Chapters 7 and 11

Acid-Base Titrations

Titration:

Increments of reagent solution-the titrant-are added to analyte until their reaction is complete.

Titration type/endpoint determination:

•Volumetric: volume of standard is measured
•Gravimetric: mass of standard is measured, e.g., Mohr method (Cl-Ag-CrO_4).
•Coulometric: time at constant current is measured, i.e., amount of charge.
•Spectrophotometric: Beer's Law, the absorbance

Terms

Titration: Performed slowly by adding standard solution from a buret until the reaction is judged to be complete.

Standard Solution (Standard Titrant): Reagent of known concentration that is used to carry out the analysis.

Indicators: Added to a titration to give an observable physical change at or near the equivalence point. Usually a color or turbidity change.

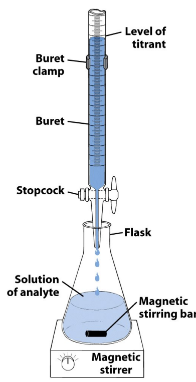


Figure 7-1
Quantitative Chemical Analysis, Seventh Edition

Terms

Equivalence Point: The point when the amount of added titrant is chemically equivalent to the amount of analyte in the sample.

End Point: The point at which an indicator physically changes representing the estimated equivalence point (color or turbidity change).

Titration error = Vep - Veq

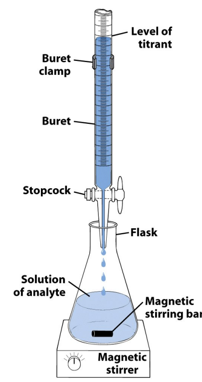


Figure 7-1
Quantitative Chemical Analysis, Seventh Edition

Terms

Blank titration:
Carry out the same procedure without analyte. To estimate the titration error.

Back-titration:
Add a known excess of one standard titrant to the analyte, and then titrate a second standard titrant to determine the excess reagent. May be required when a reaction is slow or the standard solution lacks stability.

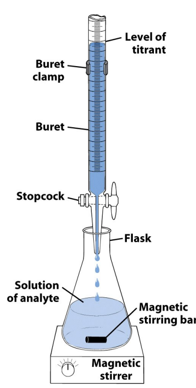


Figure 7-1
Quantitative Chemical Analysis, Seventh Edition

Standard Solutions (Titrants)

Desirable Properties of Standard Solutions

1. Sufficiently stable (only need to determine concentration once).
2. React rapidly with the analyte (less time between additions).
3. React more or less completely with the analyte (satisfactory end points).
4. Undergo a selective reaction with analyte described by a simple chemical equation

Standard Solutions (Titrants)

Methods for Establishing the Concentration of Standard Solutions

1. Direct Method: A carefully weighed quantity of primary standard is diluted to a known volume. First choice if possible.
2. Standardization: A titrant to be standardized is used to titrate a weighed quantity of a primary, secondary standard or a known volume of another standard solution.

Standard Solutions (Titrants)

Primary Standard:
Highly purified compound that serves as a reference material.
• High purity, stability (air, heat, vacuum),
• Standard solution (direct method)
• To standardize a standard solution (standardization)

Secondary Standard:
A reference material (a compound) whose purity has been established by a chemical analysis. Often used in lieu of a primary standard because there are not many primary standards.

Acid-Base Titrations

How does the pH change as titrant is added?

Titration Curve: A graph showing how the concentration of one of the reactants varies as titrant is added. (how the pH changes as titrant is added in acid and base titration)

Titration of Strong Base with Strong Acid

Table 11-1 Calculation of the titration curve for 50.00 mL of 0.020 00 M KOH treated with 0.100 0 M HBr

	mL HBr added (V_a)	Concentration of unreacted OH^- (M)	Concentration of excess H^+ (M)	pH
Region 1 (excess OH^-)	0.00	0.020 0		12.30
	1.00	0.017 6		12.24
	2.00	0.015 4		12.18
	3.00	0.013 2		12.12
	4.00	0.011 1		12.04
	5.00	0.009 09		11.95
	6.00	0.007 14		11.85
	7.00	0.005 26		11.72
	8.00	0.003 45		11.53
	9.00	0.001 69		11.22
	9.50	0.000 840		10.92
	9.90	0.000 167		10.22
	9.99	0.000 016 6		9.22
Region 2	10.00	—	—	7.00
Region 3 (excess H^+)	10.01		0.000 016 7	4.78
	10.10		0.000 166	3.78
	10.50		0.000 826	3.08
	11.00		0.001 64	2.79
	12.00		0.003 23	2.49
	13.00		0.004 76	2.32
	14.00		0.006 25	2.20
	15.00		0.007 69	2.11
	16.00		0.009 09	2.04

Table 11-1
Quantitative Chemical Analysis, Seventh Edition

Titration of Strong Base with Strong Acid

1. Before the equivalence point: excess OH^-
2. At the equivalence point: pH = 7.00
3. After the equivalence point: excess H^+

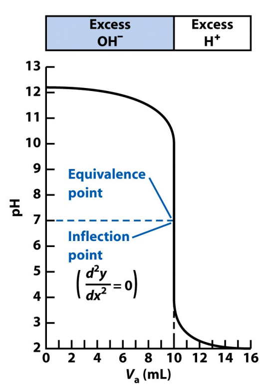
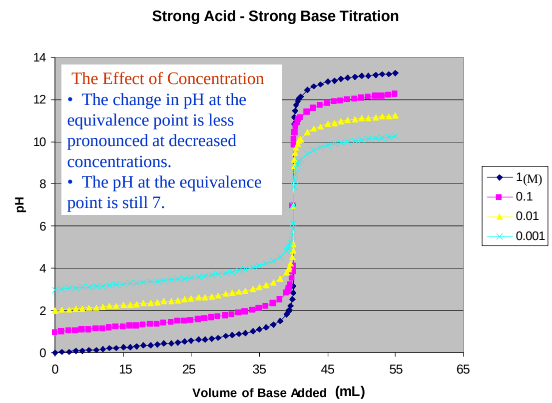


Figure 11-1
Quantitative Chemical Analysis, Seventh Edition

Titration of Strong Acid with Strong Base

EXAMPLE: Derive the titration curve for the titration of 20.00 mL of 0.1000 M HCl with 0.00, 10.00, 19.98, 20.00, 20.02 and 40.00 mL of 0.1000 M NaOH.

0.00,	initial point
10.00 ml,	50% titration
19.98 ml,	half-drop before equivalence point
20.00 ml,	100% titration (equivalence point)
20.02 ml,	half-drop after equivalence point
40.00 ml,	200% titration (far-over)



Titration of Weak Acid with Strong Base

Table 11-2 Calculation of the titration curve for 50.00 mL of 0.020 00 M MES treated with 0.100 0 M NaOH

	mL base added (V_b)	pH
Region 1 (weak acid)	0.00	3.99
Region 2 (buffer)	0.50	4.99
	1.00	5.32
	2.00	5.67
	3.00	5.90
	4.00	6.09
	5.00	6.27
	6.00	6.45
	7.00	6.64
	8.00	6.87
	9.00	7.22
	9.50	7.55
	9.90	8.27
Region 3 (weak base)	10.00	9.25
Region 4 (excess OH^-)	10.10	10.22
	10.50	10.91
	11.00	11.21
	12.00	11.50
	13.00	11.67
	14.00	11.79
	15.00	11.88
	16.00	11.95

Table 11-2
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Titration of Weak Acid with Strong Base

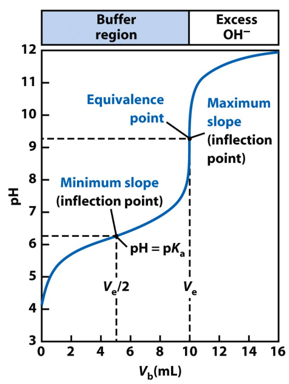


Figure 11-2
Quantitative Chemical Analysis, Seventh Edition

Titration of Weak Acid with Strong Base

•The pH change at the equivalence point decreases (the end point become less distinct) as the acid becomes weaker or more dilute

•The Effect of Concentration: the pH at the equivalence point is lower for lower initial weak acid concentrations and initial pH is higher.

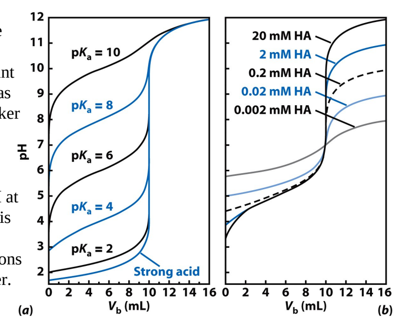


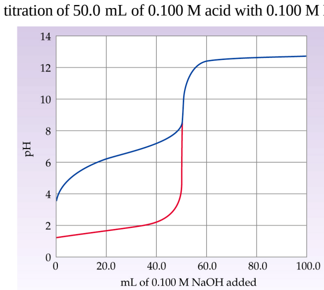
Figure 11-3
Quantitative Chemical Analysis, Seventh Edition

Titration of Weak Acid with Strong Base

EXAMPLE: Derive the titration curve for the titration of 35.00 mL of 0.1000 M HAc with 0.00, 15.00, 35.00, and 50.00 mL of 0.1000 M NaOH. $K_a = 1.75 \times 10^{-5}$ M

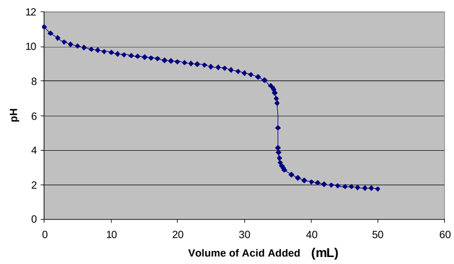
0.00,	initial point
15.00 ml,	before equivalence point
35.00 ml,	100% titration (equivalence point)
50.00 ml,	after equivalence point

The following plot shows two titration curves, each representing the titration of 50.0 mL of 0.100 M acid with 0.100 M NaOH:



(a) Which of the two curves represents the titration of a strong acid, and which a weak acid?
(b) What is the approximate pH at the equivalence point for each of the acids?
(c) What is the approximate pK_a of the weak acid?

Titration of Weak Base with Strong Acid



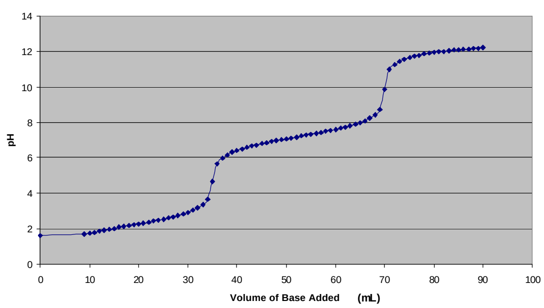
Much the same shape, except the titration would start at high pH and decrease as acid is added

Diprotic Systems: Titration of Weak Acid Base with Strong Base

EXAMPLE: Derive the titration curve for the titration of 35.00 mL of 0.1000 M H_2A with 0.00, 15.00, 35.00, 50.00, 70.00, and 90.00 mL of 0.1000 M NaOH. K_{a1} = 7.11 x 10^{-3} M; K_{a2} = 6.34 x 10^{-8} M

0.00,	Initial point
15.00 ml,	Before the 1st equivalence point
35.00 ml,	At the 1st equivalence point
50.00 ml,	After the 1st equivalence point
70.00 ml,	At the 2nd equivalence point
90.00 ml,	After the 2nd equivalence point

Diprotic Systems: Titration of Weak Acid Base with Strong Base



Diprotic Systems: Titration of Weak Base with Strong Acid

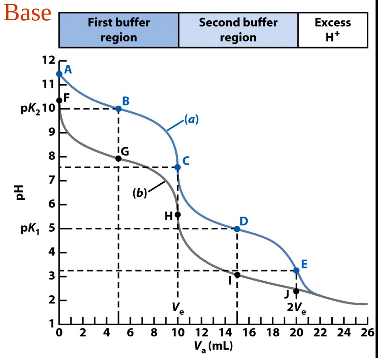


Figure 11-4
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Standard Solutions for Acid/Base Titrations

Standard acid or base reagents are always strong acids or bases

- HCl, $HClO_4$, H_2SO_4, NaOH, and KOH
- They yield sharper end points.
- Weak reagents react incompletely.
- Nitric acid and hot sulfuric and perchloric yield undesirable ox/red side reactions.

Primary standards for acid standardization *(see Table 11-5)*

- Na_2CO_3
- Tris (THAM) – tris(hydroxymethyl)aminomethane, $(HOCH_2)_3CNH_2$
- Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10H_2O$

Endpoint Determination

1. Indicators
2. Derivatives of titration curve
3. Gran Plot

Using Indicators to Determine the End Point

Acid/Base Indicators

- Weak acids or bases themselves
- The conjugate forms differs in color

$$HIn \rightleftharpoons In^- + H^+$$

acid — Color1; base — Color2

Indicators

Indicator Behavior

acid color shows when pH + 1 = pK_a

and base color shows when pH - 1 = pK_a

Color change range is (Transition range) **pH = pK_a ± 1**

Choosing the Proper Indicator

- Color change range should be in area where titration curve is most vertical.
- Indicator error: the difference between the observed end point (color change) and the true equivalence point.

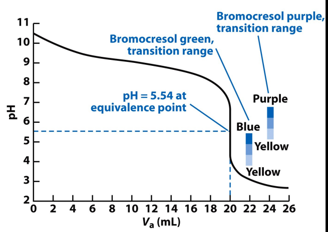

Figure 11-9
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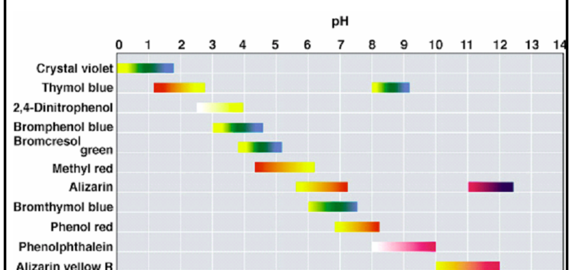
Common Indicators



See also p.215 Table 11-4

Using Derivatives of Titration Curve to Determine the End Point

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

µL NaOH	pH	First derivative: µL	First derivative: ΔpH/µL	Second derivative: µL	Second derivative: Δ(ΔpH/ΔµL)/ΔµL
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				

Table 11-3
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Using Derivatives of Titration Curve to Determine the End Point

Titration curve for a diprotic acid - strong base titration.

First derivative of a weak acid- strong base titration

Second derivative of a weak acid - strong base titration

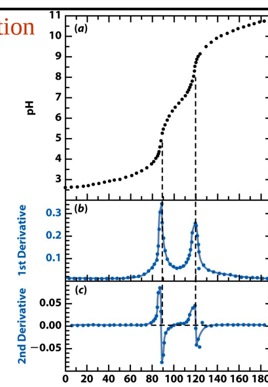

Figure 11-6
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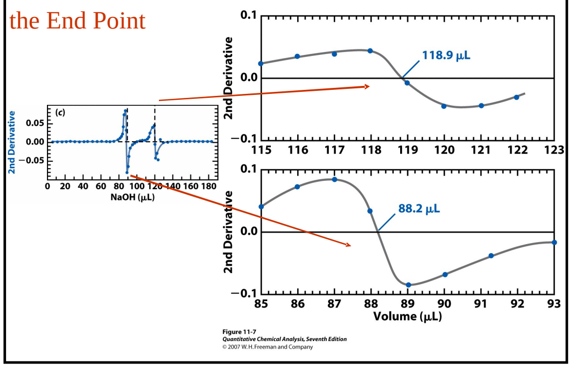
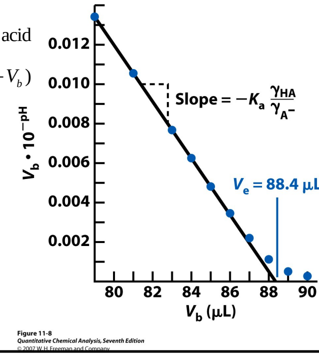
Using Derivatives of Titration Curve to Determine the End Point



Using the Gran Plot to Determine the End Point

The titration of a weak acid

$$V_b \cdot 10^{-pH} = \frac{\gamma_{HA}}{\gamma_{A^-}} K_a (V_e - V_b)$$



Using the Gran Plot to Determine the End Point

The titration of a weak acid

$$V_b \cdot 10^{-pH} = K_a \frac{\gamma_{HA}}{\gamma_{A^-}} (V_e - V_b)$$

The titration of a weak base

$$V_a \cdot 10^{+pH} = \frac{1}{K_a} \frac{\gamma_B}{\gamma_{BH^+}} (V_e - V_a)$$