

Chapter 5: strong acid-strong base; pH-metric titration.

- **Conjugate acid/base pair:** acid/ its conjugate base
- **Aqueous solution:** A solution that contains water.

- **Auto ionization of water:**



Ion product constant of water: $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

$K_w = 10^{-14}$ at $T = 25^\circ\text{C}$; $\text{p}K_w = -\log K_w$; $K_w = 10^{-\text{p}K_w}$; At $T=25^\circ\text{C}$ $\text{p}K_w = 14$

As temperature increases, K_w increases \Rightarrow the auto ionization of water is endothermic.

Acid-base pairs involved: $\text{H}_2\text{O}/\text{OH}^-$; $\text{H}_3\text{O}^+/\text{H}_2\text{O}$

Water is said to be amphoteric (Amphoteric means a substance that can act as acid or base).

- **pH** measures the acidity of the medium; $\text{pH} = -\log [\text{H}_3\text{O}^+] = \text{p}K_w + \log [\text{OH}^-]$

At $T = 25^\circ\text{C}$; $\text{pH} = 14 + \log [\text{OH}^-]$

$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$; $[\text{OH}^-] = 10^{\text{pH}-\text{p}K_w}$

- **Nature of medium:**

Neutral $\Rightarrow [\text{H}_3\text{O}^+] = [\text{OH}^-] \Rightarrow [\text{H}_3\text{O}^+] = \sqrt{K_w}$; $\text{pH} = \frac{1}{2} \text{p}K_w$

Acidic $\Rightarrow [\text{H}_3\text{O}^+] > [\text{OH}^-] \Rightarrow [\text{H}_3\text{O}^+] > \sqrt{K_w}$; $\text{pH} < \frac{1}{2} \text{p}K_w$

As pH decreases, the acidity of the solution increases

Basic $\Rightarrow [\text{H}_3\text{O}^+] < [\text{OH}^-] \Rightarrow [\text{H}_3\text{O}^+] < \sqrt{K_w}$; $\text{pH} > \frac{1}{2} \text{p}K_w$

As pH increases, the basicity of the solution increases

- **Acid:** a substance that gives H_3O^+ when dissolves in water

- **Strong acid:** acid that dissociates completely in water to give H_3O^+

$[\text{H}_3\text{O}^+] = x = C_a$; Degree of conversion $\alpha (\text{HA}) = 1$

Dissociation equation	$\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$		
Initial	C_a	0	0
Final	0	C_a	C_a

Acid-base pairs involved: HA/A^- ; $\text{H}_3\text{O}^+/\text{H}_2\text{O}$

If a strong acid is diluted by 10^n times, then pH will increase by n

- **How to identify if an acid is strong or weak?**

Strong acid $\Rightarrow [\text{H}_3\text{O}^+] = C_a$ where $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

Or $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log C_a$

Weak acid $\Rightarrow [\text{H}_3\text{O}^+] < C_a$ where $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

Or $\text{pH} = -\log [\text{H}_3\text{O}^+] > -\log C_a$

If two acids have the same concentration, the stronger acid is the one that has lower pH.

- **Base:** a substance that gives OH^- or receives H^+ when dissolves in water
 - **Strong base:** base that dissociates completely in water to give OH^- or receives H^+

Dissociation equation	H_2O $\text{BOH} \rightarrow \text{B}^+ + \text{OH}^-$ $\text{B} + \text{H}_2\text{O} \rightarrow \text{BH}^+ + \text{OH}^-$		
Initial	C_b	0	0
Final	0	C_b	C_b

Acid-base pairs involved: B^+/BOH or BH^+/B ; $\text{H}_2\text{O}/\text{OH}^-$

$[\text{OH}^-] = x = C_b$; Degree of conversion $\alpha (\text{BOH}) = 1$

If a strong base is diluted by 10^n times, then pH will decrease by n

- **How to identify if a base is strong or weak?**

Strong base $\Rightarrow [\text{OH}^-] = C_b$ where $[\text{OH}^-] = 10^{\text{pH}-\text{pK}_w}$

Or $\text{pH} = \text{pK}_w + \log [\text{OH}^-] = \text{pK}_w + \log C_b$

Weak base $\Rightarrow [\text{OH}^-] < C_b$ where $[\text{OH}^-] = 10^{\text{pH}-\text{pK}_w}$

Or $\text{pH} = \text{pK}_w + \log [\text{OH}^-] < \text{pK}_w + \log C_b$

If two bases have the same concentration, the base that has higher pH is the stronger base.

- **Reaction of strong acid (H_3O^+) with strong base (OH^-)**



This reaction is called neutralization reaction

$$K_R = \frac{1}{[\text{H}_3\text{O}^+][\text{OH}^-]} = \frac{1}{K_w}$$

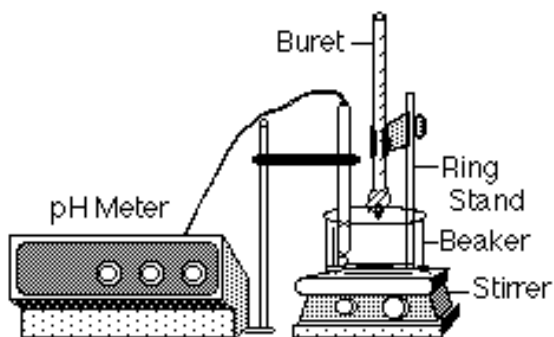
At $T=25^\circ\text{C}$ $K_R = 10^{14} \gg 10^4 \Rightarrow$ the reaction is quantitative and complete.

- **Strong acid – strong base pH-metric titration**

- **Materials:**

Graduated buret-stand-clamp-beaker-magnetic stirrer-magnetic bar-pH meter

- **pH-metric titration setup**



- **Procedure:**

- Calibrate pH-meter.
- Rinse the buret with distilled water and with the titrant.
- Fill the buret till 0.0 ml mark line.
- Rinse the volumetric pipet with distilled water and with the analyte.
- Place x ml of the analyte in the beaker using volumetric pipet (x ml) and pipet filler.
- Add 1 ml of the titrant and shake.
- Repeat this addition until the pH starts changes rapidly.
- Add drop by drop of the titrant and shake until the pH starts changes slowly.
 - **Why sometimes distilled water is added into the beaker before titration starts?** In order to immerse the pH-electrode.

- **Case 1: Analyte : strong acid Titrant : strong base**

Net ionic titration reaction: $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

Describing the curve:

The curve consists of three parts:

AB ($V_b = 0$ ml to 20 ml): pH increases slightly;

horizontal asymptote.

BC ($V_b = 20$ ml to 30 ml): pH increases sharply (jump).

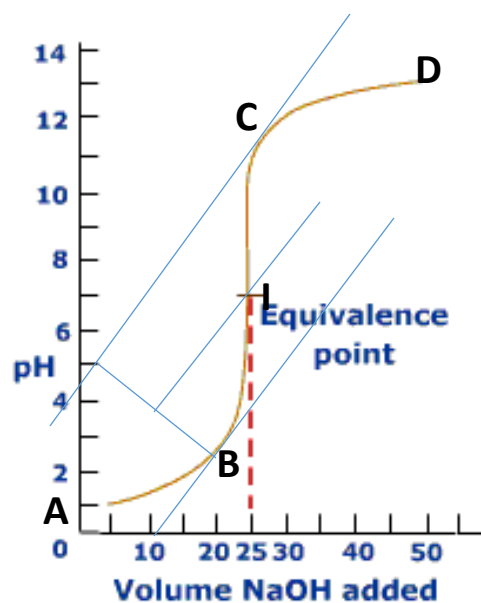
There is inflection point I ($V_b \text{Eq}$; pH eq).

CD ($V_b = 30$ ml to 50 ml): pH increases slightly;

horizontal asymptote.

Special points:

- ⇒ From A to I : acid is in excess
- ⇒ At I: acid is totally neutralized by the base according
- ⇒ to stoichiometric ratio. This point is called equivalence point.



Titration curve of strong acid (HCl) with a strong base (NaOH)

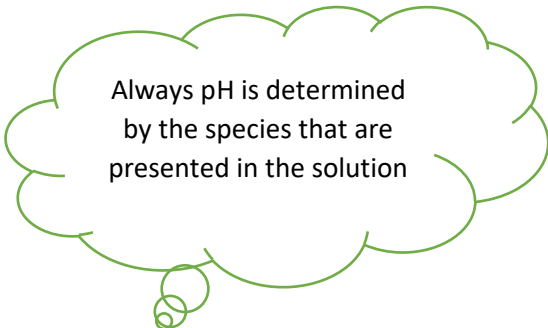
- ⇒ From I to D: base is in excess.
- ⇒ Initially $V_b = 0$ ml : $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log C_a$; (if no water was added)
 $[\text{H}_3\text{O}^+] = C_a$ (strong acid)

- ⇒ Equivalence point I: $\text{pH} = \frac{1}{2} \text{pK}_w = 7$ ($T = 25^\circ \text{C}$) \Rightarrow neutral
 The equivalence point is determined by parallel tangent method.

Species that are presented at equivalence: H_2O and spectator ions like Na^+ and Cl^-

The spectator ions have no effect pH

The medium is neutral due to the auto ionization of water which produces H_3O^+ and OH^- where $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}$
 $\Rightarrow \text{pH} = -\log [\text{H}_3\text{O}^+]$



Always pH is determined by the species that are presented in the solution

- ⇒ Adding excess strong base $\Rightarrow \text{pH} = 14 + \log [\text{OH}^-]$;
- ⇒ the asymptote tend to $\text{pH} = 14 + \log C_b$

Calculation:

At the equivalence point, according to stoichiometric ratio:

$n(\text{H}_3\text{O}^+)$ (initial in the beaker $V_a = \text{ml}$) = $n(\text{OH}^-)$ (added from buret at equivalence, V_b eq = ml)

$$\Rightarrow C_a V_a = C_b V_{b\text{Eq}}$$

- **Case 2: Analyte : strong base Titrant : strong acid**

Net ionic titration reaction: $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$

Describing the curve:

The curve consists of three parts:

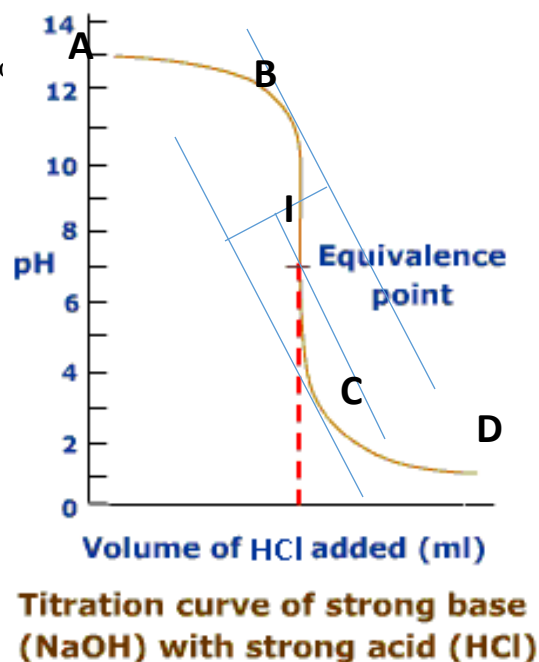
AB ($V_a = 0$ ml to x ml): pH decreases slightly; horizontal asymptote.

BC ($V_a = x$ ml to y ml): pH decreases sharply (jump). There is inflection point I (V_{aEq} ; pH eq).

CD ($V_a = y$ ml to z ml): pH decreases slightly; horizontal asymptote

Special points:

- ⇒ **From A to I :** base is in excess
- ⇒ **At I:** base is totally neutralized by the base according to stoichiometric ratio. This point is called equivalence point.
- ⇒ **From I to D:** acid is in excess.
- ⇒ **Initially** $V_a = 0$ ml : $\text{pH} = 14 + \log [\text{OH}^-] = 14 + \log C_b$;
 $[\text{OH}^-] = C_b$ (strong base)
- ⇒ **Equivalence point I:** $\text{pH} = \frac{1}{2} \text{pK}_w = 7$ ($T = 25^\circ \text{C}$)
 \Rightarrow neutral
 The equivalence point is determined by parallel tangent method.



Species that are presented at equivalence: H_2O and spectator ions like Na^+ and Cl^-

The spectator ions have no effect pH

The medium is neutral due to the auto ionization of water which produces H_3O^+ and OH^- where $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \Rightarrow \text{pH} = -\log [\text{H}_3\text{O}^+]$

- ⇒ Adding excess strong acid $\Rightarrow \text{pH} = -\log [\text{H}_3\text{O}^+]$; the asymptote tend to $\text{pH} = -\log C_a$

Calculation:

At the equivalence point, according to stoichiometric ratio:

$n(\text{OH}^-)$ (initial in the beaker $V_b =$ ml) = $n(\text{H}_3\text{O}^+)$ (added from buret at equivalence, $V_{aEq} =$ ml)

⇒ $C_b V_b = C_a V_{aEq}$

- **Effect of adding distilled water - in order to immerse the pH-electrode – on the equivalence point I (V_{eq} ; pH eq)**

- ⇒ Adding distilled water doesn't not affect V_{eq} , since the number of moles of the analyte initially presented in the beaker is not affected.
- ⇒ pH at equivalence will not be affected, since the species that are presented at equivalence are H_2O and spectator ions => adding water will keep the solution at equivalence neutral.
- ⇒ No effect for adding water on the equivalence point of strong acid with strong base.

Reactions and their calculations:
1- Auto-ionization of water. $2H_2O \rightleftharpoons H_3O^+ + HO^- \quad K_w = [H_3O^+] [HO^-]$
2- Strong acid-strong base reaction: $H_3O^+ + HO^- \rightarrow 2H_2O \quad K_r = 1/K_w$

