Fundamentals of Analytical Chemistry

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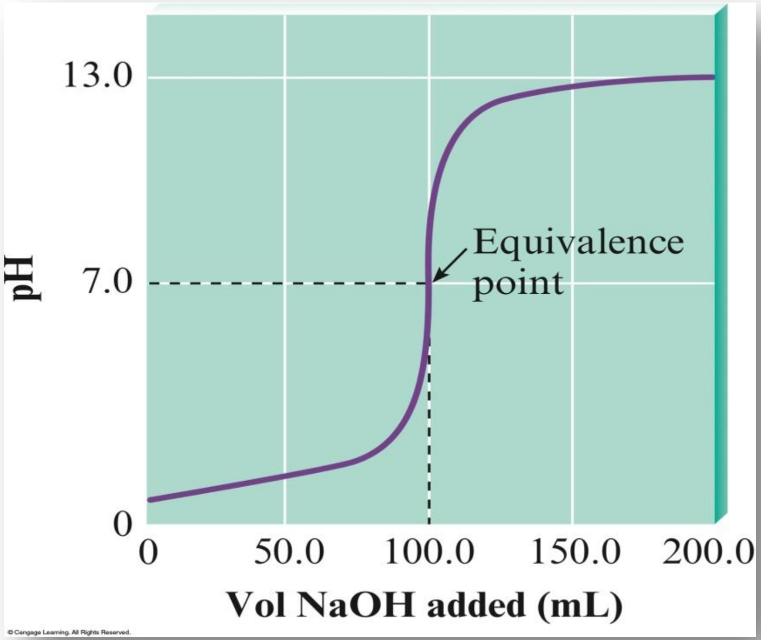
Titration Curve

- A **titration curve** is a plot of pH vs. the amount of titrant volume of titrant added.
- Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.

Features of the Strong Acid-Strong Base Titration Curve

$HCl + NaOH \rightarrow H2O + NaCl$

1. **The pH starts out low, reflecting the high $[H_3O^+]$ of the strong acid and increases gradually as acid is neutralized by the added base.**
2. **Suddenly the pH rises steeply. This occurs in the immediate vicinity of the equivalence point. For this type of titration the pH is 7.0 at the equivalence point.**
3. **Beyond this steep portion, the pH increases slowly as more base is added.**



Titration Curve

- A **titration curve** is a plot of pH vs. the amount of titrant volume of titrant added.
- Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.

Graph of How pH changes as Titrant is Added

- **Assume**
- strong acid and base completely dissociate
- *Any amount of H^+ added will consume a stoichiometric amount of OH^-*

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

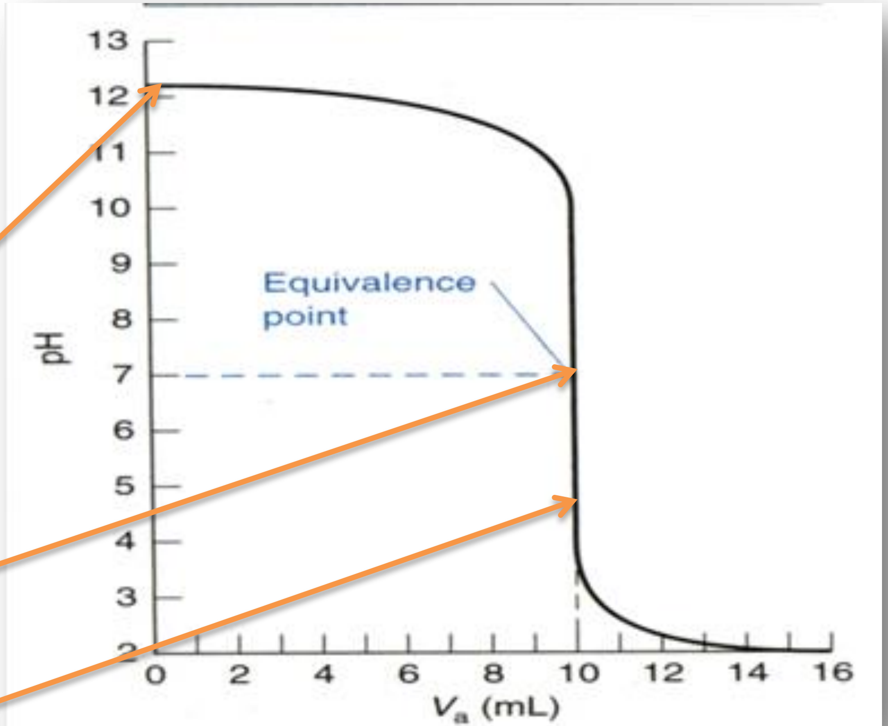
- Reaction Assumed to go to completion

-_Preequivalence or Before the equivalence point, the pH is determined by excess OH- in the solution

-At the equivalence point, H^+ is just sufficient to react with all OH^- to make H_2O

-Postequivalence or After the equivalence point, pH is determined by excess H^+ in the solution.

$$HCl + NaOH \longrightarrow H_2O + NaCl$$



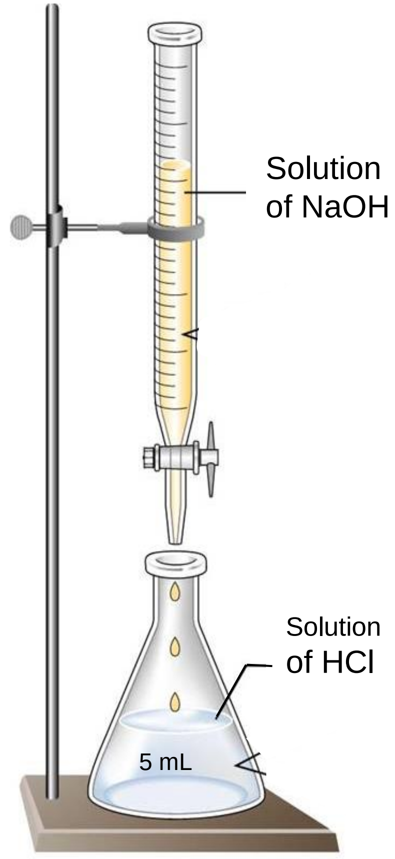
Sample Calculation: Strong Acid-Strong Base Titration Curve

Titration curve for 50.00 mL of 0.02 M HCl with 0.1 M NaOH

HCl + NaOH → NaCl+H2O

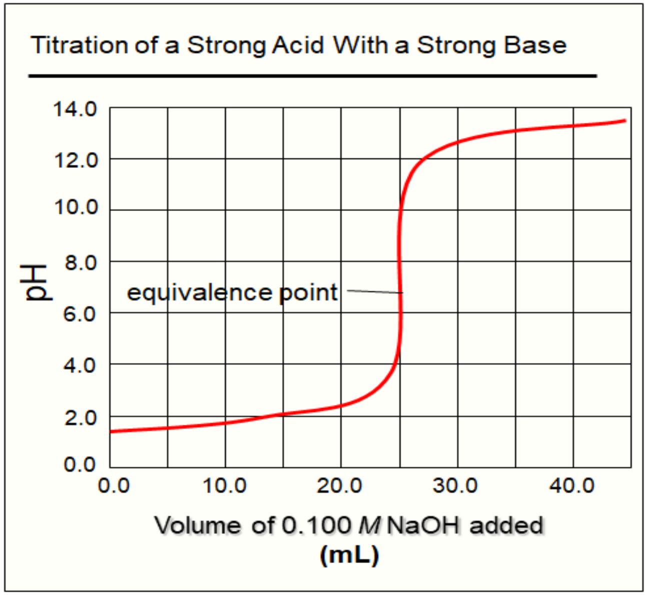
Analytic

standard



Before the Equivalence Point

1- **Before the equivalence point, we calculate the pH from the molar concentration of unreacted acid.**
2- strong acid is complete dissociation in water

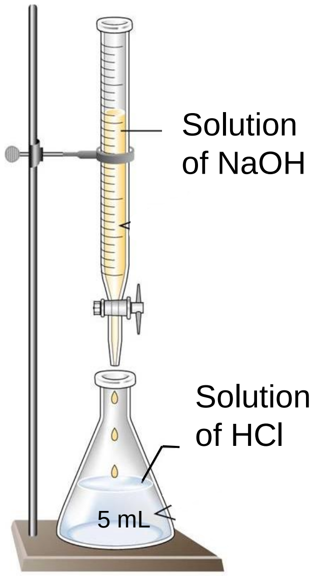


1. Initial Point:

the solution is X M in H_3O^+, pH = -log(H+)

Preequivalence Point (after addition of 10 mL reagent)

$$C_{HCl} = \frac{\text{mmol remaining (original mmol HCl – mmol NaOH added)}}{\text{total volume (mL)}}$$



Equivalence Point

$[OH^-] = [H_3O^+]$, pH = 7

Postequivalence Point (after addition of 25.10 mL reagent)

$$C_{NaOH} = \frac{\text{mmol NaOH added – original mmol HCl}}{\text{total volume solution}}$$, pH= 14-pOH

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Titration curve for 50.00 mL of 0.02 M HCl with 0.1 M NaOH , when added 4, 8 , 10, 12 ml from NaOH , Find the

HCl + NaOH → NaCl+H2O

1. Initial Point:

the solution is 0.02 M in H_3O^+,

pH = -log(H+) , pH= -log (0.02) , pH= 1.7

2- Preequivalence Point

$$C_{HCl} = \frac{\text{mmol remaining (original mmol HCl – mmol NaOH added)}}{\text{total volume (mL)}}$$

(after addition of 4 mL reagent)

$$C_{HCl} = \frac{50\ ml \times 0.02\ M - 0.1\ M \times 4\ ml)}{(50\ ml + 4\ ml)}$$

C_{HCl} = 0.01 pH= -Log (0.01) , pH=2

(after addition of 8 mL reagent)

$$C_{HCl} = \frac{50\ ml \times 0.02\ M - 0.1\ M \times 8\ ml)}{(50\ ml + 8\ ml)}$$

C_{HCl} = 0.003 pH= -Log (0.003) , pH=2.5

3- Equivalence Point

$[OH^-] = [H_3O^+]$, pH = 7

4-Postequivalence Point

(after addition of 12.00 mL reagent)

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

$$= \frac{(12\text{ mL} \times 0.1\text{ M}) - (50.00\text{ mL} \times 0.02\text{ M})}{50.0\text{ mL} + 12\text{ mL}}$$

C_{NaOH} = **0.0032 M**

pOH = **-log(0.0032) = 2.49**

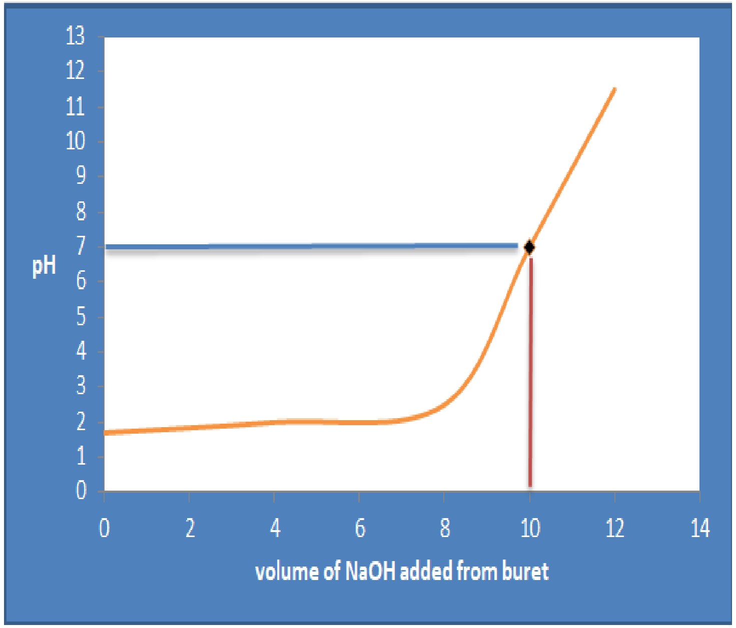
pH+pOH = 14

pH = 14 – pOH

pH = 14-2.49

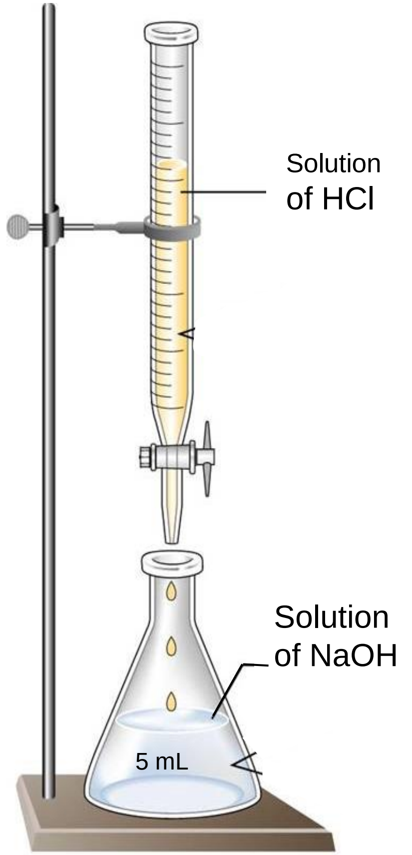
pH = 11.5

V NaOH(ml) added from buret	pH
0	1.7
4	2
8	2.5
10	7
12	11.5



Titrating a Strong Base with a Strong Acid

Titration curve for 50.00 mL of 0.05 M NaOH with 0.1 M HCl



HCl + NaOH → NaCl+H2O

standard (HCl)

Analytic (NaOH)

Before the Equivalence Point

1- Before the equivalence point, we calculate the pH from the molar concentration of unreacted acid.
2- strong base is complete dissociation in water

1. Initial Point: the solution is X M in H_3O^+, pOH = -log(OH-) , pOH + pH = 14 , pH= 14-pOH

Preequivalence Point

$$C_{NaOH} = \frac{\text{mmol remaining (original mmol NaOH – mmol HCl added)}}{\text{total volume (mL)}}$$

$$[H_3O^+] = \frac{[OH^-]}{K_w}$$

Equivalence Point

$[OH^-] = [H_3O^+]$, pH = 7

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Postequivalence Point

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

pH= -Log [H3O+]

Calculate the pH during the titration of 50 mL of 0.05 M NaOH with 0.1M HCl at 25°C after the addition of the following volumes of reagent: (a) 24.50 mL, (b) 25.00 mL, (c) 25.50 mL.

HCl + NaOH → NaCl+H2O

1. Initial Point:

pOH = -log(OH-) , pOH =-log (0.05) , pOH= 1.3

pOH + pH = 14 , pH= 14-pOH , pH= 14-1.3 , pH= 12.7

2- Preequivalence Point

$$C_{NaOH} = \frac{\text{mmol remaining (original mmol NaOH – mmol HCl added)}}{\text{total volume (mL)}}$$

(after addition of 24.5 mL reagent)

$$C_{NaOH} = \frac{50\ M \times 0.05\ ml – 0.1\ M \times 24.5\ ml)}{(50\ ml + 24.5\ ml)}$$

C_{NaOH} = 0.00067 pOH= -Log (0.00067) , pOH=3.1739

pH +pOH = 14 , pH= 14- 3.1739 , pH = 10.83

3- Equivalence Point , $[OH^-] = [H_3O^+]$, pH = 7

4-Postequivalence Point

(after addition of 25.5 mL reagent)

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

$$= \frac{(25.5\ mL \times 0.1\ M) - (50.00\ mL \times 0.05\ M)}{50.0\ mL + 25.5\ mL}$$

C_{HCl} = **0.00066 M**

pH = **-log(0.00066)**

pH = 3.18

V HCl (ml) added from buret	pH
0	12.7
24.5	10.83
25	7
25.5	3.18