

BASIC ANALYTICAL CHEMISTRY

Volumetric Analysis

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VOLUMETRIC ANALYSIS

- ♥ It is a general term for a method in quantitative chemical analysis in which the amount of a substance is determined by the measurement of the volume that the substance occupies.
- ♥ It is commonly used to determine the unknown concentration of a known reactant.
- ♥ Volumetric analysis is often referred to as titration, a laboratory technique in which one substance of known concentration and volume is used to react with another substance of unknown concentration.

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* Definition of terms

Volumetric Analysis

- Involves the preparations, storage, and measurement of volume of chemicals for analysis

Volumetric Titrimetry

- Quantitative chemical analysis which determines volume of a solution of accurately known concentration required to react quantitatively with the analyte (whose concentration to be determined).
- The volume of titrant required to just completely react with the analyte is the TITRE.

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Definition of terms

Titration

- A process in which a standard reagent is added to a solution of analyte until the reaction between the two is judged complete

Primary Standard

A reagent solution of accurately known concentration is called a standard solution.

Standardization

- A process to determine the concentration of a solution of known concentration by titrating with a primary standard

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Definition of terms

End point

- The point at which the reaction is observed to be completed is the end point
- The end point in volumetric method of analysis is the signal that tells the analyst to stop adding reagent and make the final reading on the burette.
- Endpoint is observed with the help of indicator

Equivalent point

- The point at which an equivalent or stoichiometric amount of titrant is added to the analyte based on the stoichiometric equation

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The Equipment

- Volumetric analysis involves a few pieces of equipment:

Pipette - for measuring accurate and precise volumes of solutions

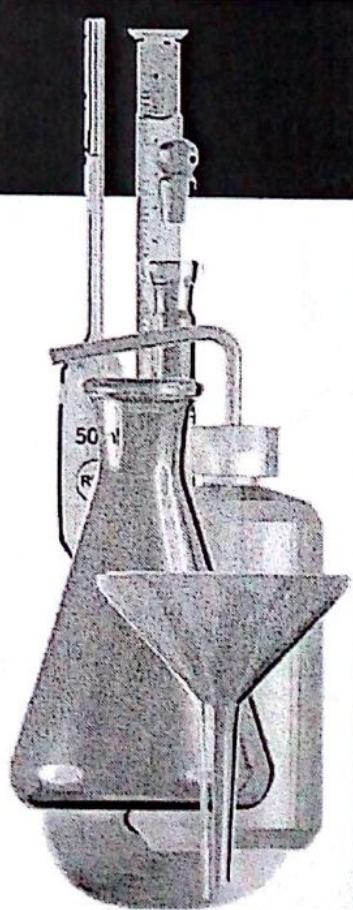
Burette - for pouring measured volumes of solutions

Conical flask - for mixing two solutions

Wash bottles - these contain distilled water for cleaning equipment

Funnel - for transfer of liquids without spilling

Volumetric flasks - a flask used to make up accurate volumes for solutions of known concentration



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The Process - Preparation

- Two solutions are used:
 - The solution of unknown concentration;
 - The solution of known concentration – this is also known as the standard solution
- Write a balanced equation for the reaction between your two chemicals
- Clean all glassware to be used with distilled water. The pipettes and burettes will be rinsed with the solutions you are adding to them

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Process – The Setup

- The burette is attached to a clamp stand above a conical flask
- The burette is filled with one of the solutions (in this case a yellow standard solution)
- A pipette is used to measure an aliquot of the other solution (in this case a purple solution of unknown concentration) into the conical flask
- Prepare a number of flasks for repeat tests
- Last, an indicator is added to the conical flask

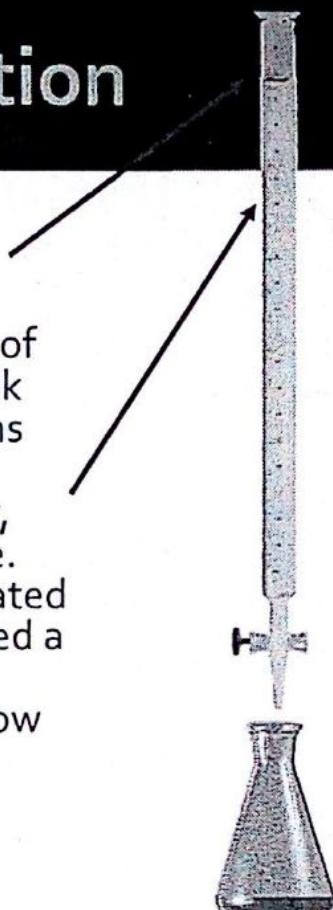


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Process – The Titration

- Read the initial level of liquid in the burette
- Turn the tap to start pouring out liquid of the burette into the flask. Swirl the flask continuously. When the indicator begins to change colour slow the flow.
- When the colour changes permanently, stop the flow and read the final volume. The volume change needs to be calculated (and written down). This volume is called a titre
- Repeat the titration with a new flask now that you know the 'rough' volume required. Repeat until you get precise results



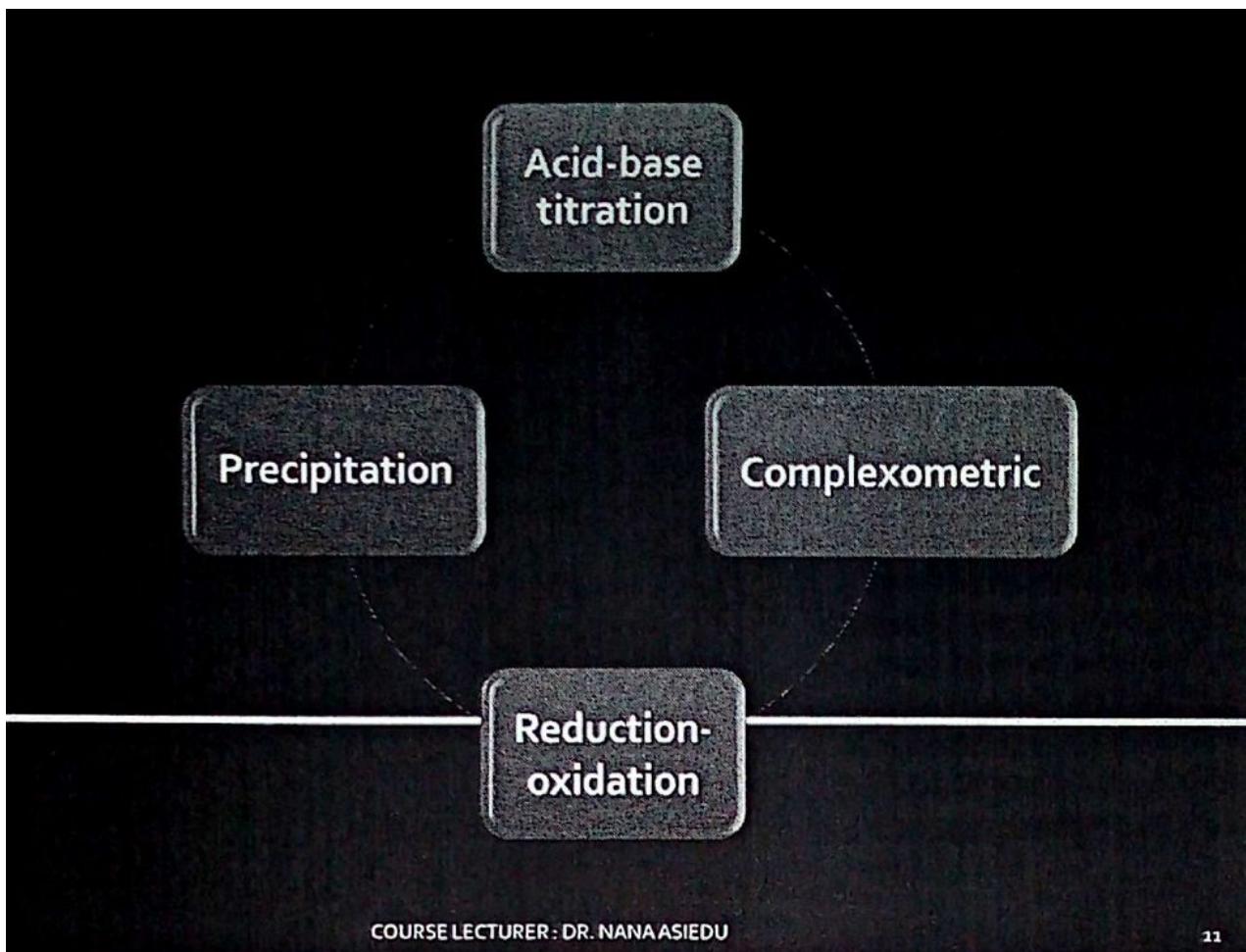
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TYPES OF VOLUMETRIC ANALYSIS

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TITRATION

- * Titration is a process in which a standard reagent is added to a solution of an analyte until the reaction between the analyte and reagent is judged to be complete.
- * When the reaction involves an acid and a base, the method is referred to as an **acid-base titration**.
- * When the reaction involves oxidation and reduction, the method is referred to as a **redox titration**.

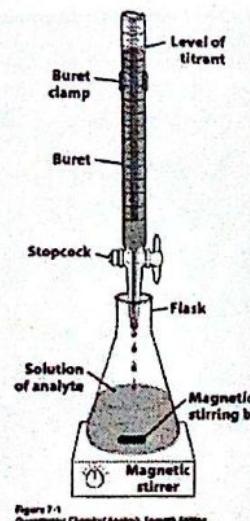


Figure 7-1
Qualitative Chemical Analysis, Seventh Edition
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ACID-BASE TITRATION

Titrations involving acid-base neutralization reactions.

- ❖ **Equivalence point:** The point in the reaction at which both acid and base have been consumed (equivalent or exactly stoichiometric amount), i.e. neither acid nor base is present in excess.
- ❖ **End point:** Actual result obtained by observation of a sudden change of physical properties, i.e. indicator changes color very near to the equivalent point.
- ❖ **Titrant:**
The known solution added to the solution of unknown concentration.
- ❖ **Titration Curve:**
The plot of pH vs. volume.

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End Point & Equivalent Point

END POINT	EQUIVALENT POINT
The point at which the reaction is <u>observed</u> to be completed	The point at which an equivalent or stoichiometric amount of titrant is added to the analyte
The end point signal frequently occurs at some point other than the equivalent point. - tells the analyst to stop adding TITRANT and record the volume.	The point at which the reaction is complete
The selected indicator should change color very near to the equivalent point.	Theoretically at the equivalence point we can calculate the amount of titrant that is required to react EXACTLY with the amount of analyte present.

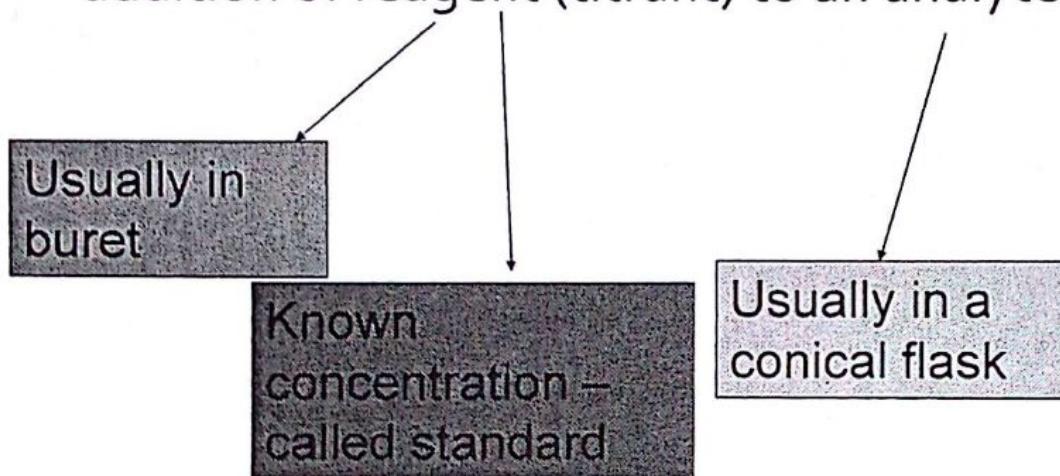
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TITRIMETRIC ANALYSIS

What is a titration :

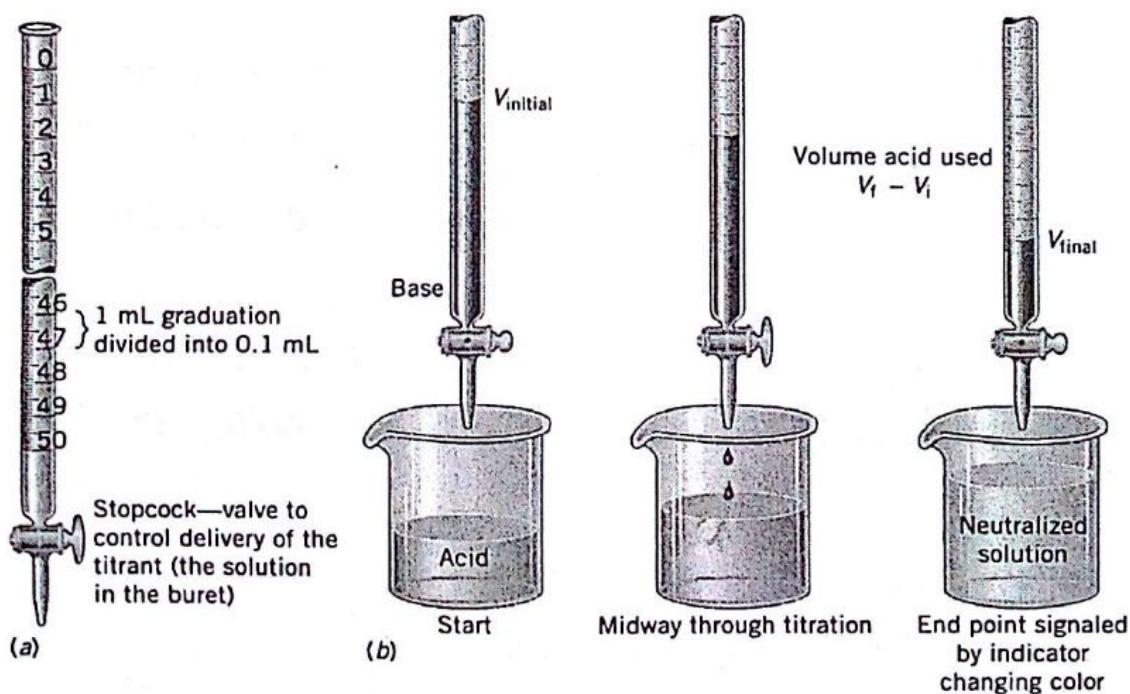
A procedure of carefully controlled addition of reagent (titrant) to an analyte.



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What happened during Titration



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Requirement For Successful Volumetric Titration

- ★ Reaction must be stoichiometric, well defined reaction between titrant and analyte.
- ★ Reaction should be rapid.
- ★ Reaction should have no side reaction, no interference from other foreign substances.
- ★ Must have some indication of end of reaction, such as color change, sudden increase in pH, zero conductivity, etc.
- ★ Known relationship between endpoint and equivalence point.

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Direct & Back Titration

- Direct Titration:
Titrant is added to the analyte until the reaction is complete.
- Back Titration:
Alternative technique to direct titration.

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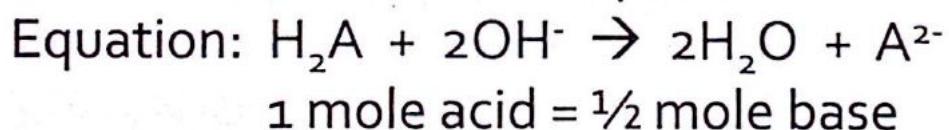
CALCULATION ACID-BASE

Example 1

A sample weighing 0.8365 g is a diprotic acid was dissolved in 75.0 mL distilled water. Indicator was added and the solution was titrated with sodium hydroxide solution. 35.35 mL was needed to reach the end point. Molar mass of acid is 150 g/mol.

1. State whether the equivalence point is greater or less than 7.
2. Name a suitable indicator that can be used in the above titration.
3. Calculate the molarity of the base.

First write the reaction equation:



$$\begin{aligned}\text{Mole acid} &= \frac{0.835}{150} = 5.5767 \times 10^{-3} \text{ mole} \\ &= 5.5767 \text{ mmole}\end{aligned}$$

$$\text{Molarity of acid} = \frac{5.5767}{75} = \underline{0.0744} \text{ M}$$

$$\frac{M_a V_a}{M_b V_b} = \frac{1}{2}$$

$$M_b = \frac{2 \times 0.0744 \times 75}{35.35} = \underline{0.3157} \text{ M} \#$$

OR

$$\begin{aligned}\text{Mmole base} &= 2 \times \text{mmole acid} \\ &= 2 \times 5.5767 \text{ mmole} \\ &= 11.1534 \text{ mmole NaOH.}\end{aligned}$$

$$\begin{aligned}\text{Molarity NaOH} &= \frac{\text{mmole NaOH}}{\text{Volume (mL)}} \\ &= \frac{11.1534}{35.35} \\ &= \underline{0.3155} \text{ M}\end{aligned}$$

CALCULATION ACID-BASE

Example 2: Calculate the concentration of vinegar in %w/v for a titration of 25 ml of vinegar which was primarily diluted 10 times (25mL into 250mL), reacted with 22.4 ml of 0.1 M NaOH standard solution.

$$\begin{aligned}\text{Mass of vinegar} &= (\text{Liters}_{\text{vinegar}})(M_{\text{vinegar}})(Fwgt_{\text{vinegar}}) \\ &= (0.25)\left(\frac{22.4 \times 0.1}{25}\right)(60) \\ &= \underline{\underline{1.34\text{g}}}\end{aligned}$$

In %w/v, concentration of vinegar is $1.34/25 = 5.4\%$

→ In g/mL

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DIRECT TITRATION

Sometime not feasible due to:

- Reaction kinetic or the reaction rate is **slow**.
- **No suitable indicator** in the direct titration.
- The **color change** is slow or delay.
- The end point is far from the equivalent point.

BACK TITRATION

- In a simple acid-base titration, a base (reagent) is added in a known quantity – greater than the amount required for acid neutralization.
- Acid and base reacts completely.
- The remaining base is titrated with a standard acid.
- The system has gone from being ACID, past the equivalent point to the BASIC (excess base), and back to the equivalent point again. The final titration to the equivalent point is called **BACK TITRATION**.

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Example Of Back Titration

- The titration of insoluble acid organic acid with NaOH is not practical because the reaction is slow.
- To overcome it add NaOH in excess and allow the reaction to reach completion and then titrate the excess NaOH with a standard solution of HCl.
- The system has gone from being ACID , past the equivalence point to the BASIC side (excess base), and then back to the equivalence point.
- The final titration to the equivalence point is called a **BACK TITRATION**.

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Calculation Examples On Analysis Using Back Titration Method

Example 1

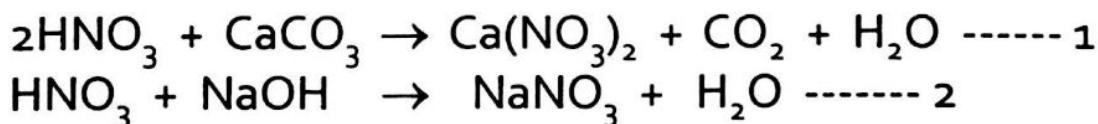
150.0 mL of 0.2105 M nitric acid was added in excess to 1.3415 g calcium carbonate. The excess acid was back titrated with 0.1055 M sodium hydroxide. It required 75.5 mL of the base to reach the end point.

Calculate the percentage (w/w) of calcium carbonate in the sample.

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First write a balance equation for the above reactions.



From Equations above:

$$1 \text{ mole HNO}_3 = \frac{1}{2} \text{ mole CaCO}_3$$

$$1 \text{ mole HNO}_3 = 1 \text{ mole NaOH}$$

Initial amount of acid:

$$\begin{aligned} \text{mmole of acid} &= 0.2105 \times 150 \\ &= 31.575 \text{ mmole acid.} \end{aligned}$$

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Remaining/excess acid during back titration:

$$\begin{aligned}\text{Mmole of excess acid} &= 0.1055 \times 75.5 \\ &= 7.965 \text{ mmole acid.}\end{aligned}$$

$$\begin{aligned}\text{Mmole of acid reacted with CaCO}_3 &= (31.575 - 7.965) \\ &= 23.61 \text{ mmole acid.}\end{aligned}$$

$$\begin{aligned}\text{Mmole of CaCO}_3 &= \frac{1}{2} \times \text{mmole acid} \\ &= \frac{1}{2} \times 23.61 \\ &= 11.805 \text{ mmole CaCO}_3.\end{aligned}$$

$$\begin{aligned}\text{Gram CaCO}_3 &= \text{mole} \times \text{molar mass} \\ &= 11.805 \times 10^{-3} \times 100 \\ &= 1.1805 \text{ g.}\end{aligned}$$

$$\begin{aligned}\% \text{CaCO}_3 &= \frac{\text{weight CaCO}_3}{\text{weight of sample}} \times 100 \\ &= \frac{1.1805}{1.3415} \times 100 \\ &= 87.99 \% (\text{w/w})\end{aligned}$$

ACID – BASE TITRATION

Arhenius



- Acid are species that can DONATE PROTON, H^+



- Base are species that can DONATE HYDROSIDE ions, OH^-
- Neutralisation is the reaction between an acid and a base :
$$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$$

Bronsted:

Acid → it can donate proton, H^+

Base → it can accept proton, H^+

CHOOSING A TITRANT

In theory, any **strong acid or strong base** can be used as titrant.

The reason for this is that most reaction involving a strong acid or a strong base is QUANTITATIVE.

Examples of strong acid titrants :

Hydrochloric acid (HCl), Nitric acid (HNO_3),

Perchloric acid (HClO_4), Phosphoric acid (H_3PO_4)

Weak acid titrant

Acetic acid ,(CH_3COOH)
Ammonium ion, (NH_4^+)
Hydrogen flouride, (HF)
Carbonic acid, (H_2CO_3)
Nitrous acid, (HNO_2)
Hydrogen sulphide, (H_2S)
Hydrogen cynide, (HCN)

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Strong & Weak Base Titrant

Strong base titrant	Weak base titrant
Sodium hydroxide, NaOH	Ammonium hydroxide, NH_4OH
Potassium hydroxide, KOH	Amine acetate.
Magnesium hydroxide, $\text{Mg}(\text{OH})_2$	Carbonate, CO_3^{2-}
Barium hydroxide , $\text{Ba}(\text{OH})_2$	Flouride ion, F^-
	Sodium carbonate, NaCO_3

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TYPES OF ACID-BASE TITRATION

1. Titration of strong acid with strong base.
2. Titration of strong acid with weak base.
3. Titration of weak acid with strong base.
4. Titration of weak acid with weak base.

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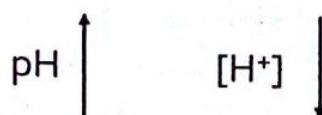
pH - A Measure of Acidity

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

Solution Is

At 25°C

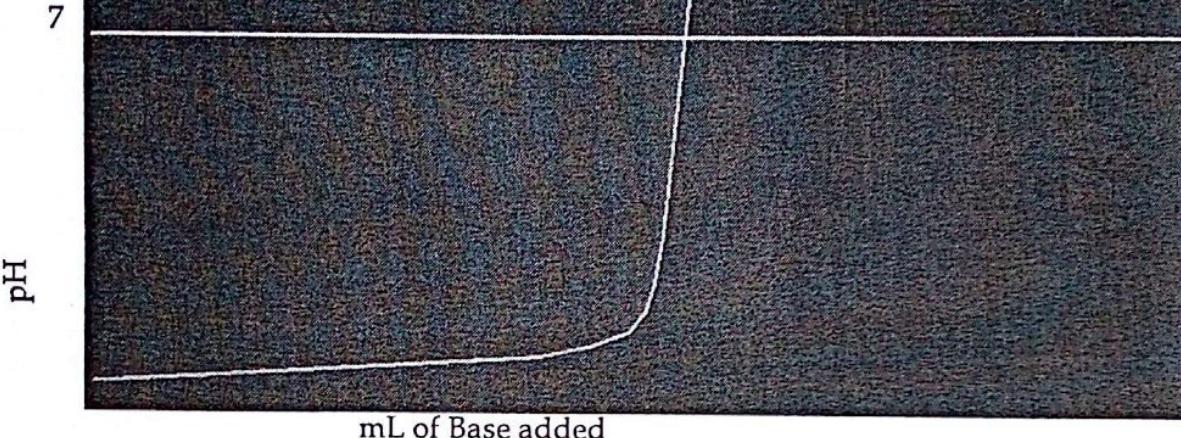
neutral	$[\text{H}^+] = [\text{OH}^-]$	$[\text{H}^+] = 1 \times 10^{-7}$	$\text{pH} = 7$
acidic	$[\text{H}^+] > [\text{OH}^-]$	$[\text{H}^+] > 1 \times 10^{-7}$	$\text{pH} < 7$
basic	$[\text{H}^+] < [\text{OH}^-]$	$[\text{H}^+] < 1 \times 10^{-7}$	$\text{pH} > 7$



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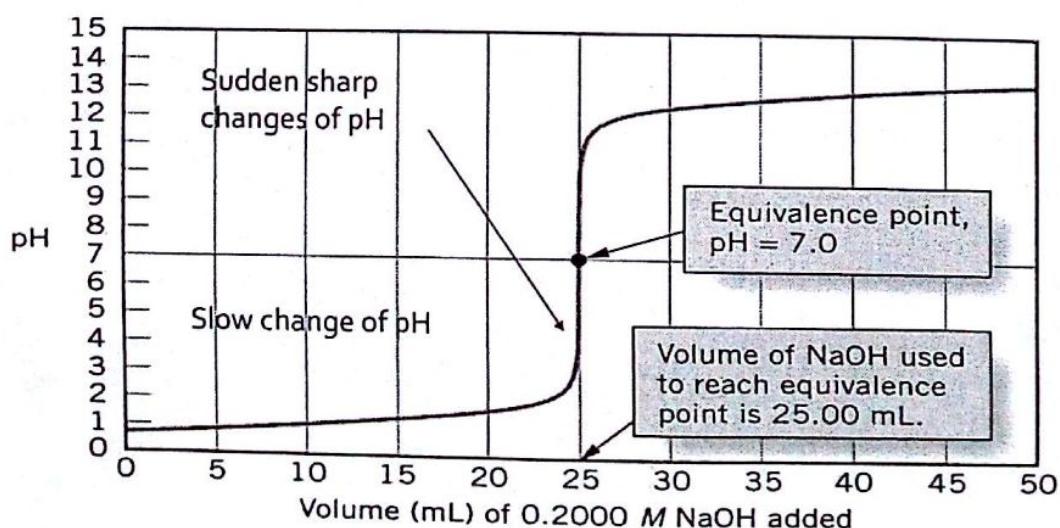
- Strong acid with strong Base
- Equivalence at pH 7



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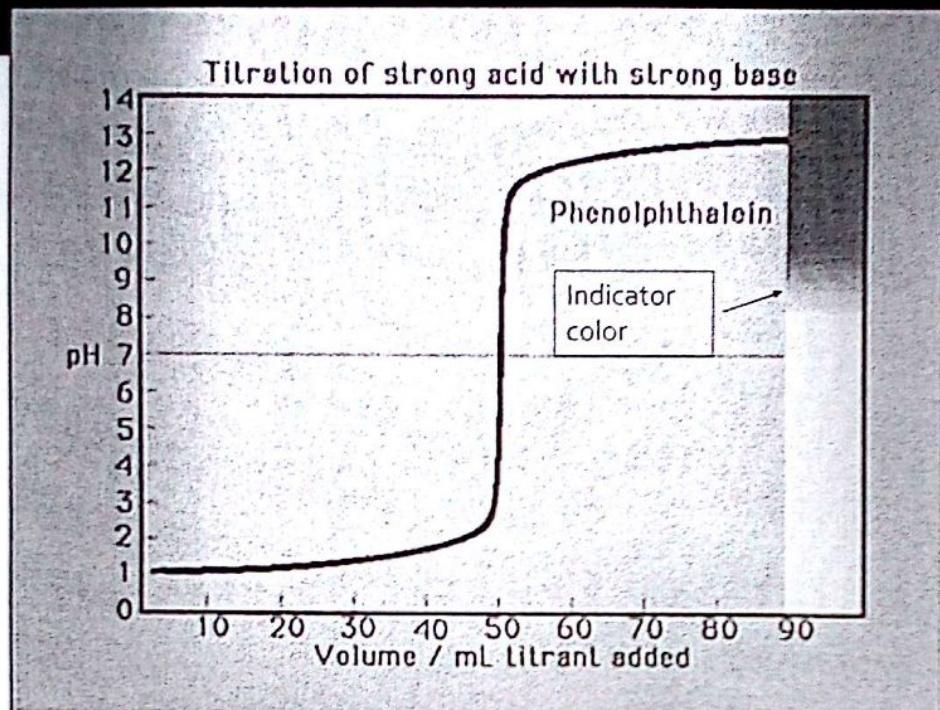
- Titration of a strong acid by a strong base



Titration curve for the titration of 25.00 mL of 0.2000 M HCl (a strong acid) with the 0.2000 M NaOH (a strong base).

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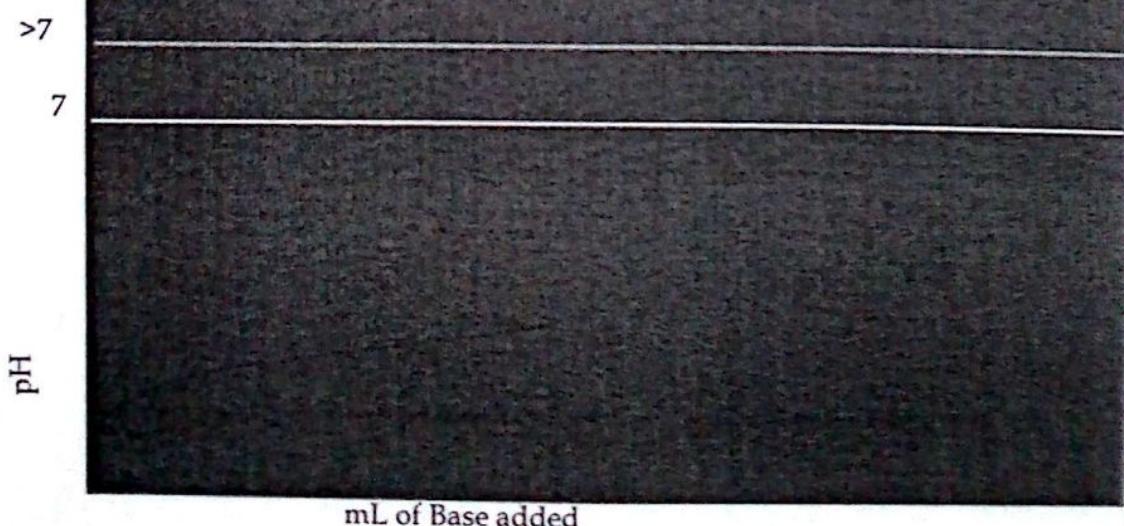
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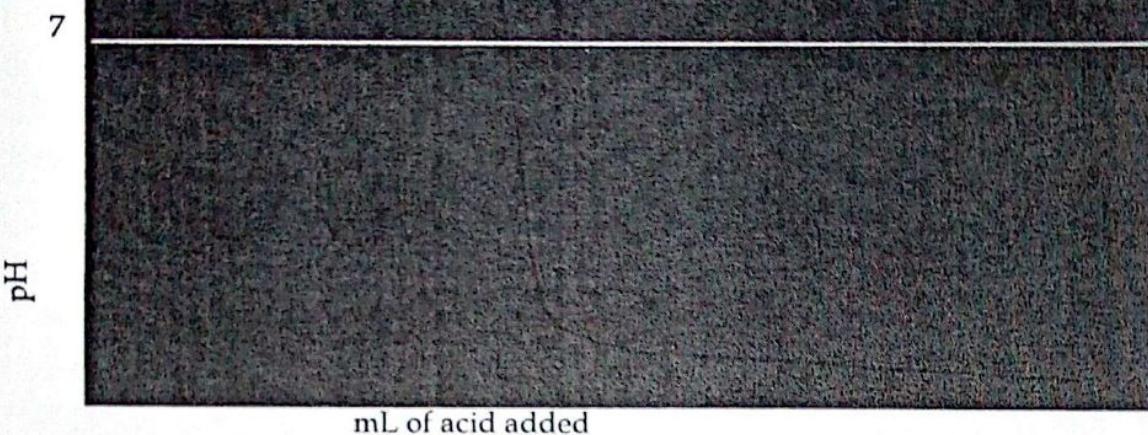
- | Weak acid with strong Base
- | Equivalence at pH >7
- | When the acid is neutralized it makes a weak base



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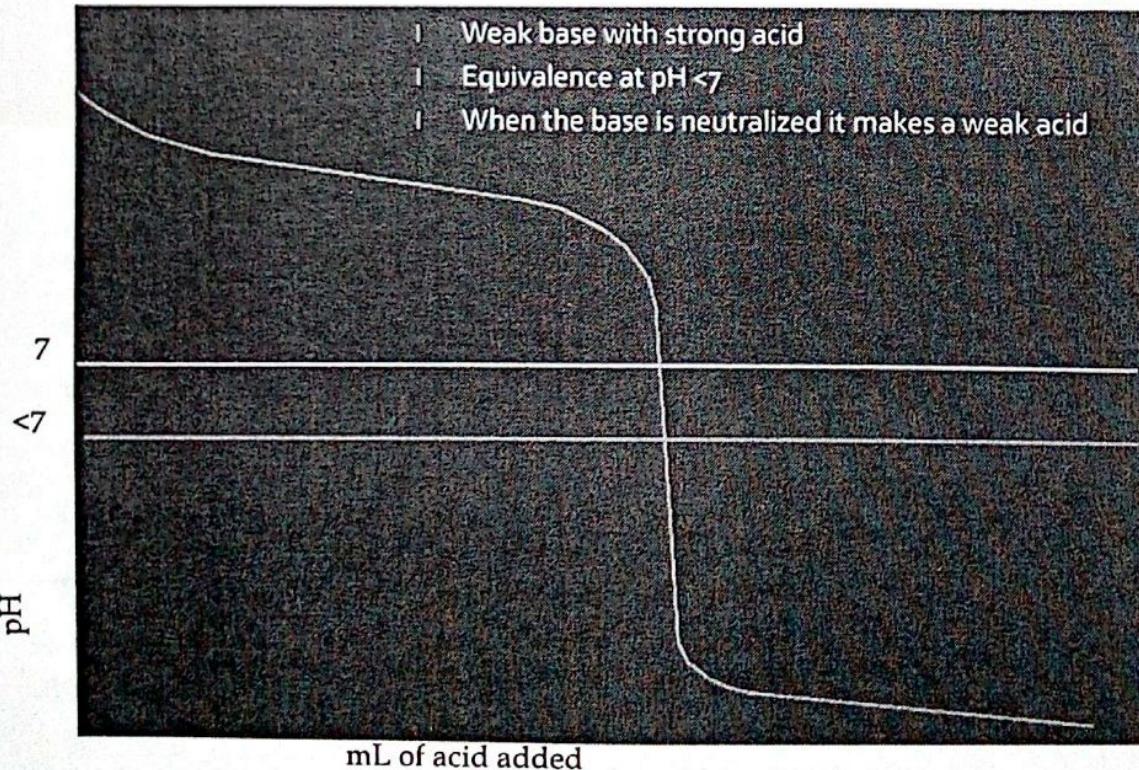
- | Strong base with strong acid
- | Equivalence at pH 7



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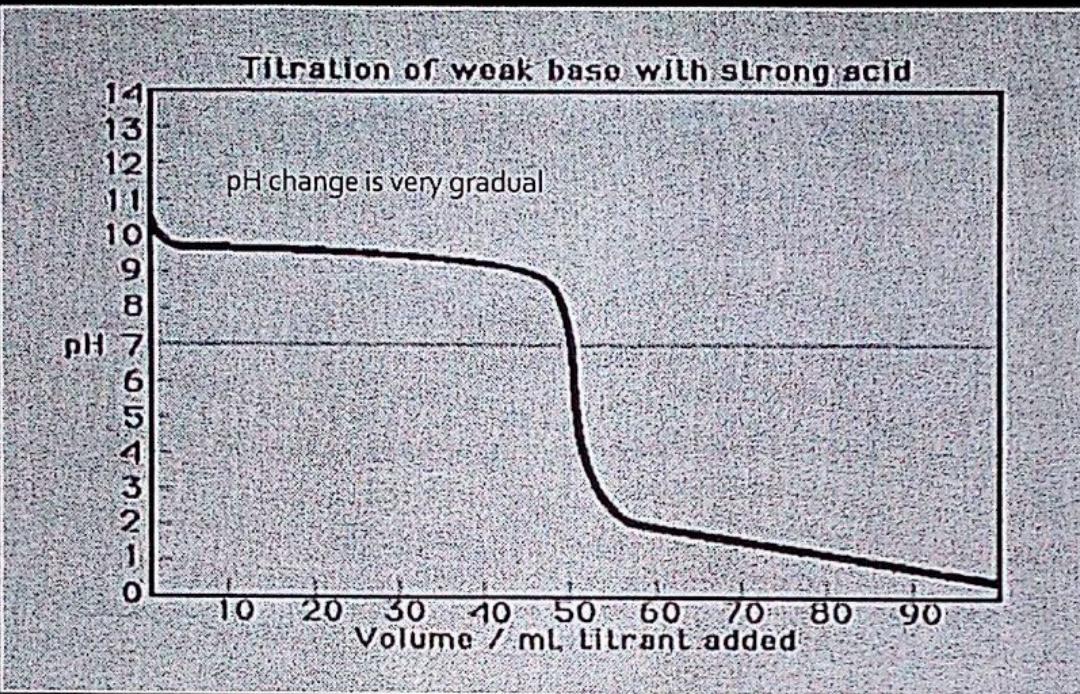
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- | Weak base with strong acid
- | Equivalence at pH <7
- | When the base is neutralized it makes a weak acid



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Strong Acid With

- ♦ Do the stoichiometry.
- ♦ $\text{mL} \times M = \text{mmol}$
- ♦ There is no equilibrium .
- ♦ They both dissociate completely.
- ♦ The reaction is $\text{H}^+ + \text{OH}^- \rightarrow \text{HOH}$
- ♦ Use $[\text{H}^+]$ or $[\text{OH}^-]$ to figure pH or pOH
- ♦ The titration of 50.0 mL of 0.200 M HNO_3 with 0.100 M NaOH

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Weak acid with Strong base

- There is an equilibrium.
- Do stoichiometry.
 - Use moles
- Determine major species
- Then do equilibrium.
- Titrate 50.0 mL of 0.10 M HF ($K_a = 7.2 \times 10^{-4}$) with 0.10 M NaOH

Summary

- Strong acid and base just stoichiometry.
- Weak acid with zero ml of base - K_a
- Weak acid before equivalence point
 - Stoichiometry first
 - Then Henderson-Hasselbach
- Weak acid at equivalence point- K_b
 - Calculate concentration
- Weak acid after equivalence - leftover strong base.
 - Calculate concentration

Summary

- Weak base before equivalence point.
 - Stoichiometry first
 - Then Henderson-Hasselbach
- Weak base at equivalence point K_a .
 - Calculate concentration
- Weak base after equivalence – left over strong acid.
 - Calculate concentration

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INDICATOR AND CHOICE OF INDICATOR

Acid –Base Indicators

The acid-base indicator function by changing colour just after the equivalence point of a titration; this colour change is called the end point.

The end point is most often detected VISUALLY. Most acid-base indicators are organic dye molecules which are either acids or bases.

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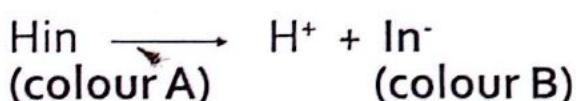
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Acid –Base Indicators

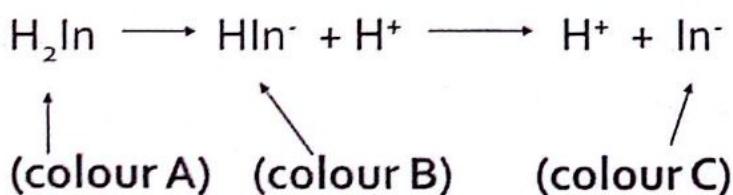
Indicators can be monoprotic (HIn) or diprotic (H_2In) acids.

The acid form of an indicator is usually coloured; when it loses a proton resulting in anion (In^-), or base form of the indicator, exhibiting different colour.

The two forms exist in equilibrium with one another as follows:



A diprotic acid indicator, H_2In , ionizes in **TWO steps** as follows:



Selecting And Using Indicators

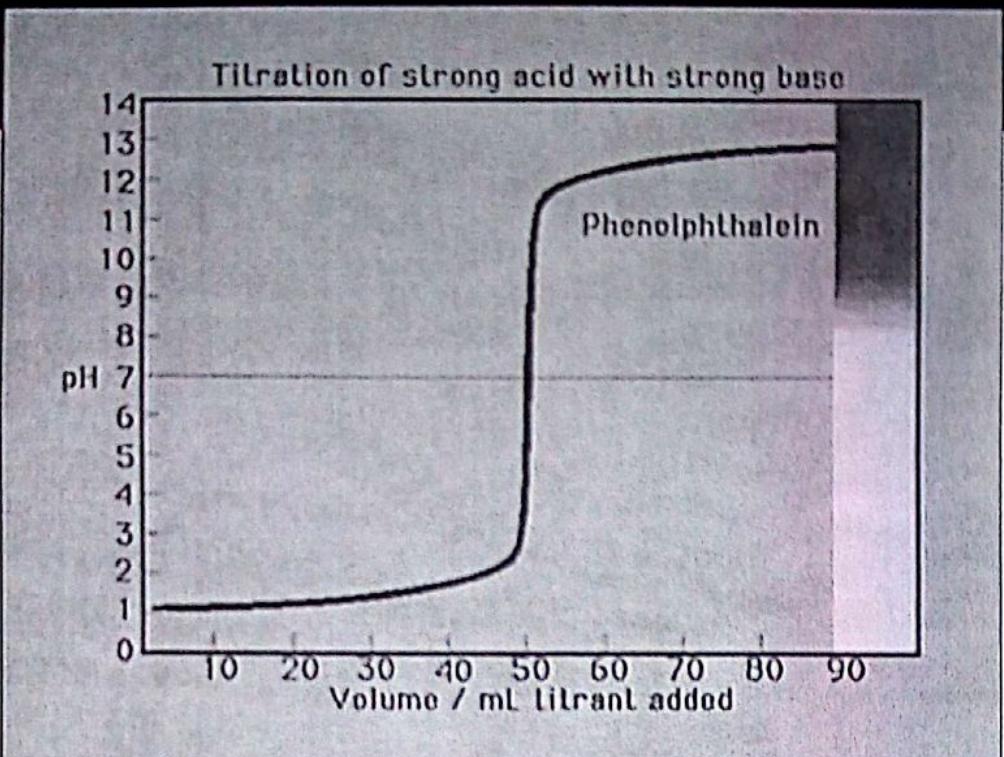
Choose an indicator that undergoes a distinct colour change at the equivalence point (true end point) of an acid-base titration .

Choose an indicator whose middle half of the pH transition range (greatest colour change) encompasses/overlap the pH at the equivalence point or the pH at the steepest part of the titration curve.

For indicator color change to be detectable by normal eyesight, a rough tenfold excess of one or the other form of the indicator must be present. This corresponds to a pH range of ± 1 pH unit about the pK of the indicator

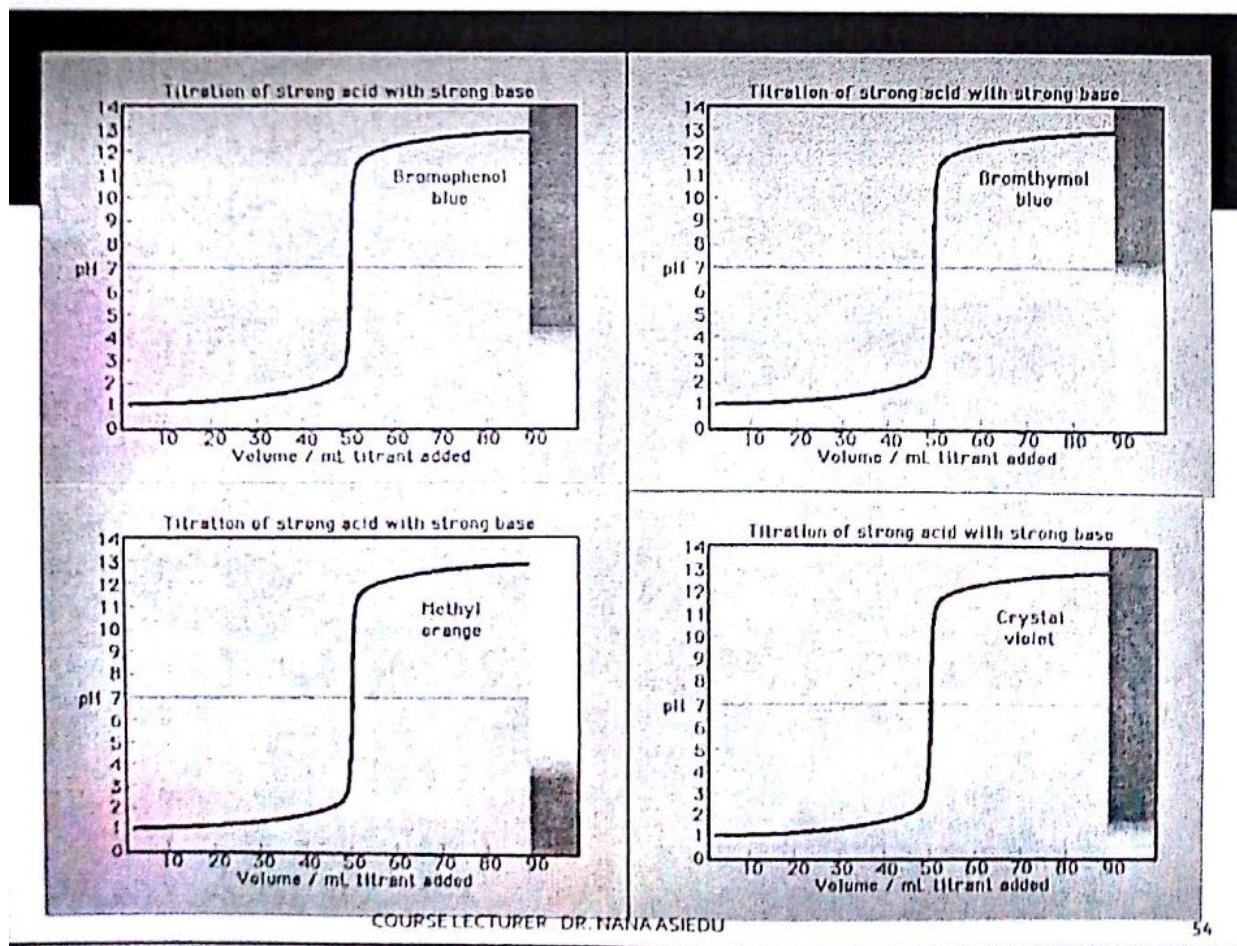
ACID-BASE INDICATORS

Common Name	Transition range	Colour Change	
		ACID	BASE
Crystal violet	0.1 – 1.5	Yellow	Blue
Thymol blue	1.2 – 2.8	Red	Yellow
Mrthyl yellow	2.4 – 4.0	Red	Yellow
Methyl orange	3.1 – 4.4	Red	Yellow
Bromocresol green	3.8 – 5.4	Yellow	Blue
Methyl red	4.2 – 6.3	Red	Yellow
Chlorophenyl red	4.5 – 6.4	Yellow	Red
Bromothymol blue	6.0 – 7.6	Yellow	Blue
Phenol red	6.4 – 8.0	Yellow	Red
Thymol blue	8.0 – 9.6	Yellow	Blue
Phenolphthalein	8.0 – 9.7	Colourless	Red



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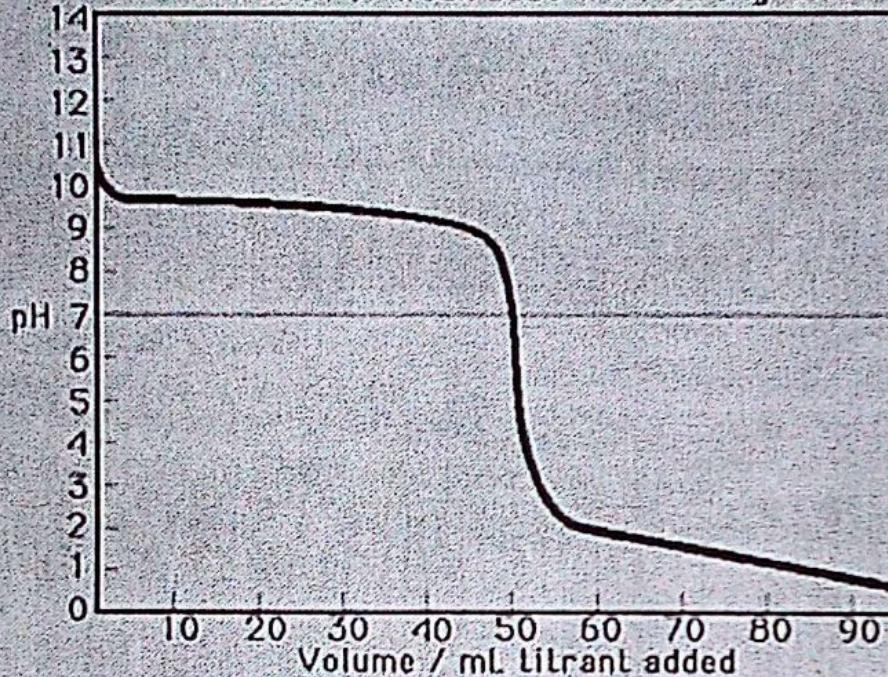
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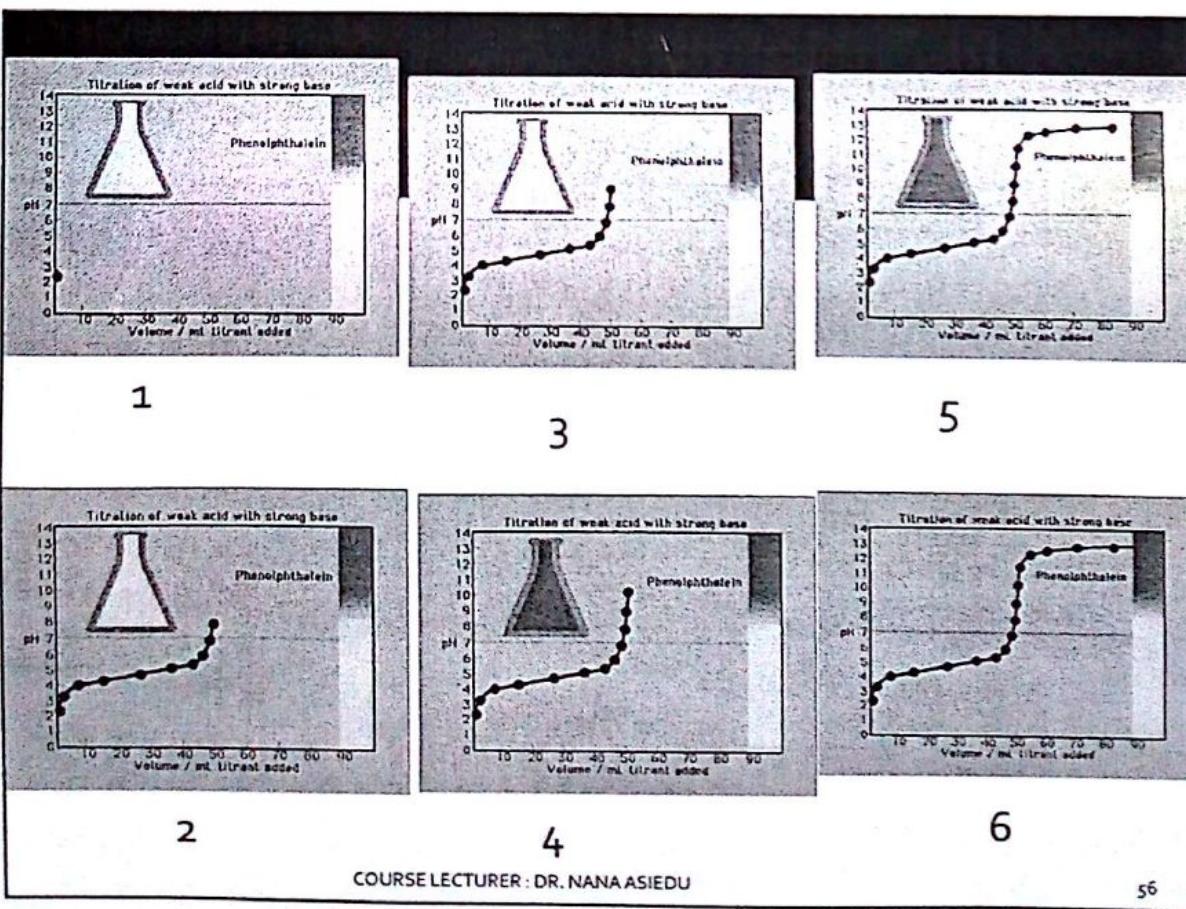
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Titration of weak base with strong acid



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