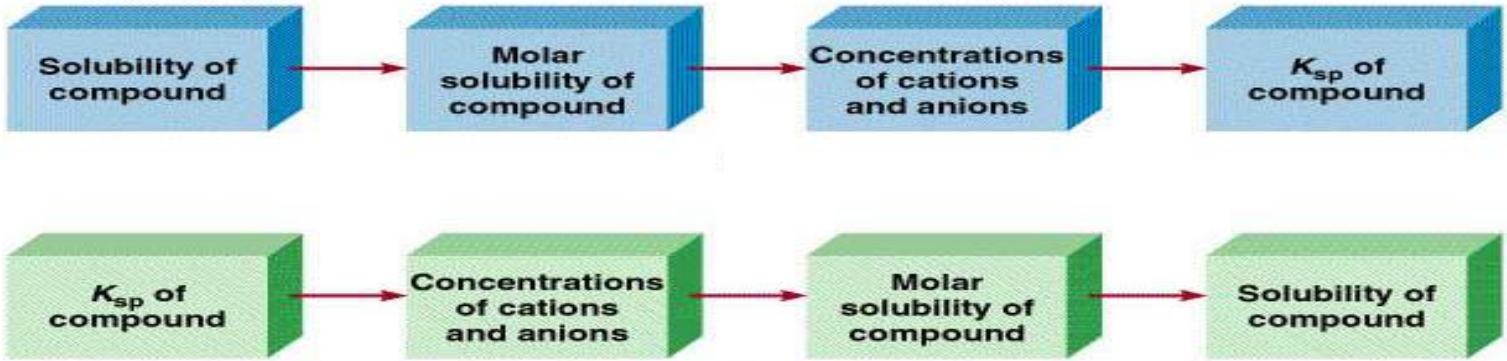
<u>Dissolution of an ionic solid in aqueous solution:</u>

$Q < K_{sp}$	Unsaturated solution	No precipitate
$Q = K_{sp}$	Saturated solution	
$Q > K_{sp}$	Supersaturated solution	Precipitate will form

Solubility Equilibria

Molar solubility (mol/L) is the number of moles of solute dissolved in 1 L of a saturated solution.

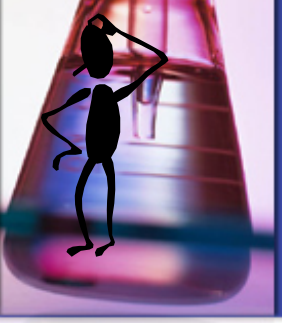
Solubility (g/L) is the number of grams of solute dissolved in 1 L of a saturated solution.



Relative Solubility

- Salts being compared produce same no. of ions, e.g., AgI, CuI, CaSO4, KSP used for comparison.

- Salts being compared produce different no. of ions, e.g., AgI, Ag_2S.. K_{SP} cannot be used for comparison.



What is the solubility of silver chloride in g/L ?

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq)$$

	Ag^+	Cl^-
Initial (*M*)	0.00	0.00
Change (*M*)	+*s*	+*s*
Equilibrium (*M*)	*s*	*s*

$[Ag^+] = 1.3 \times 10^{-5}\ M \quad [Cl^-] = 1.3 \times 10^{-5}\ M$

$K_{sp} = 1.6 \times 10^{-10}$

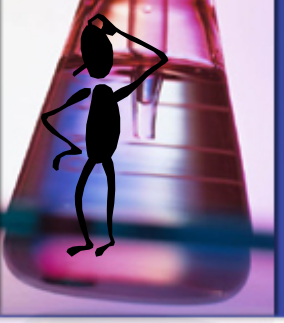
$K_{sp} = [Ag^+][Cl^-]$

$K_{sp} = s^2$

$s = \sqrt{K_{sp}}$

$s = 1.3 \times 10^{-5}$

$$\text{Solubility of AgCl} = \frac{1.3 \times 10^{-5}\ \cancel{\text{mol AgCl}}}{1\ \text{L soln}} \times \frac{143.35\ \text{g AgCl}}{1\ \cancel{\text{mol AgCl}}} = 1.9 \times 10^{-3}\ \text{g/L}$$



What concentration of Ag is required to precipitate ONLY AgBr in a solution that contains both Br^- and Cl^- at a concentration of 0.02 *M*?

$$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq) \qquad K_{sp} = 7.7 \times 10^{-13}$$

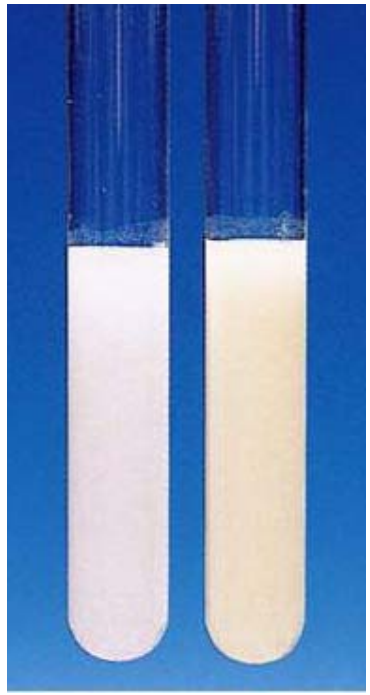
$$K_{sp} = [Ag^+][Br^-]$$

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{7.7 \times 10^{-13}}{0.020} = 3.9 \times 10^{-11}\ M$$

$$AgCl\ (s) \rightleftharpoons Ag^+\ (aq) + Cl^-\ (aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{1.6 \times 10^{-10}}{0.020} = 8.0 \times 10^{-9}\ M$$



$$3.9 \times 10^{-11}\ M < [Ag^+] < 8.0 \times 10^{-9}\ M$$

The Common Ion Effect and Solubility

The presence of a common ion **decreases** the solubility of the salt.

What is the molar solubility of AgBr in (a) pure water and (b) 0.0010 *M* NaBr?

$$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq)$$

$$K_{sp} = 7.7 \times 10^{-13}$$

$$s^2 = K_{sp}$$

$$s = 8.8 \times 10^{-7}$$

$$NaBr\ (s) \longrightarrow Na^+\ (aq) + Br^-\ (aq)$$

$$[Br^-] = 0.0010\ M$$

$$AgBr\ (s) \rightleftharpoons Ag^+\ (aq) + Br^-\ (aq)$$

$$[Ag^+] = s$$

$$[Br^-] = 0.0010 + s \approx 0.0010$$

$$K_{sp} = 0.0010 \times s$$

$$s = 7.7 \times 10^{-10}$$

pH and Solubility

- The presence of a common ion **decreases** the solubility.
- Insoluble bases dissolve in acidic solutions
- Insoluble acids dissolve in basic solutions

reactants products

$$Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2OH^-\ (aq)$$

$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$

$K_{sp} = (s)(2s)^2 = 4s^3$

$4s^3 = 1.2 \times 10^{-11}$

$s = 1.4 \times 10^{-4}\ M$

$[OH^-] = 2s = 2.8 \times 10^{-4}\ M$

pOH = 3.55 pH = 10.45

At pH less than 10.45

Lower $[OH^-]$

$OH^-\ (aq) + H^+\ (aq) \longrightarrow H_2O\ (l)$

Increase solubility of $Mg(OH)_2$

At pH greater than 10.45

Raise $[OH^-]$

Decrease solubility of $Mg(OH)_2$

15.7 Precipitation and Qualitative Analysis

If 2.00 mL of 0.200 *M* NaOH are added to 1.00 L of 0.100 *M* $CaCl_2$, will a precipitate form?

The ions present in solution are Na^+, OH^-, Ca^{2+}, Cl^-.

Only possible precipitate is $Ca(OH)_2$ (solubility rules).

Is $Q > K_{sp}$ for $Ca(OH)_2$?

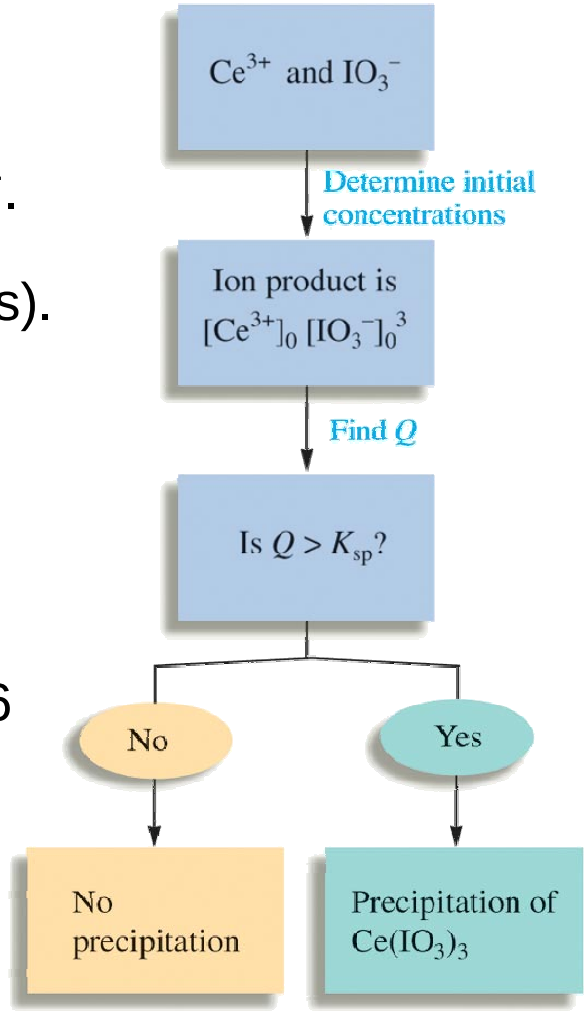
$[Ca^{2+}]_0$ = 0.100 *M*

$[OH^-]_0 = 4.0 \times 10^{-4}$ *M*

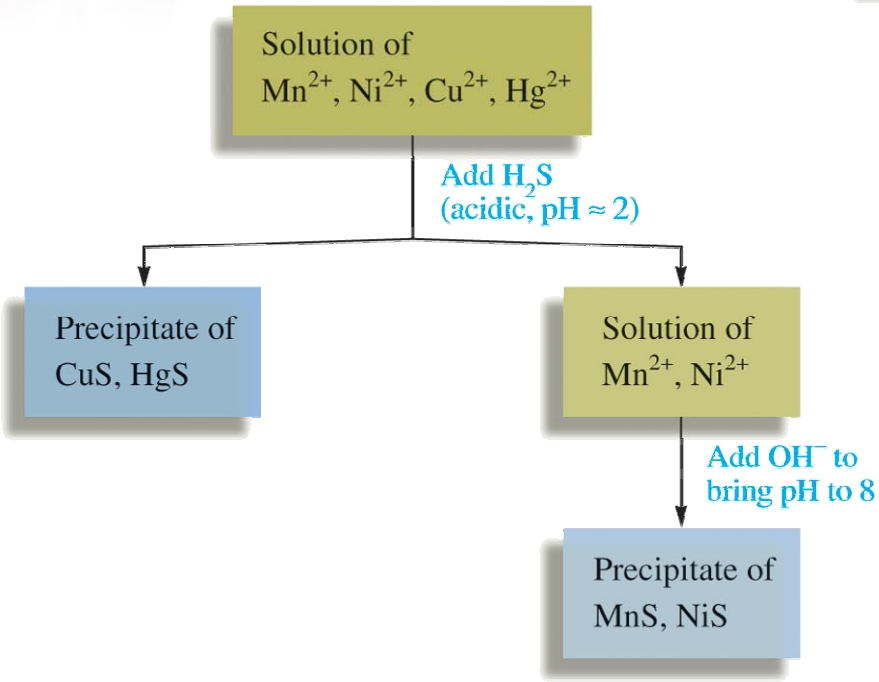
$Q = [Ca^{2+}]_0[OH^-]_0^2 = 0.10 \times (4.0 \times 10^{-4})^2 = 1.6 \times 10^{-8}$

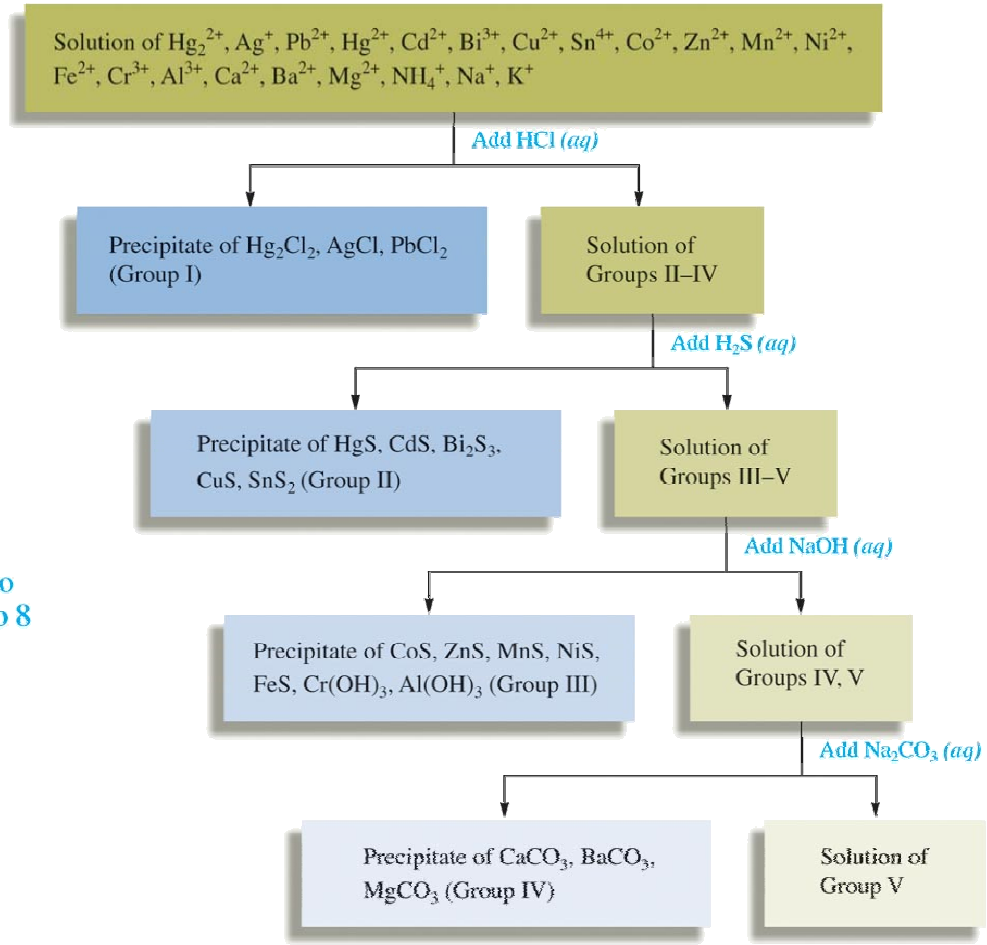
$K_{sp} = [Ca^{2+}][OH^-]^2 = 8.0 \times 10^{-6}$

$Q <$ K_{sp} No precipitate will form



Selective Precipitation and Qualitative Analysis





15.8 Complex Ion Equilibria and Solubility

A ***complex ion*** is an ion containing a central metal cation bonded to one or more molecules or ions.

$$Co^{2+}\,(aq) + 4Cl^{-}\,(aq) \rightleftharpoons CoCl_4^{2-}\,(aq)$$

The ***formation constant or stability constant (K_f)*** is the equilibrium constant for the complex ion formation.

$Co(H_2O)_6^{2+}$ $CoCl_4^{2-}$

$$K_f = \frac{[CoCl_4^{2-}]}{[Co^{2+}][Cl^{-}]^4}$$

K_f ↑ stability of complex ↑

QUESTION

Given the following values of equilibrium constants:

$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = 1.6 \times 19^{-19}$

$Cu(NH_3)_4^{2+} \rightleftharpoons Cu^{2+}(aq) + 4NH_3(aq)$ $K = 1.0 \times 10^{-13}$

What is the value of the equilibrium constant for the reaction:

$Cu(OH)_2(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq) + 2OH^-(aq)$

1) 1.6×10^{-19}
2) 6.2×10^{31}
3) 1.6×10^{-6}
4) 1.6×10^{-32}
5) 1.0×10^{13}

3) 1.6×10^{-6}

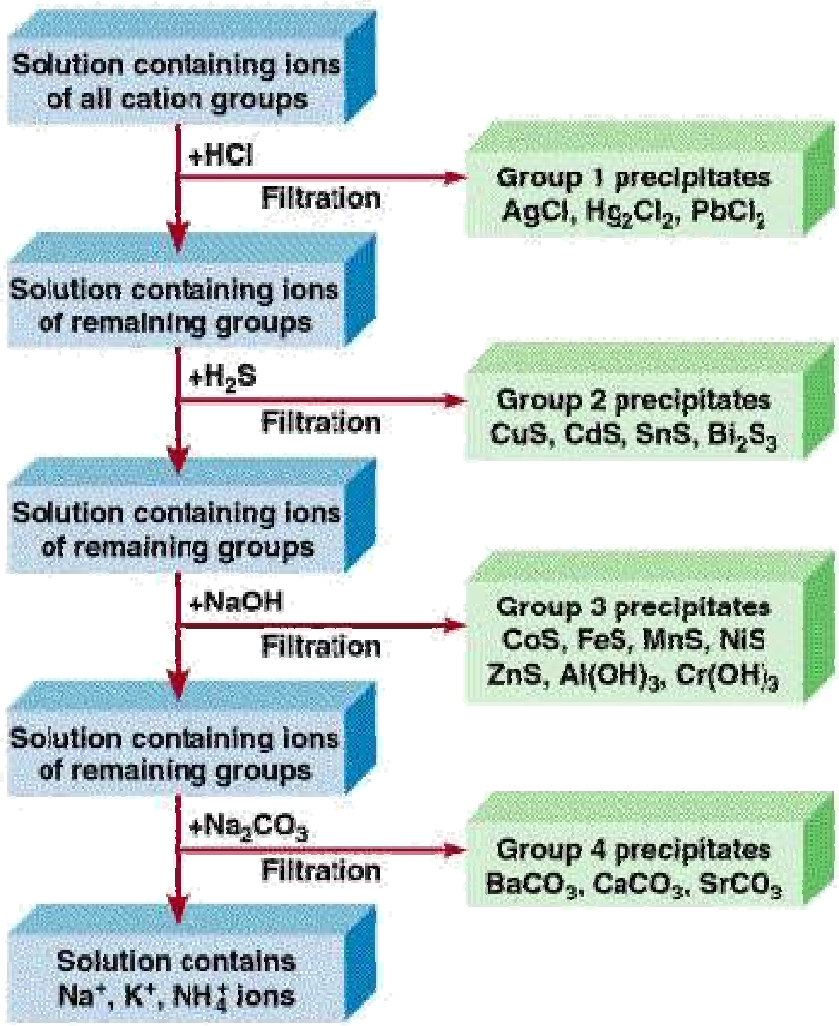
The equilibrium constant equal to K_{sp} / K

Table 16.5 Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents

Group	Cation	Precipitating Reagents	Insoluble Compound	K_{sp}
1	Ag^+	HCl	AgCl	1.6×10^{-10}
	Hg_2^{2+}	↓	Hg_2Cl_2	3.5×10^{-18}
	Pb^{2+}	↓	$PbCl_2$	2.4×10^{-4}
2	Bi^{3+}	H_2S	Bi_2S_3	1.6×10^{-72}
	Cd^{2+}	in acidic	CdS	8.0×10^{-28}
	Cu^{2+}	solutions	CuS	6.0×10^{-37}
	Sn^{2+}	↓	SnS	1.0×10^{-26}
3	Al^{3+}	H_2S	$Al(OH)_3$	1.8×10^{-33}
	Co^{2+}	in basic	CoS	4.0×10^{-21}
	Cr^{3+}	solutions	$Cr(OH)_3$	3.0×10^{-29}
	Fe^{2+}	↓	FeS	6.0×10^{-19}
	Mn^{2+}	↓	MnS	3.0×10^{-14}
	Ni^{2+}	↓	NiS	1.4×10^{-24}
	Zn^{2+}	↓	ZnS	3.0×10^{-23}
4	Ba^{2+}	Na_2CO_3	$BaCO_3$	8.1×10^{-9}
	Ca^{2+}	↓	$CaCO_3$	8.7×10^{-9}
	Sr^{2+}	↓	$SrCO_3$	1.6×10^{-9}
5	K^+	No precipitating	None	
	Na^+	reagent	None	
	NH_4^+		None	

Cation Analysis

Qualitative Analysis of Cations



Chemistry In Action:
How an Eggshell is Formed

$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightleftharpoons CaCO_3\,(s)$$

$$CO_2\,(g) + H_2O\,(l) \underset{\text{anhydrase}}{\overset{\text{carbonic}}{\rightleftharpoons}} H_2CO_3\,(aq)$$

$$H_2CO_3\,(aq) \rightleftharpoons H^+\,(aq) + HCO_3^-\,(aq)$$

$$HCO_3^-\,(aq) \rightleftharpoons H^+\,(aq) + CO_3^{2-}\,(aq)$$