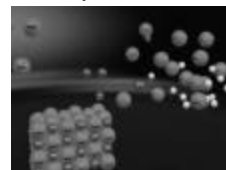


The Common Ion Effect

- 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 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

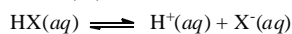
- Consider the addition of $\text{C}_2\text{H}_3\text{O}_2^-$, which is a common ion. (The source of acetate could be a strong electrolyte such as $\text{NaC}_2\text{H}_3\text{O}_2$.)
- Therefore, $[\text{C}_2\text{H}_3\text{O}_2^-]$ increases and the system is no longer at equilibrium.
- So, $[\text{H}^+]$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



- The K_a expression is

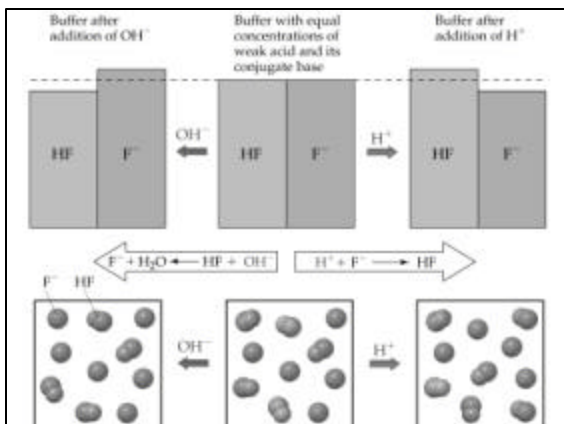
$$K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$$

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

Buffered Solutions

Composition and Action of Buffered Solutions

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

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

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

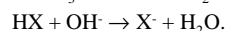
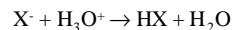
Addition of Strong Acids or Bases to Buffers

- 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:

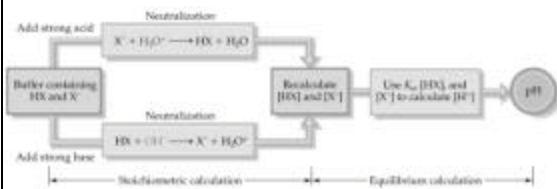


- By knowing how much H_3O^+ or OH^- was added (stoichiometry) we know how much HX or X^- is formed.
- With the concentrations of HX and X^- (note the change in volume of solution) we can calculate the pH from the Henderson-Hasselbalch equation.

Buffered Solutions

Addition of Strong Acids or Bases to Buffers

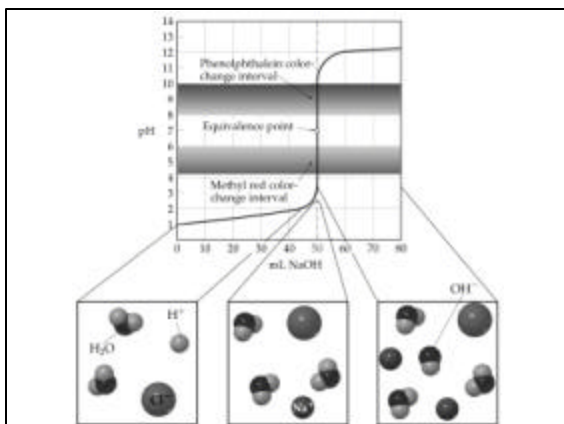
$$\text{pH} = \text{p}K_a + \log \frac{\text{conjugate base}}{\text{acid}}$$



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, $\text{pH} < 7$.



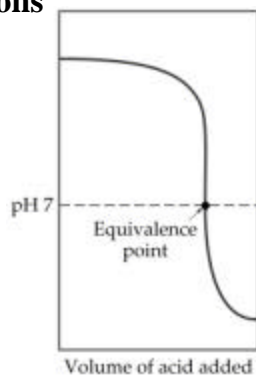
Acid-Base Titrations

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

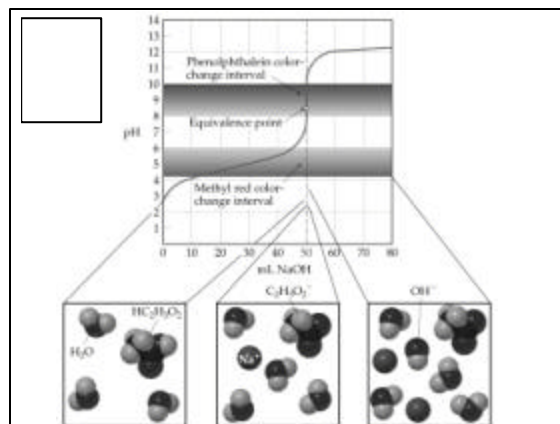
- Consider the titration of acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$ and NaOH .
- Before any base is added, the solution contains only weak acid. Therefore, pH is given by the equilibrium calculation.
- As strong base is added, the strong base consumes a stoichiometric quantity of weak acid:

$$\text{HC}_2\text{H}_3\text{O}_2(aq) + \text{NaOH}(aq) \rightarrow \text{C}_2\text{H}_3\text{O}_2^-(aq) + \text{H}_2\text{O}(l)$$

Acid-Base Titrations

Weak Acid-Strong Base Titrations

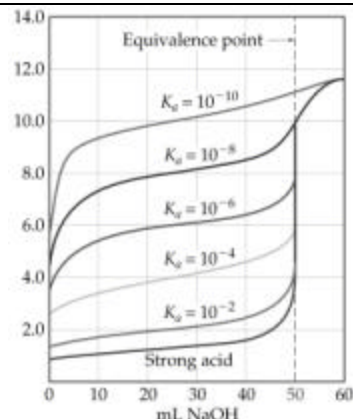
- There is an excess of acid before the equivalence point.
- Therefore, we have a mixture of weak acid and its conjugate base.
 - The pH is given by the buffer calculation.
 - First the amount of $\text{C}_2\text{H}_3\text{O}_2^-$ generated is calculated, as well as the amount of $\text{HC}_2\text{H}_3\text{O}_2$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



Acid-Base Titrations

Weak Acid-Strong Base Titrations

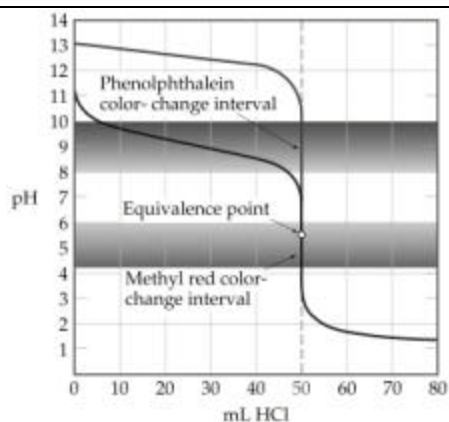
- At the equivalence point, all the acetic acid has been consumed and all the NaOH has been consumed. However, $C_2H_3O_2^-$ has been generated.
 - Therefore, the pH is given by the $C_2H_3O_2^-$ solution.
 - This means $pH > 7$.
 - More importantly, $pH \neq 7$ for a weak acid-strong base titration.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

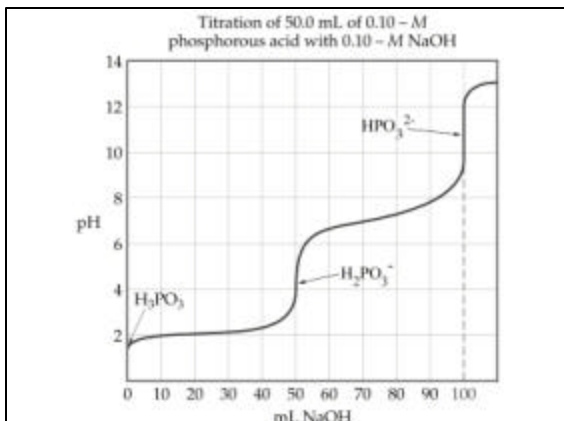
Weak Acid-Strong Base Titrations

- 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. (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 F^- is added (say, from NaF), the equilibrium shifts away from the increase.
- Therefore, $\text{CaF}_2(s)$ is formed and precipitation occurs.
- As NaF is added to the system, the solubility of 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 F^- is removed, then the equilibrium shifts towards the decrease and CaF_2 dissolves.
 - 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.
- 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 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 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
$\text{Ag}(\text{NH}_3)_2^+$	1.7×10^7	$\text{Ag}^+(aq) + 2\text{NH}_3(aq) \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+(aq)$
$\text{Ag}(\text{CN})_2^-$	1×10^{21}	$\text{Ag}^+(aq) + 2\text{CN}^-(aq) \rightleftharpoons \text{Ag}(\text{CN})_2^-(aq)$
$\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$	2.9×10^{13}	$\text{Ag}^+(aq) + 2\text{S}_2\text{O}_3^{2-}(aq) \rightleftharpoons \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}(aq)$
CdBr_4^{2-}	5×10^3	$\text{Cd}^{2+}(aq) + 4\text{Br}^-(aq) \rightleftharpoons \text{CdBr}_4^{2-}(aq)$
$\text{Cr}(\text{OH})_4^-$	8×10^{29}	$\text{Cr}^{3+}(aq) + 4\text{OH}^- \rightleftharpoons \text{Cr}(\text{OH})_4^-(aq)$
$\text{Co}(\text{SCN})_4^{2-}$	1×10^3	$\text{Co}^{2+}(aq) + 4\text{SCN}^-(aq) \rightleftharpoons \text{Co}(\text{SCN})_4^{2-}(aq)$
$\text{Cu}(\text{NH}_3)_4^{2+}$	5×10^{12}	$\text{Cu}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}(aq)$
$\text{Cu}(\text{CN})_4^{2-}$	1×10^{25}	$\text{Cu}^{2+}(aq) + 4\text{CN}^-(aq) \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}(aq)$
$\text{Ni}(\text{NH}_3)_6^{2+}$	1.2×10^9	$\text{Ni}^{2+}(aq) + 6\text{NH}_3(aq) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(aq)$
$\text{Fe}(\text{CN})_6^{4-}$	1×10^{23}	$\text{Fe}^{2+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{4-}(aq)$
$\text{Fe}(\text{CN})_6^{3-}$	1×10^{42}	$\text{Fe}^{3+}(aq) + 6\text{CN}^-(aq) \rightleftharpoons \text{Fe}(\text{CN})_6^{3-}(aq)$

Factors that Affect Solubility

Amphoterism

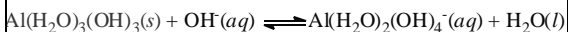
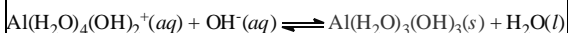
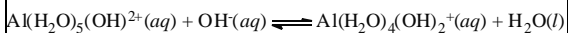
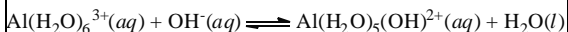
- Amphoteric oxides will dissolve in either a strong acid or a strong base.
- Examples: hydroxides and oxides of Al^{3+} , Cr^{3+} , Zn^{2+} , and Sn^{2+} .
- The hydroxides generally form complex ions with four hydroxide ligands attached to the metal:

$$\text{Al}(\text{OH})_3(s) + \text{OH}^-(aq) \rightleftharpoons \text{Al}(\text{OH})_4^-(aq)$$
- 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.

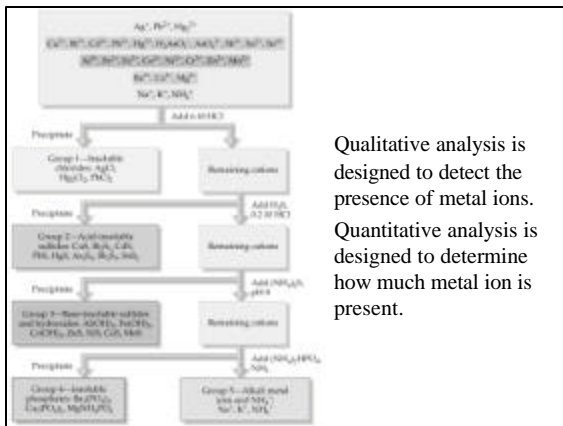
Precipitation and Separation of Ions

- Consider a mixture of $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$. CuS ($K_{sp} = 6 \times 10^{-37}$) is less soluble than ZnS ($K_{sp} = 2 \times 10^{-25}$), CuS will be removed from solution before ZnS .
- As H_2S is added to the green solution, black CuS forms in a colorless solution of $Zn^{2+}(aq)$.
- When more H_2S is added, a second precipitate of white ZnS forms.

Precipitation and Separation of Ions

Selective Precipitation of Ions

- Ions can be separated from each other based on their salt solubilities.
- Example: if HCl is added to a solution containing Ag^+ and Cu^{2+} , the silver precipitates (K_{sp} for $AgCl$ is 1.8×10^{-10}) while the Cu^{2+} remains in solution.
- Removal of one metal ion from a solution is called *selective precipitation*.



Qualitative Analysis for Metallic Elements

- We can separate a complicated mixture of ions into five groups:
 - Add 6 M HCl to precipitate insoluble chlorides ($AgCl$, Hg_2Cl_2 , and $PbCl_2$).
 - To the remaining mix of cations, add H_2S in 0.2 M HCl to remove acid insoluble sulfides (e.g. CuS , Bi_2S_3 , CdS , PbS , HgS , etc.).
 - To the remaining mix, add $(NH_4)_2S$ at pH 8 to remove base insoluble sulfides and hydroxides (e.g. $Al(OH)_3$, $Fe(OH)_3$, ZnS , NiS , CoS , etc.).

- To the remaining mixture add $(NH_4)_2HPO_4$ to remove insoluble phosphates ($Ba_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$).
- The final mixture contains alkali metal ions and NH_4^+ .