USE OF DOUBLE INDICATORS IN NEUTRALISATION Section - 4

For studying the titrations of alkali mixtures such as NaOH and Na_2CO_3 ; Na_2CO_3 and $NaHCO_3$, two indicators **phenolphthalein** and **methyl orange** are used.

- Phenolphthalein is a weak organic acid and gives end point between pH range of 8 - 10, while methyl orange, a weak base gives end point between pH range of 3 – 4.4.
- When methyl orange is used as an indicator for studying the neutralisation titrations for above mixtures, it indicates complete neutralisation for these, i.e., at the end point (colour change for indicator) the above mixtures are fully neutralised.
- When phenolphthalein is used as an indicator for the above mixtures :
  (a) it indicates complete neutralisation of NaOH (or KOH, i.e. strong alkali).
  (b) it indicates **half** neutralisation of Na_2CO_3 (at the end point $NaHCO_3$ is formed).

So, in an analysis of such alkali mixtures, both the indicators are used :

- one after the other in the same volumetric mixture

or

- two indicators are used separately in two different titrations.

FOR EXAMPLE :

1. In the Neutralisation mixture of NaOH and Na_2CO_3 :

(a) Use of methyl orange :

NaOH and Na_2CO_3, both are fully neutralised. i.e.

milliequivalent (meq or gmeq) of acid used = meq of NaOH + meq of Na_2CO_3

(b) Use of Phenolphthalein :

NaOH is fully neutralised and Na_2CO_3 is half neutralised

milliequivalent (meq. or gm.eq) of acid used = meq of NaOH + $\frac{1}{2}$ meq of Na_2CO_3

2. In the Neutralisation mixture of $NaHCO_3$ and Na_2CO_3 :

(a) Use of Methyl Orange :

$NaHCO_3$ and Na_2CO_3, both are fully neutralised. i.e.

milliequivalent (meq or gmeq) of acid used = meq of $NaHCO_3$ + meq of Na_2CO_3

(b) Use of Phenolphthalein :

Na_2CO_3 is half neutralised and $NaHCO_3$ is **not** neutralised at all.

milliquivalent (meq or gmeq) of acid used = $\frac{1}{2}$ meq of Na_2CO_3

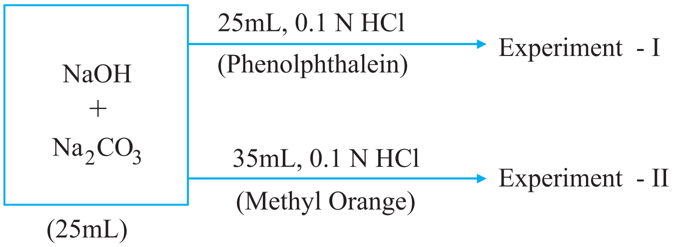
Illustration - 24 *A solution of NaOH and Na_2CO_3 is prepared. 25 mL of this solution required for neutralisation:*

(a) 25.0 mL of 0.10 N HCl when phenolphthalein is used as indicator.

(b) 35.0 mL of 0.10 N HCl when methyl orange is used as indicator.

Find the strength of NaOH and Na_2CO_3 .

Solution :



Let mmoles of NaOH be x and that of Na_2CO_3 be y in 25ml

Experiment – I :

Meq. of Acid = Meq. of Base (For complete neutralisation)

$$25 \times 0.1 = 1 \times x + 2 \times y \times \frac{1}{2}$$

[meq = n-factor × mmoles]

[**Note:** Na_2CO_3 is half neutralised with phenolphthalein as indicator]

$$\Rightarrow \quad 2.5 = x + y \qquad \text{. . . (i)}$$

Experiment – II :

Meq. of Acids = Meq. of Base (For complete neutralization)

$$35 \times 0.1 = 1 \times x + 2 \times y$$

$$\Rightarrow \quad 3.5 = x + 2y \qquad \text{. . . (ii)}$$

Solving ….(i) and …..(ii), we get : $y = 1$ and $x = 1.5$

$$x = \frac{g_{NaOH}}{M_{NaOH}} \times 1000 \Rightarrow \underset{(in\ \ 25\ \ m\ell)}{g_{NaOH}} = \frac{1.5 \times 40}{1000} = 0.06\ gm$$

$$y = \frac{g_{Na_2CO_3}}{M_{Na_2CO_3}} \times 1000 \Rightarrow \underset{(in\ \ 25\ \ m\ell)}{g_{Na_2CO_3}} = \frac{1 \times 106}{1000}\ 0.106\ \text{gm}$$

Thus, strength of NaOH $= 0.06 \times \frac{1000}{25} = 2.4\ \text{g/L}$

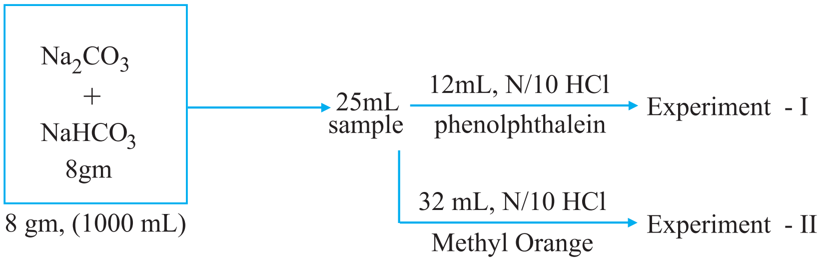
and strength of $Na_2CO_3 = 0.106 \times \frac{1000}{25} = 4.24$ g/L

Illustration - 25 *8 gm of a mixture of anhydrous Na_2CO_3 and $NaHCO_3$ was dissolved in water and made upto 1000 mL. 25 mL of this solution required for neutralisation:*

(a) 32.0 mL of N/10 HCl using methyl orange and (b) 12.0 mL of N/10 HCl using phenolphthalein.

Find the strength of $NaHCO_3$ and Na_2CO_3 .

Solution :



Let mmoles of Na_2CO_3 be x and that of $NaHCO_3$ be y in 25ml sample.

Experiment – I : Meq. of Acid = Meq. of Base (For complete Neutralisation)

$$12 \times \frac{1}{10} = 2 \times x \times \frac{1}{2} + 1 \times y \times 0 \quad \Rightarrow \quad 1.2 = x + 0 \quad \Rightarrow \quad x = 1.2 \qquad \text{. . . (i)}$$

Experiment – II : Meq. of Acids = Meq. of Base (For complete neutralization)

$$32 \times \frac{1}{10} = 2 \times x + 1 + 1 \times y \times 1 \quad \Rightarrow \quad 3.2 = 2x + y \qquad \ldots \text{(ii)}$$

Solving (i) and (ii), we get : $x = 1.2$ and $y = 0.8$

$$\text{Thus,} \quad x = \frac{g_{Na_2CO_3}}{M_{Na_2CO_3}} \times 1000 \quad \Rightarrow \quad \underset{(\text{in } 25\text{mL})}{g_{Na_2CO_3}} = \frac{1.2 \times 106}{1000} = 0.127\,\text{gm}$$

$$\text{and} \quad y = \frac{g_{NaHCO_3}}{M_{NaHCO_3}} \times 1000 \quad \Rightarrow \quad \underset{(\text{in } 25\text{mL})}{g_{NaHCO_3}} = \frac{0.8 \times 84}{1000} = 0.0672\text{ gm}$$

Thus, strength of Na_2CO_3 in the sample $= 0.127 \times \frac{1000}{25} = 5.28\,\text{gm/L}$

and strength of $NaHCO_3$ in the sample $= 0.0672 \times \frac{1000}{25} = 2.69\text{ gm/L}$

IN-CHAPTER EXERCISE-D

1. *Fill in the blanks :*

(a) *Gastric Juice contains about 3.0 gm of HCl per litre. If a person produces about 2.5 litres of gastric juice per day, number of antacid tablets each containing 400 mg of Al* $(OH)_3$ *are needed to neutralise all the HCl produced in one day are* _______

(b) *The density of 1.85 mass per cent calcium hydroxide solution is 1.025 g* cm^{-3}*. The volume of 0.1 M HCl solutions would be required to neutralise 25 mL of this solution is* ________

(c) *1 mL of* H_3PO_4 *was diluted to 250 mL. 25 mL this solution required 40.0 cc of 0.10 N - NaOH for neutralisation using phenolphthalein as indicator.The specific gravity of acid is* ___________

(d) *1.575 g, of hydrated oxalic acid* $(COOH)_2 \cdot nH_2O$ *are dissolved in water and the solution is made to 250 ml. On titration 16.68 ml of this solution are required for neutralisation of 25 ml of N/15 NaOH. The value of water crystallisation i.e. n is* ____________

(e) *The equivalent weight of a metal carbonate 0.84 gm of which reacts exactly with 40 ml of N/2* H_2SO_4 *is* _________

(f) *2.24 L of ammonia at STP is neutralised 100 mL of a solution of* H_2SO_4*. The molarity of acid is* __________

2. *500 ml of 2M HCl 100 ml of 2 M* H_2SO_4 *and one gm equivalent of a monoacidic alkali are mixed together. 30 ml of this solution required 20 ml of 143 gm* $Na_2CO_3.xH_2O$ *in one litre solution. Calculate water of crystallisation of* $Na_2CO_3.xH_2O$*.*

3. *4.0 g of a mixture of a NaCl and* Na_2CO_3 *were dissolved in water and volume made up to 250 ml. 25 ml of this solution required 50 ml of N/10 HCl for complete neutralisation. Calculate the percentage composition of the original mixture.*

4. **Choose the correct option :**

(i) *100 ml solution of 0.1N HCl was titrated with 0.2 N NaOH solutions. The titration was discontinued after adding 30 ml of NaOH solution. The remaining titration was completed by adding 0.25 N KOH solution. The volume of KOH required form completing the titration is :*

(A) 70 ml *(B)* 32 ml *(C)* 35 ml *(D)* 16 ml

(ii) *The normality of a mixture obtained by mixing 100 ml of 0.2 M* H_2SO_4 *with 100 ml of 0.2 M NaOH is :*

(A) 0.05 N *(B)* 0.1 N *(C)* 0.15 N *(D)* 0.2 N

(iii) *20 mL of x M HCl neutralises completely 10 mL of 0.1 M* $NaHCO_3$ *and a further 5 mL of 0.2 M* Na_2CO_3 *solution to methyl orange end point. The value of x is*

(A) 0.167 M *(B)* 0.133 M *(C)* 0.150 M *(D)* 0.200 M

Illustration - 26 *A mixture containing 1.0 g $CaCO_3$, 0.84 g $NaHCO_3$ and 1.06 g Na_2CO_3 is heated and the products are cooled to 27°C.*

(i) *What is the volume of gases produced at 0°C and 1 atm pressure ?*

(A) 224 *mL* (B) 336 *mL* (C) 112 *mL* (D) 448 *mL*

(ii) *The residue (after heating) is dissolved in water and titrated with 1 M H_2SO_4 solution for complete neutralization. What is the volume of H_2SO_4 consumed ?*

(A) 15 *mL* (B) 25 *mL* (C) 50 *mL* (D) 100 *mL*

Solution :

(i)-(B) $CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$

$$\text{mmoles of } CaCO_3 = \frac{1}{100} \times 1000 = 10$$

$\Rightarrow$ mmol of CO_2 = mmol of CaO = 10

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + CO_2(g) + H_2O\,(\ell)$$

$$\text{mmoles of } NaHCO_3 = \frac{0.84}{84} \times 1000 = 10$$

$\Rightarrow$ mmol of Na_2CO_3 = mmol of CO_2 = 5 (2 mmol $NaHCO_3 \equiv$ 1 mmol each of CO_2 and Na_2CO_3)

$Na_2CO_3 \xrightarrow{\Delta}$ does not decompose

$$\text{mmoles of } Na_2CO_3 \text{ (Present initially in the mixture)} = \frac{1.06}{106} \times 1000 = 10$$

Total mmoles of CO_2 = (From $CaCO_3$ + from $NaHCO_3$)

Total mmoles of $CO_2 = 10 + 5 = 15 \Rightarrow V_{CO_2}$ at STP $= 15 \times 22.4 = 336$ mL

(ii)-(B) Residue contains :

10 mmoles of CaO, 5 mmoles of Na_2CO_3 (Produced from $NaHCO_3$) and 10 mmoles of Na_2CO_3 (Present initially)

$\Rightarrow$ Total mmoles of $Na_2CO_3 = 15$

meq of CaO $= 2 \times 10 = 20$; meq of $Na_2CO_3 = 2 \times 15 = 30$ (Meq. = n-factor × mmoles)

$\Rightarrow$ meq of H_2SO_4 = meq of base mixture = 50

$\Rightarrow$ $1 \times 2 \times V_{H_2SO_4} = 50 \quad \Rightarrow \quad V_{H_2SO_4}$ consumed = 25 mL

Illustration - 27 *A solution containing 200 ml of 0.5 M $BaCl_2$ and 400 mL of 0.5 M H_2SO_4 is diluted to 1000 mL. The volume of 0.1 M $Ba(OH)_2$ required to neutralized 100 mL of above (diluted) solution is :*

(A) 200 *mL* (B) 2000 *mL* (C) 1000 *mL* (D) 100 *mL*

Solution : (A)

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2HCl$$

200 ml of 0.5 M $BaCl_2 \equiv$ 100 m mole $BaCl_2$ and 400 ml of 0.5 M $H_2SO_4 \equiv$ 200 m mole H_2SO_4

mmol after the reaction :

$$\begin{array}{ccccccc} BaCl_2 & + & H_2SO_4 & \longrightarrow & BaSO_4 & + & 2HCl \\ 100 & & 200-100=100 & & 100 & & 200 \end{array}$$

$\therefore$ H^+ ions in the solution = from $(H_2SO_4 + HCl) = (2 \times 100) + (1 \times 200) = 400$ mmol

Now 400 mmol of H^+ ions are diluted to 1000 ml.

mmole of H^+ ions in 100 mL sample $= \dfrac{100}{1000} \times 400 = 40$

mmoles of H^+ ions = meq of H^+ ions [Note that magnitude of charge over $H^+ = 1$; meq = $1 \times$ mmol]

$\Rightarrow$ meq of H^+ = meq of $Ba(OH)_2$ for complete neutralisation

$\Rightarrow$ $40 = 2 \times 0.1 \times V \Rightarrow V = 200\,mL$

Illustration - 28 ***A sample of clay contains 12% water which is partially dried and then found to contain (after drying) 40% silica and 7% water. What is the percentage of silica in the original sample ?***

(A) **47.5** **(B)** **38** **(C)** **40** **(D)** ***Cannot be said***

SOLUTION : (B)

Let the % of silica be x % in original sample. Let the mass of clay be 100 g in the original sample.

So mass of silica = x gms.

	Silica	Water	Impurity
Mass before drying (in gms)	x	12	$88 - x$
Mass after drying (in gms)	x	y	$88 - x$

% of water after drying :

$$\frac{y}{88 + y} \times 100 = 7$$

$$100y = 616 + 7y \Rightarrow y = \frac{616}{93} = 6.62\,g$$

% of silica after drying :

$$\frac{x}{88 + 6.62} \times 100 = 40$$

$$100x = 3520 + 264.8 \Rightarrow x = 37.84 \approx 38$$

Illustration - 29 ***Which of the following statements is(are) correct ?***

A mixture containing 64.0g H_2 and 64.0g O_2 is ignited so that water is formed as follows: $2H_2 + O_2 \xrightarrow{\Delta} 2H_2O$

(A) ***H_2 is the limiting reagent***

(B) ***O_2 is the limiting reagent***

(C) ***After the completion of reaction, the reaction mixture contains 72.0g of H_2O and 56.0g of unreacted H_2***

(D) ***After the completion of reaction, the reaction mixture contains 56.0g of H_2O and 72.0g of unreacted H_2***

SOLUTION : (BC)

$64\,g\ H_2 \equiv 32$ mole ; $64\,g\ O_2 \equiv 2$ mole

$$2H_2 + O_2 \xrightarrow{\Delta} 2H_2O$$

2 mol $H_2 \equiv$ 1 mol of O_2 $\Rightarrow$ 2 moles of O_2 require 4 mol of H_2 (as per stoichiometry of reaction)

Hence O_2 is the limiting reagent as it is consumed completely.

$\Rightarrow$ $32 - 4 = 28$ moles of H_2 are left $\equiv$ 56 gm of H_2

Also 2 moles of O_2 produce 4 mol of $H_2O \equiv$ 72 gm of H_2O

Illustration - 30 *A mixture of* **5.85** *gm of NaCl and* **12.25** *gm of* $KClO_3$ *is heated strongly to produce* $KClO_4$ *and KCl. The residue is dissolved in excess of* $AgNO_3$*. The mass of white precipitate formed is :*

[*Molecular mass of AgCl* = **143.5** *and* $KClO_3$ = **122.5**]

(A) **28.7** *gm* **(B)** **1.793** *gm* **(C)** **17.93** *gm* **(D)** **7.175** *gm*

SOLUTION : (C)

$$\left.\begin{aligned} 5.85\,\text{g NaCl} &\equiv 0.1\text{ mol NaCl} \\ 12.25\,\text{g KClO}_3 &\equiv 0.1\text{ mol KClO}_3 \end{aligned}\right]$$

$$\text{NaCl} \xrightarrow{\Delta} \text{nothing happens}$$

$$4\,\text{KClO}_3 \longrightarrow 3\,\text{KClO}_4 + \text{KCl} \quad \Rightarrow \quad \text{Residue is NaCl, KClO}_4 \text{ and KCl}$$

$$\left.\begin{aligned} 4\,\text{mol KClO}_3 &\equiv 1\text{ mol KCl} \\ 0.1\,\text{mol KClO}_3 &\equiv \frac{1}{4}\times 0.1\text{ mol KCl} \end{aligned}\right]$$

➤ $AgNO_3$ will precipitate out Cl^- ions from KCl and NaCl. $[Cl^- + AgNO_3 \rightarrow AgCl\downarrow + NO_3^-]$

$$\Rightarrow \quad \frac{0.1}{4}\text{mol KCl} \equiv \frac{0.1}{4}\text{ mol AgCl and } 0.1\text{ mol NaCl} \equiv 0.1\text{ mol AgCl}$$

$$\Rightarrow \quad n_{AgCl} = \frac{0.1}{4} + 0.1 = 0.125 \quad \Rightarrow \quad g_{AgCl} = 0.125 \times 143.5 = 17.93$$

Illustration - 31 **1.25** *gm of a mixture containing* $CaCO_3$ *and* $CaCl_2$ *dissolved in* **100** *ml of* H_2SO_4 *sol. To this* **400** *ml of* H_2O *is added.* **50** *ml of this solution required* **20** *ml of* **0.05** *M solution of a diacidic base. If mixture contained* **80%** $CaCO_3$ *by mass, the molarity of* H_2SO_4 *solution is :*

(A) **1.8** **(B)** **0.9** **(C)** **0.4** **(D)** **0.2**

SOLUTION : (D)

The resulting solution is acidic and $CaCl_2$ will not react with H_2SO_4 (being neutral salt). Let molarity of H_2SO_4 be x.

50 mL of solution required 20 mL of 0.05 M di-acidic base.

$\Rightarrow$ meq of excess acid in resulting solution (50 mL) = meq of di-acidic base = $(2 \times 0.05) \times 20 = 2$

Observe that original solution is 500 mL.

$$\Rightarrow \quad \text{meq of excess acid in original solution} = \frac{500}{50} \times 2 = 20$$

Now initially meq of H_2SO_4 taken = $2 \times x \times 1000 = 200x$

$\Rightarrow$ meq of H_2SO_4 used against $CaCO_3$ (only) = $200x - 20$

$$\Rightarrow \quad 200\,x - 20 = \text{meq of CaCO}_3 = \frac{g \times 1000}{E_{CaCO_3}}$$

$$g_{CaCO_3} = \frac{80}{100} \times 1.25 = 1\,; \quad E_{CaCO_3} = \frac{100}{2}$$

$$\Rightarrow \quad (200x - 20) = \frac{1}{50} \times 1000$$

$$\Rightarrow \quad x = 0.2\text{ M}$$