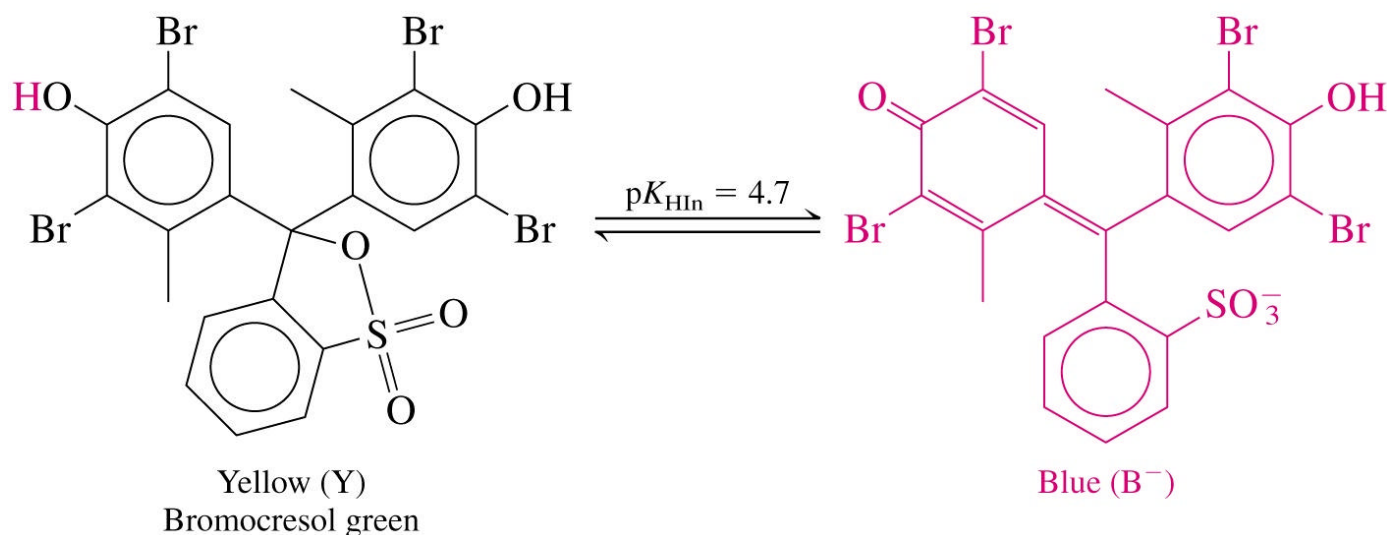# pH indicators---how they work!

pH indicators are either weak acids or weak bases---that are different in color (change in absorbance) in protonated vs. unprotonated form!

They are used at very low concentrations ----to "indicate" the pH of the solution----with the pH generally being controlled by other components!!

$$\mathrm{p}K_{\mathrm{HIn}} = 4.7$$

Yellow (Y)
Bromocresol green

Blue (B⁻)

<u>Equilibrium for indicator species:</u> Hin <------> H$^+$ + In$^-$

$$K_{HIn} = \frac{[H^+][In^-]}{[HIn]}$$

$$pH = pK_{HIn} + \log\frac{[In^-]}{[HIn]}$$

for bromocrescol green----**In$^-$** is blue and **HIn** is yellow!

at pH 4.7 (the pK$_a$) ---have half in blue form, and half in yellow form-
get a green color!!

Typically---when [Hin]/[In$^-$] > 10 ; color of solution will be color
 of Hin species; when [In$^-$] / [Hin] > 10 ; color of solution will be
color of In$^-$ species!
•By using very low concentrations of indicator---we can get
very sharp change in color at equivalence points in pH titrations!

Example of indicator that is diprotic---two different pKa values three different species possible--with three different colors!

Red (R)
Thymol blue

Yellow (Y$^-$)

Blue (B^{2-})
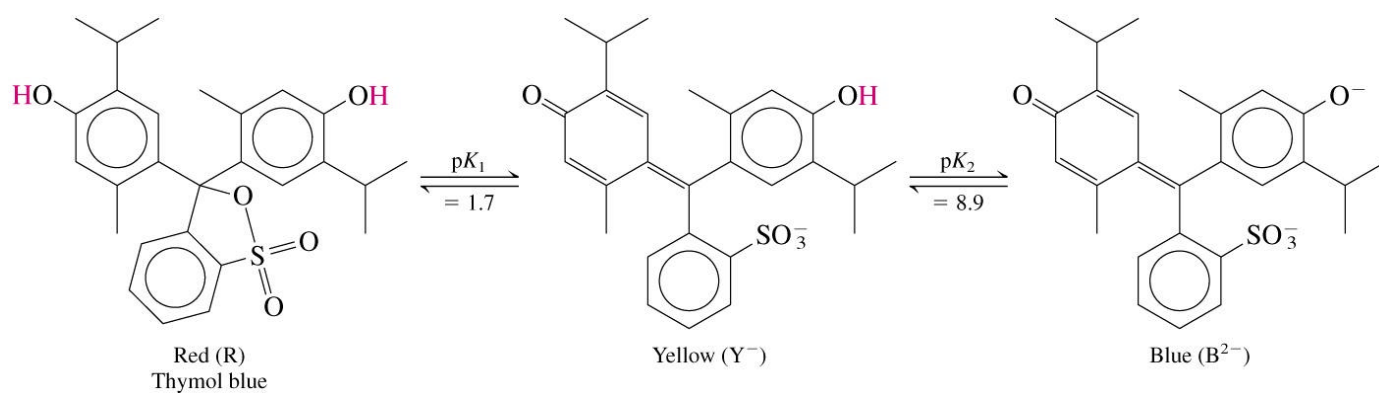
at pH $<<$ 0.7---solution will be **red**
from pH approx. 0.;7 -2.7; solution will look **orange**
from pH 2.7 --7.9; solution will be **yellow**
from pH 7.9 - 9.9 ; solution will be **green**
at pHs $>$ 9.9; solution will be **blue**!

<u>Acid-Base Titrations</u>---predicting shape and pH at given points along a titration curve!
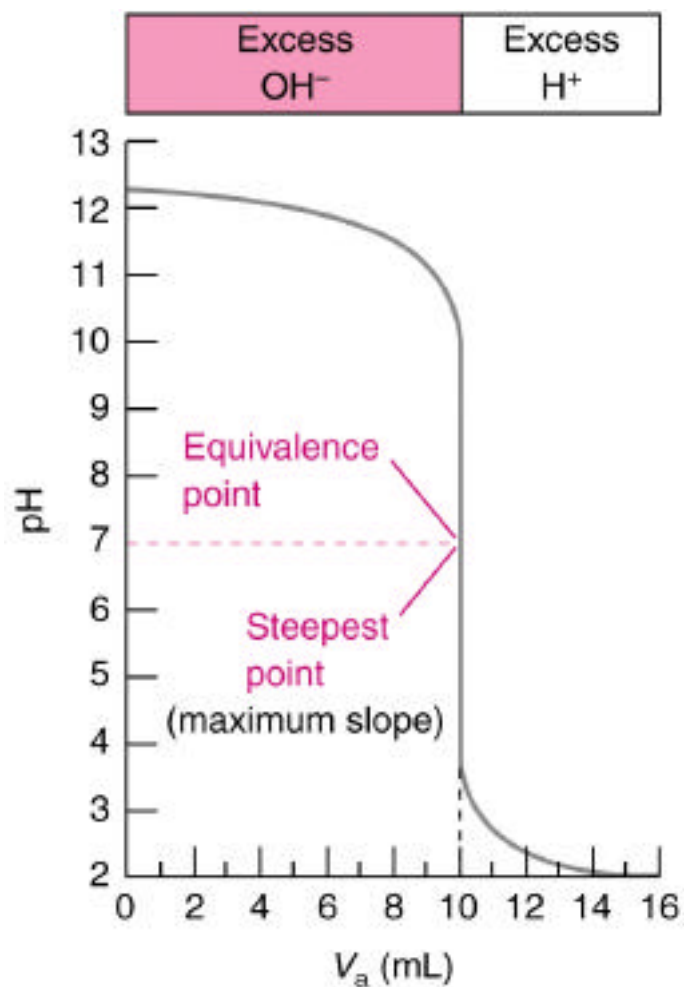
<u>Different types</u> ---
a) titration of strong acid with strong base or vica versa!
b) titration of weak acid with strong base
c) titration of weak base with strong acid

Lets start with strong acid/strong base situation--

we know that H^+ + OH^- ------> H_2O $K = 1/K_w = 10^{14}$ ---very favorable reaction---rxn goes to completion!

So if we start with base in solution---and add acid---for every proton we add---it will react with hydroxide ion to form water---until there are no more excess hydroxide ions available-**equiv. point = pH 7.0**

3-regions in titration curve-- 1) <u>before equiv. point</u>; 2) <u>at equiv. point</u>**;** 3) <u>after equiv. point</u>!

Excess OH$^-$	Excess H$^+$

pH vs V_a (mL)

Equivalence point

Steepest point (maximum slope)

titration of 50 mL of 0.02 M KOH with 0.1 M HBr---

need 1 mmole of HBr to neutralize all the base (50 mL x 0.02 = 1 mmole)

therefore at equiv. point--
$$M_{HBr} \times V_{HBr} = 1 \text{ mmole}$$
$$0.1 \times V_{HBr} = 1 \text{ mmole}$$
$$V_{HBr} = V_e = 10 \text{ mL}$$

Lets see what pH is at various points---via calculations---

when no acid added:

0.02 M KOH only present; $[OH^-] = 0.02$ M ;
    $[H^+] = 10^{-14} / 0.02 = 5 \times 10^{-13}$ M
    pH = -log $[H^+]$ = **12.30**

when 3 mL of titrant added:
   3 ml x 0.1 M = 0.3 mmoles of acid---means that you decrease
   total amount of OH^- by 0.3 mmoles---
   therefore: (1.0 mmole - 0.3 mmoles) = 0.7 mmoles OH^- still
       present in solution---but now the **total volume = 50 + 3 =53 mL**

   $[OH^-] = 0.7 / 53 = 0.013$ M ; $[H^+] = 10^{-14} / 0.013 = 7.69 \times 10^{-13}$
   pH = -log 7.69×10^{-13} = 12.11

when 9.90 mL of acid added:
9.90 x 0.1 M = 0.99 mmoles of acid;
thus OH^- left = 1.0 - 0.99 = 0.01 mmoles

$[OH^-] = 0.01/ 59.9 \text{ mL} = 1.67 \times 10^{-4}$

$[H^+] = 10^{-14}/ 1.67 \times 10^{-4} = 5.99 \times 10^{-11}$; therefore **pH = 10.22**

when 10.0 mL of acid added (equivalence point):

   10 mL x 0.1 M = 1.0 mmoles-; no more OH^- from the base is present at this point---only OH^- is from autoprotolysis of water!-- $[OH^-] = 10^{-7}$; $[H^+] = 10^{-7}$; **pH = 7.00**

when 10.1 mL of acid added---just beyond equiv. point:

   10.1 mL x 0.1 M = 1.01 mmoles; excess H^+ by 0.01 mmoles

   $[H^+] = 0.01 \text{ mmole} / 60.1 \text{ mL} = 1.66 \times 10^{-4}$ M

   therefore: pH = -log (1.66×10^{-4}) = **3.78**

when 11 mL of acid added---far beyond equiv. point:

   11 mL x 0.1 M = 1.1 mmoles; excess H^+ by 0.1 mmoles

   $[H^+] = 0.1 \text{ mmole} /61.0 \text{ mL} = 1.64 \times 10^{-3}$ M

   pH = -log(1.64×10^{-3}) = **2.79**

For titration of strong acid with base--the same exact approach is taken to find the pH at various points along the titration curve!

Sample problem: Find the pH when 12.75 mL of 0.0501 M NaOH have been added to 25.00 mL of 0.0506 M $HClO_4$!

- how many moles of **$HClO_4$** originally present?
  25 mL x 0.0506 M = **1.265 mmoles**
- after 12.75 mL base--how many moles of base?
  12.75 mL x 0.0501 M = **0.639 mmoles** of base---so there
   must be excess acid still left!
  <u>How much acid left?</u>   1.265 - 0.639 = **0.626 mmoles**
  What pH? ; [H⁺] = 0.626 mmoles / 37.75 mL = 0.0166 M
        pH = -log (0.0166) = 1.78   <u>total volume</u>

Find pH after 50 mL of base added?--50 mL x 0.0501 M = 2.505 mmole
  now have excess base- : 2.505 - 1.265 = 1.24 mmoles NaOH excess
  [OH⁻] = 1.24 mmoles / 75 mL = 0.0165 M ; [H⁺] = 10^{-14} /0.0165 =
       [H⁺] = 6.06 x 10^{-13} ; **pH = 12.22**

Titration of weak acid with strong base:

$$HA + OH^- \text{------>} H_2O + A^- \qquad K'? = 1/K_b \text{ for } A^-$$

let's say pK_a of HA $= 6.15$; $K_a = 7.08 \times 10^{-7}$

What is K_b for A^-? recall---$K_b = 10^{-14} / K_{a(HA)}$
  then $K_b = 1.41 \times 10^{-8}$ ----for rxn in opposite in direction of above-
  therefore $K' = 1/(1.41 \times 10^{-8}) = \mathbf{7.1 \times 10^7}$
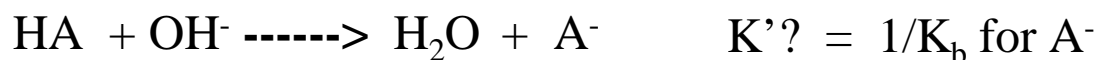   since K' is large---neutralization reaction goes completely to right

Let's say we have 50.00 mL of 0.0200 M of HA to start in solution!

how much volume of 0.1000 M NaOH is needed to reach equiv. point?
  50.00 mL x 0.0200 M $= \mathbf{1\ mmole}$ of acid present---need $\mathbf{1\ mmole}$ of
  base to reach equivalence point---
  Therefore--- 0.1000 M x $V_{base} = 1$ mmole; $\mathbf{V_{base} = 10\ mL}$

<u>Titration of weak acid with strong base:</u>

$$HA + OH^- \text{ ------>} H_2O + A^- \qquad K'? = 1/K_b \text{ for } A^-$$

let's say pK_a of HA = 6.15; K_a = 7.08 x 10^{-7}

What is K_b for A$^-$? recall---K_b = 10^{-14} / $K_{a(HA)}$
  then K_b = 1.41 x 10^{-8} ----for rxn in opposite in direction of above-
  therefore K' = 1/(1.41 x 10^{-8}) = **7.1 x 10^7**
  since K' is large---neutralization reaction goes completely to right

Let's say we have 50.00 mL of 0.0200 M of HA to start in solution!

how much volume of 0.1000 M NaOH is needed to reach equiv. point?
  50.00 mL x 0.0200 M = **1 mmole** of acid present---need **1 mmole** of
  base to reach equivalence point---
  Therefore--- 0.1000 M x V_{base} = 1 mmole; **V_{base} = 10 mL**

four regions of the titration curve----

1) <u>no base added;</u> what is starting pH?
   Calculate like weak acid problem- for F= 0.0200 M with
   K_a = 7.08 x 10^{-7}

   x^2 / (0.0200 -x) = 7.08 x 10^{-7} ; x = 1.19 x 10^{-4} = $[H^+]$; **pH = 3.93**

2) <u>initial addition of base to titrate weak acid---becomes buffer system</u>
   <u>calculation problem</u>----some of HA + OH^- -----> A^- + H_2O
   For example---say 2 mL of 0.1000 M NaOH---
   produce 2 mL x 0.1000 M = 0.2 mmoles of A^-
   starting HA = 1 mmole ; therefore after 2 mL of NaOH solution
   possesses 1.000 - 0.200 = 0.800 mmoles HA and 0.2 mmoles A^-

   Can use HH eqn to calculate pH in this region of titration curve--
   pH = pK_a + log ($[A^-]$ / [HA]) = 6.15 + log (0.2 / 0.8) = **5.55**
   note: don't need to calculate conc. of A^- and HA--only need
   mmoles for numerator and demoninator!

when you have added 5 mL of titrant ---then $V_{base} = 1/2\ V_{eq}$
Exactly 1/2 of the HA has been titrated----
This means that $[HA] = [A^-] \sim= 1/2\ F$ --the initial conc. of HA

Special situation---since $pH = pK_a + \log\ ([A^-]\ /\ [HA])$ ---but
   log term -----> 0 since $[HA] = [A^-]$; **$pH = pK_a = 6.15$**

3. <u>At equivalence point</u> (10 mL of NaOH added):
  All the HA ------> A^- and water----Hence the pH at equiv. point
   is a weak base problem-----$A^- + H_2O$ <-----> $HA + OH^-$
   must calculate $[OH^-]$ using K_b value---
  **But-- initial F concentration of A^- is less than initial [HA] due
   to dilution by titrant volume**!
  $[A^-]_{eq} = $ 1 mmole / 60 mL = **0.01667 M = F' (new formal conc.)**

         initial moles of HA at start of titration!

             total vol. at equiv. point!

K_b for $A^- = 1.41 \times 10^{-8} = x^2 / (F' - x)$; $F' = 0.01667$ M

$X = 1.53 \times 10^{-5} = [OH^-]$; $[H^+] = 10^{-14} / (1.53 \times 10^{-5}) = 6.54 \times 10^{-10}$

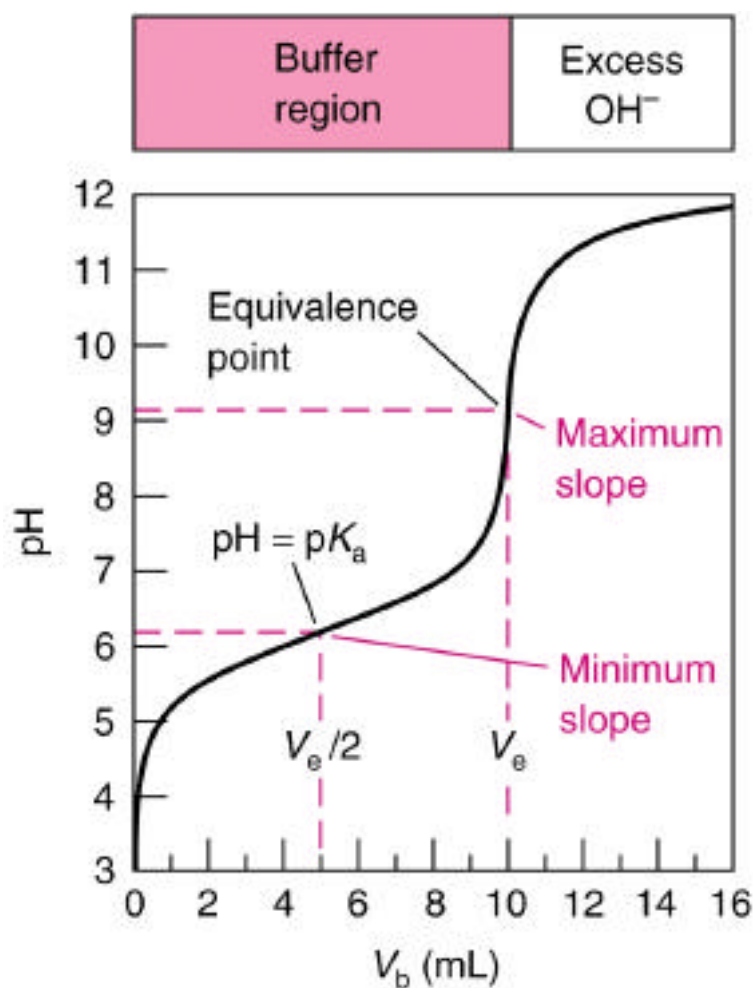**pH = -log(6.54 x 10^{-10}) = 9.18 = pH at equiv. point**

4) pH when there is excess strong base----; can assume contribution from weak base A$^-$ is negligible!

e.g. **11 mL of NaOH added**; total volume now = 61.00 mL
excess base = 1 mL x 0.1000 M = 0.1 mmole;
Therefore: 0.1000 / 61.00 = 0.0016 M = [OH$^-$]
thus--[H$^+$] = 10^{-14} / 0.0016 = 6.25 x 10^{-12} ; **pH = 11.20**

This is the actual titration curve for 0.02 M HA with pKa = 6.15 with 0.1000 M NaOH ---we calculated several of the points along the way--on the previous pages!!

Titration of weak base with strong acid---Analogous treatment
to titration of weak acid with strong base!!

Titration reaction:

Pyridine (B) BH^+
$K_b = 1.69 \times 10^{-9}$ $K_a = 5.92 \times 10^{-6}$
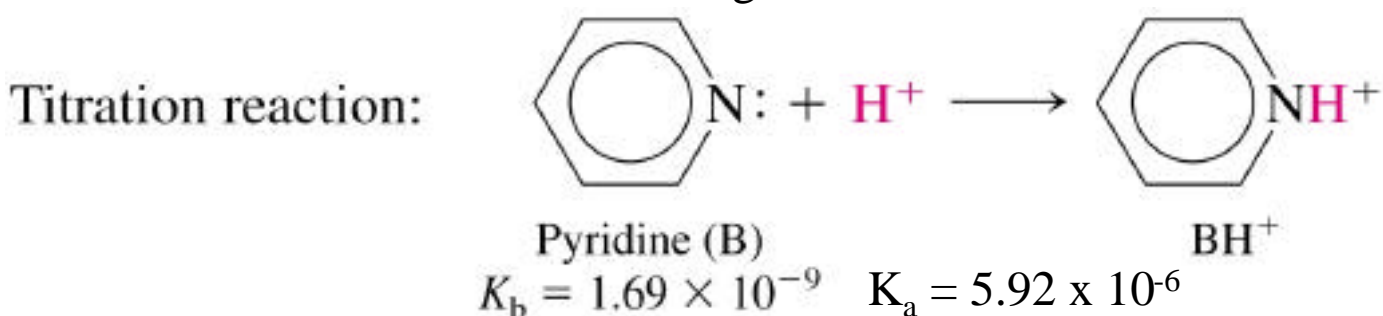
e.g.---25.00 mL of 0.08364 M pyridine titrated with 0.1067 M HCl
        mmoles pyridine base = 0.08364 x 25.00 = **2.091 mmoles**
at equiv. point:
V_{HCl} x 0.1067 M = 25.00 mL x 0.08364 ; $V_{e(HCl)}$ = **19.60 mL HCl**

What is pH after 4.63 mL of acid added:
mmoles acid = 4.63 x 0.1067 = **0.4940 mmole** of Pyridinium cation;
therefore free base left = 2.091 - 0.4940 = **1.597 mmole** Pyridine left
thus pH = pK$_a$ + log ([pyr] /[[Hpyr$^+$]) = 5.23 + log (1.597 / 0.4940) =
pH = 5.74

What would be pH at equivalence point?

This is weak acid problem---all of the pyridine converted to $Hpyr^+$;
-started with 2.091 mmoles pyridine---will have 2.091 mmoles of pyridinium ion at equivalence point!

$K_a = 5.92 \times 10^{-6} = x^2 / (F' - x)$

$F' = 2.091$ mmoles $/ (25.0$ mL $+ 19.6$ mL$) = 0.0469$ M $Hpyr^+$

$x_1 = 1.67 \times 10^{-4}$; x_2 (second. approx.) $= 1.66 \times 10^{-4} = [H^+]$
                                                  pH = 3.78

note: pH at equivalence point is quite low--why? ---because pyridine is very weak base!!---if you calculated pH at start of titration what would it be? $1.69 \times 10^{-9} = x^2 / (F - x)$; F$= 0.08364$
                    $x = [OH^-] = 1.19 \times 10^{-5}$; $[H^+] = 8.40 \times 10^{-10}$
   **pH = 9.08**

Detecting end points!---use of indicators

-choose indicator that has pK_a near the equivalence point pH of for titration---so that color change occurs in steepest region of titration curve!

- always use small amount of indicator---since they are also
  acids and bases---hence using high concentrations will consume
  analyte or titrant!

titration of
weak base with
$pK_b = 5.00$ with
(100 mL of 0.0100 M)
with 0.0500 M HCl
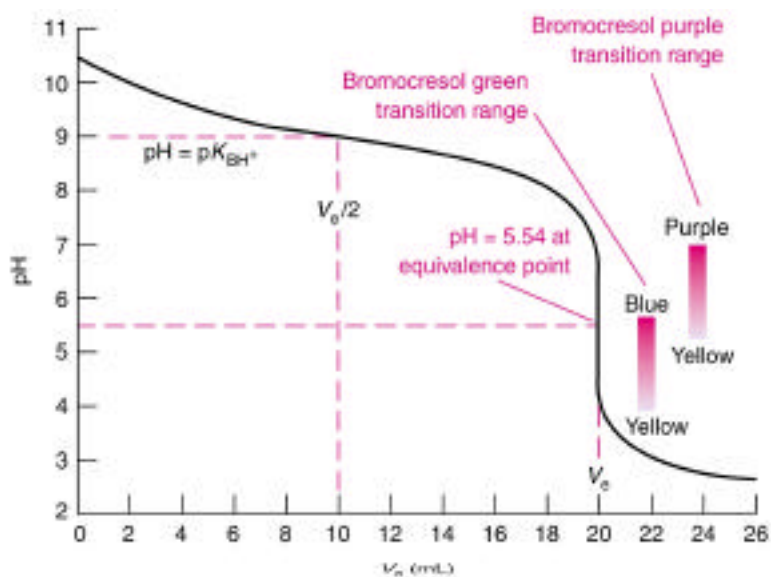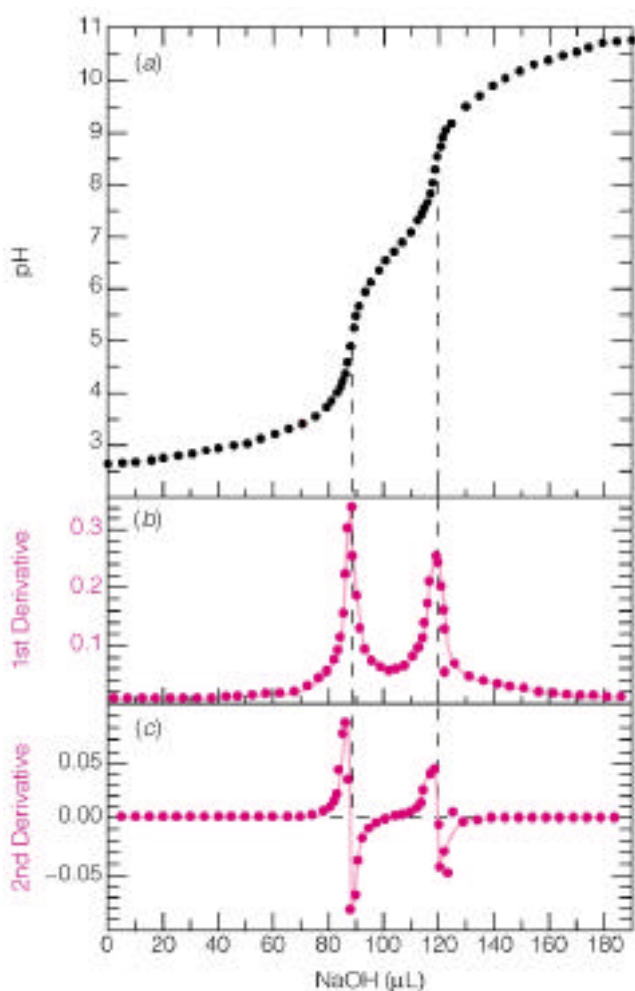
With indicators--can only see
pH change at end point of titration

Use pH electrode to monitor
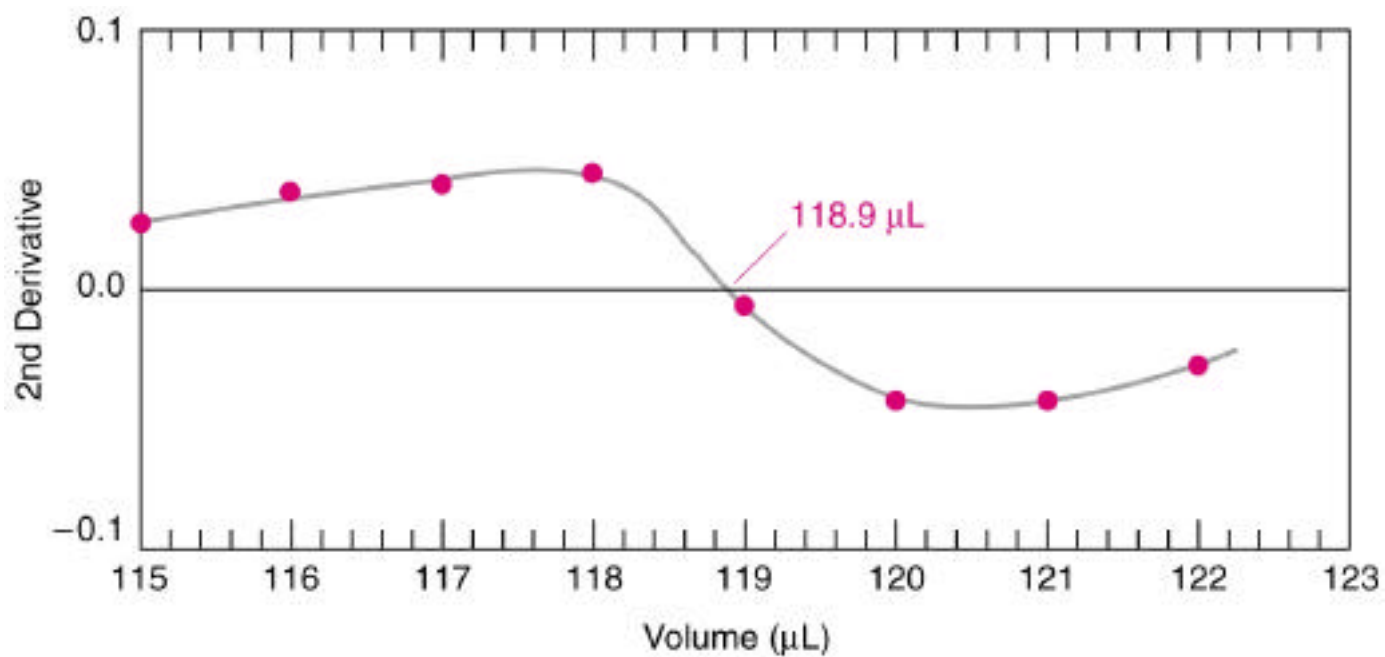pH of solution throughout titration

End point/equivalence point
can be determined by either
first or second derivative method!

slope = ΔpH / Δvol = 1st derivative

second deriv = $\dfrac{\Delta(\Delta pH/\Delta V)}{\Delta V}$

endpoint = volume at which
second deriv. goes to 0 after inflection

blow-up of second derivative plot near equiv. point!

Can model and predict complete titration of weak base with strong acid---or weak acid with strong base! Results in equations that can be put into Excel spread sheet!

for weak acid titrated by strong base:

$$\phi = \frac{C_b V_b}{C_a V_a} = \frac{\alpha_{A^-} - \dfrac{[H^+]-[OH^-]}{C_a}}{1 + \dfrac{[H^+]-[OH^-]}{C_b}}$$

where: $\alpha_{A^-} = \dfrac{K_a}{[H^+]+K_a}$
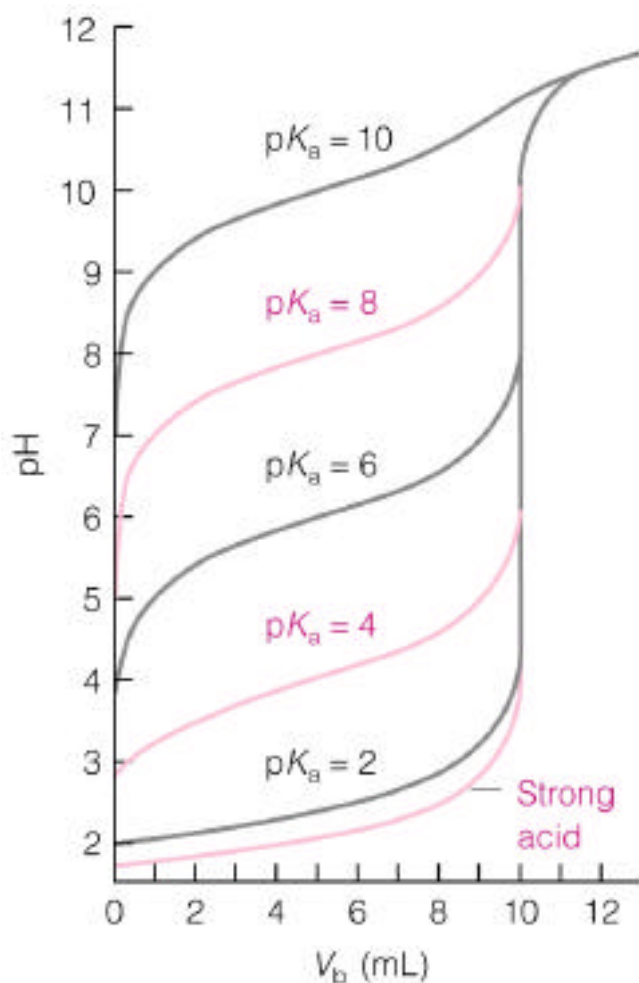
= fraction of way to equivalence point

$-$ = fraction of HA in A⁻ form!

C_b = conc. of base
C_a = conc. of acid
V_a = volume of acid
V_b = volume of base

for weak base titrated by strong acid:

$$\phi = \frac{C_a V_a}{C_b V_b} = \frac{\alpha_{BH^+} - \dfrac{[H^+]-[OH^-]}{C_b}}{1 + \dfrac{[H^+]-[OH^-]}{C_a}}$$

$\alpha_{BH^+} = \dfrac{[H^+]}{[H^+]+K_{a(BH^+)}}$

example calculated curves for titration of acids with strong base--

note: as strength of acid decreases---end points are not sharp, and would be difficult to obtain!

obtain curves by putting in different pH values in eqn (then can calc.   , [$^-$], etc.) and finally V_b values for x-axis!