Solubility and Acid-Base

Solubility

$$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq)} + Cl^-_{(aq)}$$

The **solubility protduct (K_{sp})** of this reaction would be $K_{sp} = [Ag^+][Cl^-]$

We can use ICE tables (see previous outline) to solve solubility problems.

To predict whether or not a reaction will precipitate, we can calculate the Q_{sp} and compare to the K_{sp}.

$$Q_{sp} = K_{sp}\ Equilibrium$$
$$Q_{sp} < K_{sp}\ No\ precipitation$$
$$Q_{sp} > K_{sp}\ Precipitation\ occurs$$

when $Q_{sp} > K_{sp}$ The system becomes super saturated and as a result, precipitate forms.

The **common ion effect** is simply the application of Le Chatliers principle to a solution that already containt an ion involved in a dissolution reaction. e.g. if we were to predict the shift in the above equation in a sodium chloride solution rather than pure water, the equilibrium would shif to precipitate becuase there is already chloride present, making the AgCl less soluble

Brønsted-Lowry acids and bases

In acid-base theory, a **Brønsted-Lowry acid** is a molecule that gives up a proton (H^+) and a **Brønsted-Lowry base** is a molecule that accepts a proton. A **conjugate base** is the basic anion that occurs upon deprotonating an acid and a **conjugate acid** is the cation that occurs when a base accepts a proton.

Example:

$$\underbrace{NH_3}_{Base} + \underbrace{H_2O}_{Acid} \leftrightharpoons \underbrace{NH_4^+}_{Conj.Acid} + \underbrace{OH^-}_{Conj.Base}$$

Water is an example of an **amphoteric** substance, it is capable of either donating or accepting a proton. It can also **autoionize** in which 2 water molecules can form a charged hydronium ion (H_3O^+) and hydroxide ion (OH^-). The reaction and ion product constant K_w are shown below.

$$2H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + OH^-_{(aq)} \qquad K_w = [H_3O^+][OH^-] = 10^{-14}\ @\ 25^oC$$

pH and pOH

pH and **pOH** are measures of the acidity and bascicity of a solution respectively. Both are simply the negative logarithm base 10 of either the hydronium or hydroxide ion concentration in the solution.

$$pH = -log([H_3O^+])$$

The pH scale is a common metric of gauging the acidity of solutions. Values less than 7 are acidic, values higher than 7 are basic, with 7 being the pH of pure water. A similiar metric, pOH exists for hydroxide;

$$pOH = -log([OH^-])$$

If we take the negative log of K_w we find;

$$K_w = [H_3O^+][OH^-]$$

$$-log(K_w) = -log([H_3O^+]) + (-log([OH^-]))$$
$$pK_w = pH + pOH$$
$$14 = pH + pOH$$

Relative Strengths of Acids and Bases

K_a is the acid-ionization constant and can gauge how stong an acid is. For the below reaction

$$HA_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

The base-ionization constant, K_b, is the same, but for bases.

Relating these values to K_w for conjugate pairs;

$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [[H_3O^+][OH^-] = K_w$$

Since a stong acid will completely dissociate, $[HA]$ will be 0, and thus K_a will approach infinity. If K_a = infinity, than if $K_b = K_w/K_a = K_w/\infty = 0$

Polyprotic Acids

Acids that can donate one proton are called **monoprotic**, acids that can donate multiple protons are **polyprotic** (di,tri,etc). For a polyprotic acid, each proton has it's own associated K_a value (K_{a1}, K_{a2}, etc.)

Buffers

Buffers are mixtures of roughly the same amount of a weak acid/base and it's conjugate (acid/conjugate base or vis a versa) such that the solution resists pH changes from adding small amounts of acids or bases to the solution. If acid is added to an acid/conjugate base buffer, than the equilibrium would shift left, away from acidity, if base is added, the equilibrium shifts right towards acidity, effectively neutralizing a pH change.

Henderson-Hasselbeck Equation

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

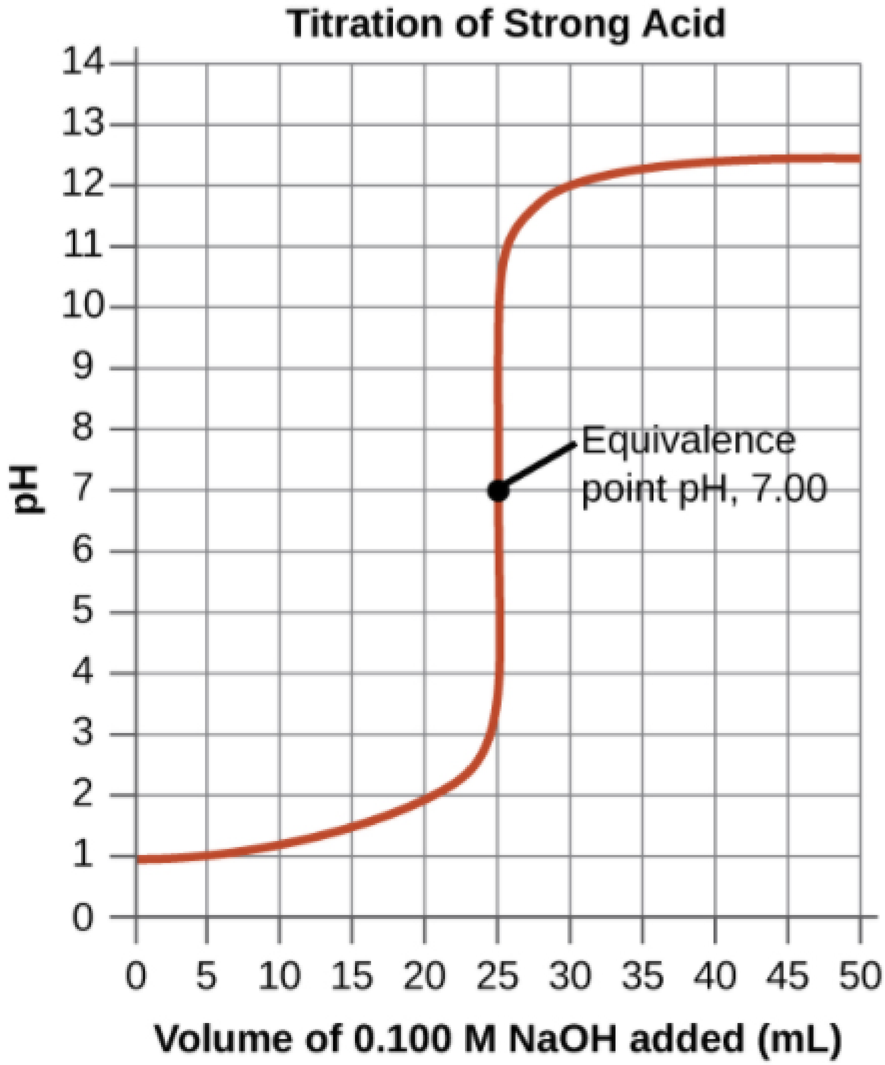
take the -log() of the whole thing;

$$pH = pK_a + log\frac{[A^-]}{[HA]}$$

Titrations

A **titration** curve is a plot of pH as a function of addition of a **titrant**.

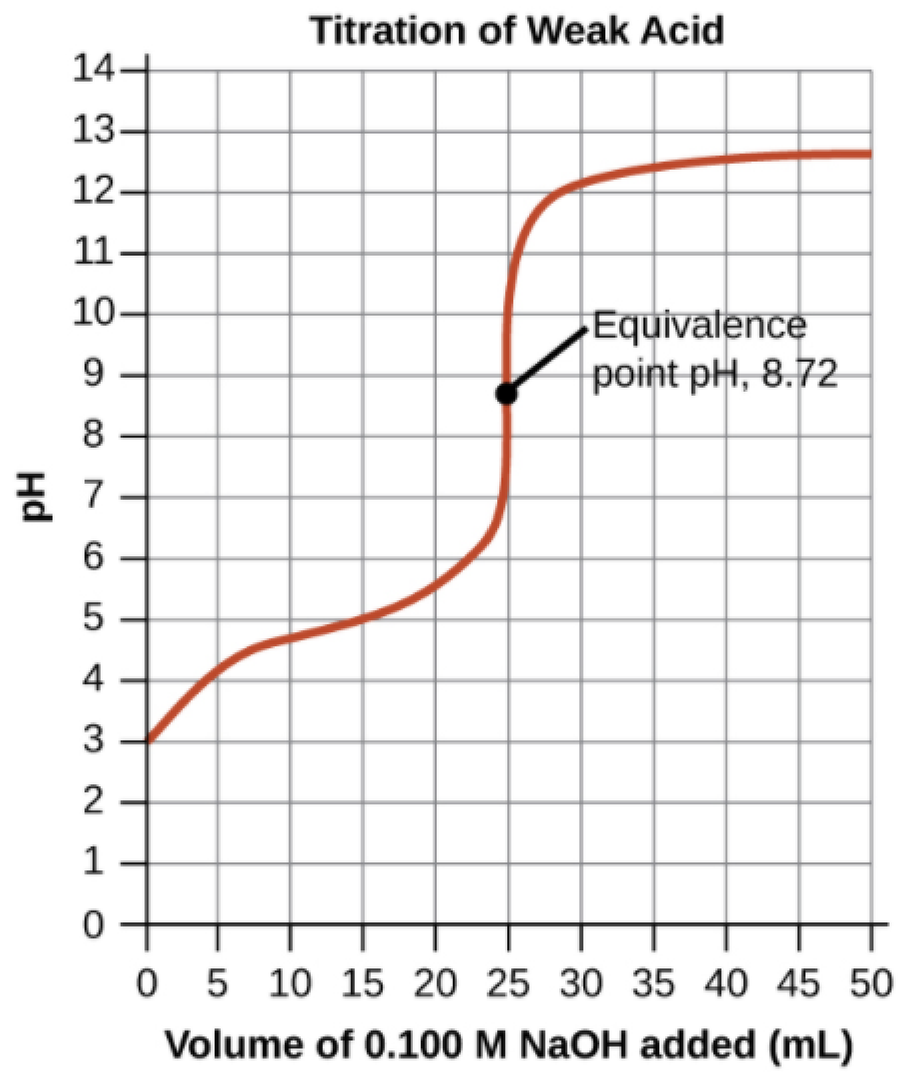
Strong Acid/Strong Base



Take an example of a 25 mL sample of 0.1 M HCl being titrated by 0.1 M NaOH. They both fully dissociate and the molar ratio of the 2 molecules in the neutralization reaction is 1 to 1 (i.e. 1 proton to 1 hydroxide). Since this is the case, once you add 25 mL of base, the solution will reach the equivalence point at a pH of 7.

Weak Acid/Strong Base

Example 25 mL of 0.1 CH3COOH and 0.1 mL NaOH.



Since the acid dissociates based on its K_a value ($1.8 \times 10^-5), we can mathematically calculate the equivalence point using an ICE method.

We start with $0.025L \times 0.1MCH3COOH = 0.0025molCH3COOH$

After adding 25 mL of NaOH, we have [CH3COOH] = 0.0025 mol/0.05 L = 0.05 M

$$K_b = K_w/K_a = \frac{10^-14}{1.8 \times 10^-5} = 5.6 \times 10^-10$$

Using ICE, assuming that the idssociation is sufficiently small;

$$K_b = \frac{x^2}{0.05}$$

$$x = 5.3 \times 10^-6 = [OH^-]$$
$$pOH = -log(5.3 \times 10^-6) = 5.28$$

pH = 14 - pOH = 14 - 5.28 = 8.72 $$

At half the equivalence point, half of the acid has been neutralized by the base, so that the concentrations of conjugate base is equal to that of the acid;

$$pH = pK_a + log\frac{[CH_3COO^-]}{CH_3COOH} = pK_a + log(1) = pK_a$$

Acid-Base Indicators

Acid-base indicators are weak organic acids or bases that experience a color change at a specific pH. Typically one will select an indicator that has a color change in the range of the region of interest.