

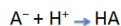
**17.1 The Common-Ion Effect**

- Common ion is produced by both acid and salt
  - Strong electrolyte added to a weak electrolyte with an ion in common
- Imposes a stress on system (salt completely dissociates in water)
- Shifts equilibrium to left (thus less dissociation of weak acid than before)
- Equilibrium is depressed, can assume that the  $[ \text{H}^+ ]_0 \ll [ \text{HA} ]_0$
- Same is true of the conjugate base



Add strong base to a solution of weak acid

Add strong acid to a solution of weak base



Calculate the pH of a solution containing 1.00 M HF ( $K_a = 7.2 \times 10^{-4}$ )

$\text{HF}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{F}^-_{(\text{aq})}$		
1.00M	0	0
-x	+x	+x
1.00-x	x	+x

$$7.2 \times 10^{-4} = \frac{x^2}{1.00-x} \quad 7.2 \times 10^{-4} = \frac{x^2}{1.00}$$

$$7.2 \times 10^{-4} = x^2$$

$$x = 0.027$$

$$\text{pH} = -\log(0.027) = 1.57$$

If 0.100 moles of  $\text{NaC}_2\text{H}_3\text{O}_2$  are added to a 1.00L of 0.100M solution of acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , what is the reactant pH?  $K_a = 1.8 \times 10^{-5}$

$\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-$			
0.30M	~	0	0.30M
-x M	~	+ xM	+ xM
(0.30-x)M	~	x M	(0.30+x)M

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{x(0.100+x)}{(0.100-x)}$$

$$1.8 \times 10^{-5} = \frac{0.100x}{0.100}$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) = 4.74$$

**17.2 Buffered Solutions**

- Buffered solutions resist a change in pH upon addition of small amounts of acid or base
  - Contain an acidic species to neutralize  $\text{OH}^-$  ions and a basic one to neutralize  $\text{H}^+$  ions
- May be buffered at acidic or basic pH
- Weak acid and conjugate base (salt has high solubility)
- Weak base and conjugate acid (salt has high solubility)
- pH in the buffered solution is determined by the ratio of concentration of weak acid and weak base
- pH is determined by: value of  $K_a$  for a weak acid component of buffer and ratio of concentrations of acid to conjugate base pair
- $\text{OH}^- + \text{HA} \rightarrow \text{H}_2\text{O} + \text{A}^-$
- As long as concentrations of HA and  $\text{A}^-$  are large compared to the amount of  $\text{OH}^-$  added, the ratio of  $[\text{HA}]/[\text{A}^-]$  and pH don't change much

**Buffer Capacity and pH**

- Buffer capacity – amount of acid or base the buffer can neutralize before the pH begins to change
- Henderson-Hasselbalch equation:  $\text{pH} = \text{p}K_a + \log [\text{base}]/[\text{acid}]$

What is the pH of a buffer that is 0.12M in lactic acid,  $\text{HC}_3\text{H}_5\text{O}_3$ , and 0.10M in sodium lactate?

$$K_a = 1.4 \times 10^{-4}$$

$$\text{pH} = \text{p}K_a + \log(\text{base/acid})$$

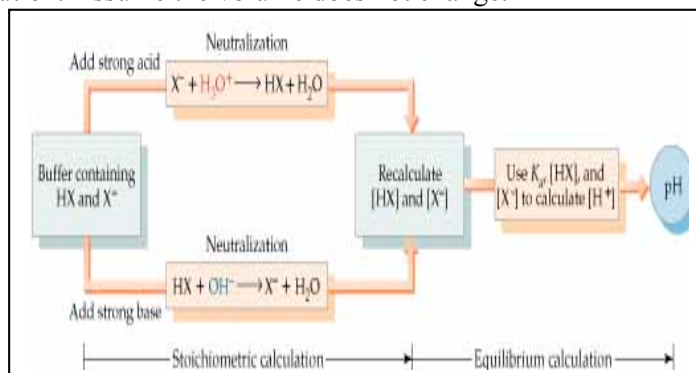
$$\text{pH} = -\log(1.4 \times 10^{-4}) + \log(0.10/0.12) \text{pH} = \underline{3.77}$$

A buffered solution is created by dissolving 0.30mol of sodium cyanide, NaCN, in 510mL of 0.55M HCN. ( $K_a = 6.2 \times 10^{-10}$ ) Assume that the volume of the solution does not change.

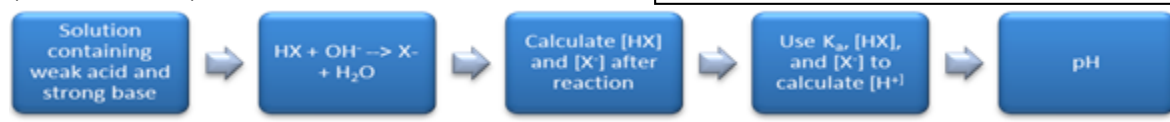
- Find the pH of the solution
- Find the pH after 0.25mol HNO<sub>3</sub> is added to the solution. Assume the volume does not change.

a.  $\text{NaCN} = (0.30\text{mol}/0.510\text{L}) = 0.59\text{M}$   
 $\text{pH} = -\log(6.2 \times 10^{-10}) + \log(0.59\text{M}/0.55\text{M})$   
 $\text{pH} = \underline{9.24}$

b.  $0.55\text{HCN} = x/0.510\text{L} = 0.28\text{mol HCN}$   
 $\text{pH} = -\log(6.2 \times 10^{-10}) + \log[(0.30-0.25)/(0.28+0.25)]$   
 $\text{pH} = \underline{8.18}$



Addition of Strong Acids or Bases to Buffers  
(see illustration)



**17.3 Acid-Base Titrations**

- Acid is added to a base or vice versa
- Strong acid (known concentration) is added to a base (with an indicator)
- Strong base (known concentration) is added to an acid (with an indicator)
- Indicator changes color to signal the arrival at the endpoint
  - Equivalence point occurs when equal amounts of acid and base have combined

Strong Acid – Strong Base Titrations

30mL of 0.50M HCl is titrated with 0.50M NaOH. Find:

- The initial pH of 0.5M HCl
- The pH after 15mL of NaOH were added

a. The initial pH is calculated using the concentration of HCl.

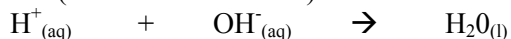
Strong Acid = 100% dissociation

$$-\log [\text{H}^+] = -\log (0.50) = \underline{0.30} = \text{pH}$$

b. Find the moles of H<sup>+</sup> and OH<sup>-</sup> that reacted

$$0.030\text{L solution} \times (0.50\text{mol HCl}/1\text{L solution}) = 0.015\text{mol HCl}$$

$$0.015\text{L} \times (0.50\text{mol}/1\text{L solution}) = 0.0075 \text{ mol NaOH}$$



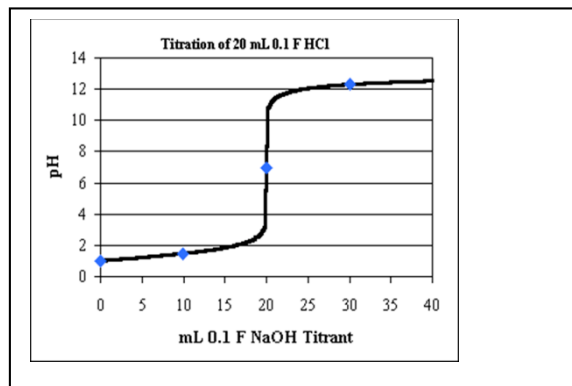
0.015mol	0.0075mol	~
-0.0075mol	-0.0075mol	~
0.0075mol	0	~

Find [H<sup>+</sup>] and pH of the new solution

$$\text{New Volume} = 0.030\text{L} + 0.015\text{L} = 0.045\text{L}$$

$$[\text{H}^+] = 0.0075\text{mol} [\text{H}^+] / 0.045\text{L} = 0.17\text{M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log(0.17) = \underline{0.77}$$



Weak Acid – Strong Base Titrations

30mL of 0.50M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> is titrated with 0.50M NaOH.  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ . Find:

- The initial pH of 0.50M acetic acid, HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>.
- The pH after 15mL of NaOH was added.
- The pH at the equivalence point.



0.50M	0	0
-x	+x	+x
0.50 - x	x	x

$$\frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = \frac{x^2}{0.50}$$

$$x^2 = [\text{H}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = \sqrt{0.50 (1.8 \times 10^{-5})} = 0.0030\text{M}$$

$$\text{pH} = -\log (0.0030) = \underline{2.52}$$

b. Moles of  $\text{HC}_2\text{H}_3\text{O}_2$ :

$$0.030\text{L solution} \times (0.50\text{mol}/1\text{L solution}) = 0.015\text{mol HC}_2\text{H}_3\text{O}_2$$

Moles of  $\text{NaOH}$ :

$$0.015\text{L solution} \times (0.50\text{mol}/1\text{L solution}) = 0.0075\text{mol NaOH}$$



0.0015mol	0.0075mol	0	~
-0.0075mol	-0.0075mol	+0.0075mol	~
0.0075mol	0	0.0075mol	~

$$\text{New Volume} = 0.030\text{L} + 0.015\text{L} = 0.045\text{L}$$

$$0.0075\text{mol}/0.045\text{L} = 0.17\text{M HC}_2\text{H}_3\text{O}_2$$

$$0.0075\text{mol}/0.045\text{L} = 0.17\text{M C}_2\text{H}_3\text{O}_2^-$$

Find pH using the Henderson – Hasselbalch equation

$$\text{pH} = \text{pK}_a + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

$$\text{pH} = -\log(1.8 \times 10^{-5}) + \log(0.17\text{M C}_2\text{H}_3\text{O}_2^- / 0.17\text{M HC}_2\text{H}_3\text{O}_2)$$

$$\text{pH} = 4.74$$

c. The equivalence point is reached when equal numbers of moles of  $\text{NaOH}$  and  $\text{HC}_2\text{H}_3\text{O}_2$  have reacted.



$$K_w = K_a + K_b \quad K_b = K_w / K_a \quad (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$$

Find moles of  $\text{C}_2\text{H}_3\text{O}_2^-$

$$0.030\text{L solution} \times (0.50\text{mol C}_2\text{H}_3\text{O}_2^- / 1\text{L solution}) = 0.015\text{mol C}_2\text{H}_3\text{O}_2^-$$

0.015mol  $\text{C}_2\text{H}_3\text{O}_2^-$  in solution as all acetic acid is reacted

$$\text{New Volume} = 0.030\text{L} + 0.030\text{L} = 0.060\text{L}$$

$$[\text{C}_2\text{H}_3\text{O}_2^-] = 0.015\text{mol}/0.060\text{L} = 0.25\text{M C}_2\text{H}_3\text{O}_2^-$$

Find  $[\text{OH}^-]$  and  $K_b$ .



0.25M	~	0	0
-x	~	+x	+x
0.25-x	~	x	x

$$K_b = (x^2/0.25-x) = (x^2/0.25)$$

$$x = [\text{OH}^-] = \sqrt{0.25 (5.6 \times 10^{-10})}$$

$$x = 1.2 \times 10^{-5}\text{M}$$

Find pOH and pH

$$\text{pOH} = -\log [\text{OH}^-] = -\log(1.2 \times 10^{-5}\text{M}) = 4.92$$

$$\text{pH} = 14 - 4.92 = 9.08$$

The solution is basic at the equivalence point (basic anion in solution)

#### Titrations of Polyprotic Acids

- When titrating with polyprotic acids or bases the substance has multiple equivalence points.
- For example, in a titration of  $\text{Na}_2\text{CO}_3$  with  $\text{HCl}$ , there are two distinct equivalence points on the titration curve.

#### 17.4 Solubility Equilibria

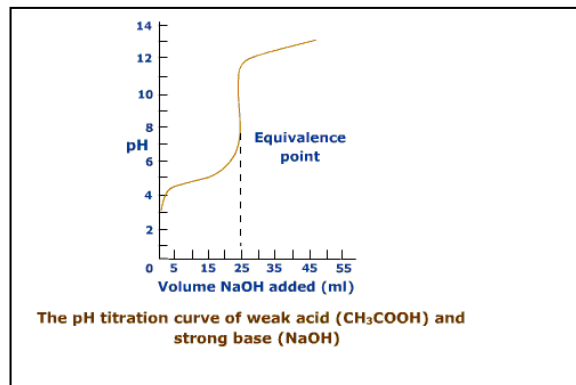
- $K_{sp}$  = Solubility Product Constant
- Expresses the degree to which the solid is soluble in water
- The equation for  $K_{sp}$  is  $K_{sp} = [\text{ion}]^a [\text{ion}]^b$

#### 17.5 Factors that Affect Solubility

- Presence of common ions
- pH of the solution
- Presence of complexing agents
  - Presence of common ions in a solution will reduce the solubility and shift the equilibrium left

#### Solubility and pH

- Solubility of slightly-soluble salts containing basic anions increases as the pH of the solution decreases
  - $\text{OH}^-$  ion is insoluble in water while the  $\text{H}^+$  ion is highly soluble
    - When a basic solution has a low concentration of  $\text{OH}^-$  ions the salt will be easy to dissolve
- The more basic the anion, the more the solubility is influenced by the pH of the solution
- Salts with anions of strong acids are unaffected by changes in pH



### Formation of Complex Ions

- Metal ions can act as Lewis acids, electron-pair acceptors toward water molecules (which act as Lewis bases), or electron-pair donors
- Lewis bases other than water can interact with metal ions, particularly with transition-metal ions
- Assembly of a metal ion and the Lewis bases bonded to it is called a complex ion
- Equilibrium constant for formation ions is called a formation constant,  $K_f$

### Amphoterism

- Amphoteric – a metal hydroxide that is capable of being dissolved in strong acids or strong bases, but not in water because it can act like an acid or a base
- Examples:  $\text{Al}^{+3}$ ,  $\text{Cr}^{+3}$ ,  $\text{Zn}^{+2}$ , and  $\text{Sn}^{+2}$ 
  - These metal ions are more accurately expressed as  $\text{Al}(\text{H}_2\text{O})_6^{+3}$ .
  - This is a weak acid and as it is added to a strong base, it loses protons and eventually forms the neutral and water-soluble  $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$

### **17.6 Precipitation and Separation of Ions**

- The reaction quotient,  $Q$ , can with the solubility product constant determine if there is a precipitation
  - If  $Q > K_{sp}$ , precipitation occurs until  $Q = K_{sp}$
  - If  $Q = K_{sp}$ , equilibrium exists (saturated solution)
  - If  $Q < K_{sp}$ , solid dissolves until  $Q = K_{sp}$
- $Q$  is sometimes referred to as the ion product because there is no denominator

### Selective Precipitation of Ions

- Selective Precipitation is the separation of ions in an aqueous solution by using a reagent that forms a precipitate with one or more of the ions.
- The sulfide ion is widely used to separate metal ions because the solubility of the sulfide salts span a wide range and are dependent on the pH of the solution

### **17.7 Qualitative Analysis for Metallic Elements**

- Qualitative Analysis determines the presence or absence of a particular metal ion, whereas quantitative analysis determines how much of a certain substance is present or produced
- 5 main groups of metal ions
  - Insoluble Chlorides, Acid-insoluble sulfides, base-insoluble sulfides and hydroxides, insoluble phosphates, and the alkali metal ions and  $\text{NH}_4^{+1}$