# **Solubility and Acid-Base**

# Solubility

$$AgCl_{(s)} 
ightleftharpoons Ag_{(aq)}^+ + Cl_{(aq)}^-$$

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  $K_{sp}$ .

$$egin{aligned} Q_{sp} &= K_{sp} \; Equilibrium \ Q_{sp} &< K_{sp} \; No \; precipitation \ Q_{sp} &> K_{sp} \; Precipitation \; occurs \end{aligned}$$

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 because 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.

$$2H_2O_{(l)} \leftrightharpoons \overset{\cdot}{H_3}O_{(aq)}^+ + OH_{(aq)}^- \qquad K_w = [H_3O^+][OH^-] = 10^{-14} \ @\ 25^oC$$

### 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 similar metric, pOH exists for hydroxide;

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

If we take the negative log of  $K_w$  we find;

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

$$egin{aligned} -log(K_w) &= -log([H_3O^+]) + (-log([OH^-])) \ pK_w &= pH + pOH \ 14 &= pH + pOH \end{aligned}$$

## **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

$$HA_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O_{(aq)}^+ + A_{(aq)}^- \ K_a = rac{[H_3O^+][A^-]}{[HA]}$$

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

Relating these values to  $K_w$  for conjugate pairs;

$$K_a imes K_b = rac{[H_3O^+][A^-]}{[HA]} imes rac{[HA][OH^-]}{[A^-]} = [[H_3O^+][OH^-] = K_w$$

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**

$$K_a = rac{[H_3 O^+][A^-]}{[HA]} \ [H_3 O^+] = K_a imes rac{[HA]}{[A^-]}$$

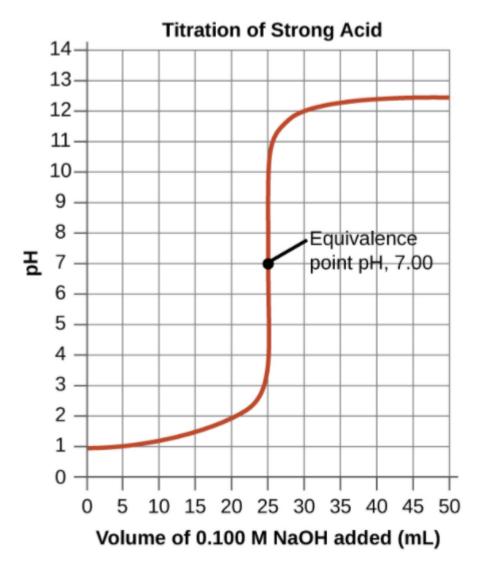
take the -log() of the whole thing;

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

#### **Titrations**

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

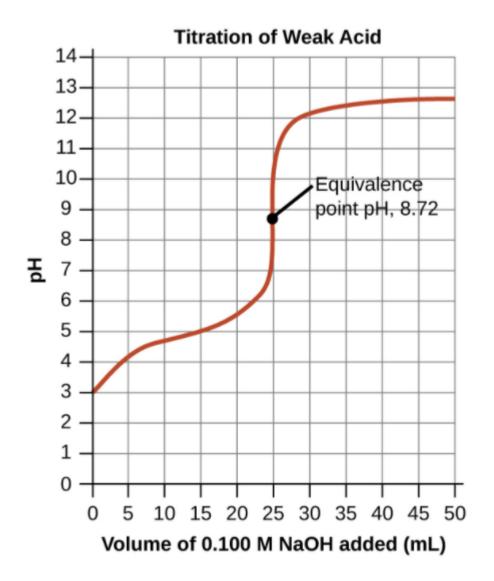
#### Strong Acid/Strong Base



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

$$K_b = K_w/K_a = rac{10^-14}{1.8 imes 10^-5} = 5.6 imes 10^-10$$

Using ICE, assuming that the idssociation is sufficiently small;

$$K_b=rac{x^2}{0.05}$$

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

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

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;

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

#### **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.

