15.1 Solutions of Acids or Bases Containing a Common Ion

common ion effect- a shift in equilibrium position due to the addition of an ion already involved in the equilibrium reaction

Example HF and NaF

$HF_{(s)} \rightarrow Na^{+}_{(aq)} + F^{-}_{(aq)}$

$HF_{(aq)} \quad H^{+}_{(aq)} + F^{-}_{(aq)}$

$\leftarrow$ Equilibrium Shift $\leftarrow$

The additional F^{-} decrease the pH by increasing the formation of molecular HF

15.2 Buffered Solutions

Buffered Solutions- resist pH changes when additional OH^{-} or H^{+} are added**.**

Buffered solutions contain weak acids or bases with their salts

(ex. HF and NaF, or NH_3 and NH_4Cl)

SAMPLE EXERCISE 15.3

Calculate the pH change that occurs when 0.010 mol solid NaOH is added to 1.0 L of a buffered solution containing 0.50 M acetic acid and 0.50 M sodium acetate.

	OH^{-}	+	$HC_2H_3O_2$	$C_2H_3O_2^{-}$ + H_2O
Before	0.010 mol		0.50 mol	0.50 mol
After	0.010-0.010		0.50-0.010	0.50+0.010
	0 mol		0.49 mol	0.51 mol

mol/L	HC_2H_3O	H^{+}	+	$C_2H_3O_2^{-}$
initial	0.49	0		0.51
x	-x	+x		+x
equilibrium	0.49	x		0.51

$$1.8 \times 10^{-5} = \frac{x(0.51)}{0.49}$$

$1.7 \times 10^{-5} = x$ (5% rule satisfied)

pH= -log[H+] = -log[1.7×10^{-5}] = 4.76

*pH without the addition of excess OH^{-} is 4.74 (only an increase of +0.002 pH units)

Hints in Solving Buffer Problems

1. Determine what the new concentrations of the species involved in equilibrium after the addition of H^{+} or OH^{-} ions. Assume the reaction between H and OH goes to completion.
2. Proceed with equilibrium calculations to determine pH

Buffering: How does it work?

- pH is governed by the ratio of [HA]/[A^{-}]

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

- If the amounts of HA and A are large in comparison to the amount of H or OH added, then the change in the ratio is small.

- If we can assume that the changes of concentration of H^+ and A^- are insignificant (initial concentrations are equal to equilibrium concentrations), then we can use the Henderson-Hasselbalch equation to solve for pH.

$$\mathbf{pH = pK_a + \log([base]/[acid])}$$

see SAMPLE EXERCISES 15.4, 15.5, 15.6

15.3 Buffer Capacity

Buffer Capacity represents the amount of protons and hydroxide ions that can be absorbed without a significant change in pH

- Buffer solutions containing large quantities of buffering components will have a high buffering capacity
- Optimal buffering occurs when the ratio of $[A^-]$ and [HA] is 1. (the concentrations are equal).
- The best buffer will be a weak acid with a pKa similar to the desired pH

see SAMPLE EXERCISE 15.8

15.4 Titrations and pH Curves

pH curve (titration curve)- a curve based on the plotting of the pH of solution being analyzed as a function of the amount of titrant (standard) added.

<u>Strong Acid-Strong Base Titrations</u>
net ionic equation: $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$
millimole (mmol) is one thousandth of a mole
Number of mmol is equal to: volume (in mL) X molarity
1 mmol = 1 x 10^{-3} mol

equivalence point- the point in a titration where the amount of OH^- added completely reacts with H^+ originally present

- after H^+ and OH^- react completely the number of moles of excess ion (H^+ or OH^-) is divided by the final volume to obtain molarity (to then figure for pH)

<u>Weak Acid-Strong Base Titrations</u>

1. The reaction between the OH^- with the weak acid is assumed to go to completion.
2. The concentrations of the acid remaining and conjugate base formed can then be figured out.
3. The concentrations of HA and A^- can then be fit into the equilibrium expression to figure for pH

- the pH at the equivalence point of the titration of a weak acid and strong base is always greater than 7
- the equivalence point is defined by the stoichiometry, not by the pH

SAMPLE EXERCISE 15.9
Hydrogen cyanide gas has a Ka of 6.2 x 10^{-10} when dissolved in water. If a 50.0 mL sample of 0.100 M HCN is titrated with 0.100 M NaOH, calculate the pH of the solution

a. After 8.0 mL of 0.100 M NaOH has been added.

	OH^-	+	HCN	→	CN^-	+	H_2O
Before	0.80 mmol		5.0 mmol		0		0
After	-0.80 mmol		-0.80 mmol		+0.80 mmol		
	0 mol		4.20 mmol		0.80 mmol		

mol/L	HCN	H^+	+	CN^-
initial	[0.0724] 4.20 mmol	0		0.80 mmol
	58.0 mL			58.0 mL
x	-x	+x		+x
equilibrium	0.0724	0.0138		0.0138

6.2 x 10-10 = 0.0138 [H+]
0.0724
3.3 x 10-3 = [H+]
8.49 = pH

b. At the halfway point of the titration.

	OH^-	+	HCN	CN^- +	H_2O
Before	2.50 mmol		5.00 mmol	0	0
After	-2.50		-2.50	+2.50	
	0 mmol		2.50 mmol	2.50 mmol	

mol/L	HCN	H^+	+	CN^-
initial	2.50 [0.0333]	0		2.50 [0.0333]
	75.0			75.0
x	-x	+x		+x
equilibrium	0.0333	x		0.0333

6.2 X 10-10 = 0.0333 $[H^+]$
0.0333
9.21 = pH

c. At the equivalence point of the titration.

	OH^-	+	HCN	→	CN^-	+	H_2O
Before	5.00 mmol		5.00 mmol		0		0
After	-5.00		-5.00		+5.00 mmol		
	0 mmol		0.49 mmol		5.00 mmol		

mol/L	CN-	+	H_20	HCN	+	OH^-
initial	5.00 mmol			0		0.51
x	-x			+x		+x
equilibrium	0.0500			x		x

K_b = 1.0 x 10-14/ 6.2 x 10-10
K_b = 1.6×10^{-5}
$1.6 \times 10^{-5} = x^2 / 0.0500$
$9.0 \times 10^{-4} = x$ or $[OH^-]$
3.05 = pOH
10.95 = pH

- the greater the conjugate base strength (smaller acid strength or Ka) will result in a higher pH at the equivalence point.

Calculations of Ka
see SAMPLE EXERCISE 15.10

Weak Base-Strong Acid Titrations
-Calculations are similar to that of “Weak Acids With Strong Bases”

15.5 Acid-Base Indicators

Indicators mark the endpoints of titrations by changing color. The endpoint is not necessarily the same as the equivalence point.

- For most indicators, about a tenth of the initial form (HA) must be converted to the other form (In^-) before a new color is apparent

$$\frac{[In-]}{[HIn]} = \frac{1}{10}$$

- Most common acid-base indicators are weak acids themselves that change color with the presence of a proton, or absence thereof.

$$HIn_{(aq)} \qquad H^+_{(aq)} + In^-_{(aq)}$$

see SAMPLE EXERCISE 15.11
When a basic solution is titrated, In is converted to HIN, so the color change will be visible when

$$\frac{[In^-]}{[HIn]} = \frac{10}{1}$$

Now the Henderson-Hasselbalch equation changes (pH=pKa + log(10/1)) to give $pH=pK_a + 1$

- Typical acid-base indicators have a pH range of $pK_a \pm 1$
- When choosing an indicator for a titration, you want the endpoint to be as close as possible to the titration equivalence point
- Strong Acid-Strong Base titrations have dramatic changes in pH near the equivalence point (many suitable indicators may be used)
- Weak Acid-Strong Base titrations (or vice versa) less dramatic pH changes near the equivalence point (much less flexibility in choosing an indicator)

Solubility Equilibria

15.6 Solubility and the Solubility Product

- Assume typical ionic solids dissociate completely to form separate hydrated cations and anions

Example $CaF_{2\,(s)} \rightarrow Ca^{2+}_{(aq)} + 2F_{(aq)}$
$Ca^{2+}_{(aq)} + 2F^-_{(aq)} \rightarrow CaF_{2(s)}$ reverse dissolution

$CaF_{2(s)}$ $Ca^{2+}_{(aq)}$ + $2F_{(aq)}$ dynamic equilibrium

K_{sp} = [Ca] [F] solubility product constant

- Neither the amount of excess solid nor the size of the particles present will shift the position of the solubility equilibrium

SAMPLE EXERCISE 15.14

The K_{sp} value for copper (II) iodate is 1.4 X 10^{-7} at 25 degrees C. Calculate its solubility at this temperature.

	$Cu(IO_3)_2$	Cu^{2+} +	$2IO^{3-}$
initial	------	0	0
change x	------	+x	+2x
equilibrium	------	x	2x

K_{sp} = $[Cu^{2+}][IO_2]^2$

1.4×10^{-7} = $[x][2x]^2$

1.4×10^{-7} = $4x^3$

3.3×10^{-3} M = x

Relative Solubilities

- K_{sp} values can be compared to determine relative solubilities if the ionic solids produce the same number of hydrated ions

Common Ion Effect

- The solubility of a solid is lowered if the solution already contains ions common to the solid

pH and Solubility

- The presence of H^+ or OH^- can greatly affect a salt's solubility

Example $Mg(OH)_{2(s)}$ $Mg^{2+}_{(aq)}$ + $2OH^-_{(aq)}$

a. lower K_{sp}, adding OH^- (increasing pH) **equilibrium shifts left**
b. higher K_{sp}, adding H^+ (decreasing pH) **equilibrium shifts right (makes H_20)**

Example $Ag_3PO_{4(s)}$ $3Ag^+_{(aq)}$ + $PO_4{}^{3-}_{(aq)}$

- Adding H^+ will react with the strong base $PO_4{}^{3-}_{(aq)}$ to form HPO_4^{3-} , thus lowering, the concentration of PO_4^{3-} and shifts the solubility equilibrium to the right
- As a general rule, if the anion X^- is a conjugate base of a weak acid (HX), the MX will show increased solubility in an acidic solution

15.7 Precipitation and Qualitative Analysis

(Q) Ion Product- similar to K_{sp}, but initial concentrations are used instead of equilibrium concentrations

Example CaF_2 Q= $[Ca^{2+}]_0\,[F^-]_0{}^2$

The relationship between Q and K_{sp} is used to predict whether or not a precipitate will form

1. If Q is greater than K_{sp}, precipitation occurs
2. If Q is less than K_{sp}, precipitation does not occur

Steps in Calculating Equilibrium Concentrations after Precipitation Occurs

1. Calculate Q to compare with K_{sp} to see if precipitation occurs
2. Determine if dissolution or the reverse is favored to do stoichiometric calculations
3. Calculate initial concentrations to figure for equilibrium concentrations
4. By substituting K_{sp} into the equilibrium expression will yield equilibrium concentrations.

Selective Precipitation- a process by which a reagent is used to selectively precipitate out metal ions within an aqueous mixture

Qualitative Analysis- a selective precipitation procedure used to separate common cations within a mixture by grouping them based on their solubilities.

Group 1- insoluble chlorides (Ag^+, Pb^{2+}, Hg_2^{2+})
Group 2- insoluble sulfides in acidic solution
(most insoluble sulfides Hg_2^{2+} , Cd^{2+} , Bi^{3+}, Cu^{2+} , Sn^{4+})
Group 3- insoluble sulfides in basic solutions
(more soluble sulfides Co^{2+} , Zn^{2+}, Mn^{2+} , Ni^+, Fe^{2+} , and any Cr^{3+} and Al^{3+} due to the OH^- present)
Group 4- insoluble carbonates
Group 5- alkali metals and ammonium ions (identified by flame tests)

Complex Ion Equilibria

15.8 Equilibria Involving Complex Ions

Complex Ion- a charged species consisting of a metal ion surrounded by ligands

Ligand- a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond (basically, a Lewis base)

Common Ligands- H_2O, NH_3 , Cl^- and CN^-

Coordination Number- Number of ligands attached to a metal ion

Example 6- $Co(H_2O)_6^{2+}$; 4- $Cu(NH_3)_4^{2+}$

-metal ions add ligands one at a time and each step is characterized by equilibrium constants called formation constants or stability constants

Example $Ag^+ + NH_3$ $Ag(NH_3)^+$ $K_1 = 2.1 \times 10^3$
$Ag(NH_3)^+ + NH_3$ $Ag(NH_3)_2^+$ $K_2 = 8.2 \times 10^3$

Calculate the concentrations of Ag^+, $Ag(NH_3)^+$ and $Ag(NH_3)^{2+}$ in a solution by mixing 100.0 mL of 2.0 M NH_3 with 100.0 mL of 1.0×10^{-3} M $AgNO_3$.

$NH_{3\,(aq)}$ + $H_2O_{(l)}$ $NH_{4(aq)}$ + $OH^-_{(aq)}$

This reaction is negligible based on the K_b value

$$[Ag^+] = \frac{100.0\text{ mL} \times 1.0 \times 10^{-3}\text{ mmol/ mL}}{200.0\text{ mL (total volume)}} = 5.0 \times 10^{-4}\text{ M}$$

$$[NH^3]_0 = \frac{100.0\text{ mL} \times 2.0\text{ mmol/mL}}{200.0\text{ mL}} = 1.0\text{ M}$$

We assume both steps go to completion based upon the large values of K_1 and K_2, so . . .

	Ag^+	+	$2NH_3$	$Ag(NH_3)_2^+$
Before	5.0×10^{-4} M		1 M	0
After	0		$1.0 – 2(5.0 \times 10^{-4})$	5.0×10^{-4}

$$K_2 = \frac{[Ag(NH_3)^{2+}]}{[Ag(NH_3)^+][NH_3]}$$

$$8.2 \times 10^3 = \frac{5.0 \times 10^{-4}}{[Ag(NH_3)^+]\ 1.0}$$

$[Ag(NH_3)^+] = 6.1 \times 10^{-8}$ M

$$K_1 = \frac{[Ag(NH_2)^+]}{[Ag^+][NH_3]}$$

$$2.1 \times 10^3 = \frac{6.1 \times 10^{-8}}{[Ag^+]\ 1.0}$$

$[Ag^+] = 2.9 \times 10^{-11}$M

Complex Ions and Solubility

- Water-insoluble solids can often be dissolved in a solution containing a ligand that forms stable complex ions with its cation.

Example $AgCl_{(s)} \quad Ag^+ + Cl^-$

(we can lower the concentration of Ag by adding the ligand NH the increasing the solubility of $AgCl_{(s)}$)

$Ag^+ + NH_3 \quad Ag(NH_3)^+$

$Ag(NH_3) + NH_3 \quad Ag(NH_3)_2^+$

- Extremely insoluble solids can sometimes be dissolved by using a mixture of concentrated HCl and HNO_3 called aqua regia

Example HgS ($K_{sp}= 10^{-54}$)

$Hg_{(s)} \quad Hg^{2+} + S^{2-}$

$2H^+ + S^{2-} \quad H_2S$

$Hg^{2+} + 4Cl^- \quad HgCl_4^{2-}$ promotes the solubility of HgS

- Solubility for many salts increase with temperature