pH Calculations for Titration Curves
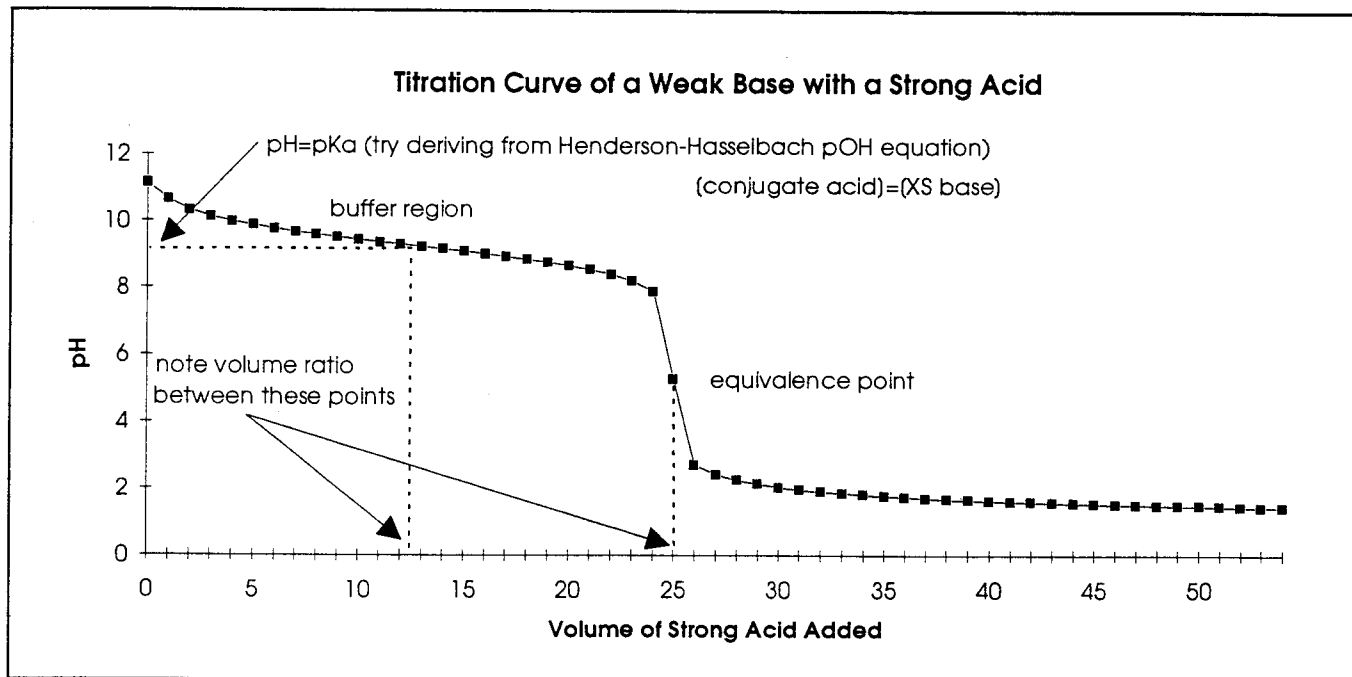# of Weak Base with Strong Acid

There are 4 regions of interest: (1) Before the addition of any acid, (2) After some acid 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 new volume.

Titration Curve of a Weak Base with a Strong Acid

pH=pKa (try deriving from Henderson-Hasselbach pOH equation)

(conjugate acid)=(XS base)

buffer region

note volume ratio between these points

equivalence point

x-axis: **Volume of Strong Acid Added**
y-axis: **pH**

1. Initial pH (Before any acid is added)

pH is dependent only upon the concentration of the base, [B], and its ionization in water.

$$B + H_2O \rightleftarrows BH^+ + OH^-$$ gives expression $K_b = \dfrac{[BH^+][OH^-]}{[B]}$
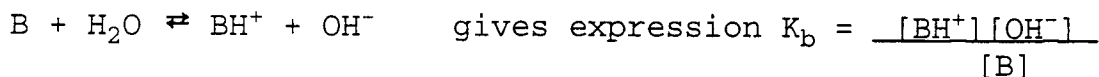
since: $[BH^+] = [OH^-]$ $K_b = \dfrac{x^2}{[B]-x}$ and if [B]>>x then ignore x on bottom

so: $K_b = \dfrac{x^2}{[B]}$ **and** $x = \sqrt{(K_b[B])}$ **and** $x = [OH^-] = [BH^+]$

and: $pOH = -Log[OH^-]$

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

All acid added reacts immediately with the base to form salt (conjugate acid) and there is still some XS (excess) base.

K_b expression is still $K_b = \dfrac{[BH^+][OH^-]}{[B]}$ but... $[BH^+] \neq [OH^-]$

so: We must determine the Molarity of the BH^+ ion formed and that of the XS B. To do this, one must use solution stoichiometry and a balanced equation (refer to limiting/excess reactant problems). The moles of acid added and the volume of acid added and the total volume must be considered at the point of interest.

$K_b = \dfrac{[BH^+][OH^-]}{[B]}$ where $[BH^+]$ concentration of the salt formed
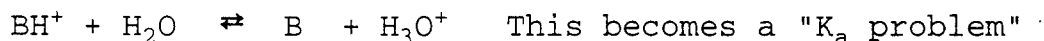where $[B]$ concentration of the XS base

solve for $[OH^-]$ and find pOH then find pH.

3. At the Equivalence Point

All the base has reacted with the acid and there is no XS of either.

$$B + HA \rightleftarrows BHA \quad \textbf{for example} \quad NH_3 + HCl \rightleftarrows NH_4Cl$$

Therefore the only species present (of interest) is the salt formed, the cation of which (BH^+) undergoes hydrolysis.

$BH^+ + H_2O \rightleftarrows B + H_3O^+$ This becomes a "K_a problem"

$K_a = \dfrac{[B][H_3O^+]}{[BH^+]}$

Since: $[B] = [H_3O^+]$ (formed by the hydrolysis reaction above)

$K_a = \dfrac{x^2}{[BH^+]-x}$ ...where $[BH^+]$ = concentration of the salt formed, and usually the x on the bottom is small enough when compared to $[BH^+]$ to allow us to ignore it.

Solve for x which is equal to $[H_3O^+]$.

$x = \sqrt{(K_a[BH^+])}$ **and** $pH = -Log[H_3O^+]$

4. pH above the equivalence point.

Solution contains XS acid and the salt formed from the neutralization reaction. Since the concentration of the H_3O^+ from the XS acid is much, much greater than the contribution of H_3O^+ ions from the hydrolysis of the salt cation, the pH = $-Log[$XS $H_3O^+]$, which is really the concentration of the strong acid in excess.

To solve, find XS moles of H_3O^+ 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).