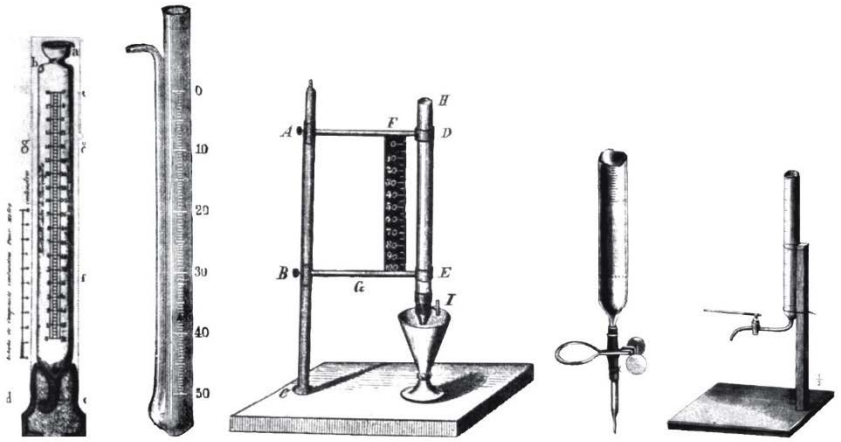
Titrations

Harris 7-1–7-2, 11-3, 11-5–11.6

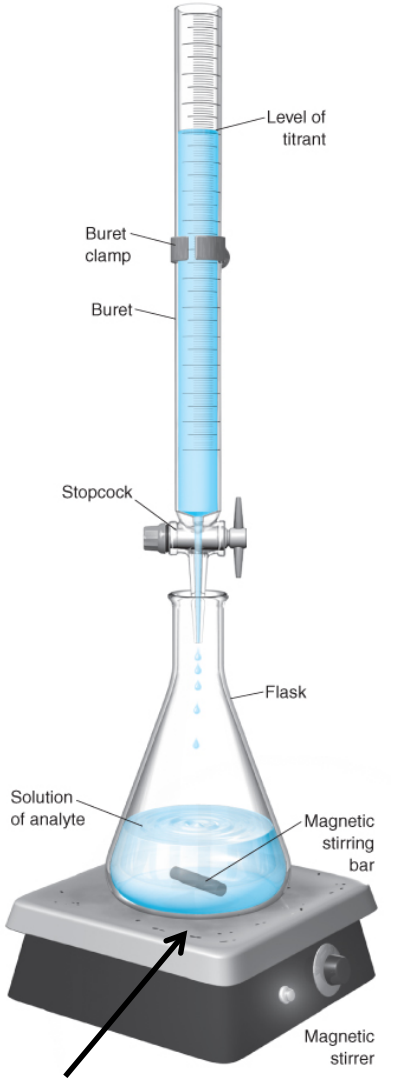
Stoichiometry of Titrations, 7-1 – 7-2

- balanced equation
- concentrations
- end point = equivalence point

acid/base titrations

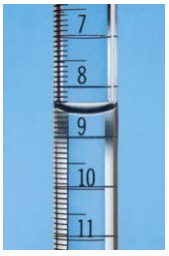


Descroizilles (1806) Pour out liquid | **Gay-Lussac (1824)** Blow out liquid | **Henry (1846)** Copper stopcock | **Mohr (1855)** Compression clip | **Mohr (1855)** Glass stopcock



The Phenolphthalein End Point

reading a meniscus

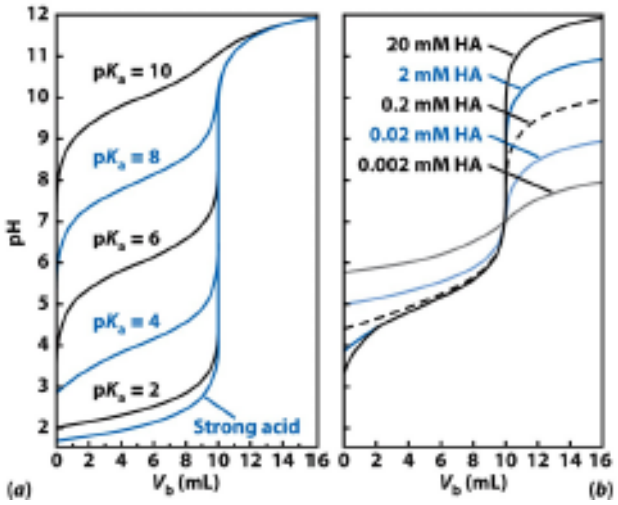


place a piece of white paper or kimwipe under flask to better aid detection of end point

Effect of Ka and dilution upon end point detection, 11-3

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

Acetic acid is used as the solvent for the tobacco lab since the base in tobacco is too weak to be observed in water.



Finding the End Point with a pH Electrode, 11-5 - use of derivatives

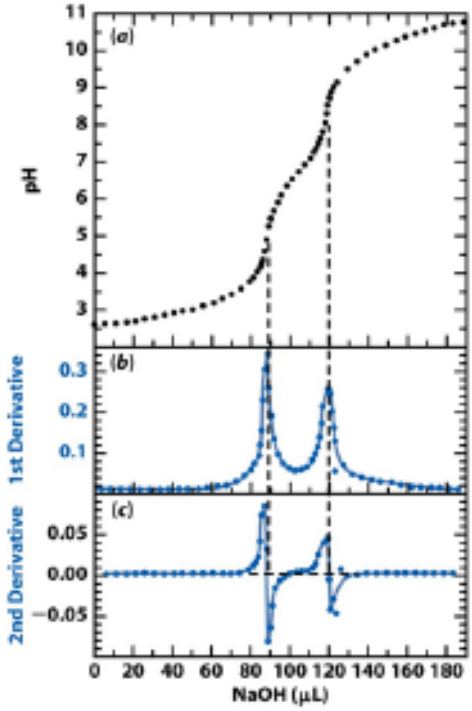
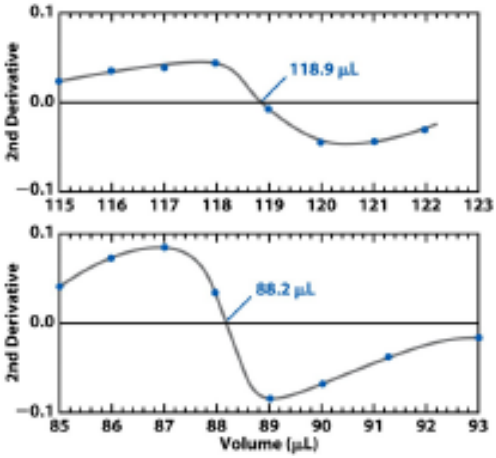


Table 11-3 Computation of first and second derivatives for a titration curve

		First derivative		Second derivative	
μL NaOH	pH	μL	$\frac{\Delta pH}{\mu L}$	μL	$\frac{\Delta(\Delta pH/\Delta\mu L)}{\Delta\mu L}$
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				

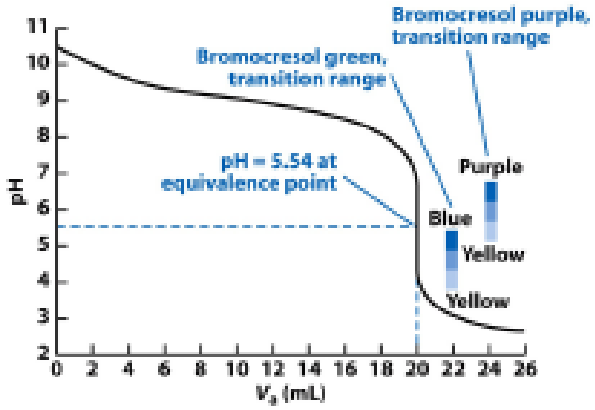


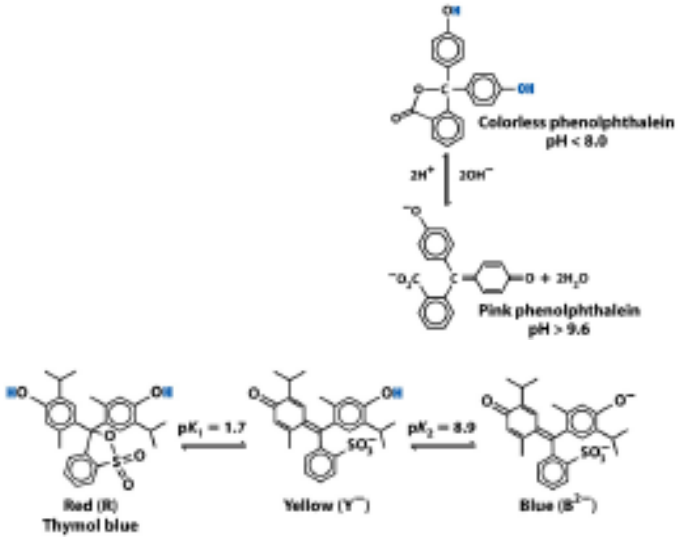
end points given by

1. maxima of first derivative
2. where second derivatives pass through zero

(generally requires drawing a straight line through the two points on either side of zero to more accurately determine the crossing point)

Finding the End Point with Indicators, 11-6 - indicators are weak acids or bases





The Leveling Effect, 11-9

$$H_2O(l) + H_2O(l) \iff H_3O^+(aq) + OH^-(aq)$$

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 (bases) stronger than the conjugate acid (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
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^+

The strongest acid (base) that can exist in a given solvent is the acidic (basic) autoprotolysis species of the solvent. In water $HClO_4$ is leveled to H_3O^+. As a strong acid it is not leveled to $CH_3COOH_2^+$ in acetic acid and we use this in the tobacco lab.

conjugate bases stronger than OH^-