ACID-BASE TITRATIONS_____

"Learn to recognize buffers! They lurk in every corner of acid-base chemistry."

Acid-Base Titrations

Solution of a base of known concentration is added to an acid of unknown concentration (or acid of known concentration added to a base of unknown concentration)

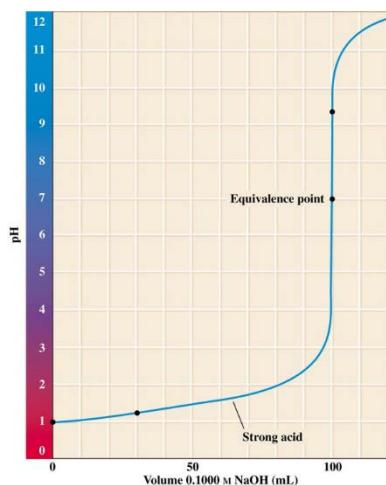   titrant
    titration curve
    equivalence point   half-equivalence point

      pH > 7 titrating weak acid
      pH = 7 titrating strong acid or base
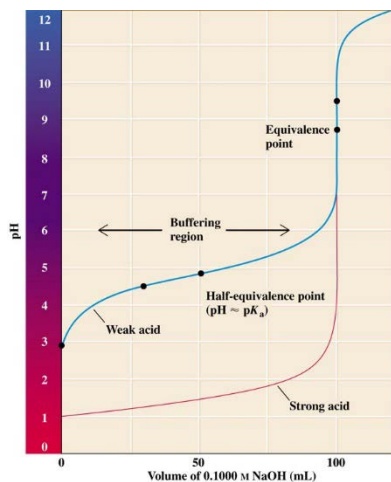   pH < 7   titrating weak base

    endpoint

strong acid or strong base titration overview
classic Arrhenius neutralization reaction characterized by

1.   strong acid (base):

2.   strong base (acid) titrant:

3.   total ionic equation:

4.   net ionic equation (what is K?):

5.   titration curve – one inflection point (equivalence point)

weak acid or weak base titration overview
weak acid (base) titrated with strong base (acid) characterized by

1.   weak acid (base):

2.   strong base (acid) titrant:

3.   total ionic equation:

4.   net ionic equation (what is K?):

5.   titration curve - two inflection points

      half-equivalence point (perfect 1/1 buffer)

      equivalence point, solution identical to conjugate base (acid) dissolved in wate)

To find the **pH as a function of added titrant** develop the exact expression (**systematic treatment**) for the hydronium (hydroxide) ion in terms of the concentrations of titrant and analyte.

SUGGESTION: do not use the dilution factor method of Harris Equation 11-1

Titration of a Strong Base with a Strong Acid, 11-1

EX: 50.00 mL of 0.02000 M KOH titrated with 0.1000 M HBr.

chemistry and equilibrium equations

charge balance   material balance

solve for $[OH^-]$ from $K_w = [H_3O^+][OH^-]$

governing equations

$$\text{base analyte: } [OH^-]^2 - (F_{KOH} - F_{HBr})[OH^-] - K_w = 0$$

$$\text{acid analyte: } [H_3O^+]^2 - (F_{HBr} - F_{KOH})[H_3O^+] - K_w = 0$$

without F_{HBr} (or F_{KOH}) term, equations are identical to systematic approach for strong base (or strong acid) dissociation

Equations simplify since for most of the titration K_w can be ignored so that the monitored hydroxide (hydronium) ion concentration is just the stoichiometric excess concentration.
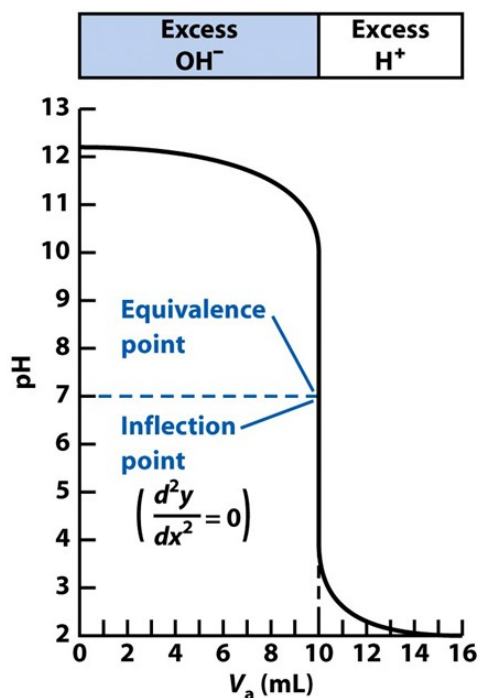
$$\text{base analyte: } [OH^-] - (F_{KOH} - F_{HBr}) = 0$$

$$\text{acid analyte: } [H_3O^+] - (F_{HBr} - F_{KOH}) = 0$$

EX 1. Determine the pH for the above example
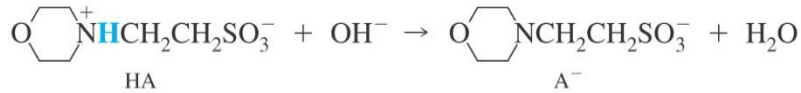 **FIND EQUIVALENCE POINT**
a) before any acid is added

b) when 3.00 mL of HBr is added

c) at the equivalence point

d) when 10.50 mL of HBr is added

Titration of a Weak Acid with a Strong Base, 11-2

EX: 50.00 mL of 0.02000 M MES [2-(N-morpholino)ethanesulfonic acid, $pK_a = 6.27$] titrated with 0.1000 M NaOH.

chemistry and equilibrium equations

$$O\bigcirc\overset{+}{N}HCH_2CH_2SO_3^- \ + \ OH^- \ \rightarrow \ O\bigcirc NCH_2CH_2SO_3^- \ + \ H_2O$$

$$\text{HA} \qquad\qquad\qquad\qquad\qquad \text{A}^-$$

charge balance   material balance

solve for [H_3O^+] from K_a

governing equation

$$K_a \ = \ \frac{[H_3O^+](F_{NaOH} + [H_3O^+] - [OH^-])}{F_{HA} - (F_{NaOH} + [H_3O^+] - [OH^-])}$$

$$[H_3O^+]^3 + (K_a + F_{NaOH})[H_3O^+]^2 - \{(F_{HA} - F_{NaOH})K_a + K_w\}[H_3O^+] - K_aK_w = 0$$

(without F_{NaOH} term, equation is identical to systematic approach for weak acid dissociation)

Do not focus on cubic equation! K_a expression simplifies in most of the titration (buffer region) as [H_3O^+] and [OH^-] are far smaller than F_{NaOH} and can be ignored. Recognizing that F_{NaOH} is just the concentration of conjugate base results in the normal buffer equation.

EX 2. Determine the pH for the above example

   FIND EQUIVALENCE POINT

a) before any base is added

b) when 3.00 mL of NaOH is added

c) at the equivalence point
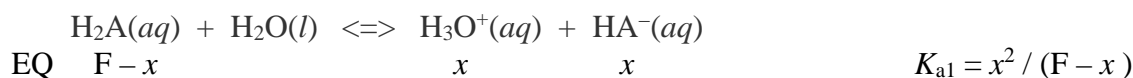
d) when 10.10 mL of NaOH is added
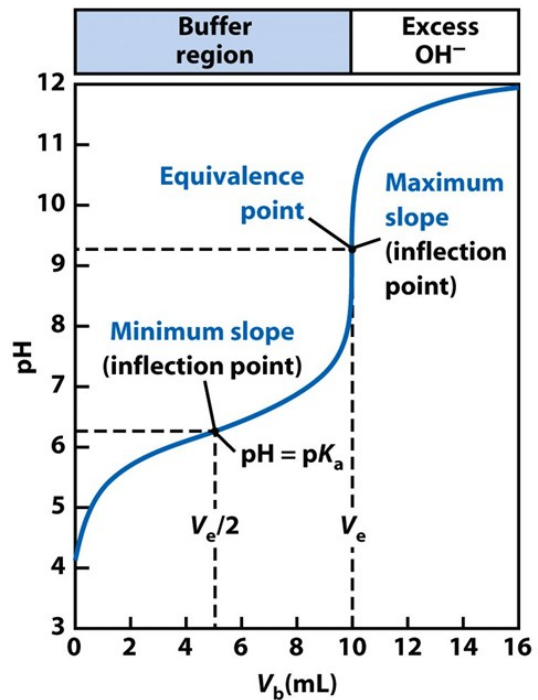
Titration of Polyprotics, 11-4 (Review of Polyprotic Acids, 10-1 and 10-3)

The titration of systems having more than one titratable acidic or basic group requires an understanding of an intermediate form. We briefly encountered these when we surveyed polyprotic acids and will now return to the material in H Ch 10-1 and 10-3.
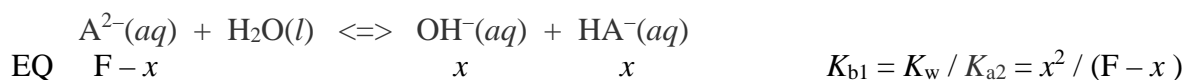
Consider determining the pH of H_2A, NaHA, or Na_2A which are all part of a diprotic system

K_{a1} $\qquad\qquad$ $H_2A(aq) + H_2O(l) \iff H_3O^+(aq) + HA^-(aq)$

K_{a2} $\qquad\qquad$ $HA^-(aq) + H_2O(l) \iff H_3O^+(aq) + A^{2-}(aq)$

1) The pH of a solution of H_2A, whose formal concentration is F, can be treated as if it were a monoprotic acid ($x = [H^+]$).

$\qquad$ $H_2A(aq) + H_2O(l) \iff H_3O^+(aq) + HA^-(aq)$

EQ $\quad$ $F - x$ $\qquad\qquad\qquad\qquad$ x $\qquad\quad$ x $\qquad\qquad\qquad$ $K_{a1} = x^2 / (F - x)$

2) The pH of solution of a salt containing the basic anion A^{2-} (such as Na_2A), whose formal concentration is F, can be treated as if it were a monobasic base ($x = [OH^-]$).

$\qquad$ $A^{2-}(aq) + H_2O(l) \iff OH^-(aq) + HA^-(aq)$

EQ $\quad$ $F - x$ $\qquad\qquad\qquad\qquad$ x $\qquad\quad$ x $\qquad\qquad$ $K_{b1} = K_w / K_{a2} = x^2 / (F - x)$

3) The species HA^- (as in a solution of NaHA) is an intermediate form as it can behave as an acid (K_{a2} expression) or as a base

$\qquad\qquad$ $HA^-(aq) + H_2O(l) \iff OH^-(aq) + H_2A(aq)$ $\qquad\qquad$ $K_{b2} = K_w / K_{a1}$
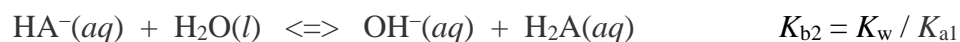
(conjugate base of H_2A in the K_{a1} expression) and both its acidity and basicity must be taken into account. A systematic approach to equilibrium addresses this. We will accept the results of this derivation without going through the proof (analysis given on Harris p. 216) where it can be shown that, generally with $K_1 = K_{a1}$ and $K_2 = K_{a2}$

$$[H^+] = \sqrt{\frac{K_1 K_2 [HA^-] + K_1 K_w}{K_1 + [HA^-]}}$$

However, if one started with a solution of NaHA where the salt dissociates into its ions Na^+ and HA^- in solution, then the principle species in solution would be HA^- since the very small values of K_{a2} and K_{b2} insure that it has not reacted much. Therefore, the equilibrium concentration of HA^- can just be replaced by its formal concentration.

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

Due to the very small value of K_w it is often found that $K_w \ll K_2 F$ so that the term with K_w can be ignored and we have

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F}{K_1 + F}}$$

Furthermore, if H_2A is not too strong of an acid or the concentration of HA^-, F, is not too dilute so that $K_1 \ll F$ then
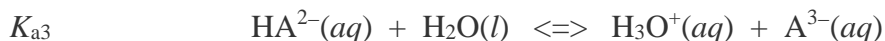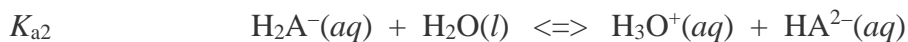
$$[H^+] \approx \sqrt{K_1 K_2}$$

or

$$pH \approx \frac{1}{2}(pK_1 + pK_2)$$

EX 3. What is the pH of a 0.050 F aqueous solution of NaHSO$_3$? For sulfurous acid $K_{a1} = 1.39 \times 10^{-2}$, $K_{a2} = 6.73 \times 10^{-8}$

To determine the pH in any of the species present in a triprotic system you still have H$_3$A treated as a monoprotic acid with K_{a1} and A^{3-} treated as a monobasic base with $K_{b1} = K_w / K_{a3}$

K_{a1} H$_3$A(aq) + H$_2$O(l) <=> H$_3$O$^+$(aq) + H$_2$A$^-$(aq)

K_{a2} H$_2$A$^-$(aq) + H$_2$O(l) <=> H$_3$O$^+$(aq) + HA^{2-}(aq)

K_{a3} HA^{2-}(aq) + H$_2$O(l) <=> H$_3$O$^+$(aq) + A^{3-}(aq)

H$_2$A$^-$ is an intermediate form sandwiched in between K_{a1} and K_{a2}. Now there is another intermediate form HA^{2-}. If one started with a solution of Na$_2$HA where the salt dissociates into its ions Na$^+$ and HA^{2-} in solution, the principle species in solution would be HA^{2-} since the very small values of K_{a3} and K_{b2} insure that it has not reacted much. As done for the diprotic system, the equilibrium concentration of HA^{2-} can just be replaced by its formal concentration.

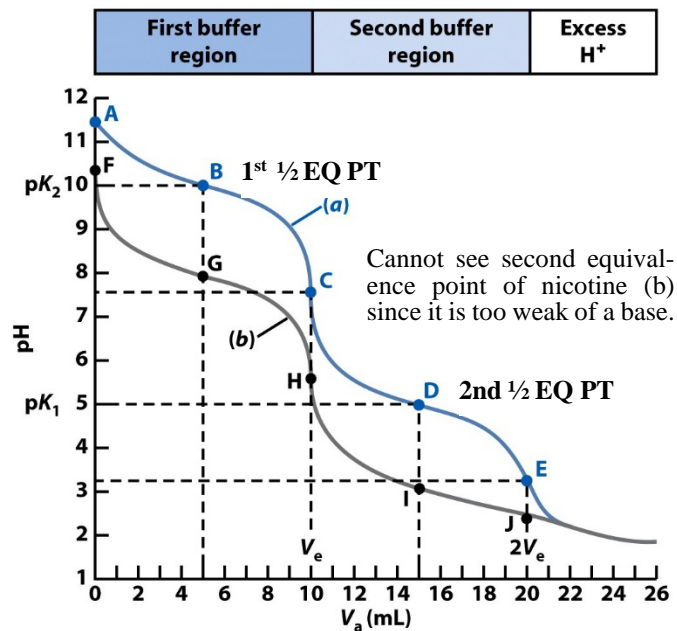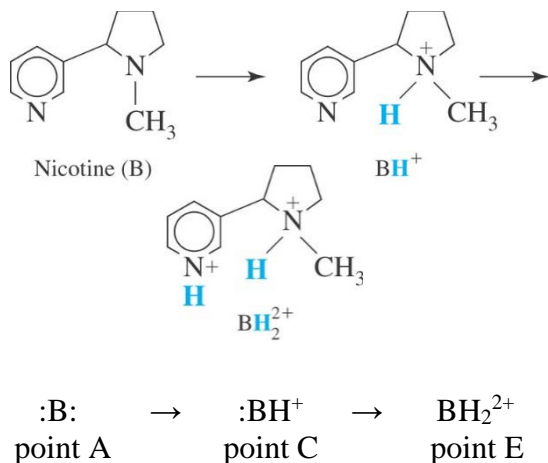$$[H^+] \approx \sqrt{\frac{K_2 K_3 F + K_2 K_w}{K_2 + F}}$$

As for the diprotic, if $K_w \ll K_3 F$ and $K_2 \ll F$ then

$$pH = \frac{1}{2}(pK_2 + pK_3)$$

Titration of a Dibasic Base with a Strong Acid, 11-4

EX: 10.00 mL of 0.100 M base a) ($pK_{b1} = 4.00$, $pK_{b2} = 9.00$) and b) nicotine ($pK_{b1} = 6.15$, $pK_{b2} = 10.85$) titrated with 0.100 M HCl.

chemistry and equilibrium equations

First buffer region	Second buffer region	Excess H^+

Nicotine (B)

BH^+

BH_2^{2+}

Cannot see second equivalence point of nicotine (b) since it is too weak of a base.

B 1st ½ EQ PT

D 2nd ½ EQ PT

:B:	→	:BH$^+$	→	BH$_2$$^{2+}$
point A		point C		point E

$pK_{a1} = pK_w - pK_{b2} = -\log(1.01 \times 10^{-14}) - 9.00 = 5.00$ $\qquad\qquad$ $pK_{a2} = pK_w - pK_{b1} = 10.00$

EX 4. Determine the pH for the above example   **FIND EQUIVALENCE POINTS**

a) before any acid is added (point A)

b) when 1.5 mL of HCl is added

c) when 10.0 mL of HCl is added (first equivalence point, point C)

d) when 15.0 mL of HCl is added

e) when 20.0 mL of HCl is added (second equivalence point, point E)

f) when 25.0 mL of HCl is added (excess strong acid)

Principal Species (10-4) and Fractional Composition Plots (10-5)

There are other ways of observing the effect of pH on a solution of an acid or a base. We briefly encountered the principal species (predominant form) when we surveyed polyprotic acids and it may now be more meaningful in the context of polyprotic tritrations. When used in conjunction with the Henderson-Hasselbalch equation, the principal species becomes even more apparent.
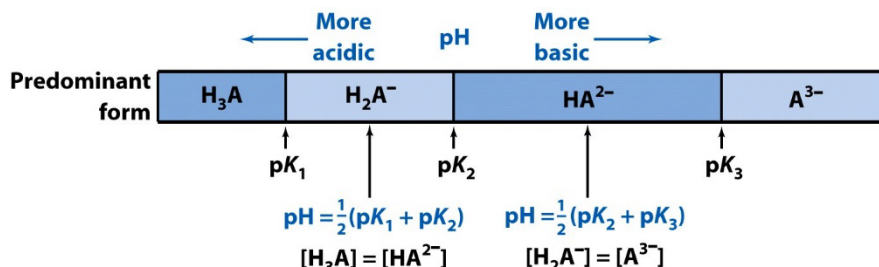

Fractional compositions were introduced when studying weak acids and weak bases. Their plots show how an acid (or base) systematically ionizes as the pH is increased by plotting the fractions of the various species present in solution. The pK_a's are very apparent as the pH at which the fraction of the acid crosses the curve for the fraction of its conjugate base.
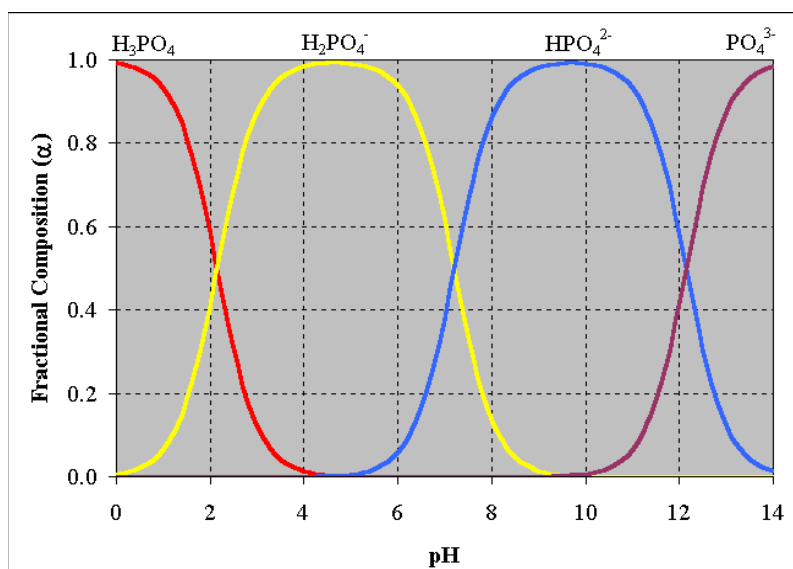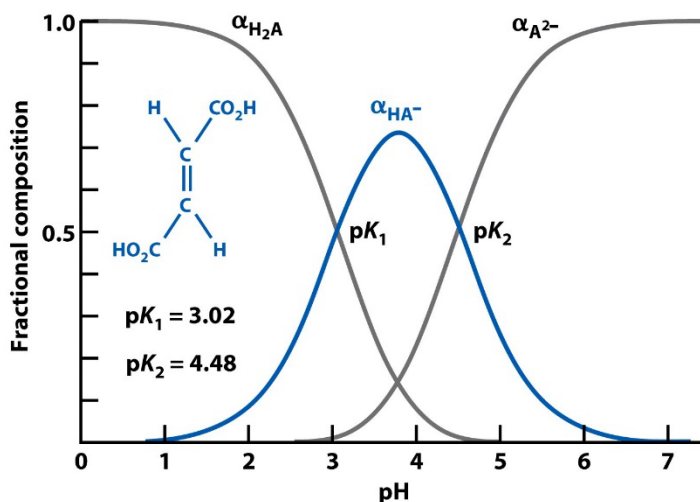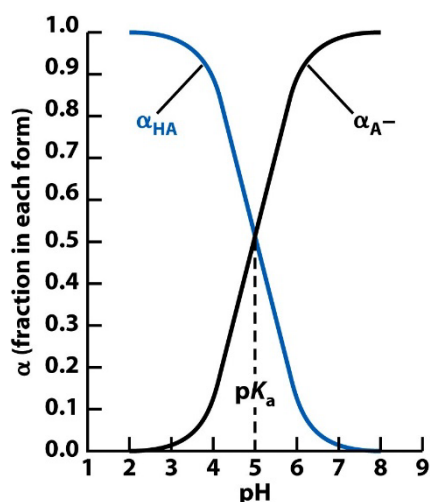
effect of K_a and dilution upon end point detection

As acid strength decreases or solution becomes more dilute the inflection at the equivalence point becomes less distinct.

(a) (b)
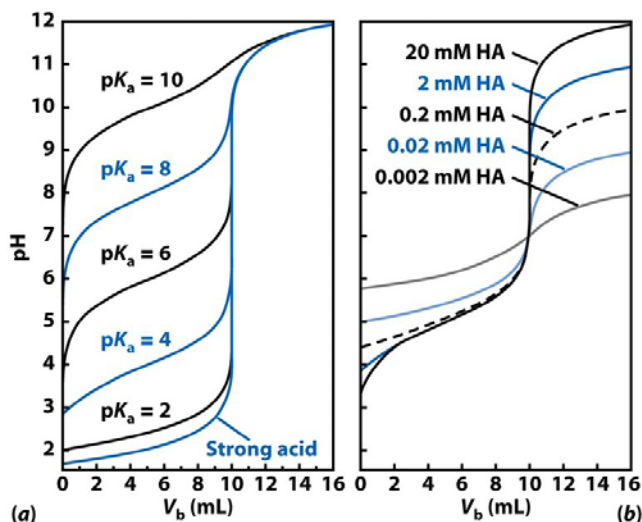
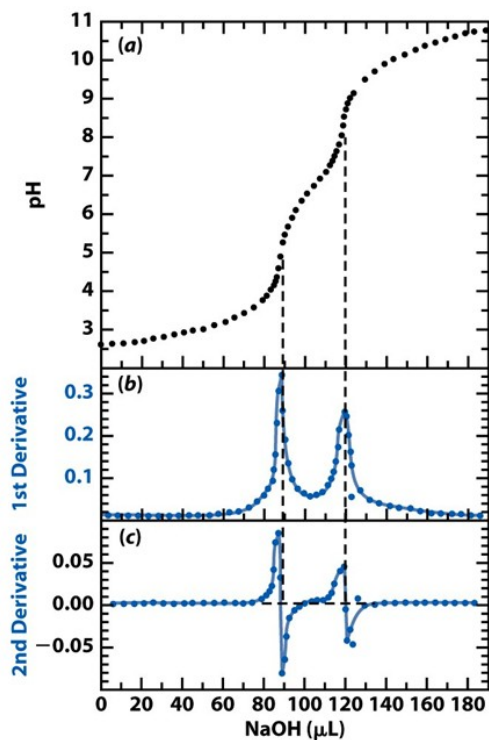# Finding the End Point with a pH Electrode, 11-5 (Lab Experiment H_Exp 7)

use of derivatives

Table 11-3 Computation of first and second derivatives for a titration curve

		First derivative		Second derivative	
μL NaOH	pH	μL	$\dfrac{\Delta pH}{\mu L}$	μL	$\dfrac{\Delta(\Delta pH/\Delta \mu L)}{\Delta \mu L}$
85.0	4.245				
		85.5	0.155		
86.0	4.400			86.0	0.071 0
		86.5	0.226		
87.0	4.626			87.0	0.081 0
		87.5	0.307		
88.0	4.933			88.0	0.033 0
		88.5	0.340		
89.0	5.273			89.0	−0.083 0
		89.5	0.257		
90.0	5.530			90.0	−0.068 0
		90.5	0.189		
91.0	5.719			91.25	−0.039 0
		92.0	0.130		
93.0	5.980				

end points given by

1. maxima of first derivative

2. where second derivatives pass through zero (generally requires drawing a straight line through two points on either side of zero to better determine the crossing point)
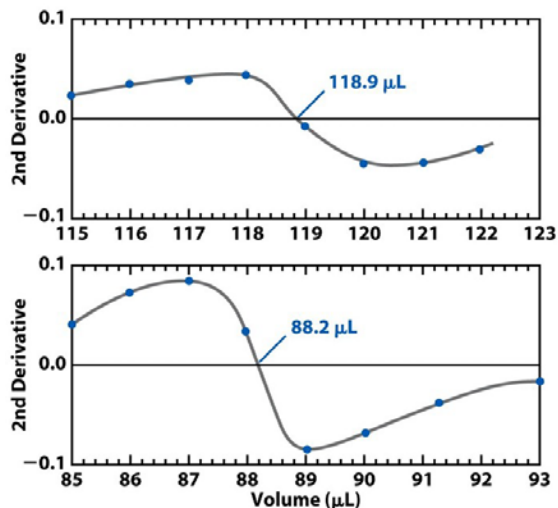
Finding the End Point with Indicators, 11-6

indicators are weak acids or bases
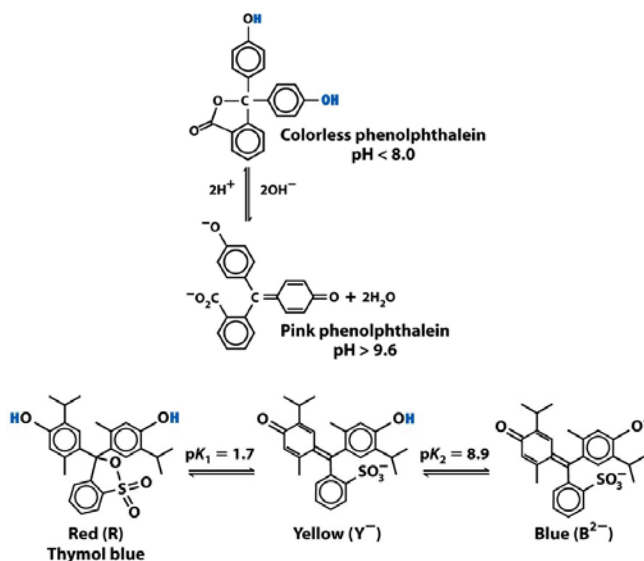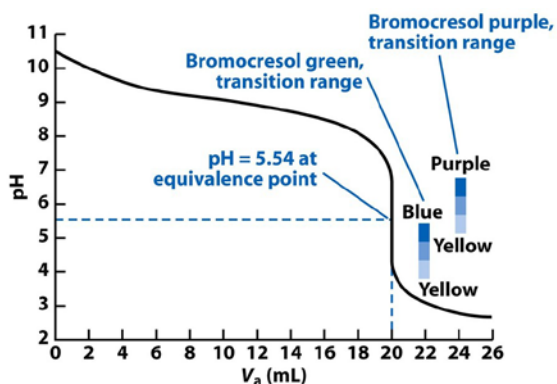

The Leveling Effect, 11-9

The strongest acid (base) that can exist in a given solvent is the acidic (basic) autoionization species of the solvent.

Leveling effect: Acids stronger than the hydronium ion or bases stronger than the hydroxide ion have the same effective strength in water, that of a strong acid or a strong base, since the equilibrium lies so far to the right that it cannot be accurately measured. In general all acids (or bases) stronger than the conjugate acid (or base) of the solvent have the same effective strength in that solvent and the solvent is said to have a leveling effect on those acids and bases.

Acidity Constants in Water at 25°C

Acid	Formula	Conjugate Base	K_a	pK_a
Hydriodic	HI	I⁻	$\approx 10^{11}$	≈ -11
Hydrobromic	HBr	Br⁻	$\approx 10^{9}$	≈ -9
Perchloric	$HClO_4$	ClO_4^-	$\approx 10^{7}$	≈ -7
Hydrochloric	HCl	Cl⁻	$\approx 10^{7}$	≈ -7
Chloric	$HClO_3$	ClO_3^-	$\approx 10^{3}$	≈ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\approx 10^{2}$	≈ -2
Nitric	HNO_3	NO_3^-	≈ 20	≈ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Urea acidium ion	$(NH_2)CONH_3^+$	$(NH_2)_2CO$ (urea)	6.6×10^{-1}	0.18
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.5×10^{-2}	1.82
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Phosphoric (1)	H_3PO_4	$H_2PO_4^-$	7.5×10^{-3}	2.12
Arsenic (1)	H_3AsO_4	$H_2AsO_4^-$	5.0×10^{-3}	2.30
Chloroacetic	$ClCH_2COOH$	$ClCH_2COO^-$	1.4×10^{-3}	2.85
Hydrofluoric	HF	F⁻	6.6×10^{-4}	3.18
Nitrous	HNO_2	NO_2^-	4.6×10^{-4}	3.34
Formic	HCOOH	HCOO⁻	1.8×10^{-4}	3.74
Benzoic	C_6H_5COOH	$C_6H_5COO^-$	6.5×10^{-5}	4.19
Oxalic (2)	$HC_2O_4^-$	$C_2O_4^{2-}$	6.4×10^{-5}	4.19

Acidity Constants in Water at 25°C

Acid	Formula	Conjugate Base	K_a	pK_a
Hydrazoic	HN_3	N_3^-	1.9×10^{-5}	4.72
Acetic	CH_3COOH	CH_3COO^-	1.8×10^{-5}	4.74
Propionic	CH_3CH_2COOH	$CH_3CH_2COO^-$	1.3×10^{-5}	4.89
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N (pyridine)	5.6×10^{-6}	5.25
Carbonic (1)	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.0×10^{-7}	7.00
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS⁻	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.2×10^{-8}	7.21
Hypochlorous	HClO	ClO⁻	3.0×10^{-8}	7.52
Hydrocyanic	HCN	CN⁻	6.2×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	2.3×10^{-11}	10.64
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	3.0×10^{-12}	11.52
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.66
Water	H_2O	OH⁻	1.0×10^{-14}	14.00
Hydrogen sulfide ion	HS⁻	S^{2-}	1.0×10^{-19}	19.00
Hydrogen	H_2	H⁻	1.0×10^{-33}	33.00
Ammonia	NH_3	NH_2^-	1.0×10^{-38}	38.00
Hydroxide ion	OH⁻	O^{2-}		

acids stronger than H_3O^+

conjugate bases stronger than OH⁻