ANALYTICAL CHEMISTRY

Acid Base Titration

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Chapter Description

- Expected Outcomes
  - Understand and state the principles of titrations.
  - Define and identify Arrhenius and Brönsted-Lowry acids and bases
  - Define and identify the conjugate of a given acid or base
  - Describe and apply the titration curves, calculations and indicators to solve the problem regarding acid base titration.

Contents

- Acid-Base Theories
- Autopyrolysis of Solvents
- Acidity of Solution
- Acid-Base Titration
- End Point Detection
- Indicators for titration

APPLICATIONS OF NEUTRALIZATION TITRATIONS

- General flow:
  - Preparation of standard solution (acid/base) → Standardization of solution with primary standards → Titration → Results
- Applications:
  - Elemental analysis
  - Determination of inorganic substances
  - Determination of organic functional groups
  - Determination of salts

ACID – BASE THEORIES

- Arrhenius Theory (Nobel Prize 1894)
  - Acid: any species that can produce hydroxonium ions (H_3O^+) – abbreviated H^+ or proton.
  - Base: produce hydroxyl ions (OH^-) in aqueous solution.
  - Does not include acids or bases that can not produce H^+ and OH^- ions.

- Brönsted – Lowry Theory
  - Acid = proton (H^+) donor
  - Base = proton acceptor
  - Amphoteric substance = function as an acid or a base

- Lewis Theory
  - Acid = accept a pair of electrons
  - Base = donate a pair of electrons

Strong electrolyte : completely dissociated.

Weak electrolyte : partially dissociated.

Strong acid	Weak acid
HCl	CH_3COOH
HBr	H_2CO_3
HI	$HOCN$
HNO_3	HCN
H_2SO_4	HF
$HClO_4$	H_2S
	$HOOH$
	$HOCl$
	$HON{=}O$
	$HOOCCOOH$
	H_3PO_4
	CH_3CH_2COOH

Strong base	Weak base
$NaOH$	NH_3
KOH	N_2H_4
$LiOH$	CH_3NH_2
$RbOH$	
$CsOH$	
$Sr(OH)_2$	
$Ba(OH)_2$	
$Ca(OH)_2$	
$Mg(OH)_2$	

Source: Christian G.D., Dasgupta, P., Schug, K. (2014) Analytical Chemistry. Wiley-VCH

AUTOPYROLYSIS OF SOLVENTS

- **Autopyrolysis** : self-ionization – acts as both an acid and a base.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^- \qquad K_w = 1.0 \times 10^{-14} mol^2 L^{-2}$$

$$\mathrm{K} = \frac{[H^+][OH^-]}{[H_2O]}$$

$$K_w = [H^+][OH^-]$$

- **Protic** solvent : a solvent that involves the transfer of H+ from one molecule to another. Can undergo self-ionization. i.e. H_2O, CH_3OH, C_6H_5OH

$$2CH_3COOH \rightleftharpoons CH_3C(OH)_2{}^+ + CH_3COO^-$$

AUTOPYROLYSIS OF SOLVENTS

- **Polyprotic** acids and bases: compounds that can donate or receive more than one proton. i.e. phosphoric acid, phosphate

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4{}^- + H_3O^+ \qquad K_{a1} = 7.11 \times 10^{-3}$$

$$H_2PO_4{}^- + H_2O \rightleftharpoons HPO_4{}^{-2} + H_3O^+ \qquad K_{a2} = 6.32 \times 10^{-8}$$

$$HPO_4{}^{-2} + H_2O \rightleftharpoons PO_4{}^{-3} + H_3O^+ \qquad K_{a3} = 7.1 \times 10^{-13}$$

- **Aprotic** solvent : a solvent that does not have an acidic proton. i.e. CH_3CN, $(C_2H_5)_2O$

ACIDITY OF SOLUTIONS

For an aqueous solution of 0.10 M HCl:

$$HCl \rightarrow H^{+} + Cl^{-}$$

$\therefore [H^{+}] = 0.01\ M$

$[H^{+}][OH^{-}] = 1.0 \times 10^{-14}$

$[0.10][OH^{-}] = 1.0 \times 10^{-14}$

$\therefore [OH^{-}] = 1.0 \times 10^{-13}$

Acidity is related to pH scale:

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

$$pOH = \log[OH^{-}]$$

$$pK_a = -logK_a$$

Because $[H^{+}][OH^{-}] = 1.0 \times 10^{-14}$, pH is related to pOH by $pH + pOH = 14$

IONIZATION OF STRONG ACIDS & BASES

- 100% ionization
- Example: calculate the pH of a 2.0×10^{-3}M HCl

$$[H^+] = 2.0 \times 10^{-3}$$

$$pH = -\log(2.0 \times 10^{-3}) = 2.70$$

EXAMPLE

What is the pH of a solution containing 0.10 M NaOH?

The final concentrations, $[Na^{+}] = [OH^{-}] = 0.10\ M$

$$K_w = [H^{+}][OH^{-}]$$

$$[H^{+}] = K_w/[OH^{-}] = 1.0 \times 10^{-14}/0.10 = 1.0 \times 10^{-13} M$$

$$pH = -log 1.0 \times 10^{-13} = 13$$

@

$$pOH = -\log[OH^{-}] \qquad pH + pOH = 14$$

$$pOH = -\log[0.10] = 1$$

$$pH = 14 - 1 = 13$$

WEAK ACID

The dissociation of weak acid

$$HA \rightleftharpoons H^{+} + A^{-}$$

(weak acid) (conjugate base)

HA (conjugate acid) and A^{-} (conjugate base) are conjugate acid-base pair.

$$K_a = \frac{[H^{+}][A^{-}]}{[HA]}$$

EXAMPLE

A solution of acid HA (0.030 M) was found to have $[H^+] = 6.5 \times 10^{-4}$ M. Calculate the K_a value for the acid.

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = [A^-] = 6.5 \times 10{-}4\, M$$

$$[H^+] = 0.030\, M - 6.5 \times 10{-}4\, M = 2.9 \times 10^{-2} M$$

$$K_a = \frac{(6.5 \times 10^{-4})(6.5 \times 10^{-4})}{2.9 \times 10^{-2}} = 1.5 \times 10^{-5}$$

WEAK BASE

For every weak acid, there is always an associated weak base.

$$HA \rightleftharpoons H^{+} + A^{-} \qquad (K_a\ has\ a\ very\ small\ value)$$

The anion A- acts as a weak base. This anion can undergo hydrolysis:

A^{-}	+	H_2O	$\rightleftharpoons$	AH	+	OH^{-}
(conjugate base)		(weak acid)		(weak acid)		(conjugate base)

$$K_h = K_b = \frac{[HA][OH^{-}]}{[A^{-}]}$$

IONIZATION OF WEAK ACIDS & BASES

- Partially ionized

	HA	$\rightleftharpoons H^+$	$+ A^-$
Initial	C_0	0	0
Equilibrium	C_0-C_1	C_1	C_1

K_a = acidity constant

Assuming

1. Contribution of $[H^+]$ from water is negligible
2. $K_a << 1$, $C_1 << C_0 \rightarrow [HA] = C_0 - C_1 \approx C_0$
   $K_a = C_1^2/C_0$
   $[H^+] = \sqrt{(K_a C_0)}$

	B	$\rightleftharpoons BH^+$	$+ OH^-$
Initial	C_0	0	0
Equilibrium	C_0-C_1	C_1	C_1

$$K_b = \frac{[BH^+][OH^-]}{B}$$

Assuming

1. Contribution of $[OH^-]$ from water is negligible
2. $K_b<<1$, $C_1<<C_0 \rightarrow [B] = C_0-C_1 \approx C_0$

   $K_b = C_1^2/C_0$

   $[OH^-] = \sqrt{(K_bC_0)}$

IONIZATION OF WEAK ACIDS & BASES

- Partially ionized

	HA	$\rightleftharpoons H^+$	$+ A^-$
Initial	C_0	0	0
Equilibrium	C_0-C_1	C_1	C_1

$$K_a = \frac{[H_3O^+][A^-]}{HA}$$

K_a = acidity constant

Assuming

1. Contribution of $[H^+]$ from water is negligible
2. K_a<<1, C_1<<C_0 → $[HA] = C_0 - C_1 \approx C_0$

   $K_a = C_1^2/C_0$

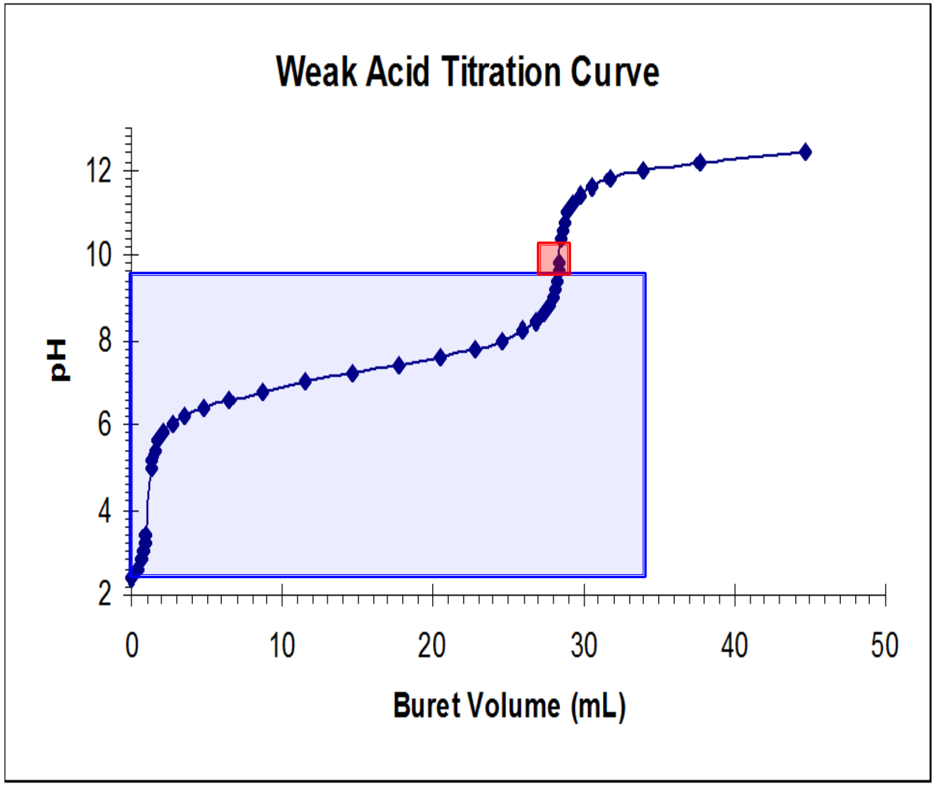
   $[H^+] = \sqrt{(K_a C_0)}$

IONIZATION OF WEAK ACIDS & BASES

$$pH = pk_a + log\frac{[A^-]}{[HA]}$$

$$[OH^-] = \sqrt{(K_w / K_a) * C_0}$$

$$[H^+] = \sqrt{(K_w / K_b) * C_0}$$



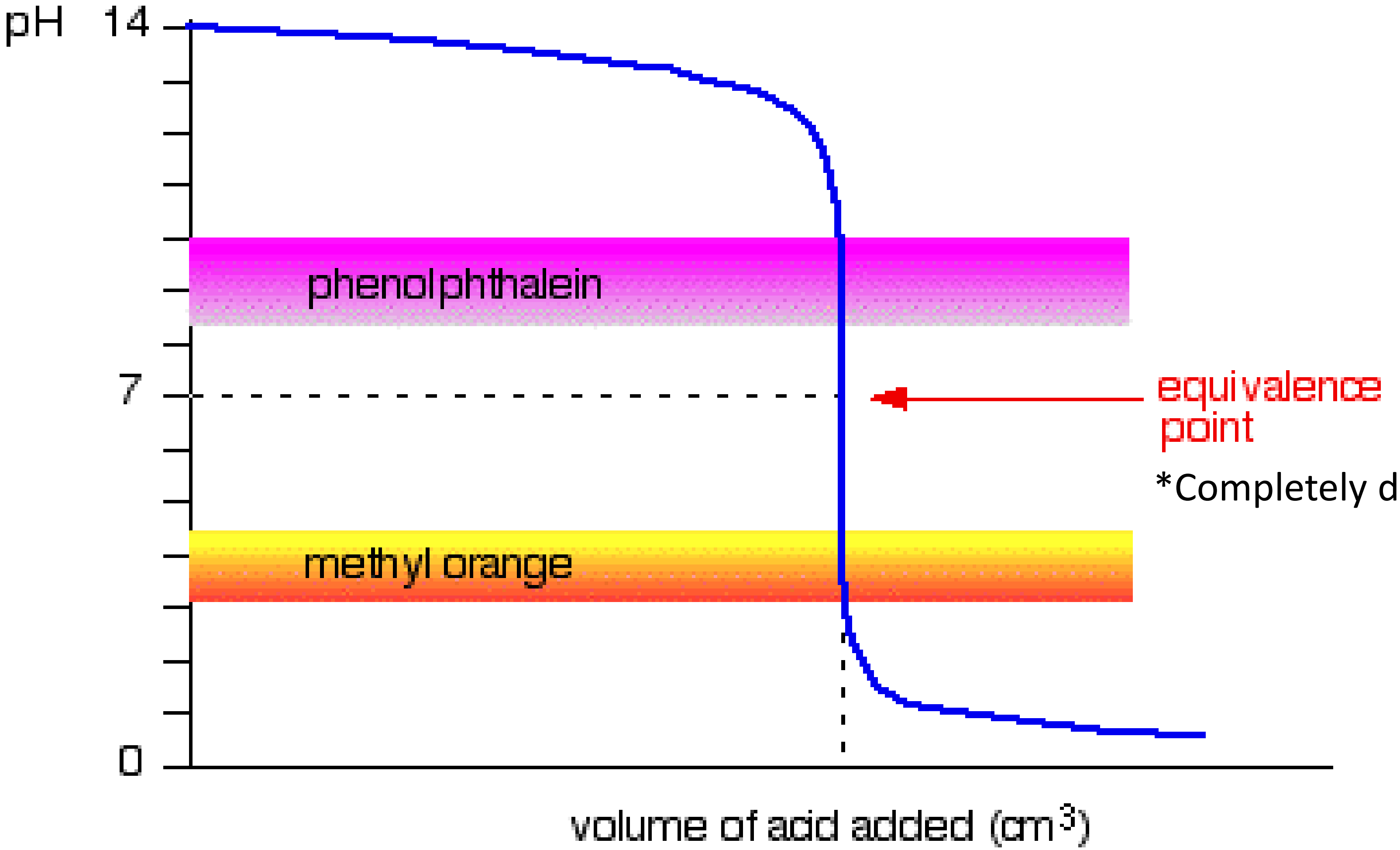
NEUTRAL IONS

- Do not reacts with water to form H^+ or OH^-.
- Are not affected by pH.
- Not many, neutral ions are only from strong acid or strong base.

Species	Neutral	
Anion	Cl^- Br^- I^-	NO_3^- ClO_4^- SO_4^{2-}
Cation	Li^+ Na^+ K^+	Ca^{2+} Ba^{2+}

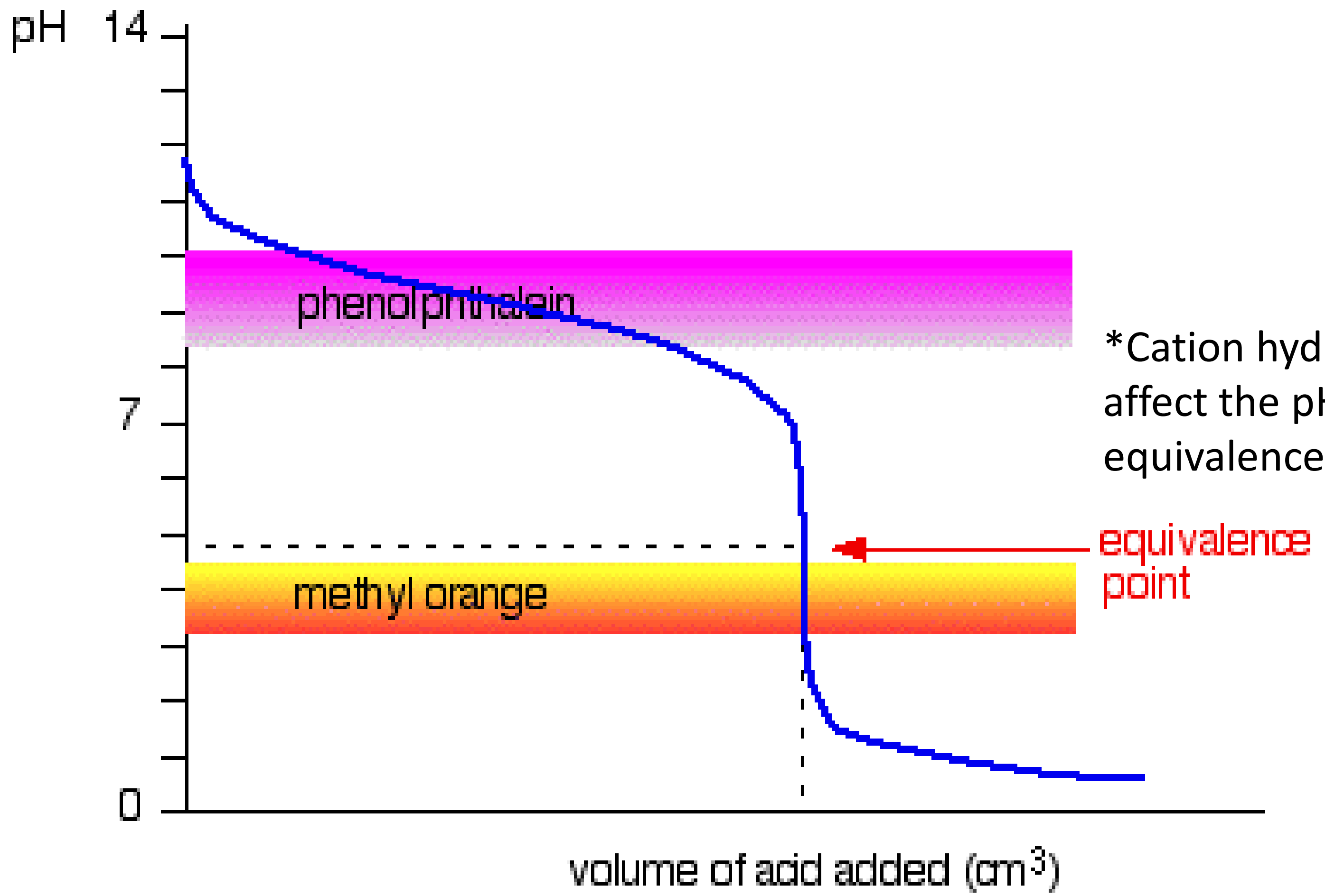
- When an acid and a base react, they **neutralize** each other to form a **salt**.

STRONG ACID VS STRONG BASE



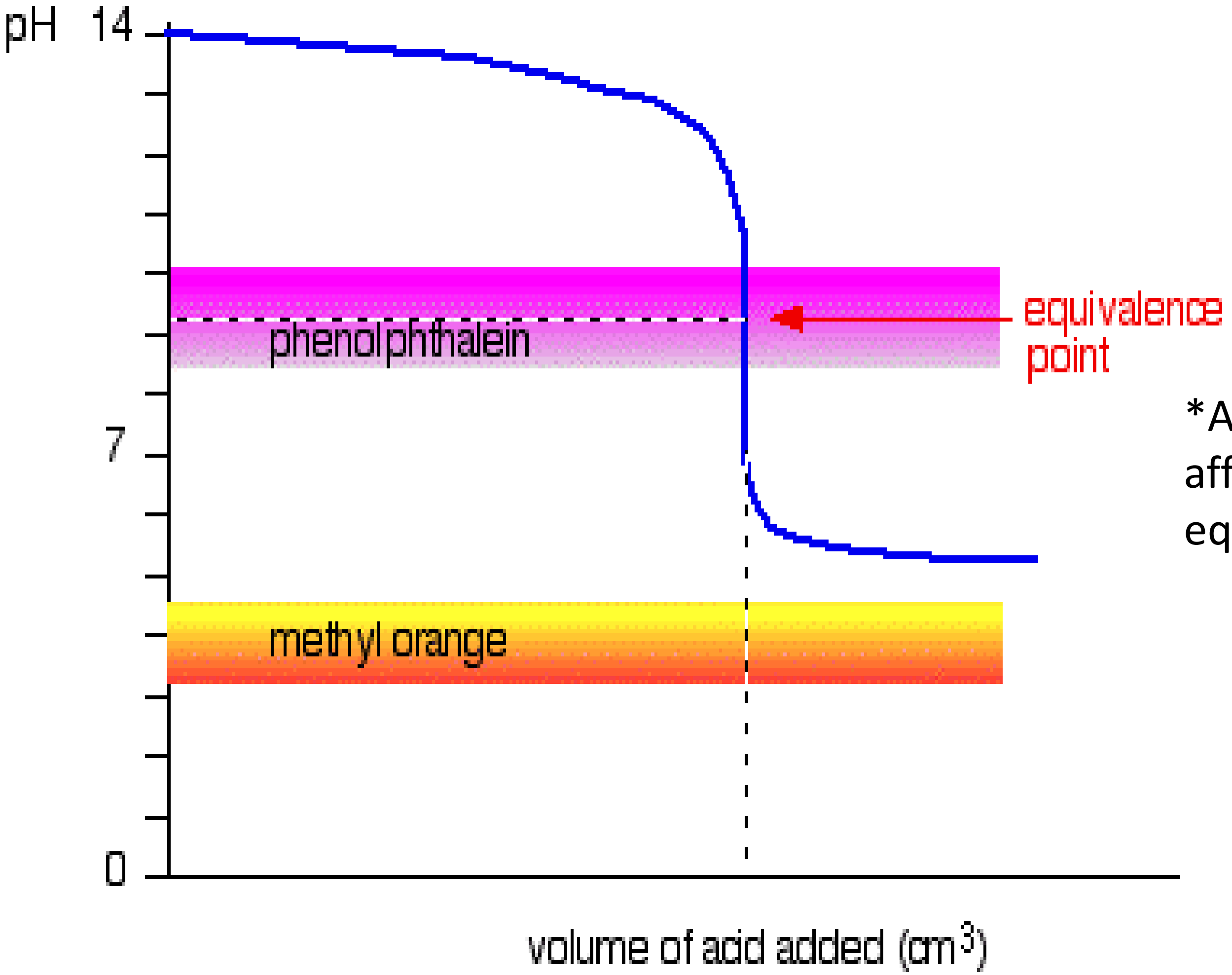
*Completely dissociated

STRONG ACID VS WEAK BASE



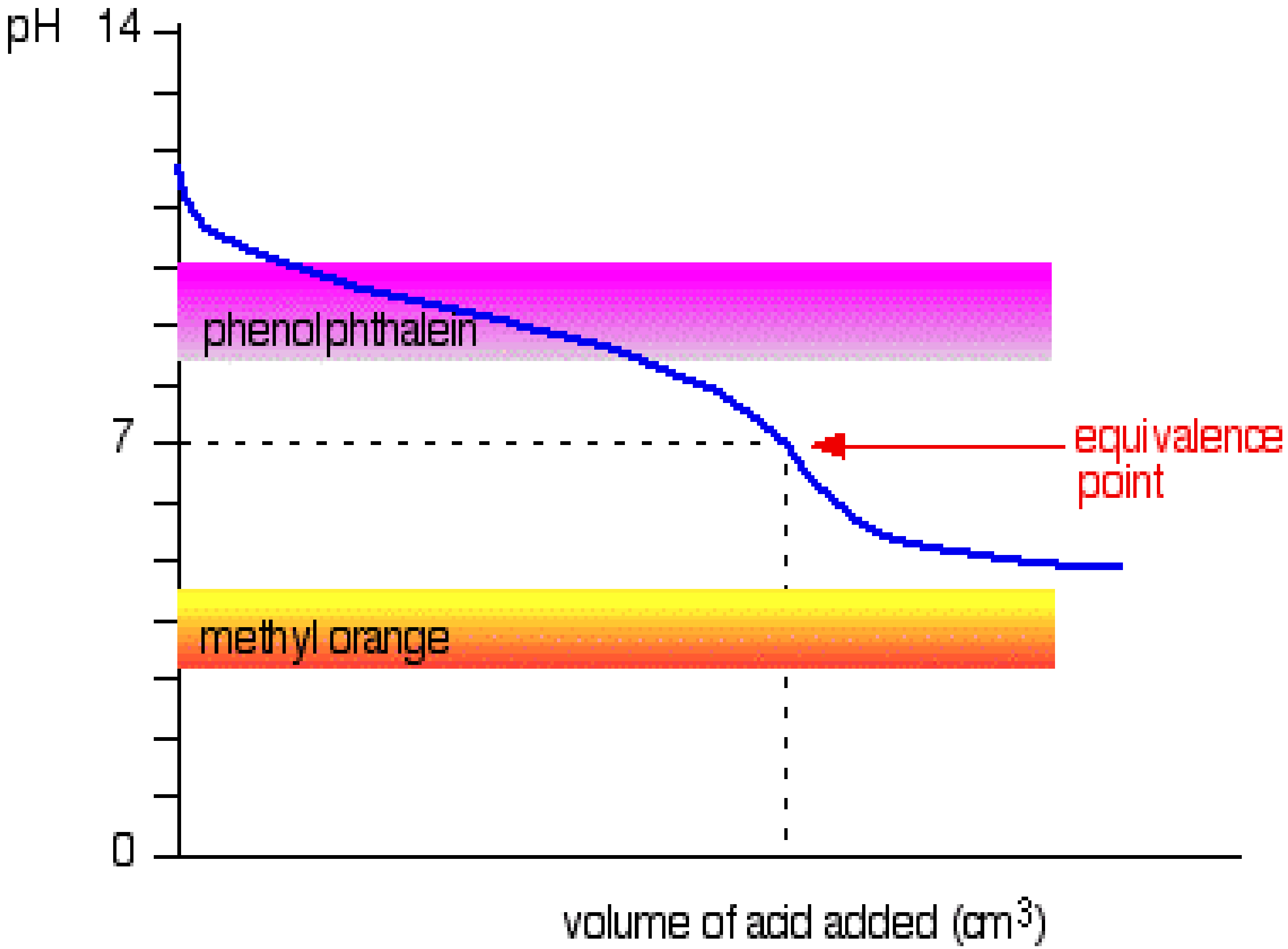
*Cation hydrolysis occurs affect the pH value at equivalence point (pH < 7)

WEAK ACID VS STRONG BASE



*Anion hydrolysis occurs affect the pH value at equivalence point (pH > 7)

WEAK ACID VS WEAK BASE



STANDARD SOLUTIONS

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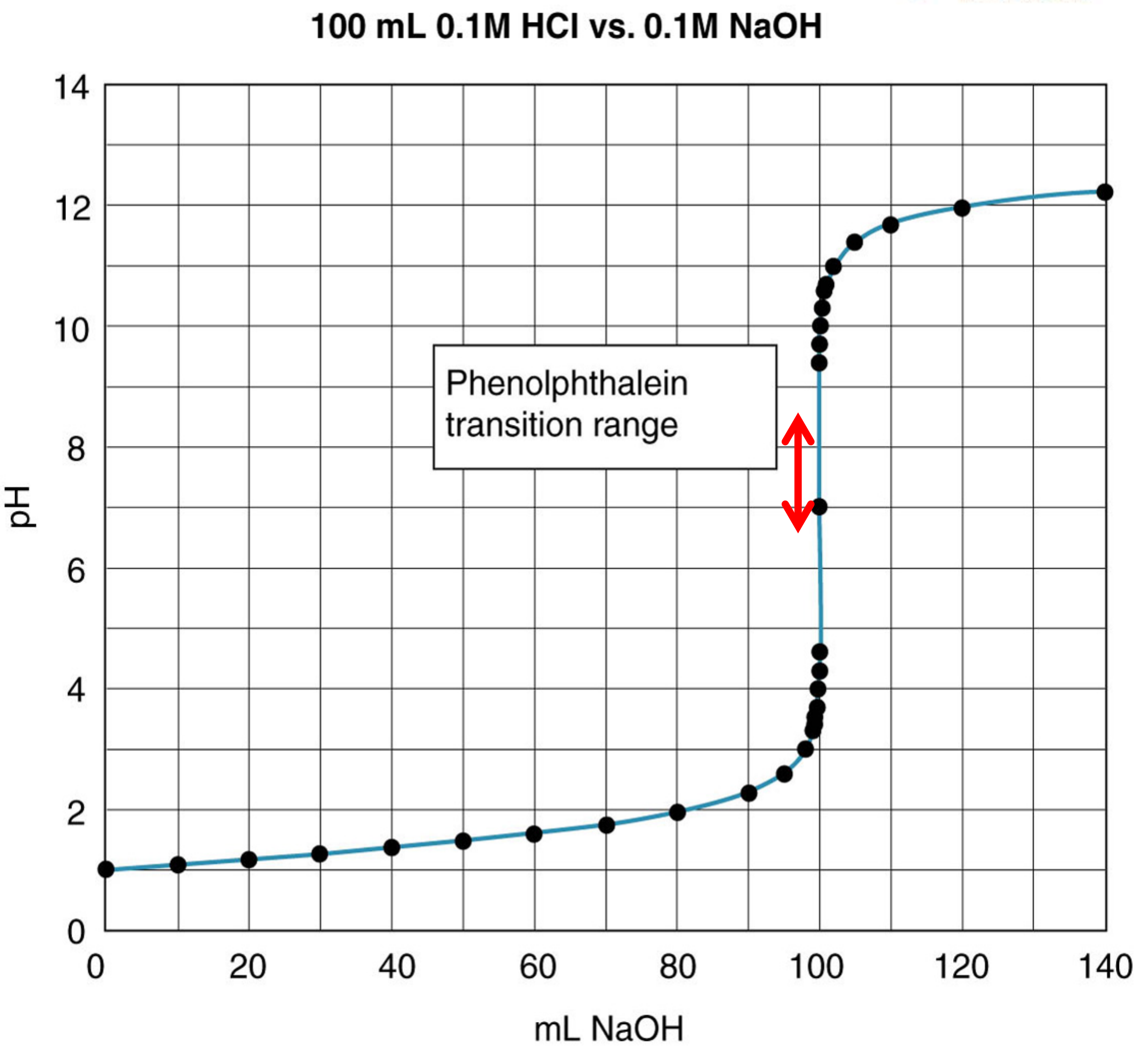
- Strong acids or strong bases
  - Complete reaction with analyte
  - Sharp end points
  - Never use weak acids & bases as standard reagents (incomplete reaction)
- Standard solutions of acids
  - Dilution of concentrated sulfuric, hydrochloric or perchloric acid.
- Standard solutions of bases
  - prepared from solid sodium or potassium and occasionally barium hydroxides. The concentrations of these bases must be established by standardization.

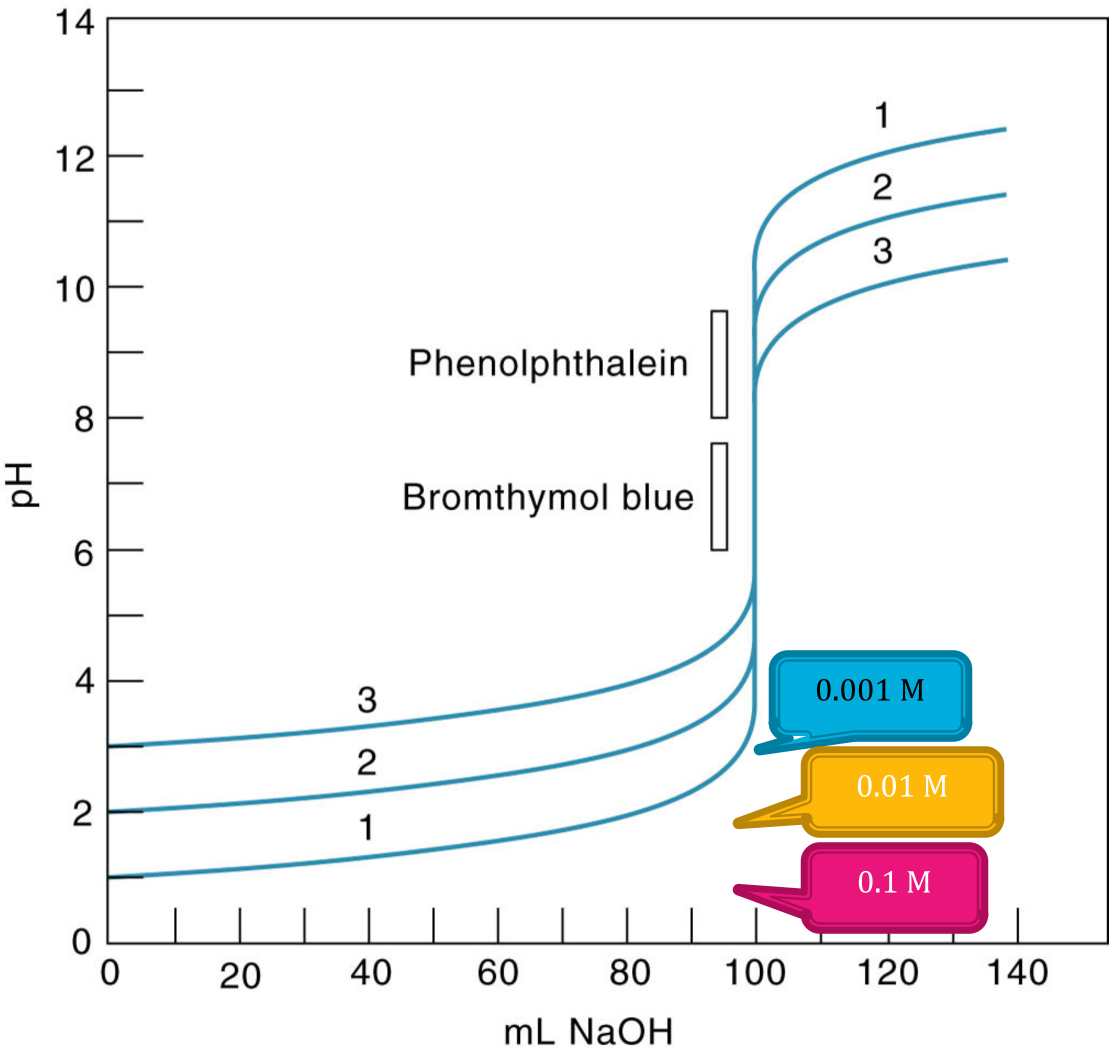
TITRATION OF STRONG ACIDS AND STRONG BASES

- A strong acid – strong base titration curve has a large end point break.
- Figure shows the titration curve for 100 mL of 0.1 M HCl versus 0.1 M NaOH.



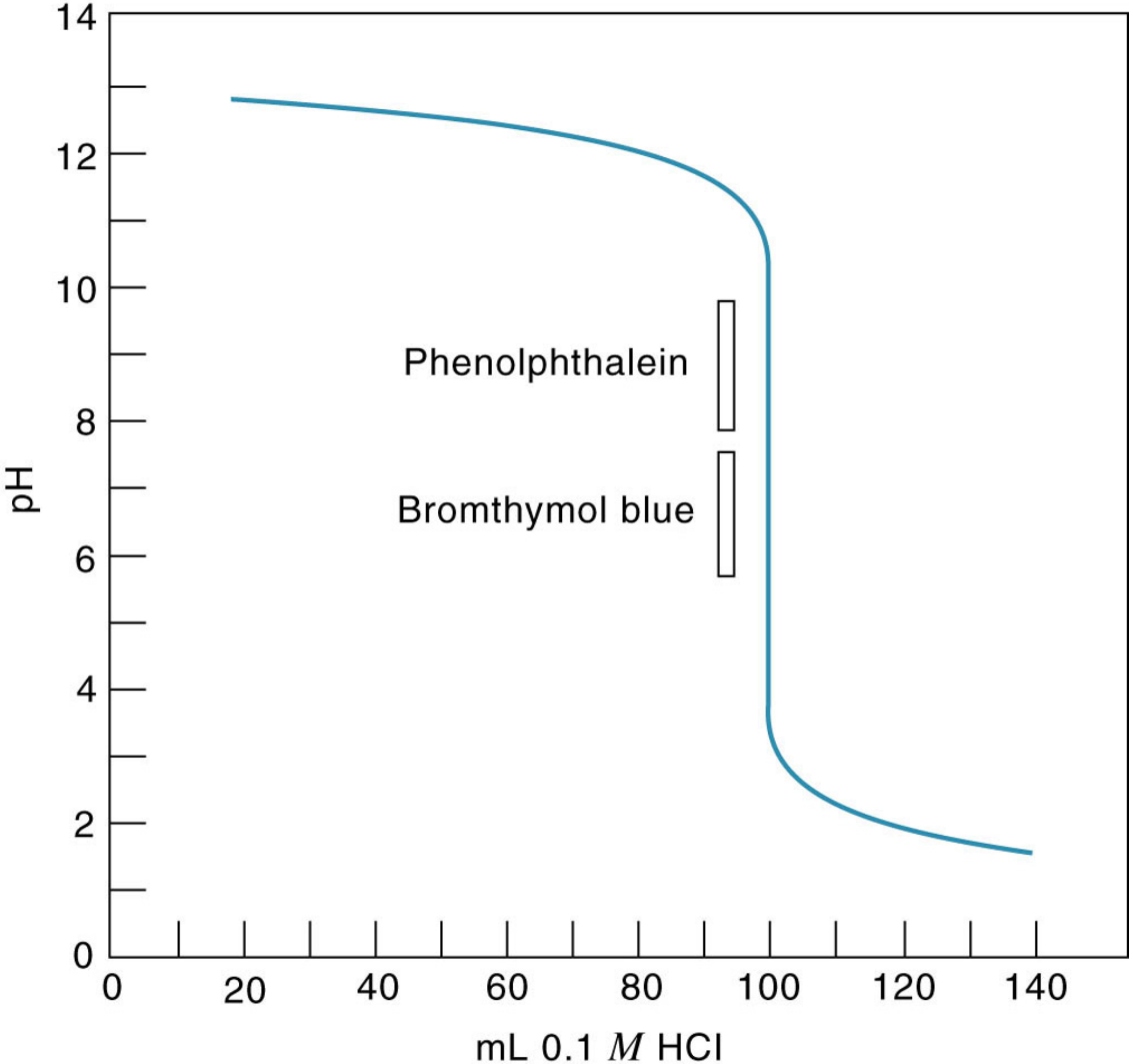
As the concentrations of acid and titrant decrease, the end point break decreases.

So the selection of indicator becomes more critical.



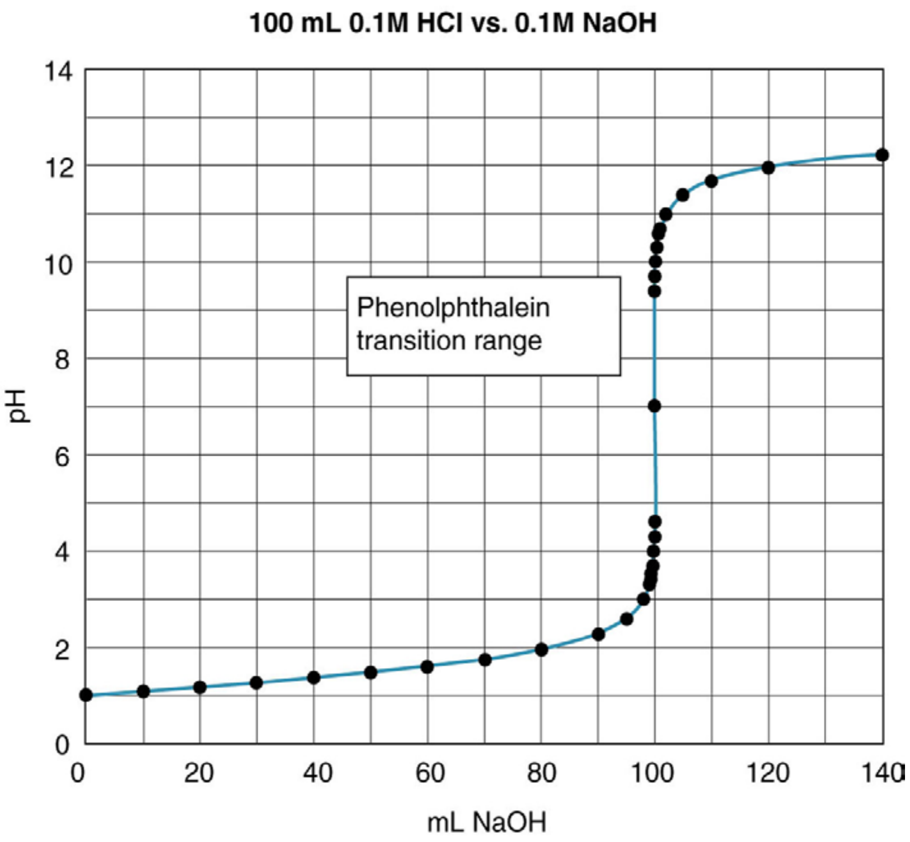
Dependence of the magnitude of end-point bread on concentration. The concentrations of acid and titrant are the same.

This is the mirror image of the HCl titration curve.



Titration curve for 100 mL of 0.1 M NaOH versus 0.1 M HCl.

STRONG ACID - STRONG BASE TITRATIONS



Approaching the equivalence point, the concentration of $[H^+]$ gets very small small

↓

Small additions of base → large ***relative*** change in the concentration of $[H^+]$

↓

Thus, near the equivalence point, greater change in pH observed

↓

This behavior make it easy by just using an indicator dye to show when we are approaching the equivalence point

↓

The indicator may change color at close to pH 7.0

TITRATION CURVES OF WEAK ACIDS WITH A STRONG BASE

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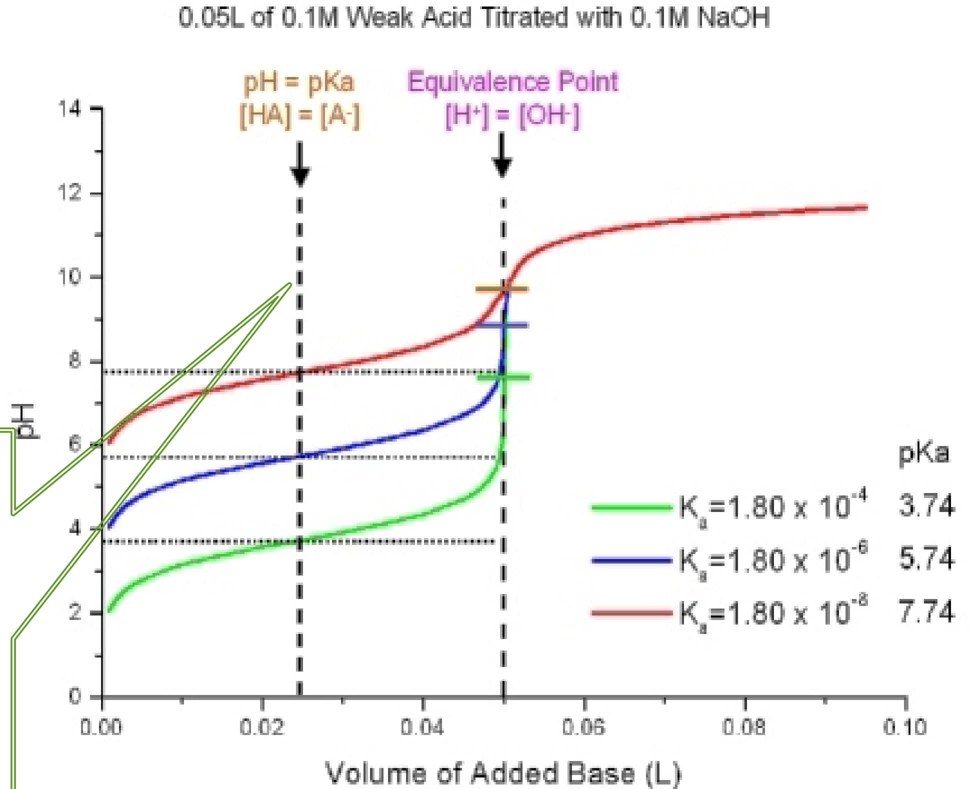
- At the equivalence point, the solution is slightly basic with the present of salt because the salt contains the conjugate base, which is able to recombine with a proton.



Source: Dr. Michael Blaber, 2000

- *After one-half : [HA] = [A–].*
- *At this point the pH = pKa.*
- *Titration profile is relatively flat around the pH = pK_a point.*
- *This means that within this region the pH is not changing much upon the addition of small amounts of base. This is the definition of a "buffered" solution, and explains why the most effective buffering is at a pH value equal to the pKa.*

FINDING EQUIVALENCE POINT

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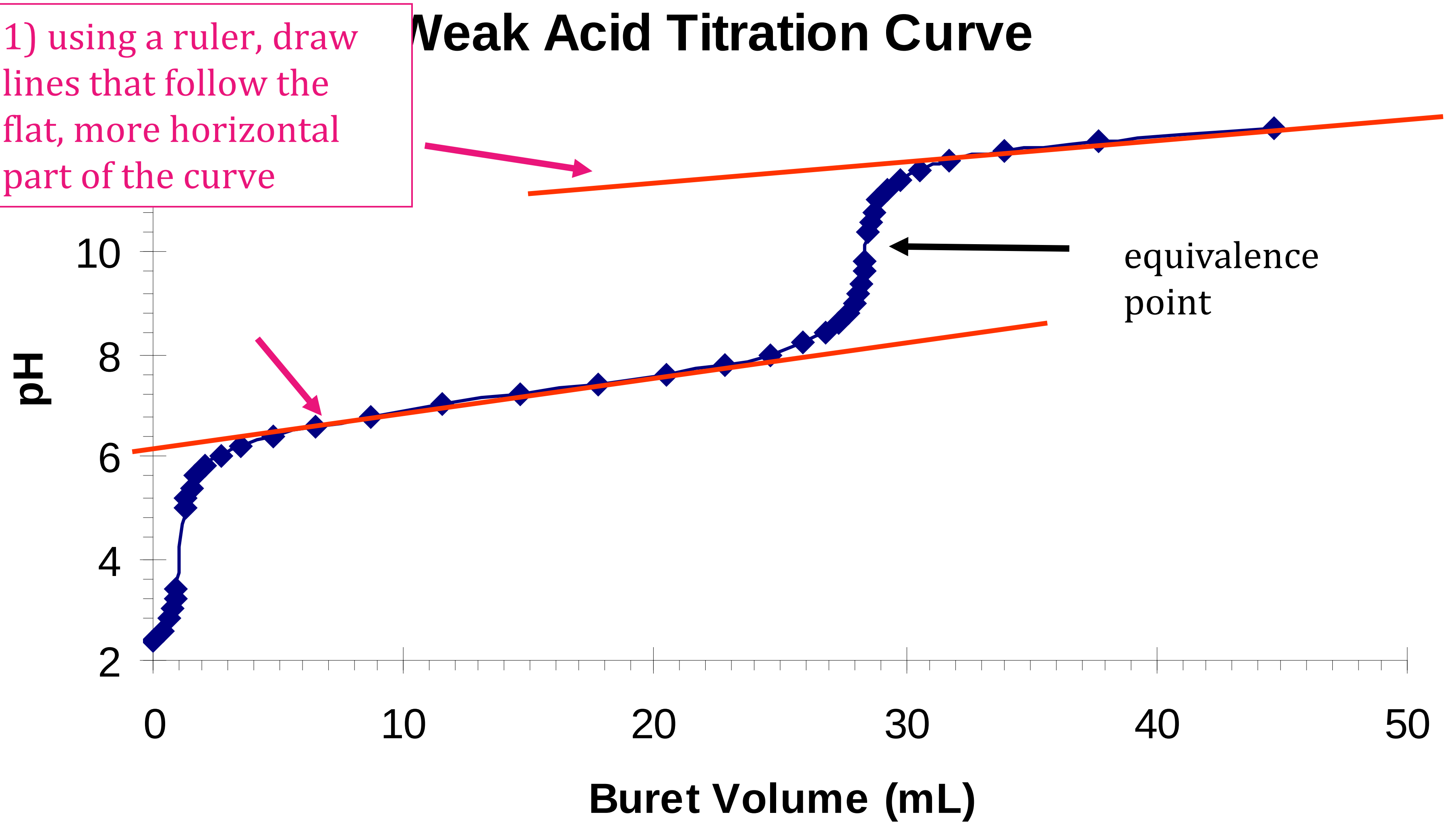
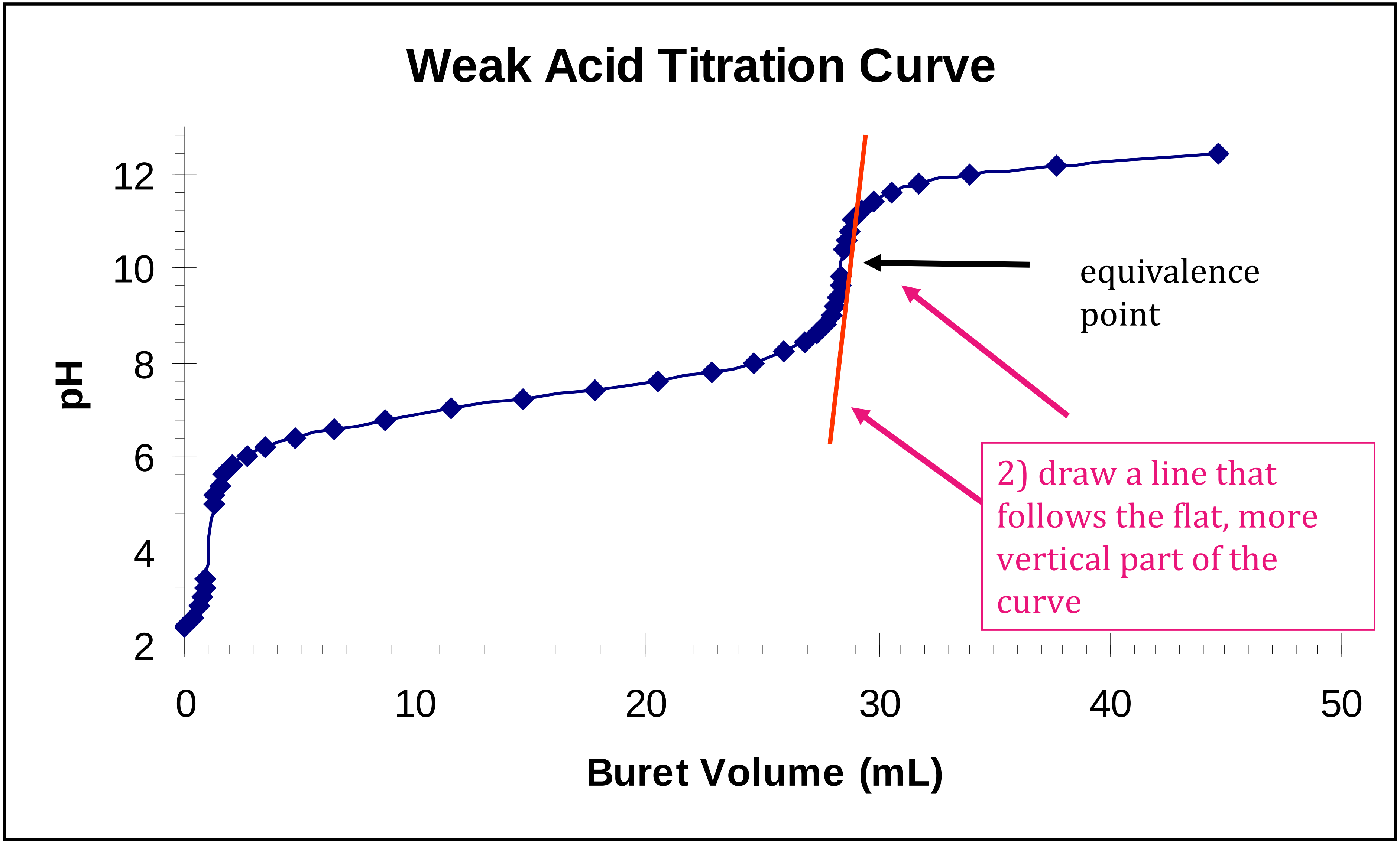
1) using a ruler, draw lines that follow the flat, more horizontal part of the curve

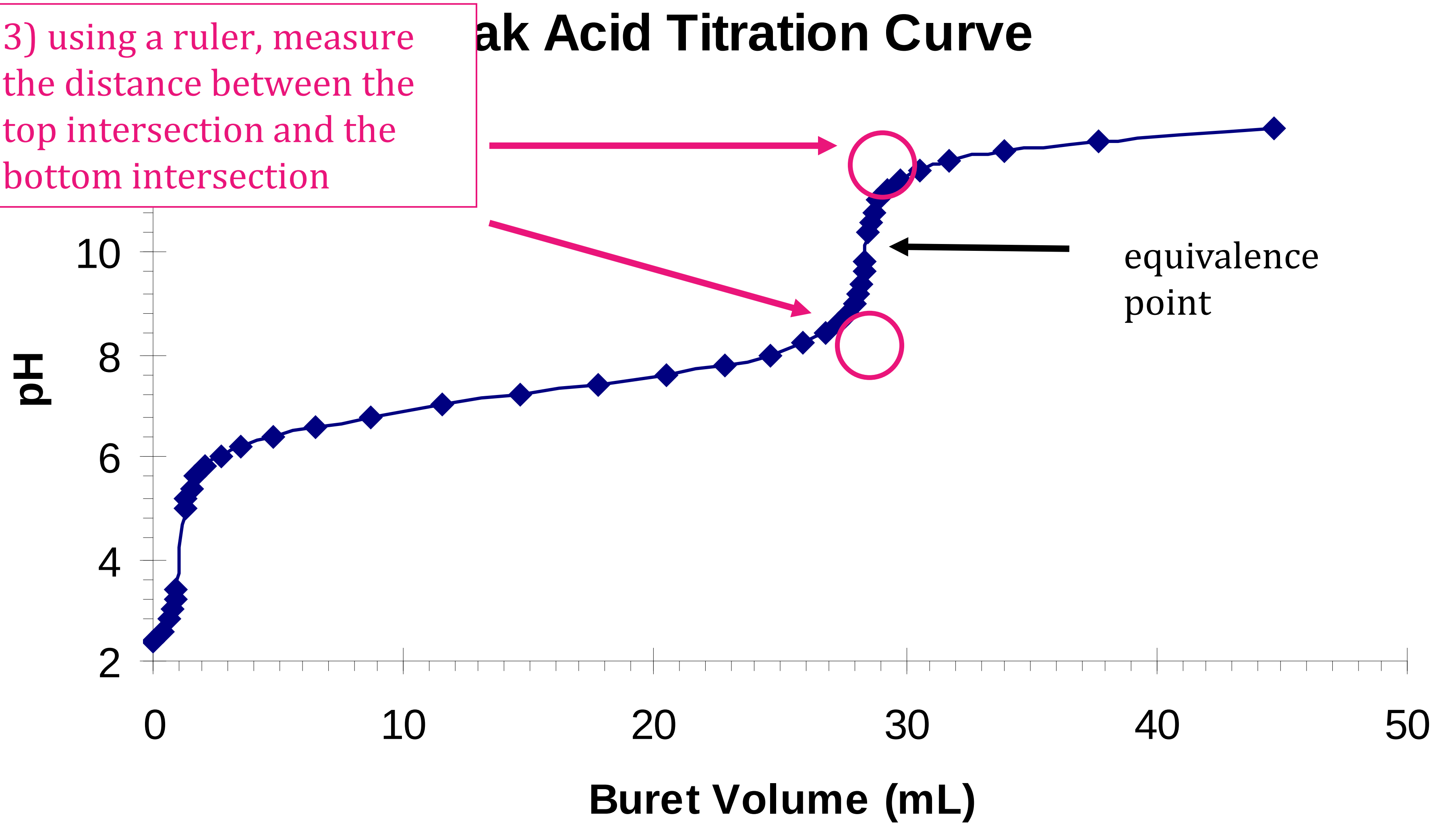


FINDING EQUIVALENCE POINT

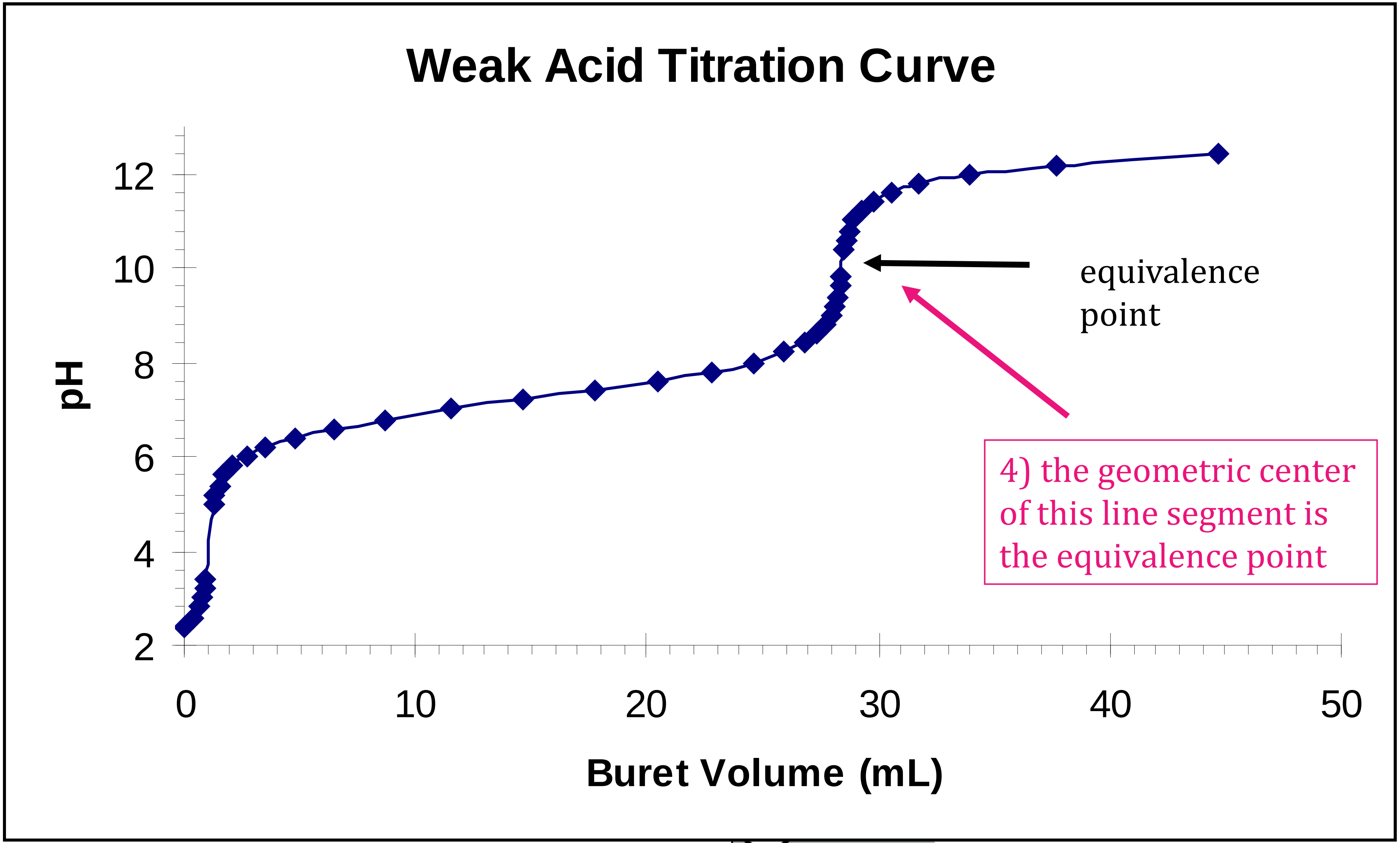


FINDING EQUIVALENCE POINT

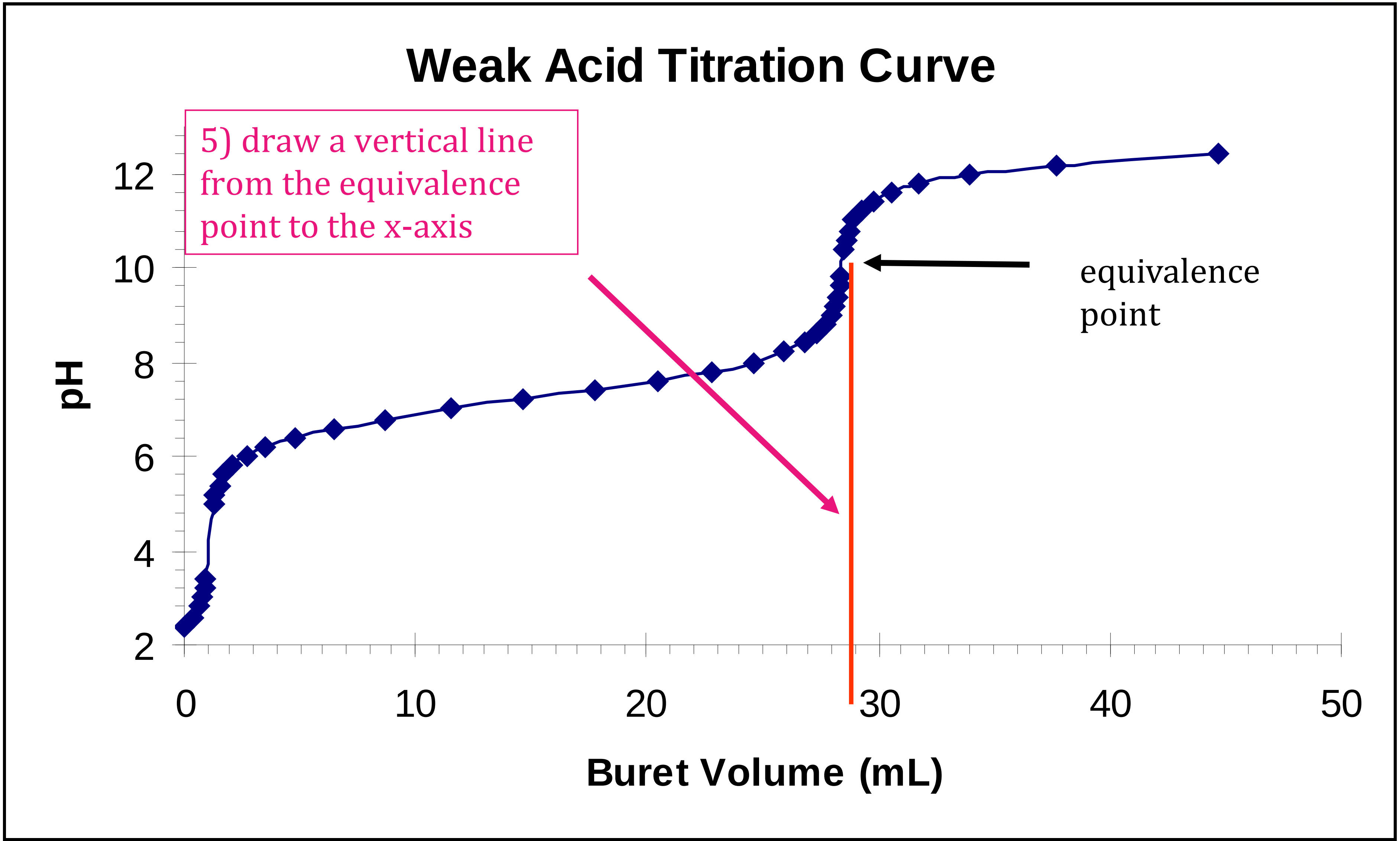
3) using a ruler, measure the distance between the top intersection and the bottom intersection



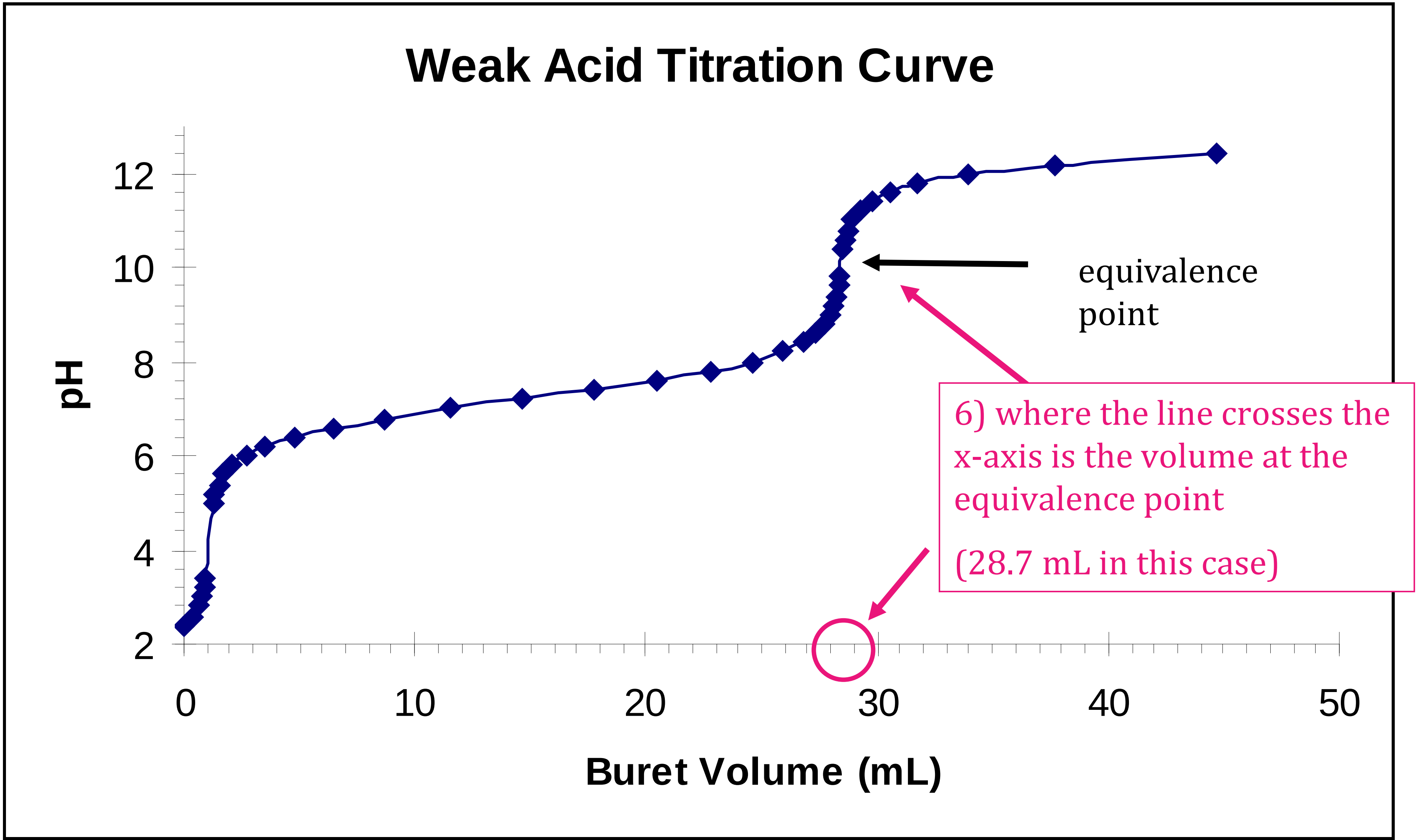
FINDING EQUIVALENCE POINT



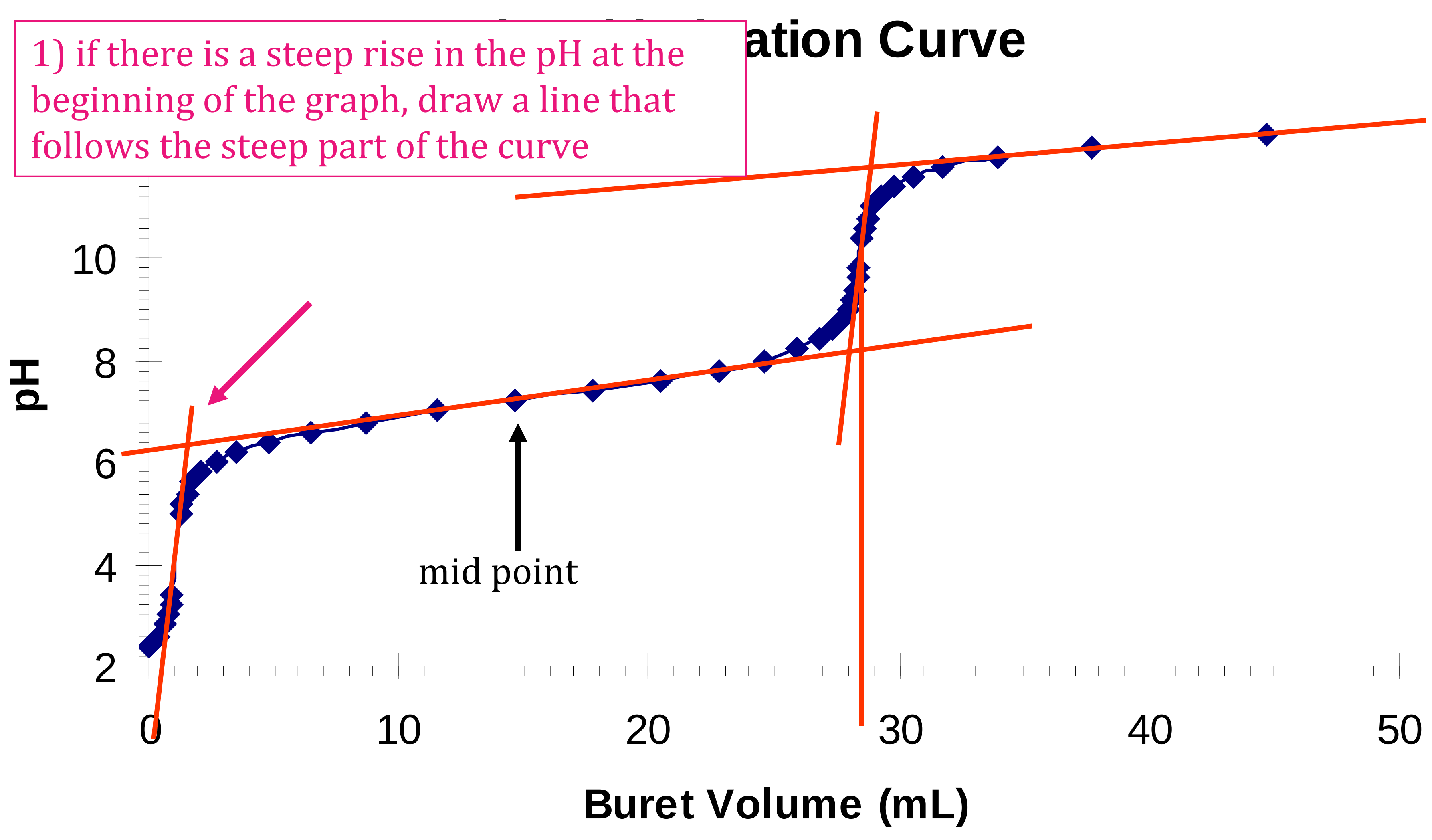
FINDING EQUIVALENCE POINT



FINDING EQUIVALENCE POINT



FIND THE MID POINT



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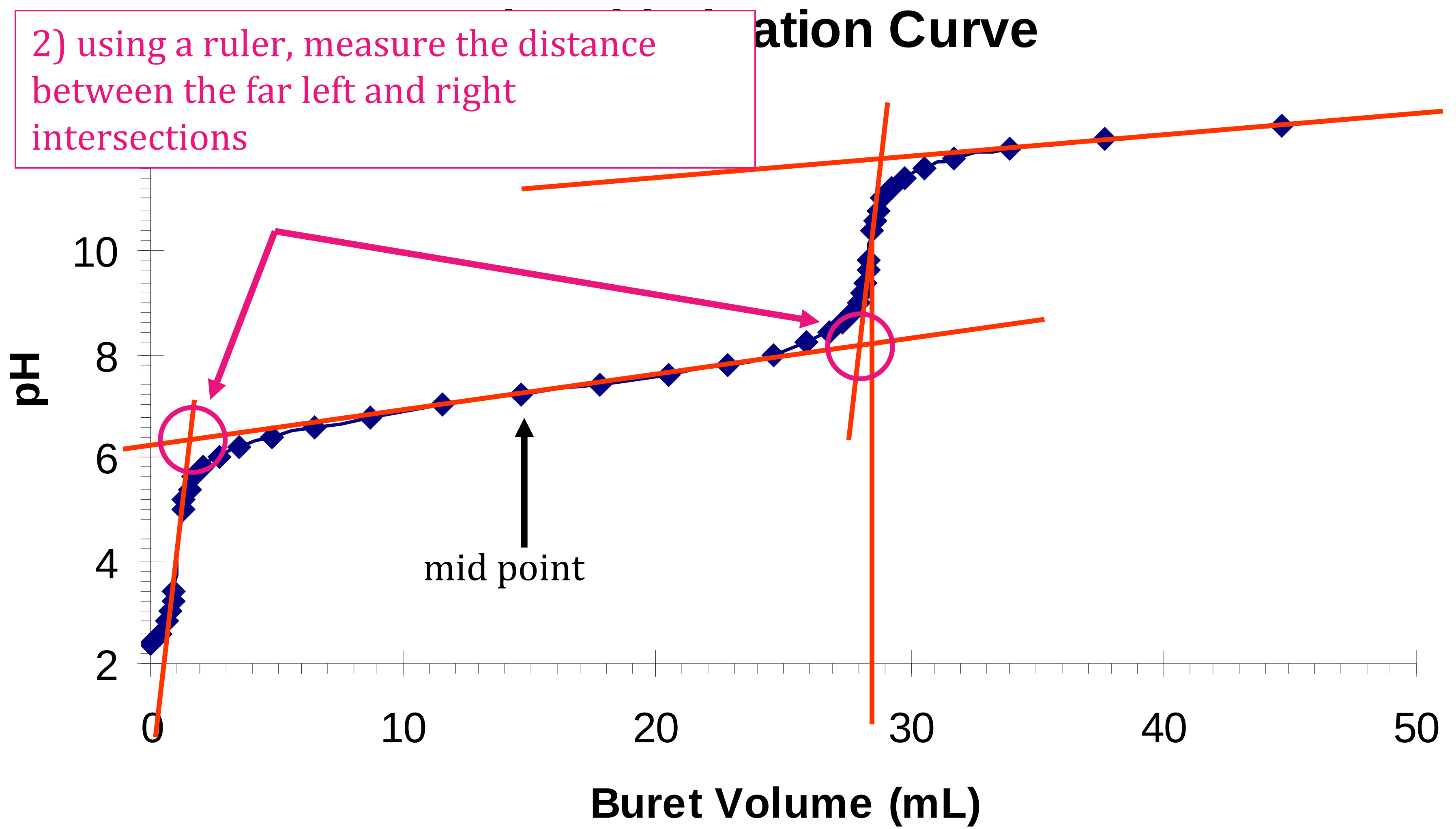

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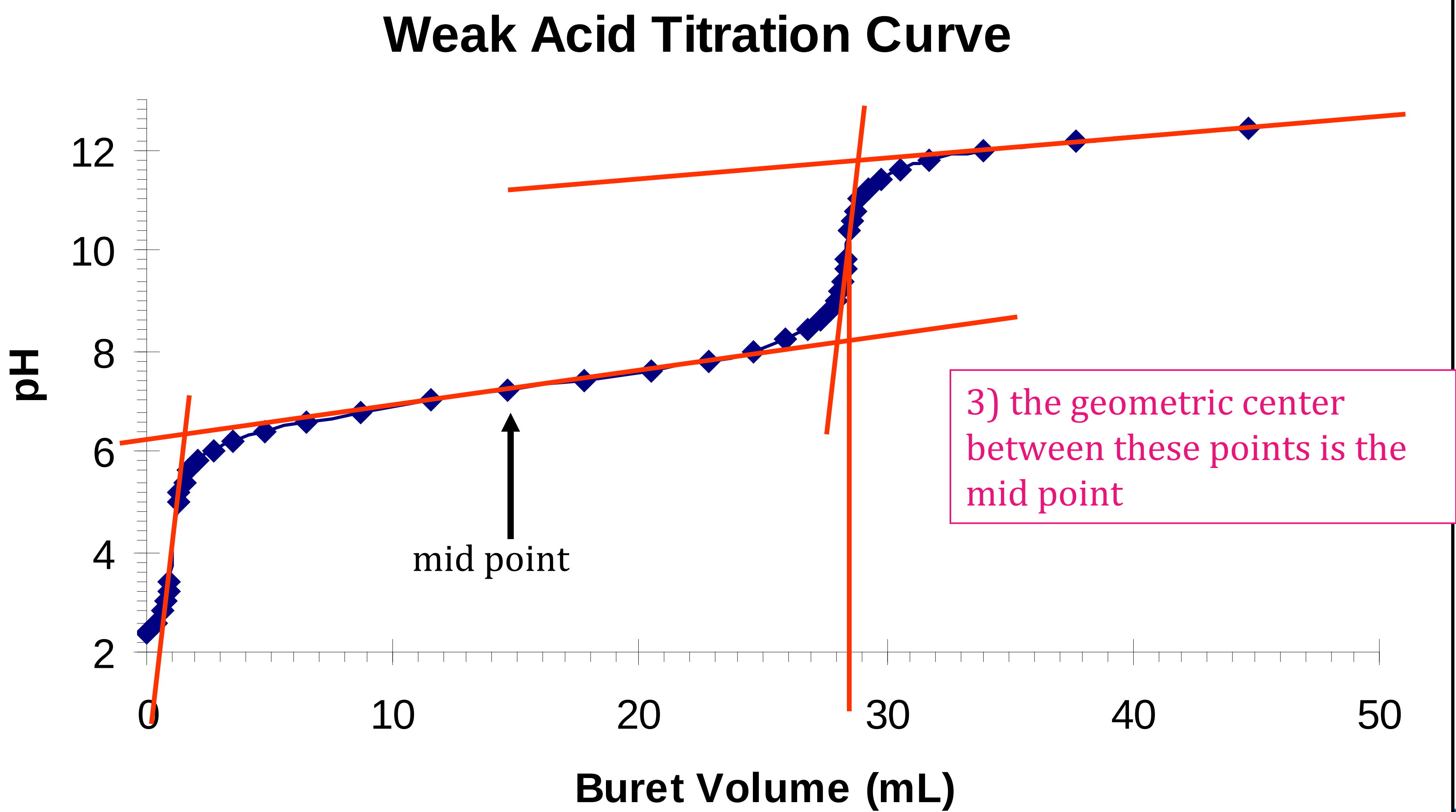

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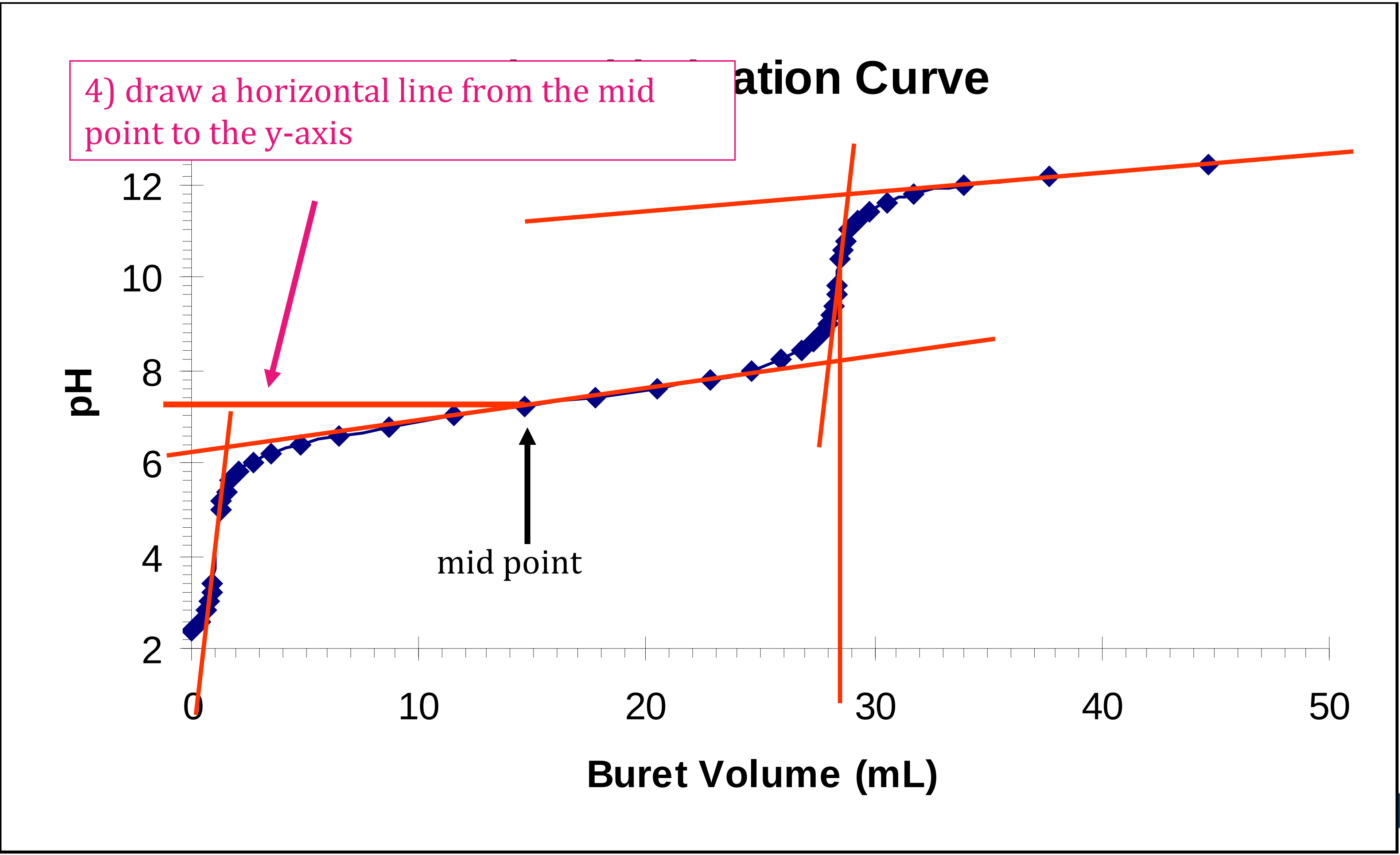

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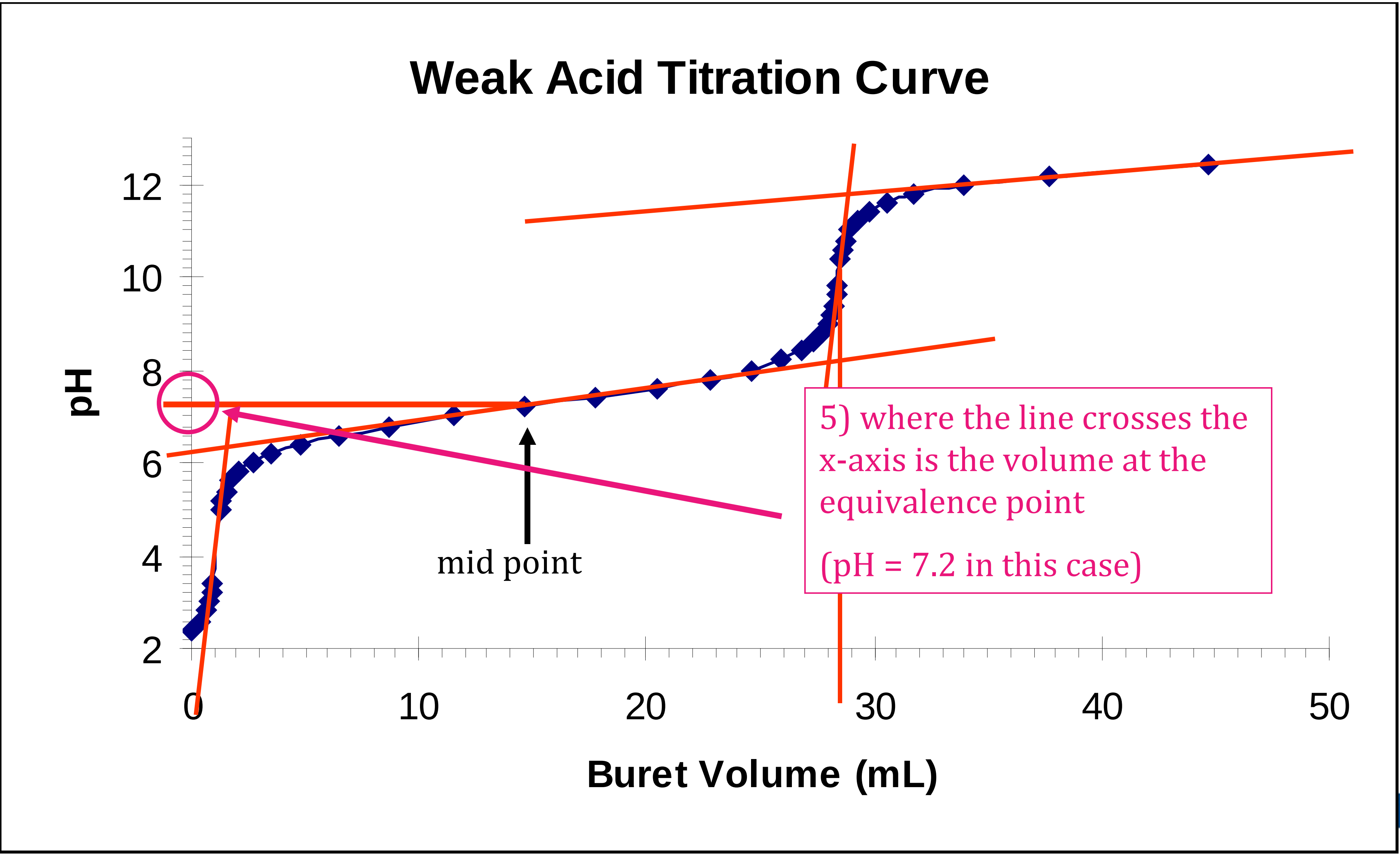


CHOOSING INDICATORS FOR TITRATIONS

- Choose an indicator which changes colour as close as possible to that equivalence point.

- That varies from titration to titration.

TABLE 14-1

Some Important Acid/Base Indicators

Common Name	Transition Range, pH	pK_a*	Color Change†	Indicator Type‡
Thymol blue	1.2–2.8	1.65§	R–Y	1
	8.0–9.6	8.96§	Y–B	
Methyl yellow	2.9–4.0		R–Y	2
Methyl orange	3.1–4.4	3.46§	R–O	2
Bromocresol green	3.8–5.4	4.66§	Y–B	1
Methyl red	4.2–6.3	5.00§	R–Y	2
Bromocresol purple	5.2–6.8	6.12§	Y–P	1
Bromothymol blue	6.2–7.6	7.10§	Y–B	1
Phenol red	6.8–8.4	7.81§	Y–R	1
Cresol purple	7.6–9.2		Y–P	1
Phenolphthalein	8.3–10.0		C–R	1
Thymolphthalein	9.3–10.5		C–B	1
Alizarin yellow GG	10–12		C–Y	2

*At ionic strength of 0.1.

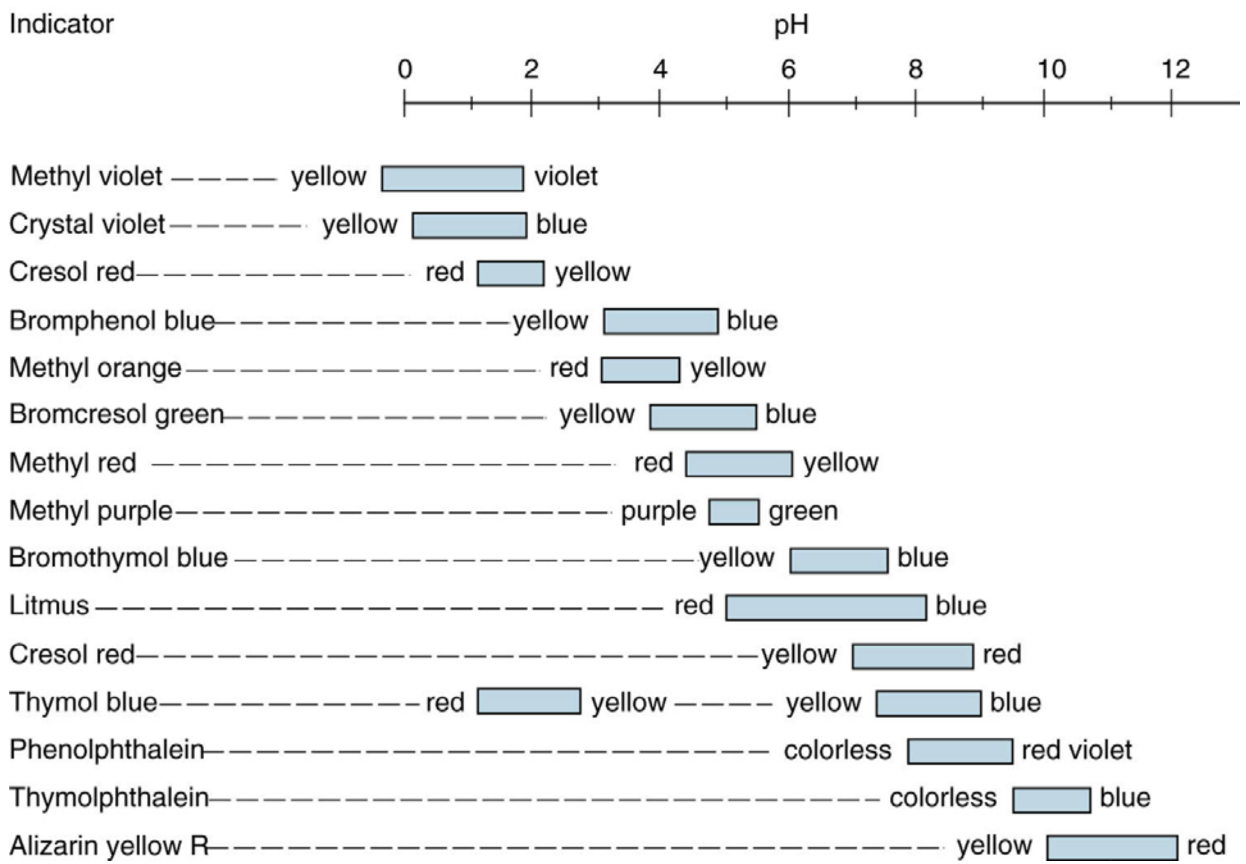
†B = blue; C = colorless; O = orange; P = purple; R = red; Y = yellow.

‡(1) Acid type: $HIn + H_2O \rightleftharpoons H_3O^+ + In^-$; (2) Base type: $In + H_2O \rightleftharpoons InH^+ + OH^-$.

§For the reaction $InH^+ + H_2O \rightleftharpoons H_3O^+ + In$.

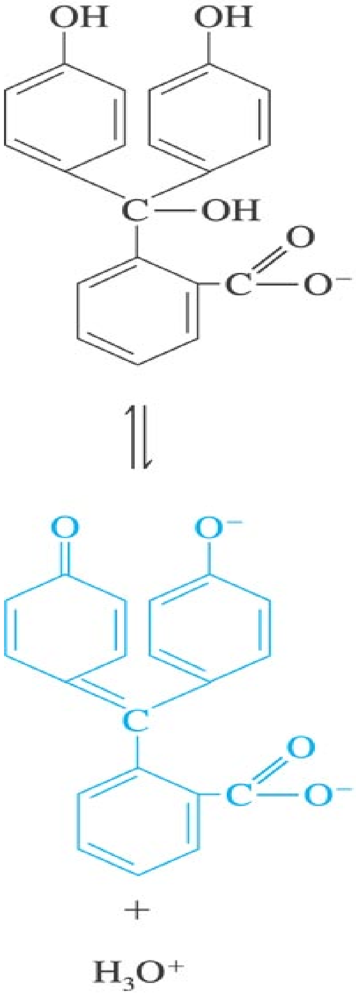
pH transition range = $pK_a \pm 1$.

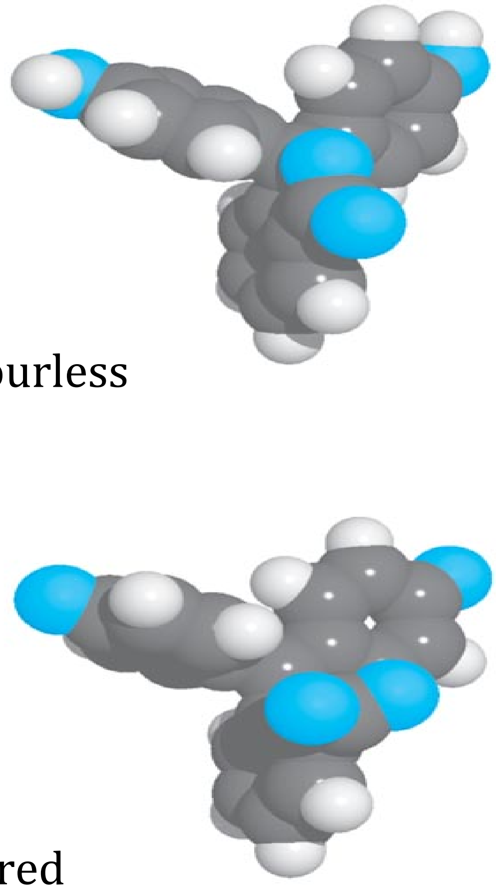
We select an indicator with a pK_a near the equivalence point pH.



pH transition ranges and colors of some common indicators.

ACID-BASE INDICATORS





colourless

red

phenolphthalein

- An acid/base indicator is a weak organic acid or a weak organic base whose undissociated form differs in color from its conjugate form.

ACID/BASE INDICATORS

- acid-type indicator, HIn :

$$HIn + H_2O \rightleftharpoons In^- + H_3O^+$$

acid color　　　　　　base color

- base-type indicator, In :

$$In + H_2O \rightleftharpoons InH^+ + OH^-$$

base color　　　　　　acid color

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

Colour A　　　　　　colour B

In acidic solution, equilibrium ←, colour A
In basic solution, equilibrium →, colour B

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