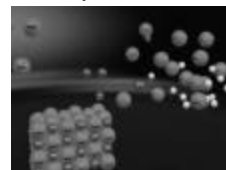


## The Common Ion Effect

- The solubility of a partially soluble salt is decreased when a common ion is added.
- Consider the equilibrium established when acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$ , is added to water.
- At equilibrium  $\text{H}^+$  and  $\text{C}_2\text{H}_3\text{O}_2^-$  are constantly moving into and out of solution, but the concentrations of ions is constant and equal.

## The Common Ion Effect

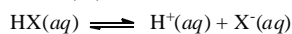
- Consider the addition of  $\text{C}_2\text{H}_3\text{O}_2^-$ , which is a common ion. (The source of acetate could be a strong electrolyte such as  $\text{NaC}_2\text{H}_3\text{O}_2$ .)
- Therefore,  $[\text{C}_2\text{H}_3\text{O}_2^-]$  increases and the system is no longer at equilibrium.
- So,  $[\text{H}^+]$  must decrease.



## Buffered Solutions

### Composition and Action of Buffered Solutions

- A buffer consists of a mixture of a weak acid (HX) and its conjugate base ( $\text{X}^-$ ):



- The  $K_a$  expression is

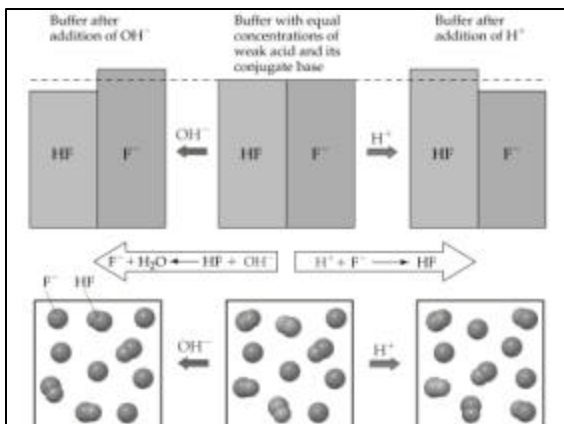
$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

$$\therefore [\text{H}^+] = K_a \frac{[\text{HX}]}{[\text{X}^-]}$$

## Buffered Solutions

### Composition and Action of Buffered Solutions

- A buffer resists a change in pH when a small amount of  $\text{OH}^-$  or  $\text{H}^+$  is added.
- When  $\text{OH}^-$  is added to the buffer, the  $\text{OH}^-$  reacts with HX to produce  $\text{X}^-$  and water. But, the  $[\text{HX}]/[\text{X}^-]$  ratio remains more or less constant, so the pH is not significantly changed.
- When  $\text{H}^+$  is added to the buffer,  $\text{X}^-$  is consumed to produce HX. Once again, the  $[\text{HX}]/[\text{X}^-]$  ratio is more or less constant, so the pH does not change significantly.



## Buffered Solutions

### Buffer Capacity and pH

- Buffer capacity is the amount of acid or base neutralized by the buffer before there is a significant change in pH.
- Buffer capacity depends on the composition of the buffer.
- The greater the amounts of conjugate acid-base pair, the greater the buffer capacity.
- The pH of the buffer depends on  $K_a$ .

## Buffered Solutions

### Buffer Capacity and pH

$$-\log[H^+] = -\log K_a - \log \frac{[HX]}{[X^-]}$$

$$\therefore \text{pH} = \text{p}K_a + \log \frac{[X^-]}{[HX]}$$

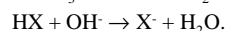
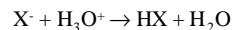
### Addition of Strong Acids or Bases to Buffers

- We break the calculation into two parts: stoichiometric and equilibrium.

## Buffered Solutions

### Addition of Strong Acids or Bases to Buffers

- The amount of strong acid or base added results in a neutralization reaction:

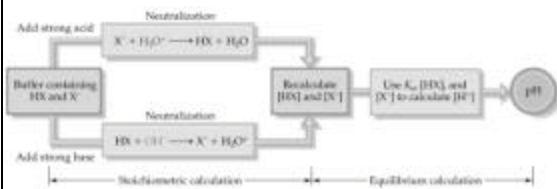


- By knowing how much  $H_3O^+$  or  $OH^-$  was added (stoichiometry) we know how much HX or  $X^-$  is formed.
- With the concentrations of HX and  $X^-$  (note the change in volume of solution) we can calculate the pH from the Henderson-Hasselbalch equation.

## Buffered Solutions

### Addition of Strong Acids or Bases to Buffers

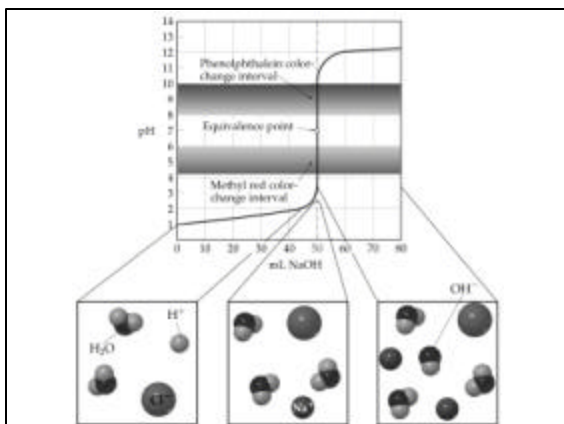
$$\text{pH} = \text{p}K_a + \log \frac{\text{conjugatebase}}{\text{acid}}$$



## Acid-Base Titrations

### Strong Acid-Strong Base Titrations

- A plot of pH versus volume of acid (or base) added is called a titration curve.
- Consider adding a strong base (e.g. NaOH) to a solution of a strong acid (e.g. HCl).
  - Before any base is added, the pH is given by the strong acid solution. Therefore,  $\text{pH} < 7$ .
  - When base is added, before the equivalence point, the pH is given by the amount of strong acid in excess. Therefore,  $\text{pH} < 7$ .



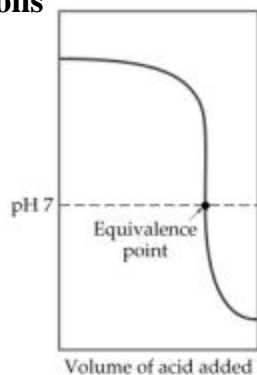
## Acid-Base Titrations

### Strong Acid-Strong Base Titrations

- At equivalence point, the amount of base added is stoichiometrically equivalent to the amount of acid originally present. Therefore, the pH is determined by the salt solution. Therefore,  $\text{pH} = 7$ .
- Consider adding a strong base (e.g. NaOH) to a solution of a strong acid (e.g. HCl).
- We know the pH at equivalent point is 7.00.
- To detect the equivalent point, we use an indicator that changes color somewhere near 7.00.

## Acid-Base Titrations

### Strong Base-Strong Acid Titrations



## Acid-Base Titrations

### Strong Acid-Strong Base Titrations

- The equivalence point in a titration is the point at which the acid and base are present in stoichiometric quantities.
- The end point in a titration is the observed point.
- The difference between equivalence point and end point is called the titration error.
- The shape of a strong base-strong acid titration curve is very similar to a strong acid-strong base titration curve.
- Initially, the strong base is in excess, so the  $\text{pH} > 7$ .

## Acid-Base Titrations

### Strong Acid-Strong Base Titrations

- As acid is added, the pH decreases but is still greater than 7.
- At equivalence point, the pH is given by the salt solution (i.e.  $\text{pH} = 7$ ).
- After equivalence point, the pH is given by the strong acid in excess, so  $\text{pH} < 7$ .

## Acid-Base Titrations

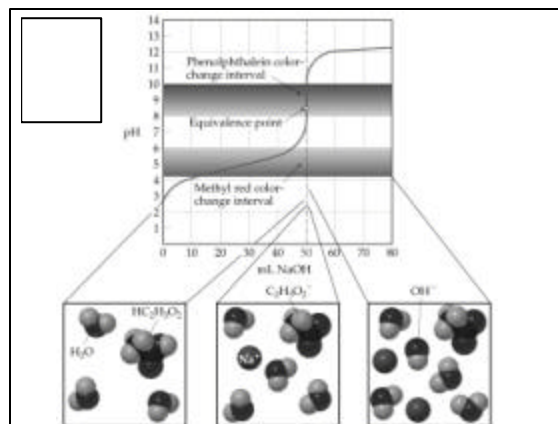
### Weak Acid-Strong Base Titrations

- Consider the titration of acetic acid,  $\text{HC}_2\text{H}_3\text{O}_2$  and  $\text{NaOH}$ .
- Before any base is added, the solution contains only weak acid. Therefore, pH is given by the equilibrium calculation.
- As strong base is added, the strong base consumes a stoichiometric quantity of weak acid:
 
$$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NaOH}(aq) \rightarrow \text{C}_2\text{H}_3\text{O}_2^-(aq) + \text{H}_2\text{O}(l)$$

## Acid-Base Titrations

### Weak Acid-Strong Base Titrations

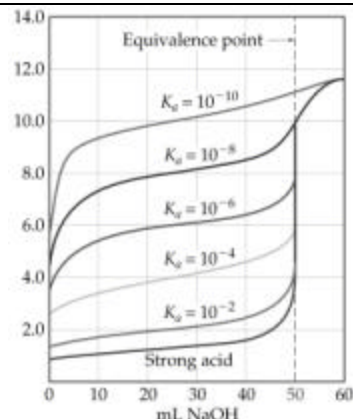
- There is an excess of acid before the equivalence point.
- Therefore, we have a mixture of weak acid and its conjugate base.
  - The pH is given by the buffer calculation.
    - First the amount of  $\text{C}_2\text{H}_3\text{O}_2^-$  generated is calculated, as well as the amount of  $\text{HC}_2\text{H}_3\text{O}_2$  consumed. (Stoichiometry.)
    - Then the pH is calculated using equilibrium conditions. (Henderson-Hasselbalch.)



## Acid-Base Titrations

### Weak Acid-Strong Base Titrations

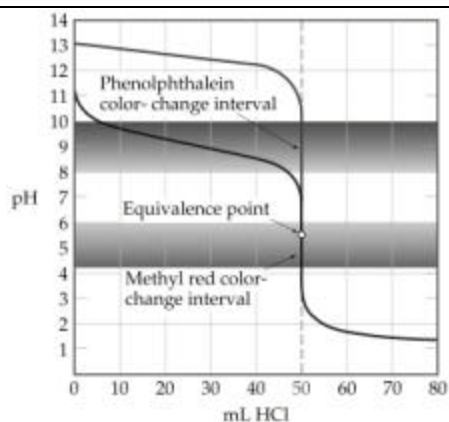
- At the equivalence point, all the acetic acid has been consumed and all the NaOH has been consumed. However,  $C_2H_3O_2^-$  has been generated.
  - Therefore, the pH is given by the  $C_2H_3O_2^-$  solution.
  - This means  $pH > 7$ .
    - More importantly,  $pH \neq 7$  for a weak acid-strong base titration.
- After the equivalence point, the pH is given by the strong base in excess.
- The equivalence point is determined by  $K_a$  of the acid.



## Acid-Base Titrations

### Weak Acid-Strong Base Titrations

- For a strong acid-strong base titration, the pH begins at less than 7 and gradually increases as base is added.
- Near the equivalence point, the pH increases dramatically.
- For a weak acid-strong base titration, the initial pH rise is more steep than the strong acid-strong base case.
- However, then there is a leveling off due to buffer effects.



## Acid-Base Titrations

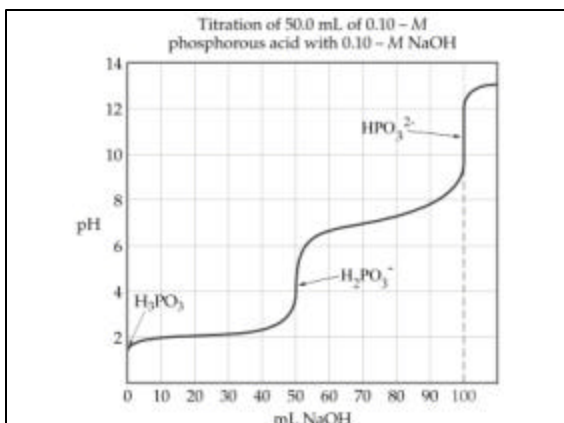
### Weak Acid-Strong Base Titrations

- The inflection point is not as steep for a weak acid-strong base titration.
- The shape of the two curves after equivalence point is the same because pH is determined by the strong base in excess.
- Two features of titration curves are affected by the strength of the acid:
  - the amount of the initial rise in pH, and
  - the length of the inflection point at equivalence.

## Acid-Base Titrations

### Titrations of Polyprotic Acids

- In polyprotic acids, each ionizable proton dissociates in steps.
- Therefore, in a titration there are  $n$  equivalence points corresponding to each ionizable proton.
- In the titration of  $H_3PO_3$  with NaOH.
  - The first proton dissociates to form  $H_2PO_3^-$ .
  - Then the second proton dissociates to form  $HPO_3^{2-}$ .



## Solubility Equilibria

### The Solubility-Product Constant, $K_{sp}$

- Consider
 
$$\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$$
- for which
 
$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$$
- $K_{sp}$  is the solubility product. ( $\text{BaSO}_4$  is ignored because it is a pure solid so its concentration is constant.)

## Solubility Equilibria

### The Solubility-Product Constant, $K_{sp}$

- In general: the solubility product is the molar concentration of ions raised to their stoichiometric powers.
- Solubility is the amount (grams) of substance that dissolves to form a saturated solution.
- Molar solubility is the number of moles of solute dissolving to form a liter of saturated solution.

## Solubility Equilibria

### Solubility and $K_{sp}$

- To convert solubility to  $K_{sp}$
- solubility needs to be converted into molar solubility (via molar mass);
- molar solubility is converted into the molar concentration of ions at equilibrium (equilibrium calculation),
- $K_{sp}$  is the product of equilibrium concentration of ions.




## Factors that Affect Solubility

### The Common Ion Effect

- Solubility is decreased when a common ion is added.
- This is an application of Le Châtelier's principle:
 
$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$$
- as  $\text{F}^-$  is added (say, from  $\text{NaF}$ ), the equilibrium shifts away from the increase.
- Therefore,  $\text{CaF}_2(s)$  is formed and precipitation occurs.
- As  $\text{NaF}$  is added to the system, the solubility of  $\text{CaF}_2$  decreases.

## Factors that Affect Solubility

### Solubility and pH

- Again we apply Le Châtelier's principle:
 
$$\text{CaF}_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{F}^-(aq)$$
  - If the  $\text{F}^-$  is removed, then the equilibrium shifts towards the decrease and  $\text{CaF}_2$  dissolves.
  - $\text{F}^-$  can be removed by adding a strong acid:
 
$$\text{F}^-(aq) + \text{H}^+(aq) \rightleftharpoons \text{HF}(aq)$$
  - As pH decreases,  $[\text{H}^+]$  increases and solubility increases.
- The effect of pH on solubility is dramatic. 

## Factors that Affect Solubility

### Formation of Complex Ions

- Consider the formation of  $\text{Ag}(\text{NH}_3)_2^+$ :  

$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$$
- The  $\text{Ag}(\text{NH}_3)_2^+$  is called a complex ion.
- $\text{NH}_3$  (the attached Lewis base) is called a ligand.
- The equilibrium constant for the reaction is called the formation constant,  $K_f$ :

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

## Factors that Affect Solubility

### Formation of Complex Ions

- Consider the addition of ammonia to  $\text{AgCl}$  (white precipitate):  

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

$$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$$
- The overall reaction is  

$$\text{AgCl}(s) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq) + \text{Cl}^-(aq)$$
- Effectively, the  $\text{Ag}^+(aq)$  has been removed from solution.
- By Le Châtelier's principle, the forward reaction (the dissolving of  $\text{AgCl}$ ) is favored.

## Factors that Affect Solubility

### Formation of Complex Ions

TABLE 17.1 Formation Constants for Some Metal Complex Ions in Water at 25 °C

Complex Ion	$K_f$	Equilibrium Equation
$\text{Ag}(\text{NH}_3)_2^+$	$1.7 \times 10^7$	$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$
$\text{Ag}(\text{CN})_2^-$	$1 \times 10^{21}$	$\text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	$2.9 \times 10^{13}$	$\text{Ag}^+(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$
$\text{CdBr}_4^{2-}$	$5 \times 10^3$	$\text{Cd}^{2+}(aq) + 4\text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$
$\text{Cr}(\text{OH})_4^-$	$8 \times 10^{29}$	$\text{Cr}^{3+}(aq) + 4\text{OH}^- \rightleftharpoons \text{Cr}(\text{OH})_4^-(aq)$
$\text{Co}(\text{SCN})_4^{2-}$	$1 \times 10^3$	$\text{Co}^{2+}(aq) + 4\text{SCN}^-(aq) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(aq)$
$\text{Cu}(\text{NH}_3)_4^{2+}$	$5 \times 10^{12}$	$\text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(aq)$
$\text{Cu}(\text{CN})_4^{2-}$	$1 \times 10^{25}$	$\text{Cu}^{2+}(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(aq)$
$\text{Ni}(\text{NH}_3)_6^{2+}$	$1.2 \times 10^9$	$\text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
$\text{Fe}(\text{CN})_6^{4-}$	$1 \times 10^{23}$	$\text{Fe}^{2+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(aq)$
$\text{Fe}(\text{CN})_6^{3-}$	$1 \times 10^{42}$	$\text{Fe}^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(aq)$

## Factors that Affect Solubility

### Amphoterism

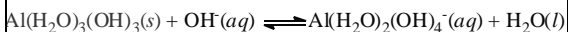
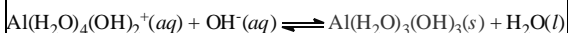
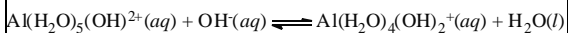
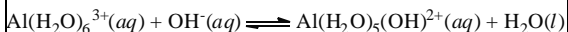
- Amphoteric oxides will dissolve in either a strong acid or a strong base.
- Examples: hydroxides and oxides of  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Sn}^{2+}$ .
- The hydroxides generally form complex ions with four hydroxide ligands attached to the metal:  

$$\text{Al}(\text{OH})_3(s) + \text{OH}^-(aq) \rightleftharpoons \text{Al}(\text{OH})_4^-(aq)$$
- Hydrated metal ions act as weak acids. Thus, the amphoterism is interrupted:

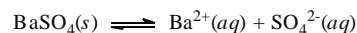
## Factors that Affect Solubility

### Amphoterism

- Hydrated metal ions act as weak acids. Thus, the amphoterism is interrupted:



## Precipitation and Separation of Ions



- At any instant in time,  $Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$ .
  - If  $Q < K_{sp}$ , precipitation occurs until  $Q = K_{sp}$ .
  - If  $Q = K_{sp}$ , equilibrium exists.
  - If  $Q > K_{sp}$ , solid dissolves until  $Q = K_{sp}$ .
- Based on solubilities, ions can be selectively removed from solutions.

