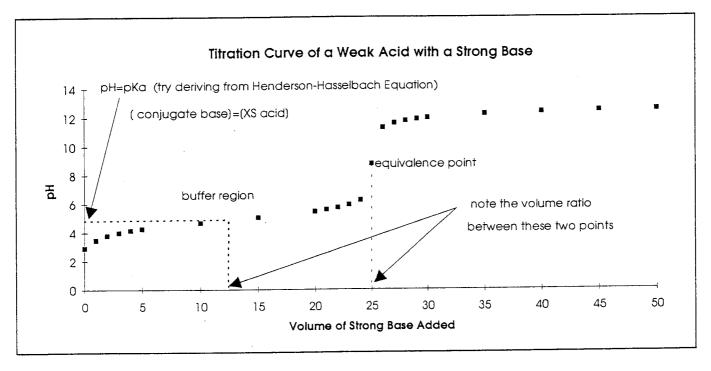
## pH Calculations for Titration Curves of Weak Acids with Strong Bases

There are 4 regions of interest: (1) Before the addition of any base, (2) After some base is added and up to the Equivalence Point, (3) The Equivalence Point, and (4) After the Equivalence Point.

To calculate the pH at any point along the curve, it is necessary to recognize which molecules and ions are present at that point, how they contribute to the pH in terms of dissociation/hydrolysis, and the concentrations of these species with regard to the <u>new volume</u>.



1. Initial pH (Before any base is added) pH is dependent only upon the concentration of the acid, [HA], and its dissociation.

$$HA \rightleftharpoons H^+ + A^-$$
 gives expression  $K_a = \frac{[H^+][A^-]}{[HA]}$ 

since: 
$$[H^+] = [A^-]$$
  $K_a = \frac{x^2}{[HA]-x}$  and if  $[HA] >> x$  then

ignore x on bottom

so: 
$$K_a = \frac{x^2}{[HA]}$$
 and  $x = \sqrt{(K_a[HA])}$  and  $x = [H^+]$ 

and:  $pH = -Log[H^+]$ 

## 2. pH after some base is added and up to the equivalence point.

All base added reacts immediately with the acid to form salt (conjugate base) and there is still some  $\underline{\rm XS}$  (excess) acid.

$$K_a$$
 expression is still  $K_a = \frac{[H^+][A^-]}{[HA]}$  but...  $[H^+] \neq [A^-]$ 

**so:** We must determine the Molarity of the  $A^-$  ion formed and that of the  $\underline{XS}$  HA. To do this, one must use solution stoichiometry and a balanced equation (refer to limiting/excess reactant problems). The moles of base added and the volume of base added and the total volume must be considered at the point of interest.

$$K_a = [H^+][A^-]$$
 where  $[A^-]$  concentration of the salt formed  $[HA]$  where  $[HA]$  concentration of the  $\underline{XS}$  acid

solve for [H+] and find pH.

## 3. At the Equivalence Point

All the acid has reacted with the base and there is no  $\underline{XS}$  of either. Therefore the only species present (of interest) is the salt formed, the anion of which  $(A^-)$  undergoes hydrolysis.

$$A^- + H_2O \Rightarrow HA + OH^-$$
 This becomes a "K<sub>b</sub> problem"

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

**Since:**  $[HA] = [OH^-]$  (formed by the hydrolysis reaction above)

$$K_b = \frac{x^2}{[A^-]-x} \qquad \qquad \dots \\ \text{where } [A^-] = \text{concentration of the salt formed} \\ \text{and the } x \text{ on the bottom is often small enough when} \\ \text{compared to } [A^-] \text{ to allow us to ignore it.}$$

Solve for  $x = [OH^-]$  and find pH.

$$x = \sqrt{(K_b[A^-])}$$
 and pOH = -Log[OH<sup>-</sup>]

## 4. pH above the equivalence point.

Solution contains  $\underline{XS}$  base and the salt formed from the neutralization reaction. Since the concentration of the OH<sup>-</sup> from the  $\underline{XS}$  base is much, much greater than the contribution of OH<sup>-</sup> ions from the hydrolysis of the salt anion, the pOH = -Log[ $\underline{XS}$  OH<sup>-</sup>].

To solve, find  $\underline{\mathrm{XS}}$  moles of  $\mathrm{OH}^-$  ions and convert to Molarity with the volume at that point. One must use solution stoichiometry and a balanced equation to accomplish this (refer to limiting/excess reactant problems).