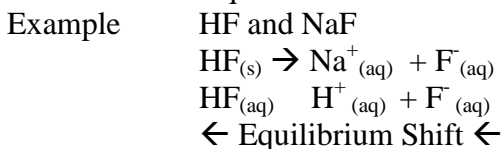


## 15.1 Solutions of Acids or Bases Containing a Common Ion

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



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

## 15.2 Buffered Solutions

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

Buffered solutions contain weak acids or bases with their salts

(ex. HF and NaF, or  $\text{NH}_3$  and  $\text{NH}_4\text{Cl}$ )

### 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.

	$\text{OH}^-$	+	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O}$
<b>Before</b>	0.010 mol		0.50 mol	0.50 mol
<b>After</b>	0.010-0.010		0.50-0.010	0.50+0.010
	<u>0 mol</u>		<u>0.49 mol</u>	<u>0.51 mol</u>

<b>mol/L</b>	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{H}^+$	+	$\text{C}_2\text{H}_3\text{O}_2^-$
<b>initial</b>	0.49	0		0.51
<b>x</b>	-x	+x		+x
<b>equilibrium</b>	0.49	x		0.51

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

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

$$\text{pH} = -\log[\text{H}^+] = -\log[1.7 \times 10^{-5}] = 4.76$$

\*pH without the addition of excess  $\text{OH}^-$  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  $\text{H}^+$  or  $\text{OH}^-$  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  $[\text{HA}]/[\text{A}^-]$   

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

$$pH = pK_a + \log\left(\frac{[base]}{[acid]}\right)$$

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  $pK_a$  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.

#### Strong Acid-Strong Base Titrations

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 =  $1 \times 10^{-3}$  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)

#### Weak Acid-Strong Base Titrations

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  $K_a$  of  $6.2 \times 10^{-10}$  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 <sup>-</sup>	+	HCN	→	CN <sup>-</sup>	+	H <sub>2</sub> O
<b>Before</b>	0.80 mmol		5.0 mmol		0		0
<b>After</b>	-0.80 mmol		-0.80 mmol		+0.80 mmol		
	<u>0 mol</u>		<u>4.20 mmol</u>		<u>0.80 mmol</u>		
<b>mol/L</b>	HCN		H <sup>+</sup>	+	CN <sup>-</sup>		
<b>initial</b>	[0.0724] <u>4.20 mmol</u>		0		<u>0.80 mmol</u>		<u>58.0 mL</u>
							58.0 mL
<b>x</b>	-x		+x		+x		
<b>equilibrium</b>	0.0724		0.0138		0.0138		

$$6.2 \times 10^{-10} = \frac{0.0138 [\text{H}^+]}{0.0724}$$

$$3.3 \times 10^{-3} = [\text{H}^+]$$

$$8.49 = \text{pH}$$

b. At the halfway point of the titration.

	OH <sup>-</sup>	+	HCN		CN <sup>-</sup>	+	H <sub>2</sub> O
<b>Before</b>	2.50 mmol		5.00 mmol		0		0
<b>After</b>	-2.50		-2.50		+2.50		
	<u>0 mmol</u>		<u>2.50 mmol</u>		<u>2.50 mmol</u>		
<b>mol/L</b>	HCN		H <sup>+</sup>	+	CN <sup>-</sup>		
<b>initial</b>	<u>2.50</u> [0.0333]		0		<u>2.50</u> [0.0333]		<u>75.0</u>
							75.0
<b>x</b>	-x		+x		+x		
<b>equilibrium</b>	0.0333		x		0.0333		

$$6.2 \times 10^{-10} = \frac{0.0333 [\text{H}^+]}{0.0333}$$

$$9.21 = \text{pH}$$

c. At the equivalence point of the titration.

	OH <sup>-</sup>	+	HCN	→	CN <sup>-</sup>	+	H <sub>2</sub> O
<b>Before</b>	5.00 mmol		5.00 mmol		0		0
<b>After</b>	-5.00		-5.00		+5.00 mmol		
	<u>0 mmol</u>		<u>0.49 mmol</u>		<u>5.00 mmol</u>		
<b>mol/L</b>	CN <sup>-</sup>	+	H <sub>2</sub> O		HCN	+	OH <sup>-</sup>
<b>initial</b>	5.00 mmol				0		0.51
<b>x</b>	-x				+x		+x
<b>equilibrium</b>	0.0500				x		x

$$K_b = 1.0 \times 10^{-14} / 6.2 \times 10^{-10}$$

$$K_b = 1.6 \times 10^{-5}$$

$$1.6 \times 10^{-5} = x^2 / 0.0500$$

$$9.0 \times 10^{-4} = x \text{ or } [\text{OH}^-]$$

$$3.05 = \text{pOH}$$

$$10.95 = \text{pH}$$

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

#### Calculations of $K_a$

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 ( $\text{In}^-$ ) before a new color is apparent

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

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



see SAMPLE EXERCISE 15.11

When a basic solution is titrated,  $\text{In}^-$  is converted to  $\text{HIn}$ , so the color change will be visible when

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

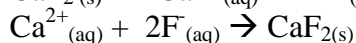
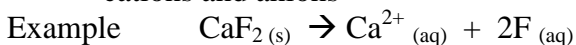
Now the Henderson-Hasselbalch equation changes ( $\text{pH} = \text{p}K_a + \log(10/1)$ ) to give  $\text{pH} = \text{p}K_a + 1$

- Typical acid-base indicators have a pH range of  $\text{p}K_a \pm 1$
- 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)

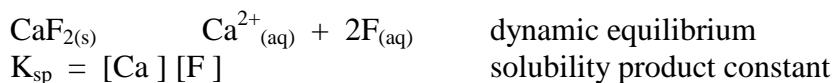
### Solubility Equilibria

#### 15.6 Solubility and the Solubility Product

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



reverse dissolution



- 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  $1.4 \times 10^{-7}$  at 25 degrees C. Calculate its solubility at this temperature.

	$\text{Cu}(\text{IO}_3)_2$	$\text{Cu}^{2+}$	+	$2\text{IO}_3^-$
initial	-----	0		0
change x	-----	+x		+2x
equilibrium	-----	x		2x

$$K_{sp} = [\text{Cu}^{2+}][\text{IO}_3^-]^2$$

$$1.4 \times 10^{-7} = [x][2x]^2$$

$$1.4 \times 10^{-7} = 4x^3$$

$$3.3 \times 10^{-3} \text{ M} = x$$

#### Relative Solubilities

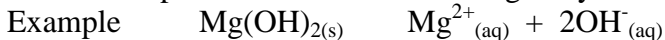
- $K_{sp}$  values can be compared to determine relative solubilities if the ionic solids produce the same number of hydrated ions

#### Common Ion Effect

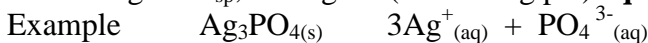
- The solubility of a solid is lowered if the solution already contains ions common to the solid

#### pH and Solubility

- The presence of  $\text{H}^+$  or  $\text{OH}^-$  can greatly affect a salt's solubility



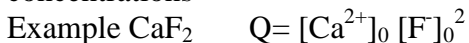
- lower  $K_{sp}$ , adding  $\text{OH}^-$  (increasing pH) **equilibrium shifts left**
- higher  $K_{sp}$ , adding  $\text{H}^+$  (decreasing pH) **equilibrium shifts right (makes  $\text{H}_2\text{O}$ )**



- Adding  $\text{H}^+$  will react with the strong base  $\text{PO}_4^{3-}_{(aq)}$  to form  $\text{HPO}_4^{2-}$ , thus lowering, the concentration of  $\text{PO}_4^{3-}$  and shifts the solubility equilibrium to the right
- As a general rule, if the anion  $\text{X}^-$  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



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

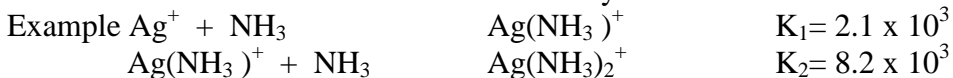
**Ligand**- a molecule or ion having a lone electron pair that can be donated to an empty orbital on the metal ion to form a covalent bond (basically, a Lewis base)

**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



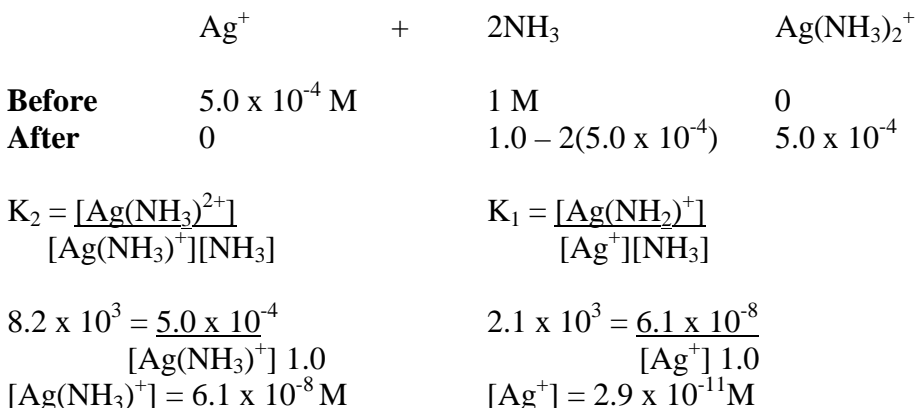
Calculate the concentrations of  $Ag^+$ ,  $Ag(NH_3)^+$  and  $Ag(NH_3)_2^+$  in a solution by mixing 100.0 mL of 2.0 M  $NH_3$  with 100.0 mL of  $1.0 \times 10^{-3}$  M  $AgNO_3$ .



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

$$[NH_3]_0 = \frac{100.0 \text{ mL} \times 2.0 \text{ mmol/mL}}{200.0 \text{ mL}} = 1.0 \text{ M}$$

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

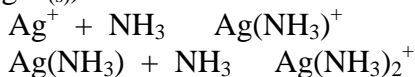


### Complex Ions and Solubility

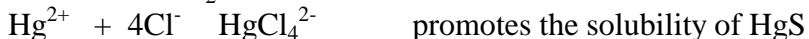
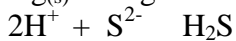
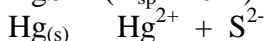
- Water-insoluble solids can often be dissolved in a solution containing a ligand that forms stable complex ions with its cation.



(we can lower the concentration of Ag by adding the ligand NH the increasing the solubility of  $\text{AgCl}_{(s)}$ )



- Extremely insoluble solids can sometimes be dissolved by using a mixture of concentrated HCl and  $\text{HNO}_3$  called aqua regia



- Solubility for many salts increase with temperature