Titrimetric analysis. Acid-base titration

Titrimetry

A method based on determination of the volume of reagent reacting stoichiometrically with the analyte

First appeared in XVIII century and did not receive wide acceptance

$$A + B \rightarrow C$$

A – determined compound;

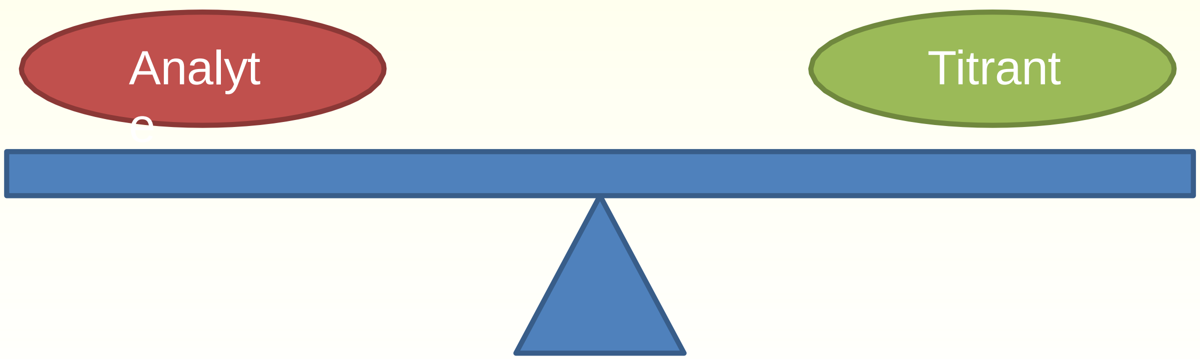
B – added reactant, totally consumed during reaction;

B is added till the moment when it stops reacting with A.

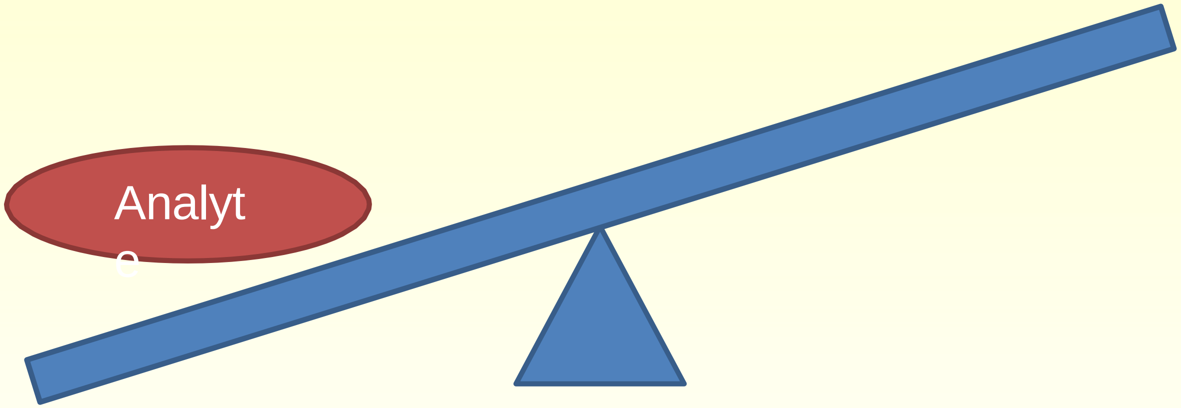
Method principle

Measures volume of a titrant at the equivalence point

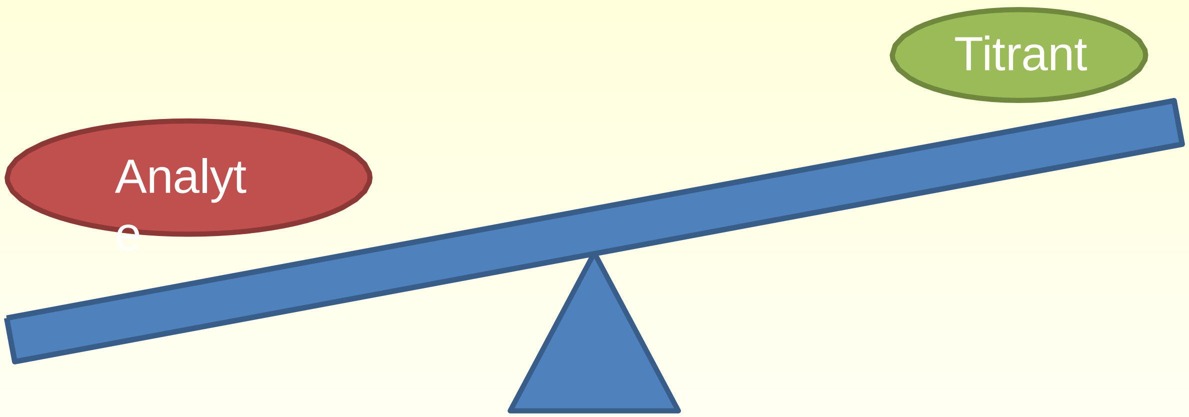
Titrant is added until all analyte is reacted



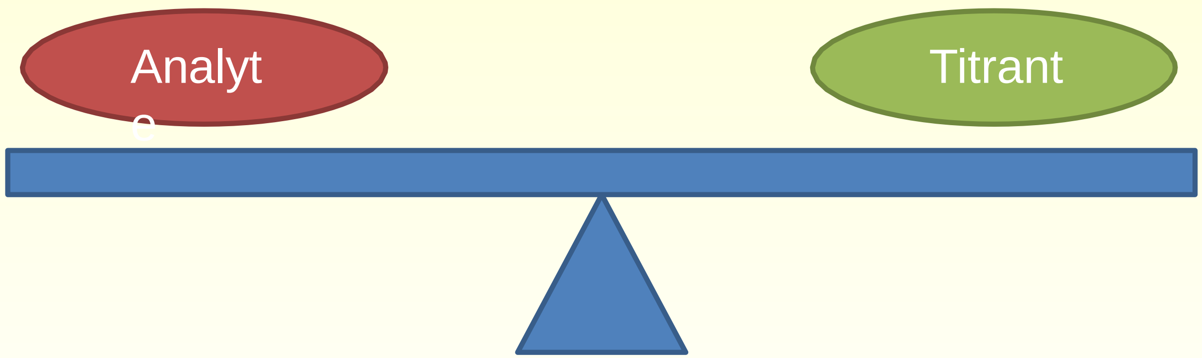
Before titration



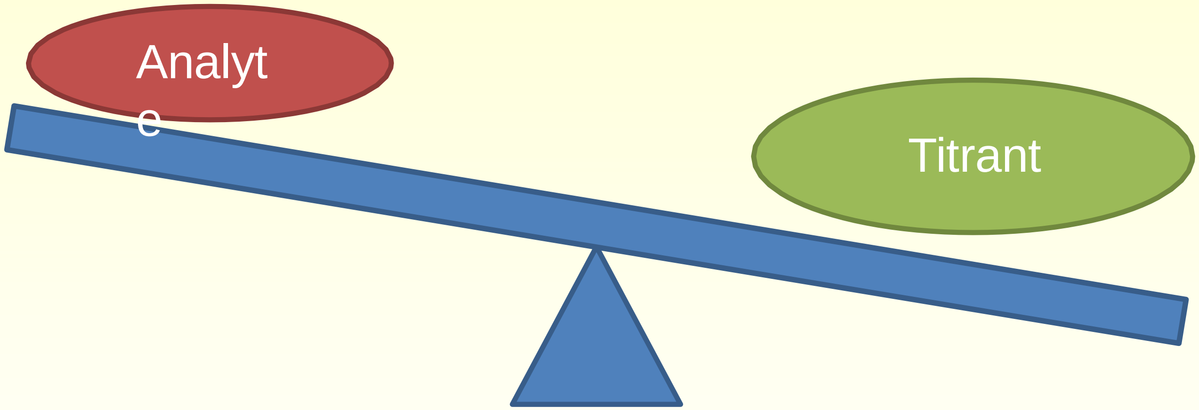
Before equivalence point



At equivalence point



After equivalence point



Back-titration

$$A + B(excess) \rightarrow C + B(unreacted)$$

After reaction ends, concentration of unreacted "B" is determined by titrimetry (or any other method)

Equivalence point

The most important part of titration – to determine equivalence point

$$\text{Moles of titrant} = V_{eq} \times C_T$$

where V_{eq} – volume of titrant at equivalence point, L (or mL);
C_T – concentration of the titrant, mol/L (or mol/mL)

Equivalence point is determined using:

- indicators (change color at the equivalence point);
- pH measurement;
- electrochemical potential measurement.

Calculation of analyte concentration

$$xA + yB \rightarrow zC$$

$$C_A \times V_A = \frac{C_B \times V_B \times X}{Y}$$

where:

C_A – concentration of analyte in sample (unknown, determined);

V_A – volume of sample (taken by analyst, known);

C_B – concentration of titrant (prepared by analyst, known);

V_B – volume of titrant at the equivalence point (determined);

X and Y – stoichiometric coefficients

Analytical signal

$$S = k \cdot C$$

Volume of titrant (V_t) is the analytical signal

$$\boldsymbol{V_t} = \frac{\boldsymbol{C_A} \times V_A \times Y}{C_t \times X}$$

$$k = \frac{V_A \times Y}{C_t \times X}$$

Exercise

10 mL of NaOH solution in water with unknown concentration was titrated with aqueous solution of HCl (C = 0.200 mol/L). Equivalence point was established at the volume of titrant 7.80 mL. What is the concentration of NaOH in the analyzed sample?

$$NaOH + HCl \rightarrow Na^{+} + OH^{-} + H_2O$$

$$C_{NaOH} = \frac{C_t \times V_t \times X}{V_{NaOH} \times Y} = \frac{0.200\,\frac{mol}{L} \times 7.8\,mL}{10\,mL} = 0.156\ mol/L$$

Answer: concentration of NaOH in the analyzed solution is 0.156 mol/L

Quick task

15 mL of H_2SO_4 solution in water with unknown concentration was titrated with aqueous solution of NaOH (C = 0.200 mol/L). Equivalence point was established at the volume of titrant 12.20 mL. What is the concentration of H_2SO_4 in the analyzed sample?

Titrant volume measurement: burette

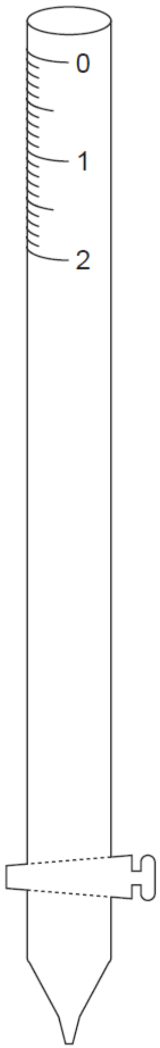
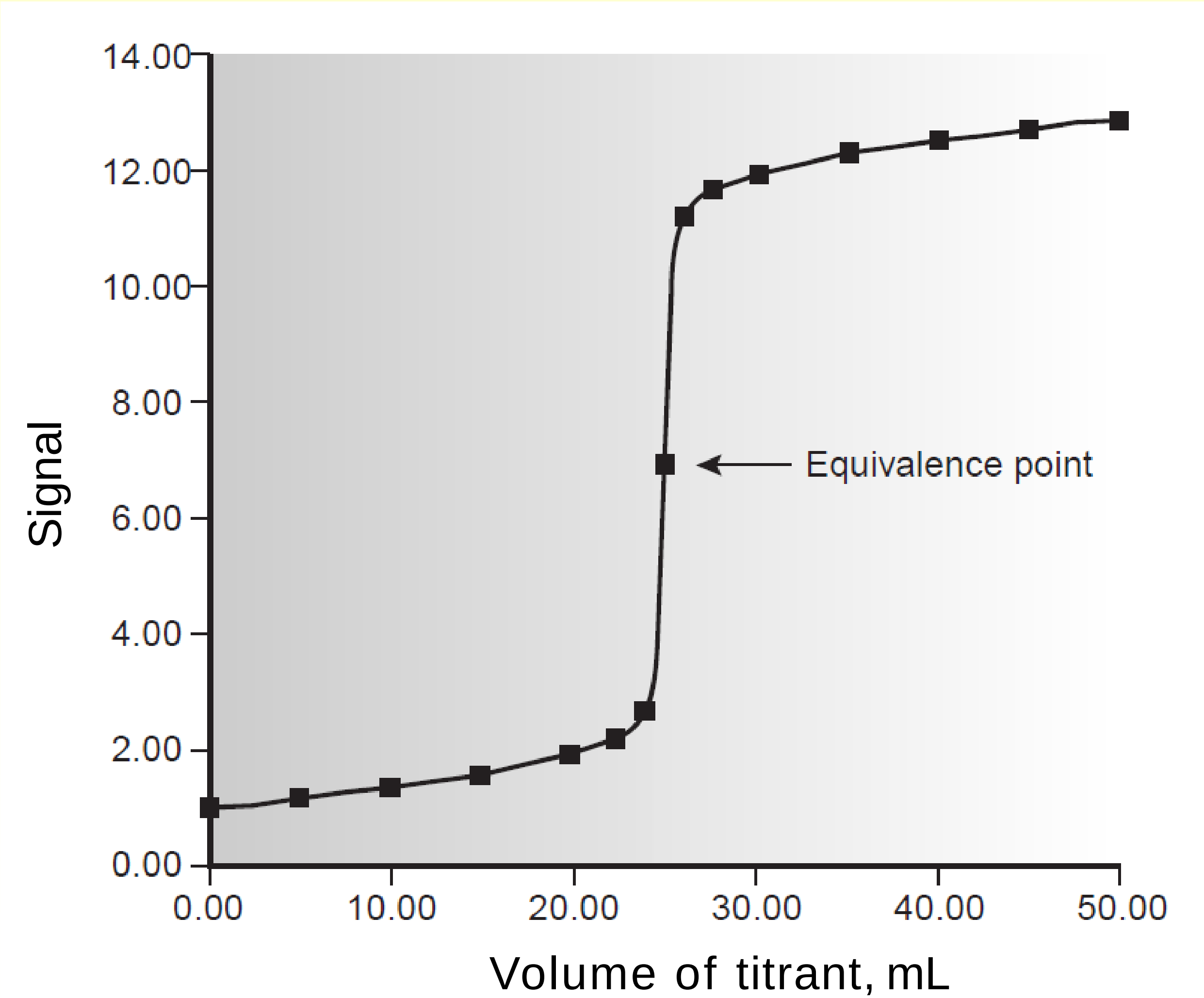


Table 9.1 Specifications for Volumetric Burets

Volume (mL)	Class[a]	Subdivision (mL)	Tolerance (mL)
5	A	0.01	±0.01
	B	0.01	±0.02
10	A	0.02	±0.02
	B	0.02	±0.04
25	A	0.1	±0.03
	B	0.1	±0.06
50	A	0.1	±0.05
	B	0.1	±0.10
100	A	0.2	±0.10
	B	0.2	±0.20

[a]Specifications for class A and class B glassware are taken from American Society for Testing Materials (ASTM) E288, E542, and E694 standards.

Titration curve



Reactions in titrimetry

Acid-base

Redox

Complexation

Precipitation

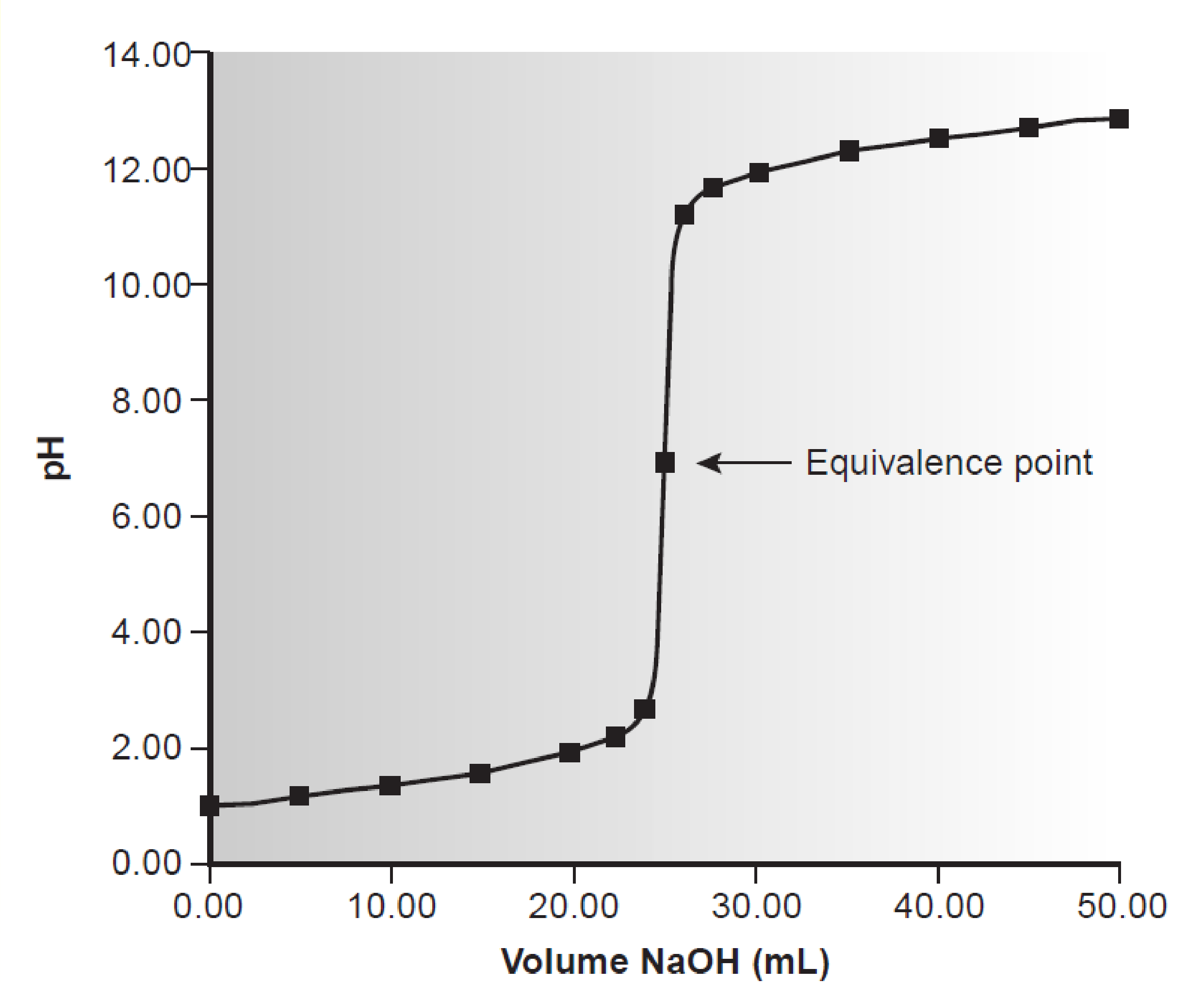
Acids-Base Titrimetry

$$H^{+} + OH^{-} \rightarrow H_2O$$

Acid is titrated by base
or
Base is titrated by acid

During acid-base titration, pH slowly changes;
At equivalence point pH rapidly changes.

Acid-base titration curve



pH during titration of strong acid

$$H^+ + OH^- \leftrightarrow H_2O$$

Before equivalence point:

$pH = -\log[H^+] = -\log[\text{unreacted HCl}]$

After equivalence point:

$pH = 14 + \log[OH^-] = 14 + \log[\text{excess NaOH}]$

At equivalence point:

$[H^+] \times [OH^-] = 10^{-14}$; $[H^+] = [OH^-] = 10^{-7}$

$pH = 7$

Table 9.2 Data for Titration of 50.00 mL of 0.100 M HCl with 0.0500 M NaOH

Volume (mL) of Titrant	pH
0.00	1.00
5.00	1.14
10.00	1.30
15.00	1.51
20.00	1.85
22.00	2.08
24.00	2.57
25.00	7.00
26.00	11.42
28.00	11.89
30.00	12.50
35.00	12.37
40.00	12.52
45.00	12.62
50.00	12.70

pH during titration of weak acid by strong base

Before titration

$$HAc \leftrightarrow H^{+} + Ac^{-}$$

$$K_A = \frac{[H^{+}] \times [Ac^{-}]}{[HAc]} = \frac{[H^{+}] \times [H^{+}]}{C_0 - [H^{+}]} = 1.75 \times 10^{-5}$$

For most weak acids: $[H^{+}] = \sqrt{K_a C_0}$

if $C_0 = 0.1M$, $[H^{+}] = 1.32 \times 10^{-3}$;

$pH = -\log [H^{+}] = 2.88$

Before an equivalence point

$$HAc + OH^- \rightarrow Ac^- + H_2O$$

immediately reacted

immediately formed

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} \rightarrow [H^+] = \frac{K_a[HAc]}{[Ac^-]}$$

$$pH = pK_a + \log \frac{[Ac^-]}{[HAc]}$$

$$[HAc] = \frac{moles\ of\ unreacted\ HAc}{total\ volume} = \frac{C_A \times V_A - C_B \times V_b}{V_A + V_B}$$

$$[Ac^-] = \frac{moles\ of\ NaOH\ added}{total\ volume} = \frac{C_B \times V_b}{V_A + V_B}$$

$$pH = pK_a + \log \frac{moles\ of\ NaOH\ added}{moles\ of\ unreacted\ HAc}$$

At and after equivalence point

$$Ac^- + H_2O \leftrightarrow HAc + OH^-$$

$$K_b = \frac{[HAc] \times [OH^-]}{[Ac^-]} = \frac{[OH^-] \times [OH^-]}{\frac{C_0 \times V_A}{V_A + V_B} - [OH^-]}$$

$$K_b = \frac{[HAc] \times [OH^-]}{[Ac^-]} = \frac{[HAc][OH^-][H^+]}{[Ac^-][H^+]} = \frac{K_w}{K_a} = \frac{10^{-14}}{1.75 \times 10^{-5}} = 5.71 \times 10^{-10}$$

$$For\ most\ weak\ bases:\ [OH^-] = \sqrt{K_b C_0}$$

After an equivalence point, pH will correspond to the concentration of excess NaOH.

$$[OH^-] = \frac{C_A \times V_A - C_B \times V_B}{V_A + V_B}$$

Table 9.3 Data for Titration of 50.0 mL of 0.100 M Acetic Acid with 0.100 M NaOH

Volume of NaOH (mL)	pH
0.00	2.88
5.00	3.81
10.00	4.16
15.00	4.39
20.00	4.58
25.00	4.76
30.00	4.94
35.00	5.13
40.00	5.36
45.00	5.71
48.00	6.14
50.00	8.73
52.00	11.29
55.00	11.68
60.00	11.96
65.00	12.12
70.00	12.22
75.00	12.30
80.00	12.36
85.00	12.41
90.00	12.46
95.00	12.49
100.00	12.52

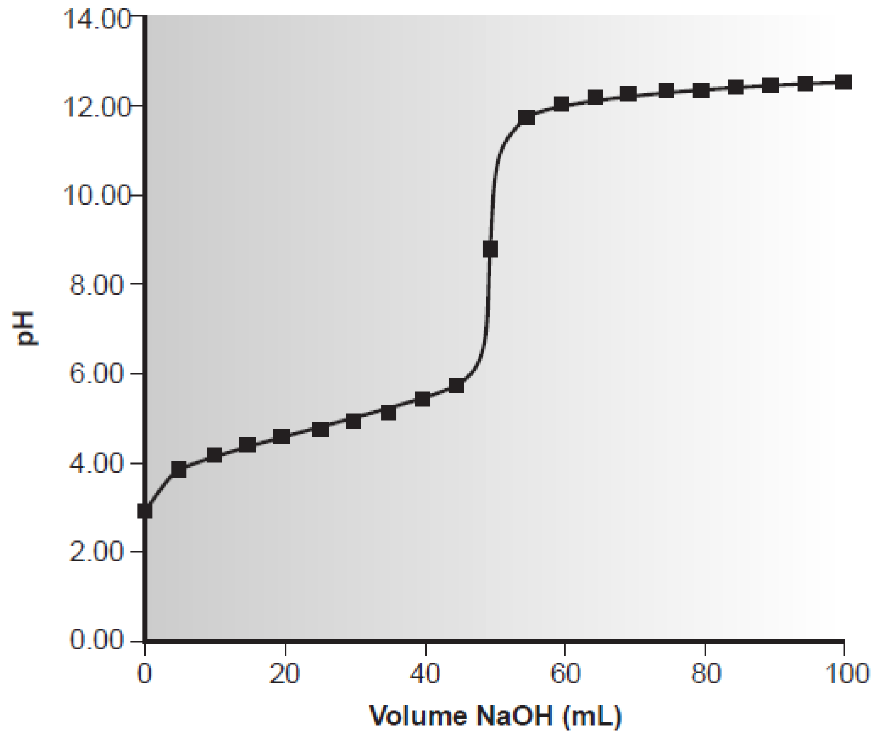


Figure 9.6
Titration curve for 50.0 mL of 0.100 M acetic acid ($pK_a = 4.76$) with 0.100 M NaOH.

pH during titration of weak base by strong acid

Before titration

$$NH_4OH \leftrightarrow NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+] \times [OH^-]}{[NH_4OH]} = \frac{[OH^-] \times [OH^-]}{C_0 - [OH^-]} = 1.76 \times 10^{-5}$$

$$For\ most\ weak\ bases:\ [OH^-] = \sqrt{K_b C_0}$$

if C_0 = 0.1M, $[OH^-] = 1.32 \times 10^{-3}$;

pOH = - log $[OH^-]$ = 2.88

pH = 14 – pH = 11.12

Before an equivalence point

$$NH_4OH + H^+ \leftrightarrow NH_4^+ + H_2O$$

immediately reacted

immediately formed

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} \quad \rightarrow \quad [OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]}$$

$$\mathrm{pOH} = \mathrm{pK_b} + \log\frac{[NH_4^+]}{[NH_4\mathrm{OH}]} \quad \rightarrow \quad \mathrm{pH} = 14 - \mathrm{pK_b} + \log\frac{[NH_4\mathrm{OH}]}{[NH_4^+]}$$

$$[NH_4OH] = \frac{moles\ of\ unreacted\ NH_4OH}{total\ volume} = \frac{C_A \times V_A - C_B \times V_B}{V_A + V_B}$$

$$[NH_4^+] = \frac{moles\ of\ HCl\ added}{total\ volume} = \frac{C_B \times V_B}{V_A + V_B}$$

$$\mathrm{pH} = 14 - \mathrm{pK_b} + \log\frac{moles\ of\ unreacted\ NH_4OH}{moles\ of\ HCl\ added}$$

At and after equivalence point

$$NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+$$

$$K_a = \frac{[NH_4OH] \times [H^+]}{[NH_4^+]} = \frac{[H^+] \times [H^+]}{\frac{C_0 \times V_A}{V_A + V_B} - [H^+]}$$

$$K_a = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{[NH_4OH]\,[H^+]\,[OH^-]}{[NH_4^+]\,[OH^-]} = \frac{K_w}{K_b} = \frac{10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}$$

$$For\ most\ weak\ acids:\ [H^+] = \sqrt{K_a C_0}$$

After equivalence point, pH will correspond to the concentration of excess HCl.

$$[H^+] = \frac{C_A \times V_A - C_B \times V_B}{V_A + V_B}$$

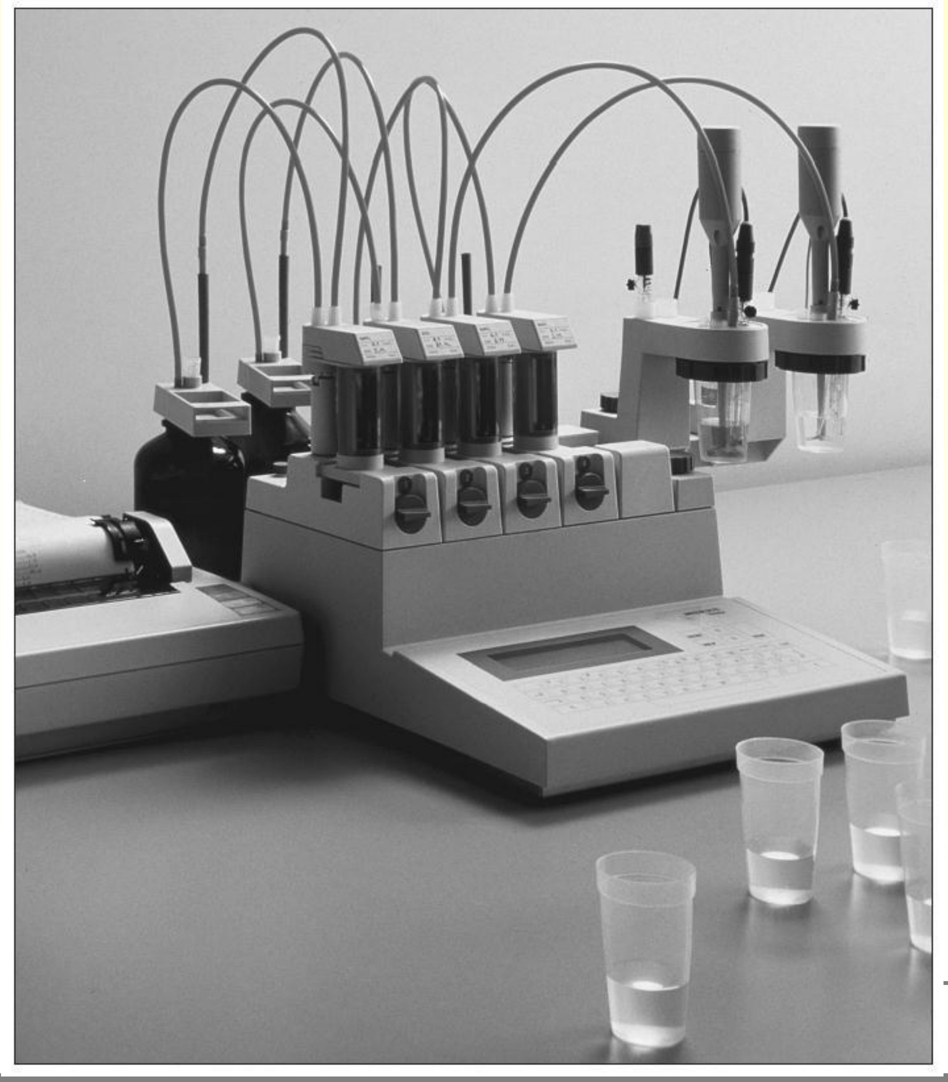
Table 9.4 Properties of Selected Indicators, Mixed Indicators, and Screened Indicators for Acid–Base Titrations

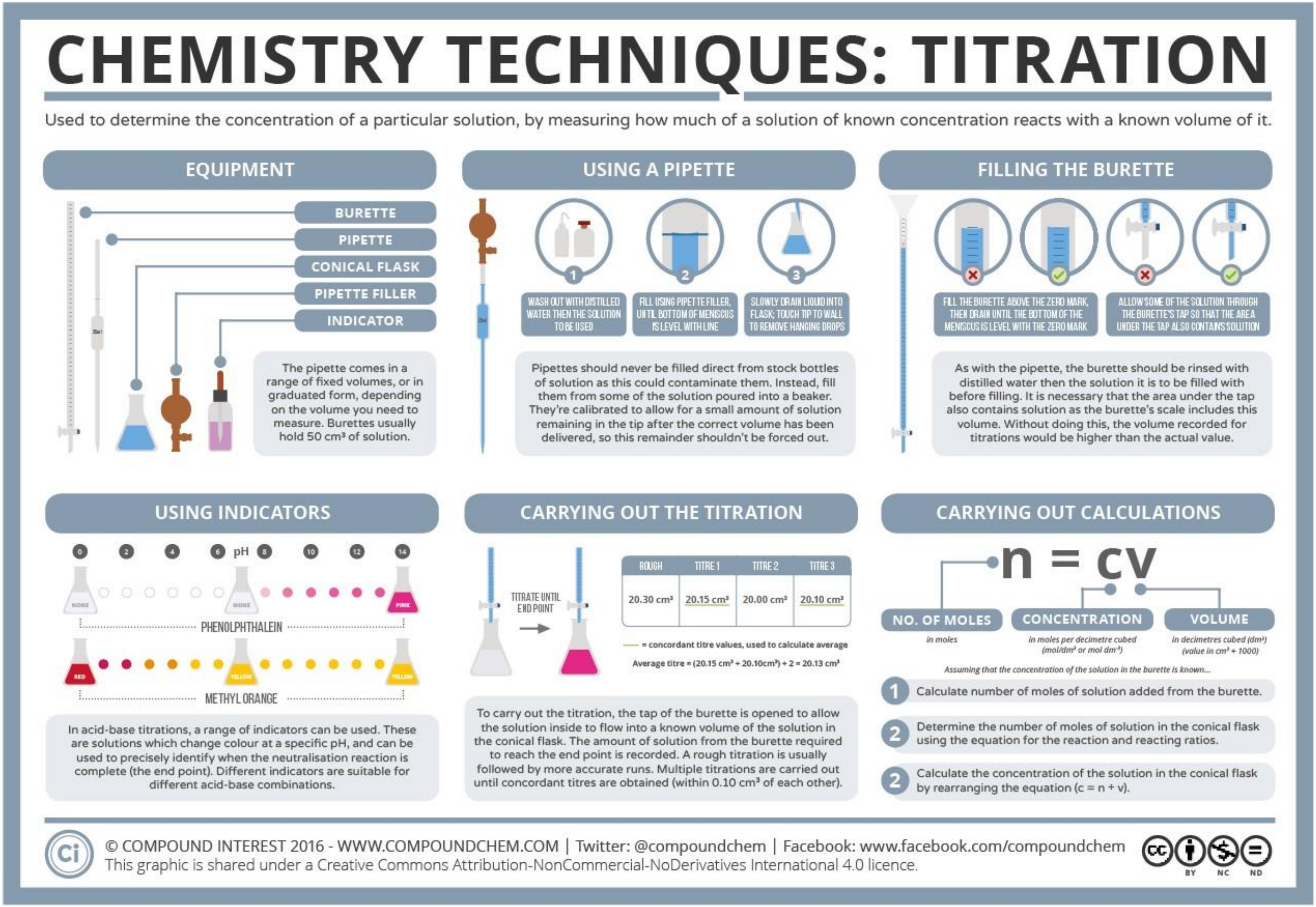
Indicator	Acid Color	Base Color	pH Range	pK_a
cresol red	red	yellow	0.2–1.8	—
thymol blue	red	yellow	1.2–2.8	1.7
bromophenol blue	yellow	blue	3.0–4.6	4.1
methyl orange	red	orange	3.1–4.4	3.7
Congo red	blue	red	3.0–5.0	—
bromocresol green	yellow	blue	3.8–5.4	4.7
methyl red	red	yellow	4.2–6.3	5.0
bromocresol purple	yellow	purple	5.2–6.8	6.1
litmus	red	blue	5.0–8.0	—
bromothymol blue	yellow	blue	6.0–7.6	7.1
phenol red	yellow	red	6.8–8.4	7.8
cresol red	yellow	red	7.2–8.8	8.2
thymol blue	yellow	blue	8.0–9.6	8.9
phenolphthalein	colorless	red	8.3–10.0	9.6
alizarin yellow R	yellow	orange/red	10.1–12.0	—

Mixed Indicator	Acid Color	Base Color	pH Range
bromocresol green and methyl orange	orange	blue-green	3.5–4.3
bromocresol green and chlorophenol red	yellow-green	blue-violet	5.4–6.2
bromothymol blue and phenol red	yellow	violet	7.2–7.6

Screened Indicator	Acid Color	Base Color	pH Range
dimethyl yellow and methylene blue	blue-violet	green	3.2–3.4
methyl red and methylene blue	red-violet	green	5.2–5.6
neutral red and methylene blue	violet-blue	green	6.8–7.3

Autotitrator




CHEMISTRY TECHNIQUES: TITRATION
Used to determine the concentration of a particular solution, by measuring how much of a solution of known concentration reacts with a known volume of it.
EQUIPMENT
BURETTE
PIPETTE
CONICAL FLASK
PIPETTE FILLER
INDICATOR
The pipette comes in a range of fixed volumes, or in graduated form, depending on the volume you need to measure. Burettes usually hold 50 cm³ of solution.
USING A PIPETTE
1 WASH OUT WITH DISTILLED WATER THEN THE SOLUTION TO BE USED
2 FILL USING PIPETTE FILLER, UNTIL BOTTOM OF MENISCUS IS LEVEL WITH LINE
3 SLOWLY DRAIN LIQUID INTO FLASK; TOUCH TIP TO WALL TO REMOVE HANGING DROPS
Pipettes should never be filled direct from stock bottles of solution as this could contaminate them. Instead, fill them from some of the solution poured into a beaker. They're calibrated to allow for a small amount of solution remaining in the tip after the correct volume has been delivered, so this remainder shouldn't be forced out.
FILLING THE BURETTE
FILL THE BURETTE ABOVE THE ZERO MARK, THEN DRAIN UNTIL THE BOTTOM OF THE MENISCUS IS LEVEL WITH THE ZERO MARK
ALLOW SOME OF THE SOLUTION THROUGH THE BURETTE'S TAP SO THAT THE AREA UNDER THE TAP ALSO CONTAINS SOLUTION
As with the pipette, the burette should be rinsed with distilled water then the solution it is to be filled with before filling. It is necessary that the area under the tap also contains solution as the burette's scale includes this volume. Without doing this, the volume recorded for titrations would be higher than the actual value.
USING INDICATORS
0 2 4 6 pH 8 10 12 14
NONE
NONE
PINK
PHENOLPHTHALEIN
RED
YELLOW
YELLOW
METHYL ORANGE
In acid-base titrations, a range of indicators can be used. These are solutions which change colour at a specific pH, and can be used to precisely identify when the neutralisation reaction is complete (the end point). Different indicators are suitable for different acid-base combinations.
CARRYING OUT THE TITRATION
TITRATE UNTIL END POINT
ROUGH
TITRE 1
TITRE 2
TITRE 3
20.30 cm³
20.15 cm³
20.00 cm³
20.10 cm³
= concordant titre values, used to calculate average
Average titre = (20.15 cm³ + 20.10cm³) ÷ 2 = 20.13 cm³
To carry out the titration, the tap of the burette is opened to allow the solution inside to flow into a known volume of the solution in the conical flask. The amount of solution from the burette required to reach the end point is recorded. A rough titration is usually followed by more accurate runs. Multiple titrations are carried out until concordant titres are obtained (within 0.10 cm³ of each other).
CARRYING OUT CALCULATIONS
n = cv
NO. OF MOLES
in moles
CONCENTRATION
in moles per decimetre cubed (mol/dm³ or mol dm⁻³)
VOLUME
in decimetres cubed (dm³) (value in cm³ ÷ 1000)
Assuming that the concentration of the solution in the burette is known...
1 Calculate number of moles of solution added from the burette.
2 Determine the number of moles of solution in the conical flask using the equation for the reaction and reacting ratios.
2 Calculate the concentration of the solution in the conical flask by rearranging the equation (c = n ÷ v).
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