

Titration

①

Titration of the solution containing both Na_2CO_3 & NaHCO_3 :

Given volume of the solution is titrated by an acid using Phenolphthalein indicators. Suppose 'a' milliequivalents of acid are used in the first end point. Then,

$$\frac{1}{2} \text{ milliequivalent of } \text{Na}_2\text{CO}_3 = \text{milliequivalent of acid} = a. \text{---(1)}$$

Now in the same already titrated solution methyl orange indicator is added and again titrated to the end point. Suppose 'b' milliequivalent of the acid are used at the second end point. Then,

$$\frac{1}{2} \text{ milliequivalent of } \text{Na}_2\text{CO}_3 + \text{milliequivalent of } \text{NaHCO}_3 = \text{milliequivalent of acid} = b \text{ ---(2)}$$

From eq (1) & (2).

milliequivalents of acid used by $\text{Na}_2\text{CO}_3 = 2a =$ milliequivalents of Na_2CO_3 .

milliequivalents of acid used by $\text{NaHCO}_3 = (b-a) =$ milliequivalent of NaHCO_3 .

Knowing the milliequivalents of the base and volume of the solution titrated, the normality (strength) of the bases can be calculated.

Example :- Both Na_2CO_3 and NaHCO_3 are present in an aqueous solution. In the presence of phenolphthalein indicator 10 ml of this solution requires 2.5 ml of 0.1 M H_2SO_4 for titration. After this methyl orange is added in the same solution & titration requires 5 ml of 0.1 M H_2SO_4 , calculate the concentration of Na_2CO_3 and NaHCO_3 in g/litre.

Solution \therefore Milliequivalent 'a' of H_2SO_4 used in the presence of the phenolphthalein indicator $= N \times V(\text{me})$
 $= 0.1 \times 2 \times 2.5 = 0.5.$

$$a = 0.5 = \frac{1}{2} \text{ milliequivalents of } Na_2CO_3.$$

Milliequivalent 'b' of $NaHCO_3 + \frac{1}{2}$ milliequivalent of Na_2CO_3

For Na_2CO_3 solution:

Milliequivalent of acid used by $Na_2CO_3 = 2 \times 0.5 = 1$

Suppose, Normality of Na_2CO_3 solution $= N$

Volume of Na_2CO_3 solution taken $= 10 \text{ ml}$

Milliequivalent of Na_2CO_3 taken $= N \times V = 10N.$

Putting the milliequivalent of H_2SO_4 and Na_2CO_3 equal,

$$1 = 10N$$

$$N = 0.1$$

Strength (s) in g/litre $= N \times E = 0.1 \times 53 = 5.3 \text{ g/litre.}$

For $NaHCO_3$ solution: $NaHCO_3 = (b - a) = 1 - 0.5 = 0.5$

Suppose, Normality of $NaHCO_3$ solution $= N.$

Volume of $NaHCO_3$ solution taken $= 10 \text{ ml.}$

meq. of $NaHCO_3$ taken $= 10N.$

Putting the meq. of H_2SO_4 and $NaHCO_3$ equal,

$$0.5 = 10N.$$

Normality of $NaHCO_3$ solution $= 0.05$

Strength (s) in g/litre $= N \times E = 0.05 \times 84$
 $= 4.2 \text{ g/litre.}$

Summary.

- 1) Phenolphthalein (weak organic Acid) : It show colour change in the pH range (8-10).
- 2) Methyl orange (weak organic Base) : It show colour change in the pH range (3.1-4.4). Due to lower pH range, it indicates complete neutralisation of whole of the base.

S.No	Base	Phenolphthalein	Methyl orange
1.	NaOH	Shows complete neutralization. $NaOH + HCl \rightarrow NaCl + H_2O$	Shows complete neutralisation, $NaOH + HCl \rightarrow NaCl + H_2O$
2.	Na ₂ CO ₃	show half neutralisation due to following reaction; $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$	shows complete neutralisation, $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
3.	NaHCO ₃	Shows no reaction	shows complete reaction $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

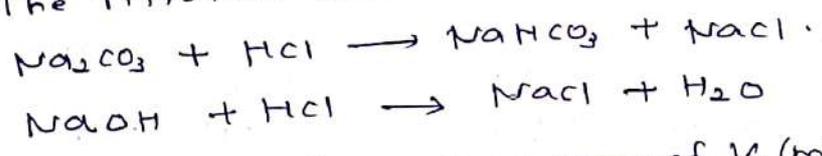
Let for complete neutralization of Na₂CO₃, NaHCO₃ and NaOH, x, y and z ml of standard HCl are required. The titration of mixture may be carried by two methods as summarised.

Mixture	Volume of HCl used with		Volume of HCl used.	
	Phenolphthalein	Methyl orange	Phenolphthalein	Methyl orange
① NaOH + Na ₂ CO ₃	$z + (x/2)$	$(x+z)$	$z + x/2$	$x/2$ (for remaining 50% Na ₂ CO ₃)
② NaOH + NaHCO ₃	$(z + 0)$	$(z+y)$	$(z + 0)$	y (for 100% remaining NaHCO ₃)
③ Na ₂ CO ₃ + NaHCO ₃	$(x/2 + 0)$	$(x+y)$	$(x/2 + 0)$	$(x/2) + y$ (for remaining 50% of Na ₂ CO ₃ and 100% NaHCO ₃ are indicated)

Example: 50ml of a solution, containing 1g each of Na_2CO_3 , NaHCO_3 and NaOH was titrated with 1N HCl . What will be the titre reading if :-

- (a) only phenolphthalein is used as indicator?
- (b) only methyl orange is used as indicator from the very beginning?
- (c) Methyl orange is added after the first end point with phenolphthalein?

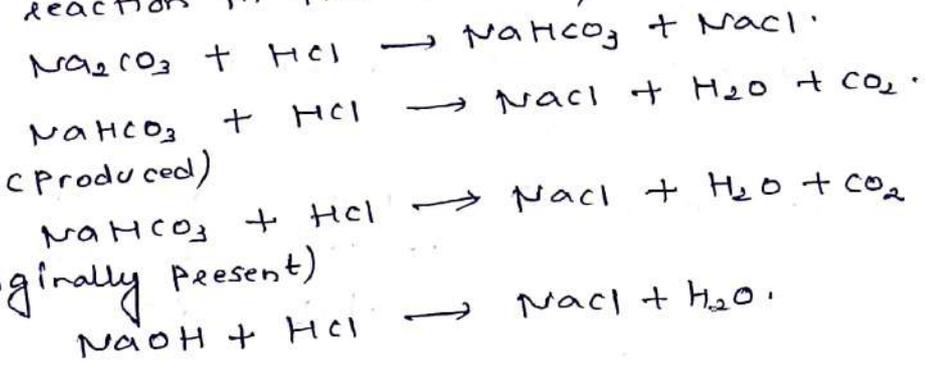
Solution: (a) The titration reaction in this case are,



meq. of Na_2CO_3 + meq. of NaOH = meq. of V_1 (mL) of 1N HCl .

$$\frac{1}{106} \times 1000 + \frac{1}{40} \times 1000 = 1 \times V_1 \quad ; \quad V_1 = 34.4 \text{ mL}$$

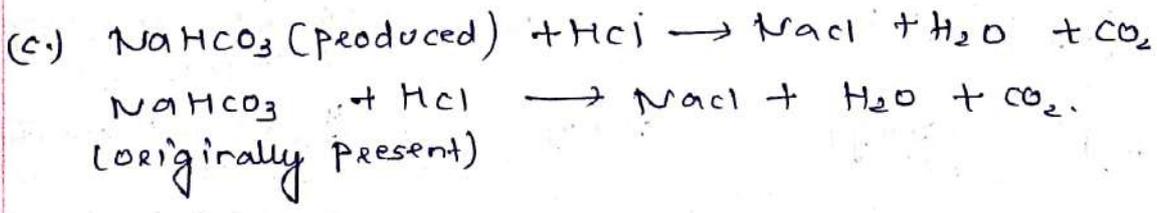
(b) The reaction in this case are;



We have, meq. of Na_2CO_3 + meq. of NaHCO_3 (Produced) + meq. of NaHCO_3 (originally present) + meq. of NaOH = meq. of V_2 (mL) of 1N HCl .

$$\frac{1}{106} \times 1000 + \frac{1}{106} \times 1000 + \frac{1}{84} \times 1000 + \frac{1}{40} \times 1000 = 1 \times V_2$$

$$V_2 = 55.8 \text{ mL}$$



We have,

$$\text{meq. of NaHCO}_3 \text{ (Produced)} + \text{meq. of NaHCO}_3 \text{ (originally present)} = \text{meq. of } V_3 \text{ mL of NHCl}$$

$$\text{OR, meq. of Na}_2\text{CO}_3 + \text{meq. of NaHCO}_3 = \text{meq. of } V_3 \text{ (mL) of NHCl}$$

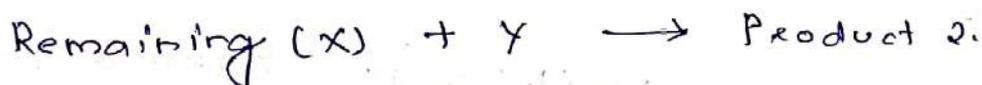
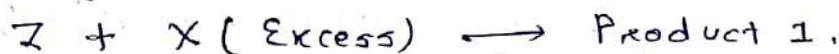
$$\frac{1}{106} \times 1000 + \frac{1}{84} \times 1000 = 1 \times V_3;$$

$$V_3 = 21.3 \text{ mL.}$$

Back Titration:

Let us consider that we have an impure solid substance 'Z' weighing 'W' g and we are required to calculate the percentage purity of 'Z' in the sample. We are also provided with two solutions 'X' and 'Y', where the concentration of 'Y' is known (N_2) and that of 'X' is unknown. For the back titration to work, following conditions are to be satisfied.

- Compound 'X', 'Y' and 'Z' should be such that 'X' & 'Y' react with each other.
- 'X' and pure 'Z' also reacts with each other but the impurity present in 'Z' does not react with 'X'.



Important Note \rightarrow Product 1 should not react with Y.

$$\text{Milliequivalent of } Y = N_2 V_2.$$

Where N_2 and V_2 (ml) is the normality and volume of Y.

$$\text{Initial milliequivalent of } X = N_1 V_1.$$

Where N_1 and V_1 (ml) is the normality and volume of X.

Remaining milliequivalents of X after reacting with

$$Y = (N_1 V_1 - N_2 V_2)$$

Remaining milliequivalents of X = milliequivalents of Z.

$$N_1V_1 - N_2V_2 = \frac{a \times 1000}{\text{Equivalent weight}}$$

Where 'a' is the weight of pure Z which is reacted.

$$a = \frac{\text{Molecular weight } (N_1V_1 - N_2V_2)}{n\text{-factor}}$$

$$\text{Percentage Purity of 'Z'} = \frac{(N_1V_1 - N_2V_2)}{n\text{-factor}} \times \frac{\text{Molar mass of 'Z'}}{W} \times 100$$

Example: 20g of a sample of Ba(OH)_2 is dissolved in 10ml of 0.5 N HCl solution. The excess of HCl was titrated with 0.2 N NaOH. The volume of NaOH used 10 cm^3 . Calculate the percentage of Ba(OH)_2 in the sample.

Solution: Meq. of HCl (initially) = $10 \times 0.5 = 5$.

$$\begin{aligned} \text{Meq. of NaOH (consumed)} &= \text{meq. of HCl in Excess} \\ &= 10 \times 0.2 = 2. \end{aligned}$$

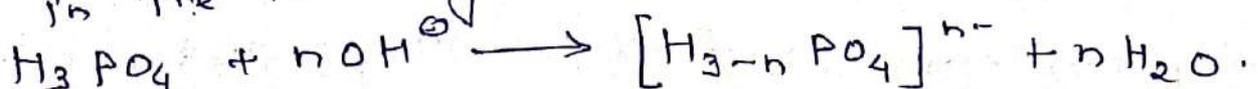
$$\begin{aligned} \text{Meq. of HCl consumed} &= \text{Meq. of Ba(OH)}_2 \\ &= (5 - 2) = 3. \end{aligned}$$

$$\text{eq. of Ba(OH)}_2 = 3/1000 = 3 \times 10^{-3}$$

$$\text{mass of Ba(OH)}_2 = 3 \times 10^{-3} \times (171/2) = 0.2565 \text{ g.}$$

$$\% \text{ Ba(OH)}_2 = (0.2565/20) \times 100 = 1.28\%$$

Question: 25 mL of 0.107 M H_3PO_4 was titrated with 0.115 M solution of NaOH to the end point identified by indicator bromocresol green. This required 23.1 mL. The titration was repeated using phenolphthalein as indicator. This time 25 mL of 0.107 M H_3PO_4 required 46.2 mL of this 0.115 M NaOH. What is the coefficient 'n' in the following reaction?



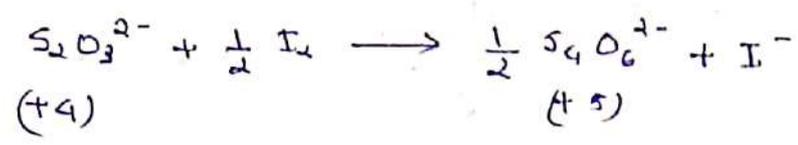
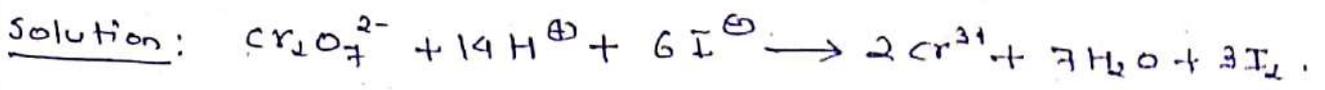
Redox Titration:

Oxidimetry: The determination of the strength of a solution of a reducing agent by titration with a standard solution of an oxidising agent is called oxidimetry.

Reductimetry: The determination of the strength of a solution of an oxidising agent by titration with standard solution of reducing agent is called reductimetry.

Species Oxidising or Reducing	Reaction Involved	(Change in oxidation number)	(Equivalent mass)
MnO_4^- (Acidic)	$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	5	mol.wt/5
MnO_4^- (Neutral)	$\text{MnO}_4^- + 2\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	3	mol.wt/3
MnO_4^- (Basic)	$\text{MnO}_4^- + \text{e}^- \rightarrow \text{MnO}_4^{2-}$	1	mol.wt/1
H_2O_2 (Oxidising)	$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}$	2	mol.wt/2
H_2O_2 (Reducing)	$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	2	mol.wt/2
$\text{S}_2\text{O}_3^{2-}$ (Reducing)	$2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$	1 (per molecule)	mol.wt/1
Cl_2 (Oxidising)	$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	2	mol.wt/2
$\text{Cr}_2\text{O}_7^{2-}$ (Oxidising)	$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	6	mol.wt/6
MnO_2 (Oxidising)	$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	2	mol.wt/2
Fe^{2+} (Reducing)	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$	1	mol.wt/1

Example: A 10ml of $K_2Cr_2O_7$ solution liberated iodine from KI solution. The liberated iodine was titrated by 16ml of $M/25$ sodium thiosulphate solution. Calculate the concentration of $K_2Cr_2O_7$ solution in gram per litre.



Equivalent weight of $K_2Cr_2O_7 = \frac{\text{mol. wt}}{\text{change in ON per mole}}$
 $= \frac{294.18}{6} = 49.03$

meq. of 10ml of $K_2Cr_2O_7$ solution = meq. of iodine
 = meq. of sodium thiosulphate
 $= \frac{1}{25} \times 16 = 0.64$.

equivalent of 10ml of $K_2Cr_2O_7$ solution = $\frac{0.64}{1000} = 0.00064$

Weight per 10ml = 0.00064×49.03
 $= 0.0313g$.

concentration of $K_2Cr_2O_7$ in gram per litre = 0.0313×100
 $= 3.13g/L$

Redox Titration

- Q1. It requires 40.05 ml of 1M Ce^{4+} to titrate 20ml of 1M Sn^{2+} to Sn^{4+} . What is the oxidation state of the cerium in the product.
- Q2. A volume of 12.53 ml of 0.05093 M SeO_2 reacted with exactly 25.52 ml of 0.1M CrSO_4 . In the reaction, Cr^{2+} was oxidized to Cr^{3+} . To what oxidation state was selenium converted by the reaction.
- Q3. A 1.0g sample of H_2O_2 solution containing x % H_2O_2 by mass requires x cm³ of a KMnO_4 solution for complete oxidation under acidic conditions. Calculate the normality of KMnO_4 solution.
- Q4. Metallic tin in the presence of HCl is oxidized by $\text{K}_2\text{Cr}_2\text{O}_7$ to stannic chloride, SnCl_4 . What volume of deci-normal dichromate solution would be reduced by 1g of tin.
- Q5. Calculate the mass of oxalic acid which can be oxidized by 100ml of M MnO_4^- solution, 10ml of which is capable of oxidizing 50ml of 1N I⁻ of I_2 .
- Q6. Exactly 40ml of an acidified solution of 0.4M iron(II) ion of titrated with KMnO_4 solution. After addition of 32ml KMnO_4 , one additional drop turns the iron solution purple. Calculate the concentration of permanganate solution.
- Q7. The iodide content of a solution was determined by the titration with Cerium(IV) sulfate in the presence of HCl, in which I⁻ is converted to ICl . A 250ml sample of the solution required 20ml of 0.058N Ce^{4+} solution. What is the iodide concentration in the original solution in gm/l.
- Q8. Potassium acid oxalate $\text{K}_2\text{C}_2\text{O}_4 \cdot 3\text{HC}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ can be oxidized by MnO_4^- in acid medium. Calculate the volume of 0.1M KMnO_4 reacting in acid solution with one gram of the acid oxalate.
- Q9. 5g sample of brass was dissolved in one litre dil. H_2SO_4 . 20 ml of this solution were mixed with KI, liberating I_2 and Cu^+ and the I_2 required 20 ml of 0.0327 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.
- Q10. 1.44g pure FeC_2O_4 was dissolved in dil. HCl and solution diluted to 100 mL. Calculate volume of 0.01M KMnO_4 required to oxidize FeC_2O_4 solution completely.
- Q11. 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromate solution for oxidizing the iron content to ferric state. Calculate the strength of dichromate solution.
- Q12. 0.5M KMnO_4 solution completely reacts with 0.05M FeC_2O_4 solution under acidic conditions where the products are Fe^{3+} , CO_2 and Mn^{2+} . The volume of FeC_2O_4 used is 125 ml. What volume of KMnO_4 was used.
- Q13. A solution is made by mixing 200 ml of 0.1M FeSO_4 , 200 gm of 0.1M KMnO_4 and 600 ml 1M HClO_4 . A reaction occurs in which Fe^{2+} is converted to Fe^{3+} & MnO_4^- to Mn^{2+} in acid solution. Calculate the concentration of each ion.
- Q14. To 100ml of KMnO_4 solution containing 0.632 gm of KMnO_4 , 200 ml of SnCl_2 solution containing 2.371 gm is added in presence of HCl. To the resulting solution excess of HgCl_2 solution is added all at once. How many gms of Hg_2Cl_2 will be precipitated. (Mn = 55; K = 39; Sn = 118.7; Hg = 201)

- Q15. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of moles of electrons taken up by the oxidant in the reaction of the above titration.
- Q16. A mixture of FeO and Fe_2O_3 is reacted with acidified KMnO_4 solution having a concentration of 0.2278 M, 100 ml of which was used. The solution was then titrated with Zn dust which converted Fe^{3+} of the solution to Fe^{2+} . The Fe^{2+} required 1000 ml of 0.13 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Find the % of FeO & Fe_2O_3
- Q17. 2 gms of FeC_2O_4 are made to react in acid solution with 0.25 M KMnO_4 solution. What volume of KMnO_4 solution would be required. The resulting solution is treated with excess of NH_4Cl and NH_4OH solution. The precipitated $\text{Fe}(\text{OH})_3$ is filtered off, washed and ignited. What is the mass of the product obtained. (Fe = 56)
- Q18. The neutralization of a solution of 1.2 g of a substance containing a mixture of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, KHC_2O_4 , H_2O and different impurities of a neutral salt consumed 18.9 ml of 0.5 N NaOH solution. On titration with KMnO_4 solution, 0.4 g of the same substance needed 21.55 ml of 0.25 N KMnO_4 . Calculate the % composition of the substance.
- Q19. A 1.0 g sample containing $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved and an excess of K_2CrO_4 solution added. After a suitable period, the BaCrO_4 was filtered, washed and redissolved in HCl to convert CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$. An excess of KI was added, and the liberated iodine was titrated with 84.7 mL of 0.137 M sodium thiosulphate. Calculate the percent purity of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.
- Q20. A sample of Mg was burnt in air to give a mix of MgO and Mg_3N_2 . The ash was dissolved in 60meq HCl and the resulting solution was back titrated with NaOH . 12 meq of NaOH were required to reach end point. An excess of NaOH was then added and the solution distilled. The NH_3 released was then trapped in 10 meq of second acid solution. Back titration of this solution required 6 meq of the base. Calculate the % of Mg burnt to the nitride.

Answer Key

- Q1. + 3 Q2. zero Q3. 0.588 N Q4. 337 mL Q5. 22.5gm Q6. 0.1M
 Q7. 0.254gm/lt Q8. $V = 31.68$ ml Q9. 41.53% Q10. 600 L MnO_4^- solution
 Q11. 0.15 N Q12. 7.5 ml Q13. $\text{Fe}^{3+} = 0.02\text{M}$; $\text{MnO}_4^- = 0.016$ M; $\text{H}^+ = 0.568$ M; $\text{Mn}^{2+} = 0.004\text{M}$;
 $\text{SO}_4^{2-} = 0.02\text{M}$; $\text{K}^+ = 0.02\text{M}$, $\text{ClO}_4^- = 0.6\text{M}$
 Q14. 1.176 gm Q15. $6.07 \approx 6$ Q16. $\text{FeO} = 13.34\%$; $\text{Fe}_2\text{O}_3 = 86.66\%$
 Q17. 33.33 ml ; 1.486 gm Q18. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O} = 14.35\%$, $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O} = 81.71\%$
 Q19. 94.38% Q20. 27.27%