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## UNIT 3 ACID-BASE TITRATIONS-II

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### 3.1 INTRODUCTION

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In Unit 2, we discussed the basic principle of acid-base titrations. Based on this, you performed three experiments for the analysis of acetic acid in vinegar using three different techniques. In this unit we are expanding acid-base titration method further for the analysis of a mixture of sodium carbonate and sodium hydroxide. This method of titration will help you in understanding the basic principle of some important industrial analyses such as that of soda ash, sodium bicarbonate, mixture of sodium carbonate—sodium bicarbonate, commercial caustic soda, washing soda, etc. The procedures, such as, conductometry, potentiometry or acid-base indicators can be used to analyse the above substances. Here we will discuss the acid-base indicator method only for the analysis of a mixture of sodium carbonate and sodium hydroxide.

#### Objectives

After performing this experiment you should be able to :

- state and explain the principle of acid-base titration with special reference to the titration of sodium carbonate and sodium hydroxide mixture,
- standardise the given solution of hydrochloric acid and use it in estimating basic solutions, and
- determine the strength of sodium carbonate and sodium hydroxide in a given solution.

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### 3.2 EXPERIMENT 4 : DETERMINATION OF SODIUM CARBONATE AND SODIUM HYDROXIDE IN A MIXTURE BY INDICATOR METHOD

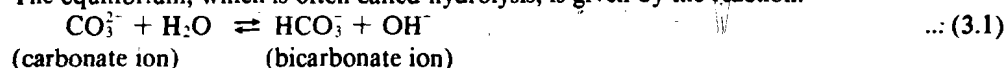
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Titration of a mixture of sodium carbonate and sodium hydroxide is basically the same as the acid-base titration discussed in Unit 2, except that there will be more than one region in which the pH varies rapidly because such a titration has more than one equivalence point. Titration curve also shows more than one sharp pH breaks. First we will discuss the principle.

#### 3.2.1 Principle

We observe two equivalence points in this titration. You may like to ask, why does a mixture of sodium carbonate and sodium hydroxide behave this way? To answer this question we should first study the behaviour of sodium carbonate solution and then the behaviour of a mixture of sodium carbonate and sodium hydroxide in acid-base titrations.

Sodium carbonate is a salt of a weak acid and a strong base; when such salts are dissolved in water, they behave as bases due to the basicity of the conjugate base  $\text{CO}_3^{2-}$  in this case. The equilibrium, which is often called hydrolysis, is given by the reaction:



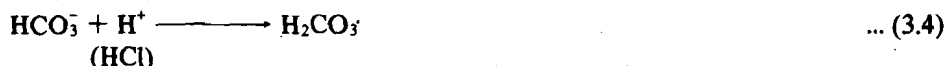
(carbonate ion)                      (bicarbonate ion)

The bicarbonate ion is further hydrolysed to carbonic acid :



The  $\text{OH}^-$  ions so produced in solution are responsible for the basic character of sodium carbonate.

When sodium carbonate is titrated with a strong acid, such as hydrochloric acid, the carbonate ions are first converted to the bicarbonate ions, and then to carbonic acid. This is due to the fact that a strong acid displaces a weak acid from the conjugate base of the latter.



Combining both the above equations we can write,



From Eq. 3.5, we can see that  $p = 1$  and  $q = 2$ , substituting these values in Eq. 1.8, we get

$$\frac{M_{\text{Na}_2\text{CO}_3} V_{\text{Na}_2\text{CO}_3}}{M_{\text{HCl}} V_{\text{HCl}}} = \frac{1}{2}$$

$$\text{i.e., } M_{\text{HCl}} V_{\text{HCl}} = 2M_{\text{Na}_2\text{CO}_3} V_{\text{Na}_2\text{CO}_3} \quad \dots (3.6)$$

Due to the neutralisation taking place in two steps as indicated by reactions in Eqs. 3.3 and 3.4, we observe two regions of sharp pH change in the titration curve (Fig. 3.1) and thus two equivalence points. Here up to the first equivalence point  $\text{CO}_3^{2-}$  is neutralised to  $\text{HCO}_3^-$  stage; and up to the second equivalence point  $\text{HCO}_3^-$  is neutralised to  $\text{H}_2\text{CO}_3$  stage. In this experiment we will utilise this behaviour of sodium carbonate in the estimation of a mixture of sodium carbonate and sodium hydroxide.

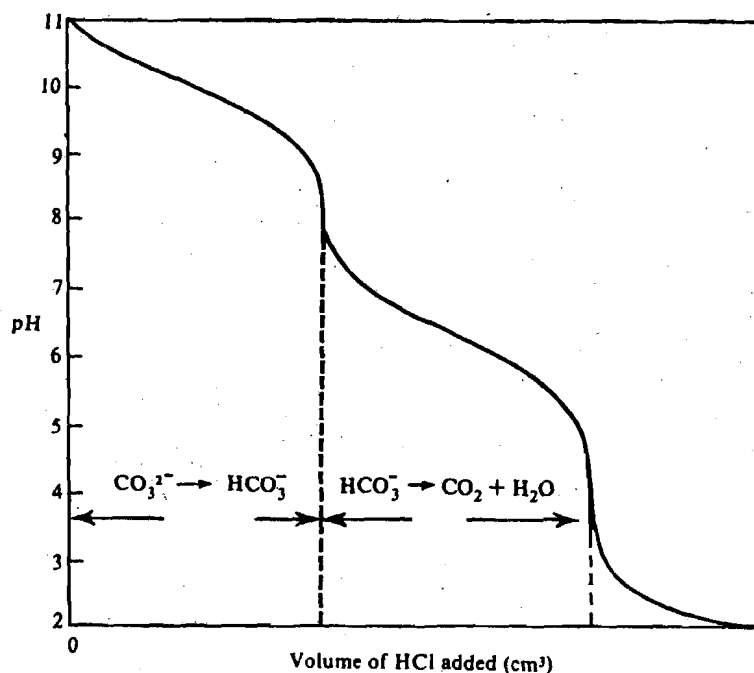


Fig. 3.1 : Titration curve for sodium carbonate titrated with hydrochloric acid.

The titration curve for a sodium carbonate and sodium hydroxide mixture is shown in Fig. 3.2. As you can see, it has two equivalence points. The first equivalence point indicates complete neutralisation of  $\text{NaOH}$  plus half neutralisation of the carbonate, i.e., its conversion to the bicarbonate (cf Eq. 3.3). The second equivalence point indicates neutralisation of the bicarbonate (cf Eq. 3.4).

From Fig. 3.2 and Table 2.3 you can see that for the detection of the first and the second end points, phenolphthalein and methyl orange, respectively, are the suitable indicators. Once these two end points are detected, volume of  $\text{HCl}$  used to titrate sodium hydroxide and sodium carbonate may be calculated. This can be further illustrated by considering Fig. 3.3.

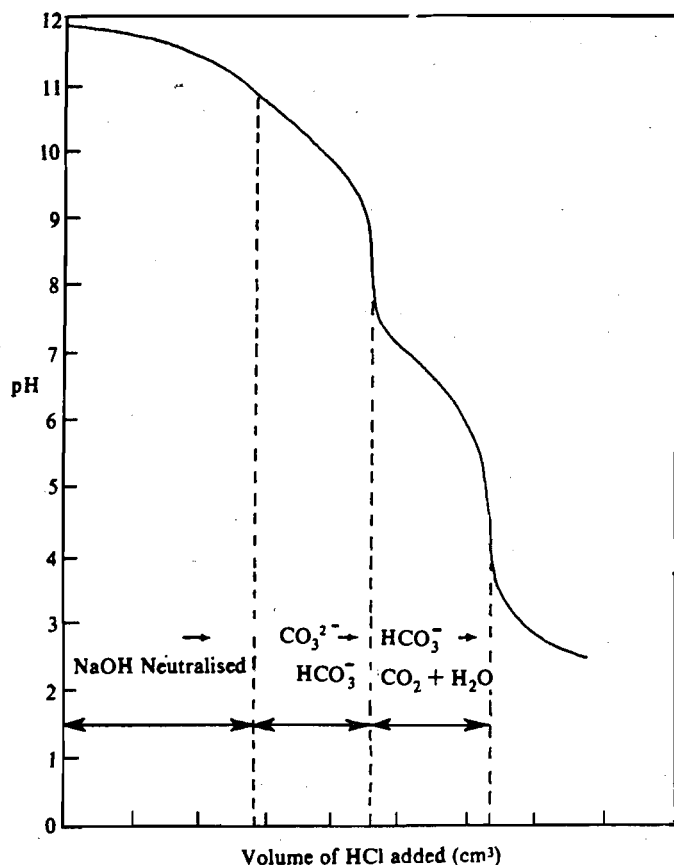


Fig. 3.2 : Titration curve for a mixture of sodium carbonate and sodium hydroxide titrated against acid.

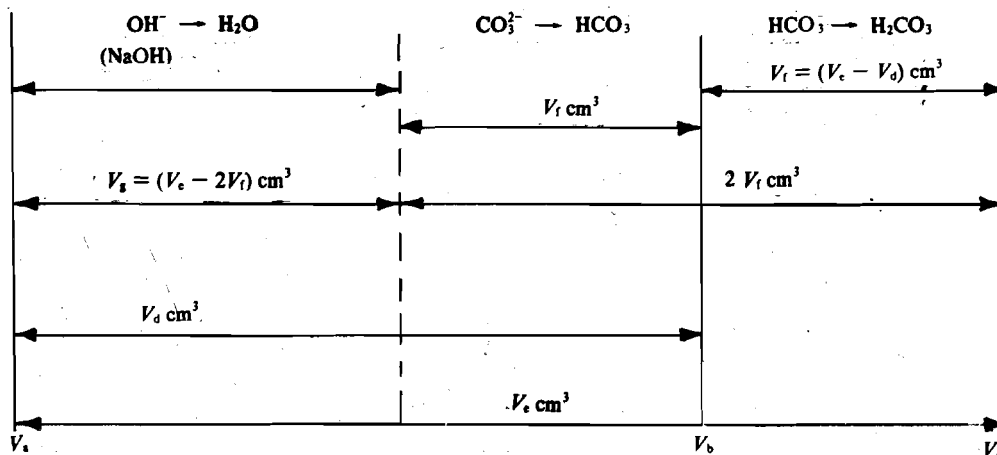
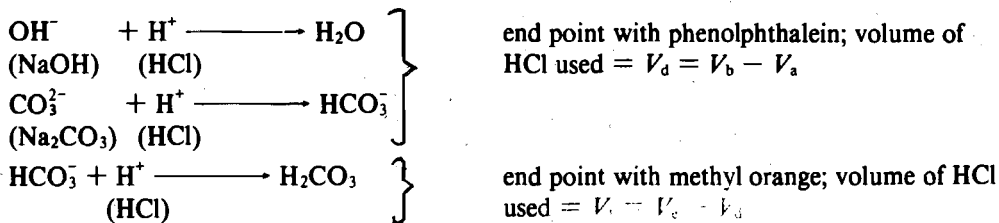


Fig. 3.3 : Titration of a mixture of sodium carbonate and sodium hydroxide with hydrochloric acid.

In this diagram  $V_a$ ,  $V_b$  and  $V_c$  refer to burette readings—initial, at the end point with phenolphthalein and at the end point with methyl orange, respectively. The values of  $V_a$ ,  $V_b$  and  $V_c$  are also used in observation Table II in calculating the volumes of HCl required for neutralising NaOH and  $\text{Na}_2\text{CO}_3$  mixtures. Thus, for the first end point we need  $V_b - V_a = V_d \text{ cm}^3$  and for the second end point  $V_c - V_a = V_c \text{ cm}^3$  of hydrochloric acid, then the titration of  $\text{HCO}_3^-$  requires  $V_c - V_d = V_t \text{ cm}^3$  of HCl. An additional  $V_t \text{ cm}^3$ , therefore, is required to titrate the original  $\text{CO}_3^{2-}$  to  $\text{HCO}_3^-$ . Titration of the  $\text{OH}^-$  in the original sample needs  $V_c - 2V_t = V_b \text{ cm}^3$  of HCl.

The corresponding chemical reactions may be summarised as :



Before using hydrochloric acid for the titration it should be standardised with a suitable primary standard, preferably sodium carbonate. The reaction between sodium carbonate and hydrochloric acid is given in Eqs. 3.3–3.5 which we have already discussed. End point of the titration is detected with methyl orange indicator.

Before proceeding further, answer the following SAQs.

**SAQ 1**

Suggest whether aqueous solutions of the following substances are acidic, basic or neutral

- a) NaCN b) NaCl c) CH<sub>3</sub>COONa d) NaHCO<sub>3</sub> e) K<sub>2</sub>CO<sub>3</sub>

.....  
 .....

**SAQ 2**

Predict the number of pH breaks observed for the following titrations.

- a) CH<sub>3</sub>COOH – NaOH  
 b) NaHCO<sub>3</sub> – HCl  
 c) K<sub>2</sub>CO<sub>3</sub> – HCl

.....  
 .....

**SAQ 3**

On the basis of Fig. 3.4 given below, suggest suitable indicators for the titration.

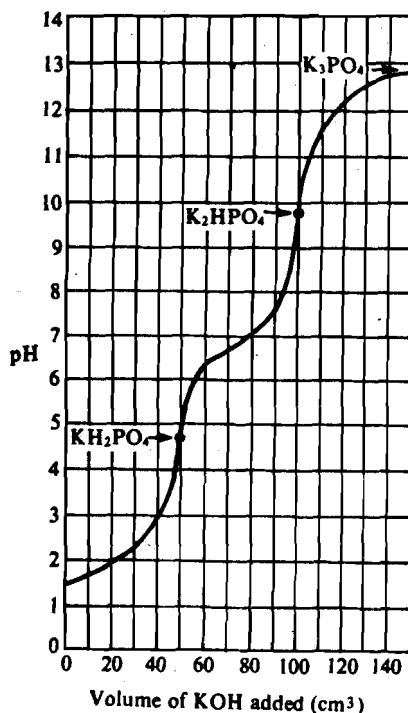


Fig. 3.4 : Titration of 50 cm<sup>3</sup> of 0.1 M H<sub>3</sub>PO<sub>4</sub> with 0.1 M KOH

**3.2.2 Requirements**

You will need the following apparatus and chemicals for this experiment.

**Apparatus**

- Burette (50 cm<sup>3</sup>) – 1
- Pipette (20 cm<sup>3</sup>) – 1
- Conical flask (250 cm<sup>3</sup>) – 1
- Weighing bottle
- Volumetric flasks (250 cm ) – 2
- Funnel – 1
- Burette stand with clamp – 1

**Chemicals**

- Sodium carbonate

**Mixture of sodium carbonate and sodium hydroxide.**

**Phenolphthalein indicator solution :** It is prepared by dissolving 5 g of the reagent in 500 cm<sup>3</sup> of ethanol and adding 500 cm<sup>3</sup> of water. If a precipitate is formed, it is filtered.

**Methyl orange indicator solution :** It is prepared by dissolving 5 g of free acid/sodium salt of the indicator in 1 dm<sup>3</sup> of water; 15.2 cm<sup>3</sup> of 0.1 M HCl is added to the sodium salt further, if necessary.

**Hydrochloric acid solution (0.1 M) :** This solution is prepared by taking 10 cm<sup>3</sup> conc. HCl in a 1 dm<sup>3</sup> volumetric flask and diluting the acid up to the mark with distilled water.

To obtain satisfactory results by double indicator method the solution titrated must be cold, and loss of carbon dioxide must be prevented as far as possible by keeping the tip of the burette immersed in the liquid.

**3.2.3 Procedure**

First collect 0.1 M hydrochloric acid in a 250 cm<sup>3</sup> bottle. Since hydrochloric acid is a secondary standard, you have to standardise it by titrating it against a primary standard, Na<sub>2</sub>CO<sub>3</sub> in this case.

**1) Standardisation of hydrochloric acid :**

- i) Take approximate mass of a clean dry weighing bottle and then weigh the weighing bottle with about 1.35 – 1.40 g of dried sodium carbonate exactly. Transfer the sodium carbonate to a clean volumetric flask of 250 cm<sup>3</sup> capacity through a glass funnel. Weigh the weighing bottle again and find the exact mass of sodium carbonate transferred by subtracting this mass from the mass of the weighing bottle plus sodium carbonate. Dissolve sodium carbonate in volumetric flask and make up the volume to the mark with distilled water.
- ii) Fill up the burette with hydrochloric acid solution and mount it on a stand. Note the reading on the burette and record it in the observation Table I under the initial reading column.
- iii) Pipette out 20 cm<sup>3</sup> of the standard sodium carbonate solution, add two to three drops of methyl orange indicator. Titrate with constant swirling against a white back-ground till a red colour is obtained. Record your reading in the observation Table I under the final reading column. Repeat the titration to get at least two concordant readings.

**2) Titration of the mixture of sodium carbonate and sodium hydroxide against standardised hydrochloric acid :**

- i) Pipette out 20 cm<sup>3</sup> of the mixture solution in a conical flask. Add 1-2 drops of phenolphthalein to it; a pink colour will be obtained.
- ii) Note the initial reading of the burette in the observation Table II under the initial reading column. Run in standardised HCl from the burette slowly into flask until the pink colour is just discharged. Note the burette reading in the observation Table II under the 'reading with phenolphthalein' column.
- iii) Now, add a few drops of methyl orange to the solution in the conical flask; a yellow colour is obtained. Run in a further quantity of the acid until the yellow colour of the solution changes to red. Note the final burette reading in the observation Table II under the 'reading with methyl orange' column. Repeat both titrations with both the indicators to get two concordant sets of readings.

**3.2.4 Observations**

Mass of the weighing bottle =  $m_1$  g = .....

Mass of weighing bottle + sodium carbonate =  $m_2$  g = .....

Mass of weighing bottle (after transferring the salt) =  $m_3$  g = .....

Amount of sodium carbonate transferred =  $m_2 - m_3 = m$  g = .....

Molar mass ( $M_m$ ) of sodium carbonate = 106 g mol<sup>-1</sup>

Volume of sodium carbonate prepared = 250 cm<sup>3</sup>

Molarity of sodium carbonate solution =  $M_1$

$$= \frac{m \times 1000}{M_m \times 250} \text{ mol dm}^{-3}$$

$$= \frac{m \times 4}{106} \text{ mol dm}^{-3}$$

$$= \dots\dots\dots \text{ mol dm}^{-3}$$

**Observation Table I**  
Sodium carbonate solutions vs. hydrochloric acid solution

S. No.	Volume of Na <sub>2</sub> CO <sub>3</sub> in cm <sup>3</sup>	Burette reading		Volume of HCl in cm <sup>3</sup> (Final - Initial)
		Initial	Final	
1	20			
2	20			
3	20			

**Observation Table II**  
Hydrochloric acid solution vs. solution of a mixture of Na<sub>2</sub>CO<sub>3</sub> and NaOH

S. No.	Volume of sodium carbonate and sodium hydroxide mixture solution in cm <sup>3</sup>	Burette Reading			Volume of HCl used in titration of NaOH + half of the Na <sub>2</sub> CO <sub>3</sub> $V_a = (V_b - V_a)$ cm <sup>3</sup>	Volume of HCl used in titration of NaOH + Na <sub>2</sub> CO <sub>3</sub> $V_c = (V_c - V_a)$ cm <sup>3</sup>	Volume of HCl used in titration of HCO <sub>3</sub> <sup>-</sup> $V_f = (V_c - V_a)$ cm <sup>3</sup>	Volume of HCl used in titration of Na <sub>2</sub> CO <sub>3</sub> $2V_f$ cm <sup>3</sup>	Volume of HCl used in titration of NaOH $V_s = (V_c - 2V_f)$ cm <sup>3</sup>
		Initial $V_a$	with phenolphthalein $V_b$	with methyl orange $V_c$					
1	20								
2	20								
3	20								

**3.2.5 Calculations**

a) **Standardisation of hydrochloric acid solution :**

Molarity of sodium carbonate solution =  $M_1$  ..... mol dm<sup>-3</sup>

Volume of sodium carbonate solution =  $V_1 = 20$  cm<sup>3</sup>

Volume of hydrochloric acid (from observation Table I) =  $V_2$  cm<sup>3</sup> = ..... cm<sup>3</sup>

Molarity of HCl solution =  $M_2 = ?$

Using Eq. 3.6,

Molarity of HCl solution

$$M_2 = \frac{2M_1 V_1}{V_2}$$

$$= \dots\dots\dots \text{ mol dm}^{-3}$$

b) **Estimation of sodium carbonate and sodium hydroxide in the mixture :** This can be done as follows :

i) **Estimation of sodium carbonate in the solution :** Volume of hydrochloric acid used in the titration of sodium carbonate in the given sample (from observation Table II) =  $2V_f = V_3 = \dots\dots\dots$  cm<sup>3</sup>

Molarity of hydrochloric acid solution =  $M_3 = M_2 = \dots\dots\dots$  mol dm<sup>-3</sup> (from standardisation of HCl solution)

Volume of HCl solution used =  $2V_f = V_3 = \dots\dots\dots$  cm<sup>3</sup>

Volume of sodium hydroxide and sodium carbonate solution =  $V_4$  cm<sup>3</sup> = 20 cm<sup>3</sup>

Molarity of Na<sub>2</sub>CO<sub>3</sub> solution =  $M_4 = ?$

Using Eq. 3.6,

$$2M_4 V_4 = M_3 V_3$$

$$M_4 = \frac{M_3 V_3}{2V_4}$$

$$= \dots\dots\dots \text{ mol dm}^{-3}$$

Strength of sodium carbonate present in the given solution =  $M_4 \times$  Molar mass

$$= \dots\dots\dots \text{ g dm}^{-3}$$

- ii) **Estimation of sodium hydroxide in the solution** : Volume of hydrochloric acid used in the titration of NaOH in the given sample (from observation Table II)

$$= V_8 = V_5 = \dots\dots\dots \text{cm}^3$$

$$\text{Molarity of hydrochloric acid solution} = M_5 = M_2 = \dots\dots\dots \text{mol dm}^{-3}$$

$$\text{Volume of HCl solution used} = V_8 = V_5 = \dots\dots\dots \text{cm}^3$$

$$\text{Volume of the solution containing sodium hydroxide and sodium carbonate} = V_6 = 20 \text{ cm}^3$$

$$\text{Molarity of sodium hydroxide solution} = M_6 = ?$$

Using following molarity equation, (sodium hydroxide and hydrochloric acid react in equimolar ratio),

$$M_6 V_6 = M_5 V_5$$

$$M_6 = \frac{M_5 V_5}{V_6}$$

$$= \dots\dots\dots \text{mol dm}^{-3}$$

Strength of sodium hydroxide in the given solution

$$= M_6 \times \text{Molar mass g dm}^{-3}$$

$$= \dots\dots\dots \text{g dm}^{-3}$$

### 3.2.6 Results

- i) Molarity of  $\text{Na}_2\text{CO}_3$  in the given solution =  $\dots\dots\dots \text{mol dm}^{-3}$   
Molarity of NaOH in the given solution =  $\dots\dots\dots \text{mol dm}^{-3}$

- ii) Strength of  $\text{Na}_2\text{CO}_3$  in the given solution =  $\dots\dots\dots$   
Strength of NaOH in the given solution =  $\dots\dots\dots$

Compare these results with the correct values for the given solution of a mixture of sodium carbonate and sodium hydroxide.

Using the experimental technique mentioned above you can also design an experiment to determine the percentage purity of commercial caustic soda. As you know sodium hydroxide absorbs  $\text{CO}_2$  from the air and gets converted into carbonate.



Therefore, a solution of caustic soda always contains some  $\text{Na}_2\text{CO}_3$ .

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## 3.3 ANSWERS TO SAQs

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- Basic
  - Neutral
  - Basic
  - Basic
  - Basic
- One
  - One
  - Two

3. Phenolphthalein for the first pH break and methyl orange for second pH break (See Fig 3.5).

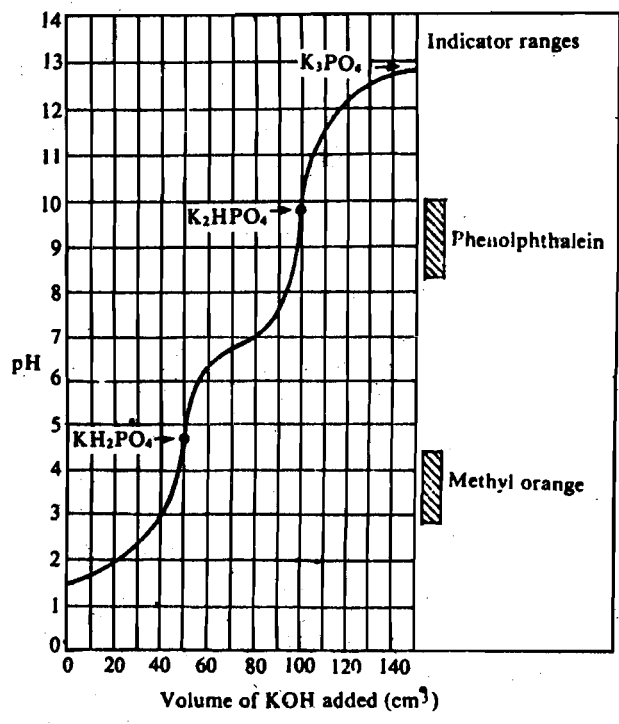


Fig. 3.5 : Titration 50 cm<sup>3</sup> of 0.1 M H<sub>3</sub>PO<sub>4</sub> with 0.1 M KOH