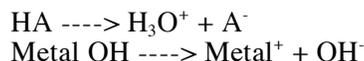


**ACID-BASE EQUILIBRIA**

## I. Titrations Curves for Strong Acids and Strong Bases.

A. Strong acids and strong bases ionize with 100% efficiency in aqueous solution.



B. The net reaction of strong acids with strong bases is the reaction of a hydronium ion with a hydroxide ion to form water.



C. Titration curves of strong acids titrated with strong bases are divided into domains:

1. Before equivalence.
2. At equivalence.
3. After equivalence.

D. Before equivalence:

1. Initially, before any base is added to the acid sample, the  $[\text{H}_3\text{O}^+]_{\text{total}} = C_{\text{HA}} + [\text{H}_3\text{O}^+]_{\text{water}}$ .
2. If the  $C_{\text{HA}}$  is greater than  $10^{-6}$  M, the  $[\text{H}_3\text{O}^+]_{\text{water}}$  can be ignored.
3. As strong base is added but **prior to equivalence**,  $[\text{H}_3\text{O}^+]$  is consumed. The remaining  $[\text{H}_3\text{O}^+]$  is calculated:

$$[\text{H}_3\text{O}^+] = \frac{\text{total\# moles H}_3\text{O}^+\text{initially} - \text{\# moles OH}^-\text{added}}{\text{total volume}} = \frac{V_{\text{HA}}C_{\text{HA}} - V_{\text{Base}}C_{\text{Base}}}{\text{total volume}}$$

E. At equivalence:

1. The acid and base have reacted at the stoichiometric ratio.
2. The  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = 10^{-7}$  M
3. The pH = 7 at equivalence.

F. Beyond equivalence:

1. All the acid is consumed; only base is present.
2. The amount of base is calculated from the excess added beyond equivalence.

$$C_{\text{Base}} = [\text{OH}^-] = \frac{\text{total\# moles OH}^-\text{added} - \text{\# moles OH}^-\text{reacted}}{\text{total volume}} = \frac{V_{\text{Base}}C_{\text{Base}} - V_{\text{acid}}C_{\text{acid}}}{\text{total volume}}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]}$$

G. Titration concentrations and titration curves of strong base with strong acid are calculated in similar fashion.

H. Note that...

1. If the  $C_{\text{Acid}}$  is greater than  $10^{-6}$  M, we have assumed that the water contribution to the hydronium ion concentration can be ignored.

2. If the  $C_{\text{Acid}}$  is less than  $10^{-8}$  M, you can also assume that the water is primarily responsible for the hydronium ion concentration, and that the added acid is insignificant.
3. Only when the  $C_{\text{Acid}}$  is between  $10^{-8}$  -  $10^{-6}$  M must the water contribution to the hydronium ion concentration be considered.

## II. Acid-Base Indicators.

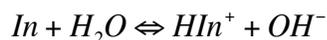
A. Acid-base indicators (pH indicators) are weak organic acids or weak organic bases that change color as a function of ionization state.

B. Acid-base indicators of two types have different ionization equilibria:

1. Acid-type indicators:



2. Base-type indicators:



C. As the pH changes, each equilibria above shifts in response, producing a color change.

D. Human visual perception only responds to dramatic color changes. Changes of less than 10% usually are not visible. Thus, the molar concentrations of the indicator species must constitute approximately 90% of the indicator before the color changes are seen clearly.

1. To see the  $In^-$  color:

$$\frac{[In^-]}{[HIn]} \geq 10$$

2. To see the HIn color:

$$\frac{[In^-]}{[HIn]} \leq 0.10$$

3. Acid-base indicators (like any ionizable molecule) are 50% ionized at the  $pK_a$ .

4. At 1 pH unit above the  $pK_a$ , 90% of the ionizable indicator is in its basic form.

5. At 1 pH unit below the  $pK_a$ , 90% of the ionizable indicator is in its acid form.

6. Thus, indicators show a full color transition  $\pm 1$  pH unit of the  $pK_a$ , and indicators are generally selected based upon the closeness of their  $pK_a$  to the endpoint pH.

## III. Buffers.

A. Buffers are solutions that resist changes in pH.

B. Buffers consist of an aqueous solution of:

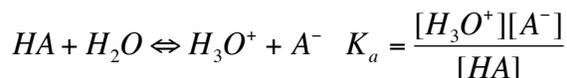
1. A weak acid and its conjugate base (e.g., acetic acid and sodium acetate).
2. A weak base and its conjugate acid (e.g., ammonia and ammonium chloride).

C. Buffers are formed when:

1. A weak acid is titrated by a strong base.
2. A weak base is titrated by a strong acid.
3. A weak acid is combined with a salt containing its conjugate base.
4. A weak base is combined with a salt containing its conjugate acid.

D. pH calculations: weak acid + salt of conjugate base

1. If HA (a weak acid) and NaA (the sodium salt of its conjugate base) are dissolved in water, two equilibria are established:



2. The resulting solution may be acidic, neutral or basic, depending upon which equilibrium predominates. ("Dominates" means that equilibrium is favored to the right as written.)

- a. If  $K_a$  dominates, the solution is acidic.
- b. If  $K_b$  dominates, the solution is basic.

3. If one assumes that the acid dissociation equilibrium ( $K_a$ ) dominates, then the concentration of  $OH^-$  may be assumed to be negligible (and the water ionization may be ignored).

4. If these simplifying assumptions are made, a "simple" equation (called the Henderson-Hasselbalch equation) can be derived from  $K_a$  and used in calculations of pH:

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

IV. Properties of Buffers.

A. The pH of a buffered solution is independent of dilution if the concentration of the buffering species stays above  $10^{-4}$  M.

B. Buffering capacity is dependent upon both the total concentration of the buffering species and the ratio of  $[A^-]$  to  $[HA]$ .

1. Buffering capacity is defined as the number of moles of strong acid or strong base that one liter of a buffer can absorb during a change in pH of 1.
2. Maximum buffering capacity is observed when the ratio of  $[A^-]$  to  $[HA]$  is 1 (i.e., the  $pH = pK_a$  or the buffer is 50% ionized).

C. A buffer should be used at a pH +/- 1 of its  $pK_a$ .

D. If properly prepared, added strong acid or strong base (in small amounts) does not significantly affect pH.

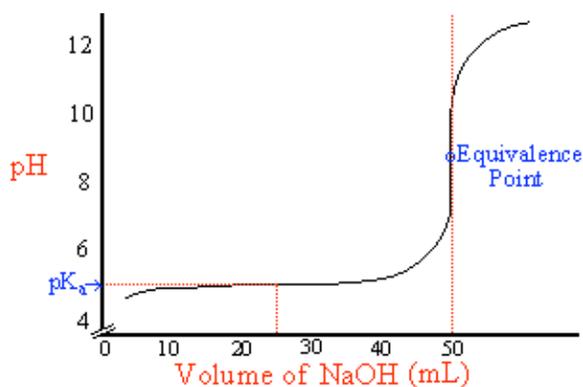
V. Titration Curves for Weak Acids Titrated with a Strong Base: Acetic Acid Titrated with NaOH

A. Acetic acid is a monoprotic acid ( $pK_a = 4.757$ ).

B. NaOH is a monohydroxy, strong base.

C. Titration of acetic acid with NaOH follows a curve similar in shape to the strong acid-strong base titration curve, but the equivalence point is not a pH 7.

D. Shown below is a titration curve for 0.100 M acetic acid titrated with 0.100 M NaOH.



E. During the titration and in the generation of a titration curve, four regions will be considered:

1. No NaOH added (i.e., 0.100 F acetic acid).
2. NaOH added, but before equivalence has been reached.
3. At the equivalence point (i.e., 0.100 F acetate ion).
4. After equivalence.

F. No NaOH added:

1.  $[H_3O^+]$  is calculated from the  $K_a$  of acetic acid:

$$K_a = \frac{[H_3O^+][Ac^-]}{[HAc]} = \frac{X^2}{C_{HAc} - X}$$

Assuming  $X \ll C_{HAc}$  and by rearrangement:

$$X = [H_3O^+] = \sqrt{K_a C_{HAc}}$$

2. If  $X$  is not  $\ll C_{HAc}$ , the quadratic formula must be used to solve for  $X$ .

G. NaOH added, but before equivalence:

1. Added NaOH reacts with HAc producing a buffer (a mixture of HAc and  $Ac^-$ ).

2. The concentrations of HAc and Ac are calculated from the volumes reacted and substituted into the  $K_a$  (or Henderson-Hasselbalch equation) to calculate  $[H_3O^+]$  and pH:

$$C_{HAc} = \frac{\# \text{ moles HAc initially} - \# \text{ moles NaOH added}}{\text{total volume}}$$

$$C_{NaAc} = \frac{\# \text{ moles NaOH added}}{\text{total volume}}$$

$$[H_3O^+] = \frac{K_a [C_{HAc}]}{C_{NaAc}}$$

a. In using these equations, check the assumptions made that allow use of  $K_a$  or the Henderson-Hasselbalch. They are:

- 1) Water equilibrium contributions are negligible.
- 2)  $C_{NaAc}$  and  $C_{HAc} \gg [H_3O^+]$  and  $[OH^-]$

H. At equivalence:

1. At equivalence, the HAc and NaOH have reacted at the stoichiometric ratio.

$$\# \text{ moles HAc initially present} = \# \text{ moles NaOH added}$$

2. The solution at the equivalence point is *identical to dissolving sodium acetate (NaAc) in water*. The  $[H_3O^+]$  may be calculated from the base hydrolysis of  $Ac^-$ .



$$K_b = \frac{[OH^-][HAc]}{[Ac^-]} = \frac{K_w}{K_a} = \frac{1.00 \cdot 10^{-14}}{1.75 \cdot 10^{-5}} = 5.71 \cdot 10^{-10} = \frac{[X][X]}{[C_{NaAc} - X]}$$

$$[X] = [OH^-] = \sqrt{K_b [C_{NaAc}]}$$

- a. Note that X is assumed to be  $\ll C_{NaAc}$ . This assumption must be checked.
- b. If the assumption is not true, the quadratic formula must be used to solve for X.

I. Beyond equivalence:

1. Beyond equivalence, all the HAc is consumed and the presence of excess  $OH^{1-}$  prevents the base hydrolysis of the  $Ac^{1-}$ .
2. The concentration of the excess  $OH^-$  is calculated from the reacted volumes and used to calculate  $[H_3O^+]$  and pH.

$$[OH^-]_{\text{excess}} = \frac{\text{total \# moles } OH^- \text{ added} - \# \text{ moles HAc initially}}{\text{total volume}}$$

J. General characteristics of weak acid titrations with strong bases:

1. If the concentrations of acid are too low, you cannot ignore the water contributions to  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$ .
2. Low acid concentrations decrease the magnitude of the pH change at the equivalence point, limiting the selection of endpoint indicator. Conversely, the higher the acid concentrations, the larger the pH change around the equivalence point.
3. As  $K_a$  gets smaller, the pH change at equivalence gets smaller. Generally, the smaller  $K_a$  gets, the more concentrated the solutions must be. Acids with  $K_a$  below  $10^{-6}$ - $10^{-7}$  M are nearly impossible to titrate easily with a burette and typically endpoint indicator.