Fundamentals of Analytical Chemistry

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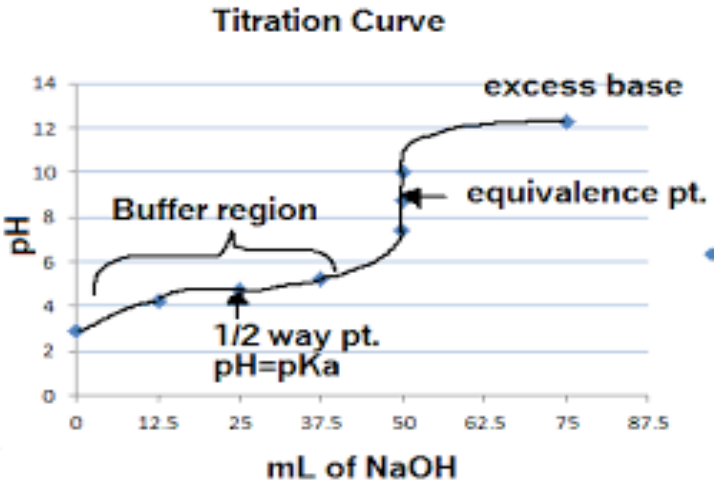
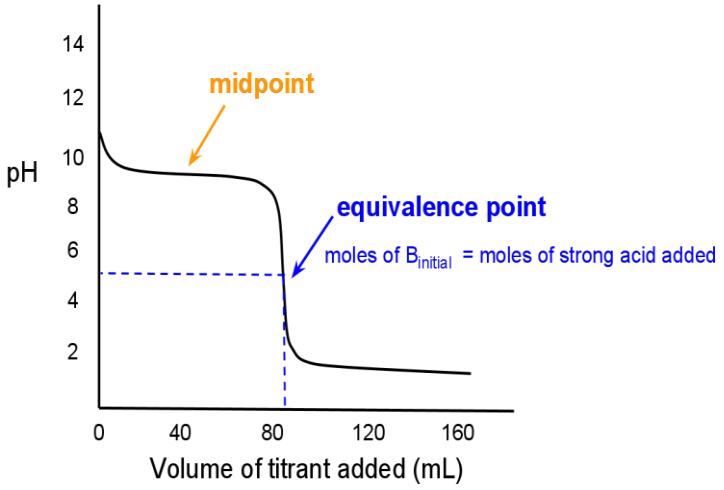
Titrating a Strong Base with a weak Acid

$CH_3COOH + NaOH \longrightarrow NaCl + H_2O$



Titration Curves for Weak Bases

$NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$



Christine Chang

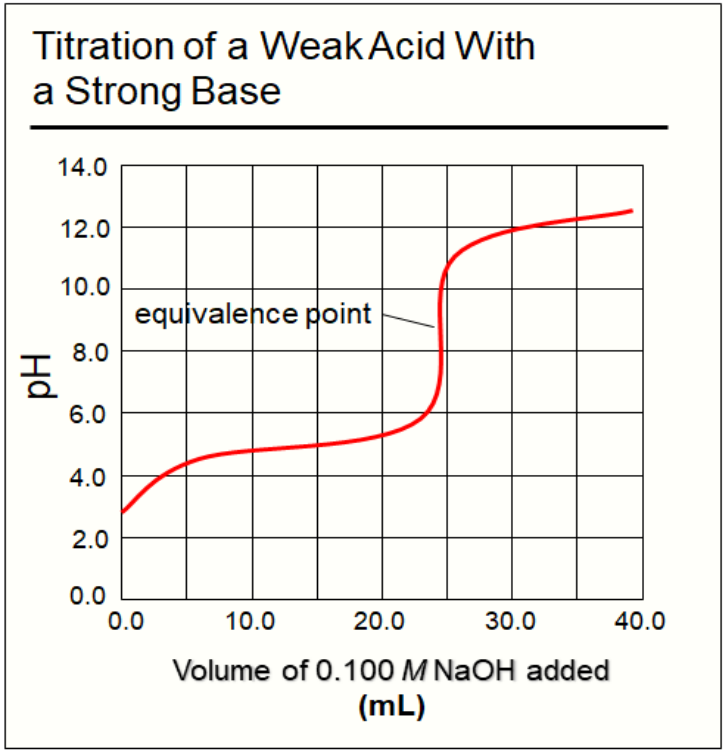
Titration Curves for Weak Acids

Buffer Solutions

Buffer: a mixture of a **weak acid** and its **conjugate base** or a **weak base** and its **conjugate acid** that resists changes in pH of a solution

Titration Data

NaOH added (mL)	pH
0.00	2.89
5.00	4.14
10.00	4.57
12.50	4.74
15.00	4.92
20.00	5.35
24.00	6.12
25.00	8.72
26.00	11.30
30.00	11.96
40.00	12.36



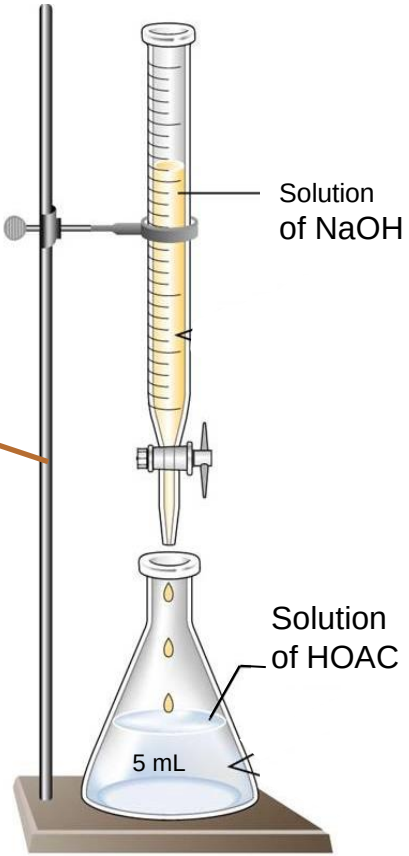
Titrating a Strong Base with a weak Acid

Titration curve for 50.00 mL of 0.1 M CH3COOH(HOAC) with 0.1 M NaOH

CH3COOH + NaOH → NaCl+H2O

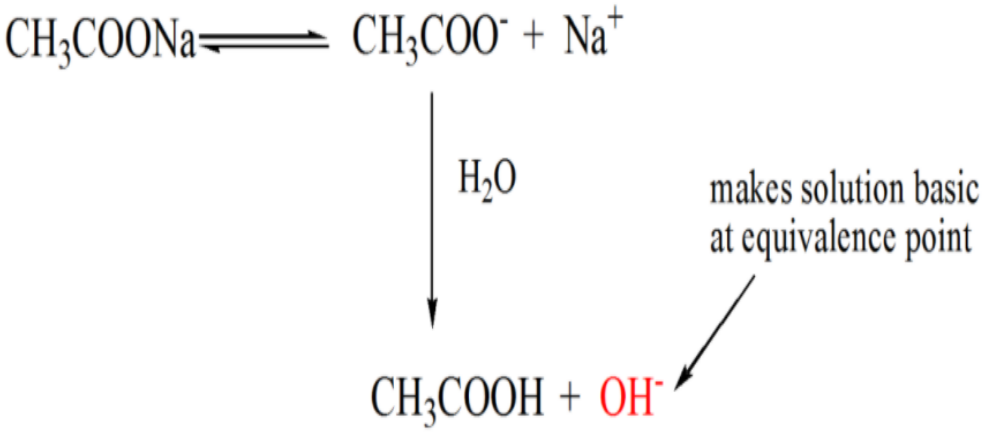
Analytic

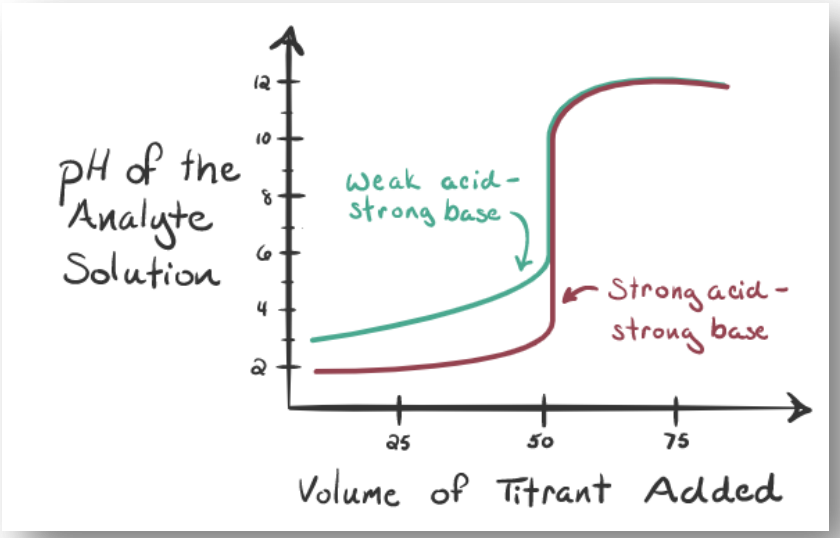
standard



Titration curves for weak acid v strong base

- At the equivalence point the solution contains **CH3COONa.**
- This dissociates into acetate ions **CH3COO-** and Na+ .
- **CH3COO-** is the conjugate base of the weak acid **CH3COOH .**
- **CH3COO-** is strong base is reacted with water to form wake acid **(CH3COOH)** and **OH-** ion as strong conjugate base .
- thus increasing the **pH to ~ 9** at the equivalence point.





Generate a curve for the titration of 50 mL of 0.1 M acetic acid (HOAc) with 0.1 M sodium hydroxide at 25°C (10,25,49,50,50.10 . Ka $=1.7 \times 10^{-5}$

1. Initial Point:

$[H_3O^+] = \sqrt{K_a C_a}$, $[H_3O^+] = \sqrt{1.7 \times 10^{-5} \times 0.1}$, $[H_3O^+] = 1.32 \times 10^{-3}$

pH = -Log$[H_3O^+]$, **pH = -log** (1.32×10^{-3}) , **pH= 2.88**

2- Preequivalence Point(after addition of 10 mL reagent)

C_{HOAC} = mmol remaining (original mmol HOAC – mmol NaOH added)

total volume (mL)

C_{HOAC} = 50 M x 0.1 ml – 0.1 M x 10 ml)

(50 ml+ 10 ml)

C_{HOAC} = **0.067 M**

C_{NaOAC} = mmol NaOH added

total volume (mL)

$C_{NaOAC} = \frac{10 \text{ ml} \times 0.1 \text{ M}}{60 \text{ ml}}$

C_{NaOAC} = 0.016 M

pH= pKa + log $\frac{[NaOAC]}{[HOAC]}$, Ka = $\frac{[H3O+]\ [OAC-]}{[HOAC]}$, pH = 4.76 + log $\frac{0.016}{0.067}$, pH= 4.15

3- Equivalence Point

- all of the acetic acid has been converted to sodium acetate.
- The solution is, therefore, similar to one formed by dissolving NaOAc in water.

$$NaOAC + H_2O \rightleftharpoons HOAC + OH^-$$

$$K_b = \frac{[HOAC]\,[OH^-]}{[OAC^-]} \Longrightarrow \frac{K_w}{K_a} = \frac{[HOAC]\,[OH^-]}{[OAC^-]}$$

suppose : $[HOAC] = [OH^-]$

from C_{NaOAC} = mmol NaOH added / total volume (mL)

$$C_{NaOAC} = \frac{50\ ml \times 0.1\ M}{100 ml}$$

$$C_{NaOAC} = 0.05\ M \Longrightarrow [OAC^-] = 0.05$$

$$\frac{1\times 10^{-14}}{1.7\times 10^{-5}} = \frac{[OH^-]^2}{[OAC^-]} \Longrightarrow 5.71 \times 10^{-6} = \frac{[OH^-]^2}{[OAC^-]}$$

$$[OH^-] = \sqrt{[OAC^-]K_b} \Longrightarrow [OH^-] = \sqrt{0.05 \times 5.71 \times 10^{-6}} \Longrightarrow [OH^-] = 5.3 \times 10^{-6}$$

4-Postequivalence Point

(after addition of 50.10 mL reagent)

$$C_{NaOHl} = \frac{\text{mmol NaOH added – original mmol HOAC}}{\text{total volume solution}}$$

$$= \frac{(50.10\ mL \times 0.1\ M) - (50.00\ mL \times 0.1\ M)}{50.0\ mL + 50.10\ mL}$$

C_{NaOH} = **0.000099 M**

pOH = **-log(0.000099)**

pOH = 4.00

pH + pOH =14

pH= 14- pOH

pH= 14- 4

pH = 10

Titration Data

NaOH added (mL)	pH
0.00	2.88
5.00	----
10.00	4.15
25.00	------
49.00	------
50.00	8.73
50.10	10.00
60.00	-------

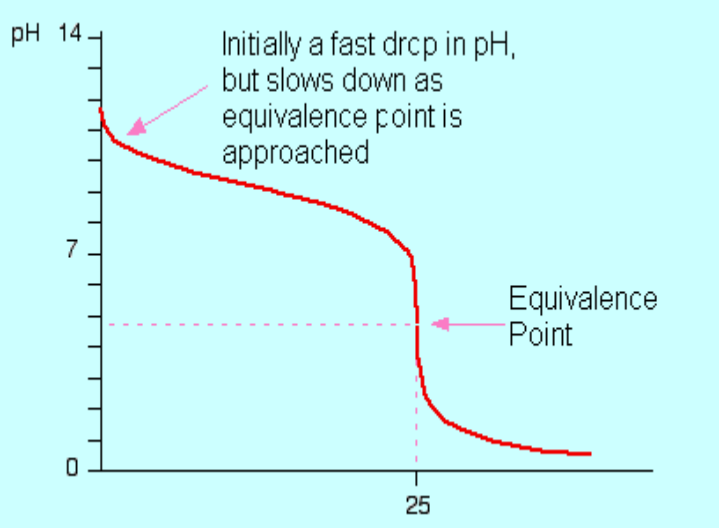
Titration of a weak base with a strong acid

- A depiction of the pH change during a titration of HCl solution into an ammonia solution.

$$NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$$

- The curve depicts the change in pH vs. the volume of HCl added in mL.
- the pH at the equivalence point is not 7 but below it. This is due to the production of a conjugate acid during the titration; it will react with water to produce hydronium (H_3O^+) ions.
- In the example of the titration of **HCl** into **ammonia** solution, the **conjugate acid** formed (**NH_4^+**) reacts as follows:

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$$

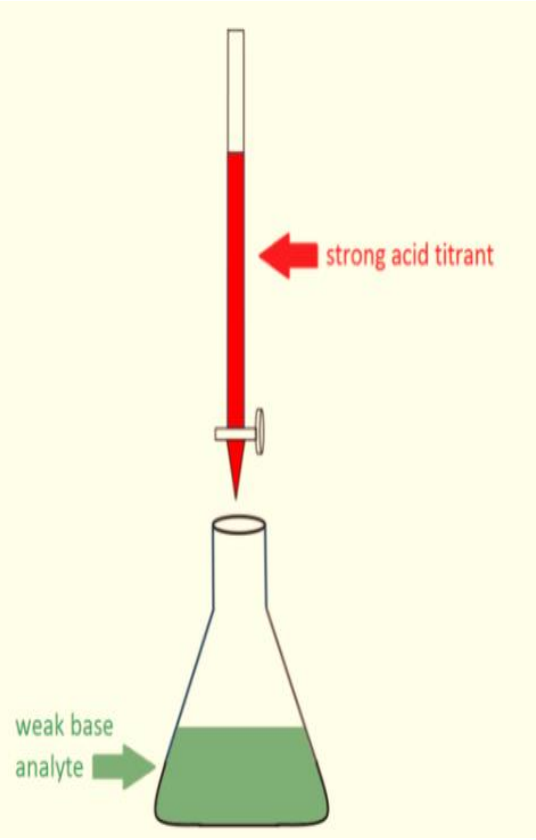


Titration Curves for Weak Bases

50. mL aliquot of 0.05 M NaCN (K_a for HCN = 6.2 * 10-10) is titrated with 0.1 M HCl. The reaction is

$$CN^- + H_3O^+ \rightleftharpoons HCN + H_2O$$

Calculate the pH after the addition of (a) 0.00, (b) 10.00, (c) 25.00, and (d) 26.00 mL of acid.



1. Initial Point: Before adding any volume from burette.

$$CN^- + H_2O \rightleftharpoons HCN + OH^-$$

Water=conjugate acid
Hydroxide = conjugate base

This is the conjugated acid of the base that you are titrating

This is the base analytic that you are titrating

Reactants	CN-	H2O	HCN	OH-
Initial	0.05 M	---	0	0
Change	-X	---	+X	+X
Equilibrium	0.05- X	---	X	X

$$K_b = \frac{[OH^-][HCN]}{[CN^-]}$$

$$K_b = \frac{K_w}{K_a} \longrightarrow K_b = \frac{1 \times 10^{-14}}{6.2 \times 10^{-10}}$$

Suppose : $[OH^-] = [HCN]$

$[CN^-]$ = NaCN = 0.05

$$[OH^-] = \sqrt{K_b \, C_{NaCN}}$$

$$[OH^-] = \sqrt{1.61 \times 10^{-5} \times 0.05}$$

$$[OH^-] = 8.97 \times 10^{-4}$$

pOH = -log $[OH^-]$

pOH = -log 8.97×10^{-4}

pOH= 3.05

pH= 14-pOH

pH= 14-3.05

pH= 10.95

2- Preequivalence Point(after addition of 10 mL reagent)

C_{NaCN} = original mmol NaCN – mmol HCl added)

total volume (mL)

C_{NaCN} = 50 M x 0.05 ml – 0.1 M x 10 ml)

(50 ml+ 10 ml)

C_{NaCN} = 0.025 M

C_{HCN} = mmol HCladded

total volume (mL)

$C_{HCN} = \frac{10\ ml \times 0.1\ M}{60\ ml}$

C_{HCN} = 0.016 M

$pH = pKa + \log \frac{[NaCN]}{[HCN]}$,

$Ka = \frac{[H3O+]\ [CN-]}{[HCN]}$,

$pH = 9.208 + \log \frac{0.025}{0.016}$,

pH= 9.4

3- Equivalence Point

- all of the NaCN has been converted to HCN.

$Ka = \frac{[H3O+]\ [CN-]}{[HCN]}$

suppose : $[H3O+] = [CN^-]$

from C_{HCN} = mmol HCL added

total volume (mL)

$C_{HCN} = \frac{25\ ml \times 0.1\ M}{25+50\ ml} = 0.033M$

$[H3O^+] = \sqrt{[HCN]K_a}$

$[H3O^+] = \sqrt{0.033 \times 6.2 \times 10^{-10}}$

$[H3O^+] = 1.32 \times 10^{-3}$

$pH = -\log (1.32 \times 10^{-3})$

pH= 5.34

4-Postequivalence Point

(after addition of 26.00 mL reagent)

$$C_{HCl} = \frac{\text{mmol HCl added} - \text{original mmol NaCN}}{\text{total volume solution}}$$

$$= \frac{(26.00\ \text{mL} \times 0.1\ \text{M}) - (50.00\ \text{mL} \times 0.05\ \text{M})}{50.0\ \text{mL} + 26.00\ \text{mL}}$$

$$[H_3O^+]C_{HCl} = 1.32 \times 10^{-3}\ \text{M}$$

$$\text{pH} = -\log(1.32 \times 10^{-3})$$

$$\text{pH} = 2.88$$

Titration Data

HCl added (mL)	pH
0.00	10.95
10.00	9.4
25.00	5.34
26.00	2.88