ACID-BASE TITRATION

PROBLEM 45 A 1.5 g sample containing oxalic acid and some inert impurity was dissolved in enough water and volume made up to 250 mL. A 20 mL portion of this solution was then mixed with 30 mL of an alkali solution. The resulting solution was then treated with stoichiometric amount of $CaCl_2$ just needed for precipitation of oxalate as CaC_2O_4. Solution was filtered off and filtrate was finally titrated against 0.1 M HCl solution. 8.0 mL of acid was required to reach the equivalence point. At last, the above neutral solution was treated with excess of $AgNO_3$ solution and AgCl obtained was washed, dried and weighed to be 0.4305 g. Determine mass percentage of oxalic acid in the original sample.

PROBLEM 46 A 1.5 g sample containing P_2O_3 and some inert impurity was dissolved in enough water and boiled gently where P_2O_3 disproportionated quantitatively into PH_3 and H_3PO_4. The solution was further boiled for some time to let-off all $PH_3\,(g)$ and finally cooled to room temperature and diluted to 100 mL. A 10 mL portion of this solution was then mixed with 20 mL 0.3 M NaOH solution. Excess alkali required 11.0 mL 0.05 M H_2SO_4 solution for back titration. Determine mass percentage of P_2O_3 in the original sample.

PROBLEM 47 2.5 g of a mixture containing $CaCO_3$, $Ca(HCO_3)_2$ and NaCl was dissolved in 100 mL water and its 10 mL portion required 10 mL 0.05 M H_2SO_4 solution to reach the phenolphthalein end point. An another 10 mL portion of the same stock solution required 32.35 mL of the same acid solution to reach the methyl orange end point. Determine mass percentage of $CaCO_3$ and $Ca(HCO_3)_2$ in the original mixture.

PROBLEM 48 A solution contain both Na_2CO_3 and $NaHCO_3$. 10 mL portion of this solution is mixed with few drops of phenolphthalein indicator and titrated against 0.08 M H_2SO_4 solution. 7.0 mL of acid was required to reach the end point A 5.0 mL portion of this solution was then taken for further analysis and a few drops of methyl orange was added to it and finally titrated against same acid solution. 3.53 mL of acid was required to reach the end point. Determine mass of Na_2CO_3 and $NaHCO_3$ per litre of solution. Ignore volume change due to addition of indicator.

PROBLEM 49 A mixture was known to contain both KNO_3 and K_2SO_3. To 0.486 g of the mixture, dissolved in enough water to give 50 mL solution, was added 50 mL of 0.15 M HCl solution. The reaction mixture was heated to expel all SO_2 and then 25 mL of the reaction mixture was titrated with 0.1 M KOH. The titration required 13.11 mL of the base. Calculate mass percentage of K_2SO_3 in the mixture.

PROBLEM 50 An amino acid isolated from a piece of animal tissue was believed to be glycine. A 0.05 g sample was treated in such a way that all nitrogen in it was converted into ammonia. This ammonia was added to 50 mL of 0.05 M HCl solution. The excess acid remaining in the solution required 30.57 mL 0.06 M NaOH solution for complete neutralization. What was the percentage by mass of nitrogen? How does this mass compare with percentage mass of nitrogen calculated from glycine (H_2NCH_2COOH)?

PROBLEM 51 In a reaction, calcium orthophosphate on heating with magnesium produced calcium phosphide, magnesium metaphosphate, calcium oxide and oxygen gas. Phosphide on hydrolysis produces PH_3 gas. The PH_3 gas is burnt completely to P_2O_5 using air, which contains 21%, by volume of oxygen. Calculate the volume of air at STP required for combustion, if 2.4 g Mg was initially reacted with calcium orthophosphate. All volumes are measured at STP.

PROBLEM 52 9.3 g of a mixture containing Li_2CO_3, $NaHCO_3$, Na_2CO_3 on strong heating produced 7.37 g of solid residue. The residue is dissolved in 200 mL water.

A 10 mL portion of this solution is mixed with 15 mL of a normal HCl solution. The excess acid required 12 mL 0.5 N NaOH solution to reach the equivalence point. Determine the mass percentage of $NaHCO_3$ and Na_2CO_3 in the original mixture. Li = 7, Na = 23.

PROBLEM 53 4.0 g of a monobasic, saturated carboxylic acid is dissolved in 100 mL water and its 10 mL portion required 8.0 mL 0.27 M NaOH to reach the equivalence point. In an another experiment, 5.0 g of the same acid is burnt completely and CO_2 produced is absorbed completely in 500 mL of a 2.0 N NaOH solution. A 10 mL portion of the resulting solution is treated with excess of $BaCl_2$ to precipitate all carbonate and finally titrated with 0.5 N H_2SO_4 solution. Determine the volume of the acid solution that would be required to make this solution neutral.

PROBLEM 54 5.0 g of a mixture containing $NaHCO_3$, NaCl and Na_2CO_3 is dissolved in 500 mL water and its 10 mL portion required 12.4 mL 0.1 M HCl solution to reach the equivalence point. In an another experiment, 10 mL portion of the same stock solution is mixed with 10 mL 0.15 M NaOH solution. Excess NaOH required 12.6 mL 0.1 M HCl solution for back titration. Determine the mass percentage of each component in the original mixture.

PROBLEM 55 6.4 g of a pure monobasic organic acid is burnt completely in excess of oxygen and CO_2 evolved is absorbed completely in one litre of an aqueous solution of NaOH. A 10 mL portion of this solution required 14.5 mL of a normal HCl solution to reach the phenolphthalein end point. An another 10 mL portion of the same solution required 18 mL of the same HCl solution to reach the methyl orange end point. If the organic acid contains 25% oxygen by weight, deduce the empirical formula of this acid and strength of original NaOH solution.

PROBLEM 56 A complex of cobalt with ammonia is analyzed for determining its formula, by titrating it against a standardized acid as follows:

$$\mathrm{Co(NH_3)_xCl_3}(aq) + \mathrm{HCl} \longrightarrow \mathrm{NH_4^+}(aq) + \mathrm{Co^{3+}}(aq) + \mathrm{Cl^-}(aq)$$

A 1.58 g complex required 23.63 mL 1.5 M HCl to reach the equivalence point. Determine formula. If the reaction mixture at equivalence point is treated with excess of $AgNO_3$ solution, what mass of AgCl will precipitate out?

PROBLEM 57 One litre solution of alkali is prepared by dissolving impure solid of alkali which contain 5% Na_2CO_3 and 8% $CaCO_3$ and 10% NaCl. A 10 mL portion of this solution required 9.8 mL of a 0.5 M H_2SO_4 solution for neutralization. Calculate weight of alkali dissolved initially.

PROBLEM 58 40 g of a sample of caustic soda containing NaOH, Na_2CO_3 and inert impurity is dissolved in water to prepare 1.0 litre solution. A 25 mL portion of this solution required 23.15 mL 1.022 N HCl for complete neutralization. To 25 mL another solution, excess of $BaCl_2$ is added, and resulting solution required 22.55 mL HCl of same strength to reach the end point. Calculate mass percentage of NaOH and Na_2CO_3 in the original sample.

PROBLEM 59 1.5 g of a sample containing Na_2CO_3 and $NaHCO_3$ is dissolved in 100 mL of water. A 25 mL portion of this solution required 22.45 mL 0.202 N HCl using methyl orange as indicator. In a separate analysis, 25 mL portion of the same stock solution is mixed with 30 mL 0.204 N NaOH and then excess of $BaCl_2$ is added resulting in precipitation of all carbonate as $BaCO_3$. Filtrate required 9.98 mL HCl of same strength. Calculate mass percentage of Na_2CO_3 and $NaHCO_3$ in the mixture.

PROBLEM 60 One gram sample of a saturated hydrocarbon is burned completely and liberated CO_2 was absorbed in a 1.0 L 0.2 N NaOH solution. To the resulting solution, excess of $BaCl_2$ crystals was added and the solution was filtered off to free from $BaCO_3$. A 10 mL portion of the extract required 12 mL 0.025 M H_2SO_4 solution for neutralization. Determine molecular formula of the hydrocarbon.

PROBLEM 61 2.0 g of a saturated, monobasic carboxylic acid was burned and liberated CO_2 was passed through a concentrated solution of NaOH. The resulting solution was separated into two equal half and analyzed. One half required 71.72 mL 1.0 N HCl to reach the end point in presence of phenolphthalein indicator. The other half required 123.44 mL 1.0 N HCl to reach the end point in presence of methyl orange indicator. Deduce formula of acid and determine mass of NaOH present initially.

PROBLEM 62 2.5 g of a mixture containing $NaHCO_3$, Na_2CO_3 and NaCl is dissolved in 100 mL water and its 50 mL portion required 13.33 mL 1.0 N HCl solution to reach the equivalence point. On the other hand its other 50 mL portion required 19 mL 0.25 M NaOH solution to reach the equivalence point. Determine mass percentage of each component.

Problem 63 2.0 g of a crystal of $CaCO_3$ is dissolved in 50 mL water and then mixed with 50 mL of a HCl solution. The resulting solution is boiled to remove all CO_2 and its 10 mL portion required 8.0 mL of a NaOH solution to make the solution neutral. Also 20 mL of original HCl solution is equivalent to 96 mL of NaOH solution. Determine molarity of both NaOH and HCl solution.

Problem 64 2.725 g of a mixture of $K_2C_2O_4$, KHC_2O_4 and $H_2C_2O_4 \cdot 2H_2O$ is dissolved in 100 mL H_2O and its 10 mL portion is titrated with 0.1 N HCl solution.

20 mL acid was required to reach the equivalence point. In another experiment, 10 mL portion of the same stock solution is titrated with 0.1 N KOH solution. 20 mL of base was required to reach the equivalence point. Determine mass percentage of each component in the mixture.

Problem 65 A 1.0 g sample containing NH_4NO_3, $(NH_4)_3PO_4$ and some inert impurity was dissolved in 100 mL water its 10 mL portion required 15 mL 0.1 M NaOH solution to reach the equivalence point. In a separate experiment, 10 mL of the same stock solution was treated with excess of $BaCl_2$ solution and 0.077 g of barium phosphate precipitate was obtained. Determine mass percentage of ammonium nitrate in the original sample.

Problem 66 10.38 mg of a diprotic acid (containing (C, H and O) is burned completely and all CO_2 was absorbed in 100 mL of alkali solution. The resulting solution is separated into two-half and one-half required 55 mL 0.005 M H_2SO_4 solution to reach the phenolphthalein end point. Other half was titrated in presence of methyl orange indicator and 80 mL H_2SO_4 solution of same strength was required to reach the end point. In a separate analysis, 0.168 g of the same acid required 16.18 mL 0.125 M NaOH solution to reach the end point. Deduce formula of the acid and determine molarity of alkali solution used initially.

Problem 67 A 3.0 g sample containing Na_2CO_3, $NaHCO_3$, NaCl and some inert impurity was dissolved in 100 mL of water and its 10 mL portion was titrated against 0.1 M HCl solution using phenolphthalein indicator. 11.32 mL of acid solution was required to reach the end point. The resulting solution was then mixed with excess of $AgNO_3$ solution resulting in formation of 0.306 g of AgCl precipitate. The solution was filtered-off and filtrate was again titrated, but now against 0.05 M NaOH solution. 42.64 mL of alkali was required to reach the end point. Determine mass percentage of Na_2CO_3, $NaHCO_3$ and NaCl in the original sample.

Problem 68 In neutralization titration of Na_3PO_4, if phenolphthalein is used as indicator, end point is indicated only when Na_3PO_4 is converted into Na_2HPO_4 while, if methyl orange is used as indicator, end point appear only when Na_3PO_4 is converted into H_3PO_4. In an experiment a 4.0 g mixture containing Na_3PO_4, Na_2HPO_4 and NaH_2PO_4 is dissolved in 50 mL water and its 10 mL portion required 24.4 mL 0.1 M HCl solution to reach the end point using phenolphthalein indicator. In a separate analysis, 10 mL portion of the same stock solution required 23.572 mL 0.5 M HCl solution to reach the end point using methyl orange as indicator. Determine mass percentage of all components in the mixture.

Problem 69 A mixture containing $LiHCO_3$, NaCl and Na_2CO_3 on gentle heating loses 26.5% of its weight. 5.0 g of this mixture was heated gently and residue was dissolved in 100 mL water. A 10 mL portion of this solution was then treated with 20 mL 0.2 M H_2SO_4 solution. A 10 mL portion of the resulting solution required 3.86 mL 0.1 M NaOH solution to reach the end point. Determine mass percentage of each component in the mixture.

Problem 70 A mixture containing $LiHCO_3$, $NaHCO_3$ and $CaCO_3$ on gentle heating loses 48.4% of its weight. In an experiment, 5.0 g of this mixture was dissolved in 100 mL water and its 10 mL portion was treated with 10 mL 0.5 M NaOH solution. The resulting solution was then treated with excess of

$BaCl_2$ solution resulting in precipitation of all carbonates as $BaCO_3$. Precipitate was separated out by filtration and filtrate required 15.3 mL 0.1 N HCl solution to reach the end point. Determine mass percentage of all components present in the mixture.

Problem 71 5.0 g of a mixture containing NaCl, $NaHCO_3$, Na_2CO_3 and $CaCO_3$ on gentle heating reduces to 4.25 g of solid residue. In a separate experiment, 1.0 g of the same mixture required 10 mL 0.2 M NaOH to reach the end point. In a 3rd experiment, 1.0 g of the same mixture was dissolved in 100 mL water and required 10 mL 1.053 M HCl solution to reach the end point. Determine mass percentage of each component in the mixture.

Problem 72 2.0 g of a sample of $CaCO_3$, $NaHCO_3$ and some volatile, inert impurity, was heated strongly where $CaCO_3$ and $NaHCO_3$, were decomposed into CaO and Na_2CO_3 respectively and all CO_2 gas produced in decomposition was absorbed in a 50 mL NaOH solution. NaOH was little less than the stoichiometric requirement therefore, CO_2 during reaction with NaOH, produced Na_2CO_3 and some $NaHCO_3$. The resulting solution was titrated first in presence of phenolphthalein indicator and 5.0 mL 1.0 M HCl was required to reach the phenolphthalein end point. Methyl orange was then added and titration continued with HCl of same strength where 15 mL HCl was required to reach the final end point.

On the other hand, the residue obtained after heating of the original sample was dissolved in water and treated with excess of $BaCl_2$, giving 0.985 g of $BaCO_3$ precipitate. Determine mass percentage of $CaCO_3$ and $NaHCO_3$ in the original sample.

Problem 73 A one gram sample containing NaOH as the only basic substance and some inert impurity was left exposed to atmosphere for a very long time so that part of NaOH got converted into Na_2CO_3 by absorbing CO_2 from atmosphere. The resulting sample was dissolved in water and volume made upto 100 mL. A 100 mL portion of this solution required 16 mL 0.25 M HCl solution to reach the equivalence point when methyl orange was used as indicator. In a separate analysis, 20 mL portion of the same solution was taken alongwith phenolphthalein indicator and mixed with 50 mL of 0.1 M HCl solution. An additional 9.00 mL 0.1 M $Ba(OH)_2$ solution was required to just restore the pink colour of solution. Determine mass percentage of NaOH in the original sample and mass percentage of Na_2CO_3 in the sample after exposure to atmosphere.

Problem 74 The monochloroacetic acid ($ClCH_2COOH$) preservative in a 100 mL of carbonated beverage was extracted by shaking with dimethyl ether and then returned to aqueous solution as $ClCH_2COO^-$ by extraction with 1.0 M NaOH. This solution was acidified and treated with 50 mL 0.0452 M $AgNO_3$ solution where the following reaction occurred:

$$ClCH_2COOH + AgNO_3 + H_2O \longrightarrow HOCH_2COOH + H^+ + NO_3^- + AgCl(s)$$

After filtering the AgCl, titration of filtrate required 10.43 mL of an NH_4SCN solution. Titration of a blank taken through the entire procedure used 22.98 mL of same NH_4SCN solution. Calculate weight in mg, of $ClCH_2COOH$ in the beverage sample.

Problem 75 2.0 g of a sample containing sodium oxalate, oxalic acid dihydrate and some inert impurity was dissolved in 100 mL water and its 20 mL portion required 23.34 mL 0.04 M acidified permanganate solution to reach the equivalence point. In a separate analysis, 20 mL portion of the same stock solution required 26.67 mL 0.1 N NaOH solution to reach the end point. Determine mass percentage of $Na_2C_2O_4$ and $H_2C_2O_4{\cdot}2H_2O$ in the original sample.

Problem 76 A 1.5 g sample containing $(NH_4)_2SO_4$, NH_4NO_3 and some inert impurity was dissolved in water and volume made upto 100 mL. A 20 mL portion of this solution was mixed with 50 mL 0.1 M NaOH solution. A 30 mL aliquot of this resulting solution required 9.00 mL 1/28 M H_2SO_4 solution for complete neutralization. In a separate analysis, 32 mL of the original stock solution on treatment with excess of $BaCl_2$ solution produced 0.466 g $BaSO_4$ precipitate. Determine mass percentage of NH_4NO_3 and $(NH_4)_2SO_4$ in the original sample.

PROBLEM 77 A 1.0 g impure sample containing $[Zn(NH_4)_4]Cl_2$ and some inert impurity was treated with 15 mL of 1 M NaOH solution where all complex is converted into $Na_2[Zn(OH)_4]$. The excess base required 10 mL $\frac{1}{6}$ M HCl solution for back titration.

(a) Determine percentage purity.

(b) If the last solution obtained after neutralization was treated with excess of $AgNO_3$, what weight of AgCl would have been produced?

PROBLEM 78 1.2 g of a salt with their empirical formula $K_xH_y(C_2O_4)_z$ was dissolved in 50 mL of water and its 10 mL portion required 11.00 mL of a 0.1 M HCl solution to reach the equivalence point. In a separate analysis, 15 mL of the stock solution required 20 mL 0.2475 M KOH to reach the equivalence point. Determine empirical formula of the salt.

PROBLEM 79 Impure phosphoric acid for use in the manufacture of fertilizer is produced by the reaction of sulphuric acid on phosphate rock of which a principal component is $Ca_3(PO_4)_2$ and rest are silica and other inert impurity. In an analysis, 2.0 g of a sample of rock salt was dissolved in 100 mL H_2SO_4 solution. Excess sulphuric acid left in 20 mL of this solution required 40 mL 0.02 M NaOH for back titration. In a separate analysis 20 mL of the above solution required 50 mL 0.04 M NaOH for complete neutralization. Determine mass percentage of $Ca_3(PO_4)_2$ in rock-sample.

PROBLEM 80 A 10 g sample of ammonium perchlorate containing some inert impurity was mixed with 3 g Al powder where all perchlorate reacted to produce Al_2O_3, N_2, HCl and H_2O. All HCl was absorbed in 100 mL 1 M NaOH solution. Determine percentage purity of perchlorate sample and volume of 0.5 M HCl required to neutralize the above solution.

PROBLEM 81 Potassium superoxide (KO_2) is utilized in closed system breathing apparatus to remove CO_2 and water from exhaled air. The removal of H_2O generate oxygen gas and KOH and this KOH in the subsequent step remove CO_2 as $KHCO_3$. 5.0 kg of an impure sample of KO_2 is just sufficient to remove all CO_2 and H_2O from a closed room of dimension $10\text{ m}\times 5\text{ m}\times 3\text{m}$. Determine mass of this KO_2 required to neutralize a 100 mL 0.1 M H_2SO_4 solution in a separate analysis. Assume room conditions to be at 1.0 atmosphere and 300 K and mole fraction of CO_2 in that room is 0.01.

PROBLEM 82 3.25 g of a saturated, tribasic carboxylic acid required 68.4 mL of a 0.750 M NaOH solution to reach the equivalence point. Determine molecular formula of acid.

Solutions

ACID-BASE TITRATION

45. Total mmol of AgCl from 20 mL solution $= \dfrac{0.4305 \times 1000}{143.5} = 3$

m moles of AgCl from HCl = 0.8 ⇒ m moles of AgCl from $CaCl_2 = 2.2$

⇒ 1.1 m mole of $CaCl_2$ was consumed for precipitation of oxalate from 20 mL solution.

Hence, total *m* mol of oxalic acid in 250 mL solution $= \dfrac{1.1}{20} \times 250 = 13.75$

$$\text{m\% of oxalic acid} = \frac{13.75 \times 10^{-3} \times 90}{1.5} \times 100 = \mathbf{82.5}$$

46. The balanced disproportionation reaction is:

$$2P_2O_3 + 6H_2O \longrightarrow PH_3 + 3H_3PO_4$$

meq of NaOH added = 6

meq of H_2SO_4 required for back titration = 1.1

⇒ 4.9 meq of NaOH neutralized 4.9 meq of H_3PO_4

⇒ Total meq of H_3PO_4 produced $= 49 = \dfrac{49}{3}$ m mol H_3PO_4

m mol of P_2O_3 present originally $= \dfrac{2}{3} \times \dfrac{49}{3}$

⇒ Mass % of $P_2O_3 = \dfrac{98 \times 10^{-3}}{9 \times 1.5} \times 110 \times 100 = \mathbf{79.85}$

47. m mol of CO_3^{2-} in 10 mL $= 10 \times 0.05 \times 2 = 1$

In presence of methyl orange 3.235 m mol H^+ is consumed in which 2 m mol H^+ would be required for CO_3^{2-}, hence 1.235 m mol H^+ for HCO_3^- ion.

$$\Rightarrow \qquad \text{m \% CaCO}_3 = \frac{10 \times 10^{-3} \times 100}{2.5} \times 100 = \mathbf{40}$$

$$\text{m \% Ca(HCO}_3)_2 = \frac{6.175 \times 10^{-3} \times 162}{2.5} \times 100 = \mathbf{40}$$

48. m mol of H^+ required to reach the phenolphthalein end point $= 1.12$

$\Rightarrow$ 1.12 m mol Na_2CO_3 is present per 10 mL of solution.

Now, $V = 17$ mL and it contain 1.12 m mol of $NaHCO_3$ produced in titration in association with original $NaHCO_3$.

$\because$ 5 mL of this solution required 3.53 mL acid to reach the methyl orange end point.

$$\therefore \quad 17 \text{ mL would require} = \frac{3.53}{5} \times 17 = 12 \text{ mL acid} = 1.92 \text{ m mol } H^+$$

$\Rightarrow$ m mol of H^+ consumed for neutralization of original bicarbonate $= 0.8$

$$\text{m (Na}_2\text{CO}_3)/\text{litre} = 112 \times 10^{-3} \times 106 = \mathbf{11.872\ g}$$

$$\text{m (NaHCO}_3)/\text{litre} = 80 \times 10^{-3} \times 84 = \mathbf{6.72\ g}$$

49. m mol of HCl taken = 7.5

m mol of HCl left unreacted = 5.244

m mol of HCl reacted = $2.256 \equiv 1.128$ m mol $K_2SO_3 = 0.178$ g K_2SO_3

$$\text{m\% } K_2SO_3 = \mathbf{36.6\%}$$

50. m mol of NH_3 from glycine $= 2.5 - 1.8342 = 0.6658 =$ m mol of nitrogen.

mass of nitrogen $= 9.3212 \times 10^{-3}$ g = **18.64%**

Theoretical mass% = **18.66**

51. Chemical reactions involved in the entire process are :

$$2Ca_3(PO_4)_2 + Mg \longrightarrow Ca_3P_2 + Mg\,(PO_3)_2 + 3CaO + \tfrac{7}{2}O_2$$

$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$$

$$2PH_3 + 4O_2 \longrightarrow P_2O_5 + 3H_2O$$

$\Rightarrow$ 2.4 g (0.1 mol) Mg will produce 0.2 mol PH_3 which would require 0.4 mol of oxygen.

$\Rightarrow$ Vol. of O_2 needed = 8.96 L, hence vol. of air needed = **42.66 L. at S. T. P.**

52. Let the mixture contain x g of Li_2CO_3, y g of $NaHCO_3$.

$\Rightarrow$ After heating $$\frac{30x}{74}+\frac{106y}{168}+9.3-(x+y)=7.37$$

$$\frac{44x}{74}+\frac{62y}{168}=1.93 \qquad \text{...(i)}$$

From titration information :

$$\frac{2x}{74}+\frac{2y}{168}+\frac{9.3-(x+y)}{106}\times 2=0.18$$

$$\Rightarrow \qquad \frac{32x}{74}-\frac{62y}{168}=0.24 \qquad \text{...(ii)}$$

Solving, Eqs. (i) and (ii) gives $x=2.11\,\text{g}$, $y=1.825\,\text{g}$

and $Na_2CO_3=5.365\,\text{g}$ $\Rightarrow$ $NaHCO_3$ = **19.62%,** Na_2CO_3 = **57.7%**

53. M (acid) $=\dfrac{4}{8\times 0.27\times 10}\times 1000=185.2$

Formula of acid $=C_nH_{2n}O_2 \Rightarrow M=14n+32=185.2 \Rightarrow n=11$

Now 5g acid will produce $\dfrac{5}{186}\times 11=\dfrac{55}{186}$ mol CO_2 after complete combustion.

Total moles of NaOH available = 1.0

Moles of NaOH left unreacted $=1-\dfrac{2\times 55}{186}=\dfrac{76}{186}$ in 500 mL

$\Rightarrow$ Molarity of NaOH after precipitation of Na_2CO_3 = 0.817

Therefore, $0.817\times 10=0.5\times V$ $\Rightarrow$ V = **16.34 mL**

54. Let 10 mL solution contain x m mol $NaHCO_3$ and y m mol Na_2CO_3 :

$$\Rightarrow \qquad x+2y=1.24 \quad \text{and} \quad x=1.5-1.26 \quad \Rightarrow \quad y=0.5$$

$$\Rightarrow \qquad m(NaHCO_3)=0.24\times 50\times 10^{-3}\times 84=1.008\text{g}=\mathbf{20.16\%}$$

$$m(Na_2CO_3)=0.5\times 50\times 10^{-3}\times 106=2.65\text{ g}=\mathbf{53\%}$$

$$m(NaCl)=1.342\text{g}=\mathbf{26.84\%}$$

55. $$\underset{\frac{6.4}{M}}{C_xH_yO_2}+O_2 \longrightarrow \underset{\frac{6.4x}{M}}{xCO_2} \xrightarrow{2NaOH} \underset{\frac{6.4x}{M}}{xNa_2CO_3}$$

Let 10 mL solution contain a m mol NaOH and b m mol Na_2CO_3 :

$$\Rightarrow \qquad a+b=14.5$$

$$a+2b=18 \quad \Rightarrow \quad b=3.5 \quad \Rightarrow \quad \frac{6.4x}{M}=0.35 \qquad \text{...(i)}$$

Also, $$\frac{25M}{100}=32 \quad \Rightarrow \quad M=128 \quad \Rightarrow \quad x=\frac{0.35\times 128}{6.4}=7$$

Also, $12x + y + 32 = 128 \quad \Rightarrow \quad y = 12$

$\Rightarrow$ Formula $= C_7H_{12}O_2$

$M(\text{NaOH}) = 1.8$

56. The balanced chemical reaction is :

$$\underset{\frac{1.58}{165.5 + 17x}}{\text{Co(NH}_3)_x\text{Cl}_3} + \underset{\frac{1.58x}{165.5 + 17x}}{x\text{HCl}} \longrightarrow x\text{NH}_4^+ + \text{Co}^{3+} + \underset{\frac{1.58\,(x+3)}{165.5 + 17x}}{(x+3)\,\text{Cl}^-}$$

$$\Rightarrow \quad \frac{1.58\,x}{165.5 + 17x} = \frac{23.63 \times 1.5}{1000} \quad \Rightarrow \quad \boldsymbol{x = 6}$$

$$m(\text{AgCl}) = 0.053 \times 143.5 = \mathbf{7.62\ g}$$

57. $$\frac{5x}{100} \times \frac{1}{53} + \frac{8x}{100} \times \frac{1}{50} + \frac{77x}{100} \times \frac{1}{40} = 0.98 \quad \Rightarrow \quad \boldsymbol{x = 45\ g}$$

58. $$\text{meq of } Na_2CO_3 = 0.6132 \times 40 = 24.528 \ \Rightarrow\ m\%\ Na_2CO_3 = \mathbf{3.25}$$

$$\text{meq of NaOH} = 23.046 \times 40 = 922 \ \Rightarrow\ m\%\ \text{NaOH} = \mathbf{92.2}$$

59. Let the sample contain x mol Na_2CO_3 and y mol $NaHCO_3$.

$$\Rightarrow \quad 2x + y = 18.1396 \times 10^{-3} \qquad \text{...(i)}$$

m mol of NaOH combined with $NaHCO_3 = 4.1$

$\Rightarrow$ Total moles of $NaHCO_3 = 16.4 \times 10^{-3} = y \quad \Rightarrow \quad x = 0.8698 \times 10^{-3}$

$$\Rightarrow \quad m\ \%\ NaHCO_3 = \frac{16.4 \times 10^{-3} \times 84}{1.5} \times 100 = \mathbf{91.84}$$

$$m\ \%\ Na_2CO_3 = \frac{0.8698 \times 10^{-3} \times 106}{1.5} \times 100 = \mathbf{6.15}$$

60. Total NaOH = 0.2 mol,NaOH left unreacted = 0.06 mol

NaOH combined with $CO_2 = 0.14$ mol producing 0.07 mol of Na_2CO_3.

Let hydrocarbon is $C_nH_{2n+2} \quad \Rightarrow \quad M = 14n + 2$

$$\Rightarrow \quad \frac{n}{14n + 2} = 0.07 \quad \Rightarrow \quad n = 7, \text{ Molecular formula} = \mathbf{C_7H_{16}}$$

61. Formula $= C_nH_{2n}O_2 : M = 14n + 32$

Let half-solution contain x m mol Na_2CO_3 and y m mol NaOH.

$$\Rightarrow \quad x + y = 71.72$$

$$2x + y = 123.44 \quad \Rightarrow \quad x = 51.72$$

$$\Rightarrow \quad \text{Total } Na_2CO_3 = 103.44 \text{ m mol}$$

$$\Rightarrow \quad \frac{2n}{14n + 32} = 103.44 \times 10^{-3} \quad \Rightarrow \quad n = 6$$

Hence, acid is $\mathbf{C_6H_{12}O_2}$

$$m(\text{NaOH}) = 123.44 \times 2 \times 10^{-3} \times 40 = \mathbf{9.87g}$$

62. Moles of $NaHCO_3 = 19 \times 0.25 \times 2 \times 10^{-3} = 9.5 \times 10^{-3} = m\%\ NaHCO_3 = \mathbf{31.92}$

$$\text{Moles of Na}_2\text{CO}_3 = (26.66-9.5)\times\frac{10^{-3}}{2} = 8.58\times10^{-3}$$

$\Rightarrow$ $m\%\ \text{Na}_2\text{CO}_3 = \mathbf{36.38};\ m\%\ \text{NaCl} = \mathbf{31.7}$

63. Let N_1 be normality of HCl and N_2 be the normality of NaOH

$\Rightarrow$ $20N_1 = 96N_2$ ...(i)

Also, $\frac{2}{50}\times1000+8N_2\times10 = 50N_1$

$\Rightarrow$ $4+8N_2 = 5N_1$

$N_2 = \mathbf{0.25},\ N_1 = \mathbf{1.2}$

64. Let the mixture contain x m mol $\text{K}_2\text{C}_2\text{O}_4$, y m mol KHC_2O_4 and z m mol of $\text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O}$.

Then, $2x+y=20$ ...(i)

$y+2z=20$ ...(ii)

$166x+128y+126z=2725$ ...(iii)

$\Rightarrow$ $\frac{166}{2}(20-y)+128y+\frac{126}{2}(20-y)=2725$

Solving, $y=10.83$

$\Rightarrow$ $x=4.585$

$z=4.585$

$\Rightarrow$ $m\ \%\ \text{KHC}_2\text{O}_4 = \mathbf{50.87}$

$m\ \%\ \text{K}_2\text{C}_2\text{O}_4 = \mathbf{27.93}$

$m\ \%\ \text{H}_2\text{C}_2\text{O}_4\cdot2\text{H}_2\text{O} = \mathbf{21.2}$

65. Let sample contain x m mol NH_4NO_3 and y m mol $(\text{NH}_4)_3\text{PO}_4$

$\Rightarrow$ $x+3y=15$ and $y=\frac{0.077}{601}\times2\times10000=2.56$

$\Rightarrow$ $x=7.32$ and $m\ \%\ \text{NH}_4\text{NO}_3 = \mathbf{58.56}$

66. Let half solution contain a m mol Na_2CO_3 and b m mol NaOH

$\Rightarrow$ $a+b=0.55$ and $2a+b=0.8$ $\Rightarrow$ $a=0.258b=0.3$

Total m mol of $\text{Na}_2\text{CO}_3 = 0.5 =$ m mol of CO_2 produced

Formula of acid $= \text{C}_x\text{H}_y\text{O}_4$ $\Rightarrow$ moles of CO_2 produced $=\frac{10.38\times10^{-3}}{M}\cdot x$

Also, 0.168 g acid $=16.18\times0.125\times10^{-3}$ equivalent $\Rightarrow$ $M=166$

$\Rightarrow$ $\frac{10.38\times10^{-3}x}{166}=0.5\times10^{-3}$ $\Rightarrow$ $x=8$

Also, $12x+y+64=166$

$\Rightarrow$ $y=6$ $\Rightarrow$ Formula $=\mathbf{C_8H_6O_4}$

$M(\text{NaOH}) = \mathbf{0.016\ M}$

67. Moles of $\text{Na}_2\text{CO}_3 = 0.1\times10\times11.32\times10^{-3} = 11.32\times10^{-3}$

$$\Rightarrow \qquad m\,\%\ \mathrm{Na_2CO_3} = \frac{11.32\times10^{-3}\times106}{3}\times100 = \mathbf{40}$$

m moles of AgCl $= \dfrac{0.306\times1000}{143.5} = 2.13$ from 10 mL stock solution.

$\Rightarrow$ Moles of NaCl in original sample $= (21.3-11.32)\times10^{-3} = 9.98\times10^{-3}$

$\Rightarrow$ Mass% of NaCl $=$ **19.46**

Total NaOH consumed for 10 mL stock solution $= 0.05\times42.64 = 2.132$

$\Rightarrow$ $NaHCO_3$ in original sample $= (21.32-11.32)\times10^{-3} = 10^{-2}$ mol.

$$\Rightarrow \qquad \text{Mass \% of } \mathrm{NaHCO_3} = 10^{-2}\times84\times\frac{100}{3} = \mathbf{28}$$

68. m mol of $Na_3PO_4 = 24.4\times0.1\times5 = 12.2$

$$\Rightarrow\ m\,\%\ (\mathrm{Na_3PO_4}) = 12.2\times10^{-3}\times164\times\frac{100}{4} = \mathbf{50}$$

Also, if the mixture contain y m mol Na_2HPO_4 and z m mol NaH_2PO_4

Then $\qquad 12.2\times3+2y+z = 23.572\times0.5\times5 = 58.93$

$\Rightarrow \qquad 2y+z = 22.33$ ...(i)

Also, $\qquad 142y+120z = 2000$ ...(ii)

Solving; $\qquad y = 6.9$ and $z = 8.53$

$$\Rightarrow \qquad m\%\ \mathrm{Na_2HPO_4} = 6.9\times142\times10^{-3}\times\frac{100}{4} = \mathbf{24.5}$$

$$m\%\ \mathrm{NaH_2PO_4} = \mathbf{25.5}$$

69. Weight loss $= 5\times0.265 = 1.325$ g

$\because$ 106 g weight is lost from 136 g of $LiHCO_3$

$\Rightarrow$ 1.325 g weight will be lost by $\dfrac{136}{106}\times1.325 = 1.7$ g $\quad\Rightarrow\quad m\%\ LiHCO_3 = 34$

m moles of H_2SO_4 used for neutralization of Li_2O and $Na_2CO_3 = 4-0.579 = 3.421$

$\Rightarrow$ Total m mol of $Li_2O + Na_2CO_3 = 34.21$

Also, moles of $Li_2O = 12.5\times10^{-3}$ $\quad\Rightarrow\quad$ moles of $Na_2CO_3 = 21.71\times10^{-3}$

$$\Rightarrow \qquad m\%\ (\mathrm{Na_2CO_3}) = \mathbf{46} \Rightarrow m\%\ \mathrm{NaCl} = \mathbf{20}$$

70. Let the mixture contain x g $LiHCO_3$, y g $NaHCO_3$

On heating :

$$\underset{168}{2\mathrm{NaHCO_3}} \longrightarrow \underset{106}{\mathrm{Na_2CO_3}} + \mathrm{H_2O} + \mathrm{CO_2}$$

$$\underset{136}{2\mathrm{LiHCO_3}} \longrightarrow \underset{30}{\mathrm{Li_2O}} + \mathrm{H_2O} + 2\mathrm{CO_2}$$

$$\underset{100}{\mathrm{CaCO_3}} \longrightarrow \underset{56}{\mathrm{CaO}} + \mathrm{CO_2}$$

$$\text{Mass of residue} = \frac{30x}{136} + \frac{106y}{168} + (5 - x - y)\frac{56}{100} = 2.58$$

$$\left(\frac{56}{100} - \frac{30}{136}\right)x + \left(\frac{56}{100} - \frac{106}{168}\right) y = 0.22$$

$\Rightarrow$ $$0.34x - 0.07y = 0.22 \qquad \text{...(i)}$$

Also, m mol of NaOH reacted with bicarbonates = 5 – 1.53 = 3.47

$\Rightarrow$ $$\text{Total m mol of } LiHCO_3 + NaHCO_3 = 34.7$$

$\Rightarrow$ $$\frac{x}{68} + \frac{y}{84} = 34.7 \times 10^{-3} \qquad \text{...(ii)}$$

Solving, Eqs. (i) and (ii) gives $y = 1.686\text{g}, x = 1$

$\Rightarrow$ $$m\%\ LiHCO_3 = \mathbf{20},\ NaHCO_3 = \mathbf{33.7}$$

71. Moles of $NaHCO_3$ in 1.0 g mixture $= 2 \times 10^{-3} \Rightarrow m\%\ NaHCO_3 = \mathbf{16.8}$

Also moles of HCl consumed by 1 g mixture $= 10.53 \times 10^{-3}$

Out of this 2×10^{-3} mol HCl will be used up by $NaHCO_3$

$\Rightarrow$ 8.53×10^{-3} mol HCl will be used up by Na_2CO_3 and $CaCO_3$

$\Rightarrow$ Moles of $(Na_2CO_3 + CaCO_3) = 4.265 \times 10^{-3}$/g of mixture.

Also 5 g mixture loses 0.75 g wt. and mixture contain 0.84 g $NaHCO_3$

$\Rightarrow$ 0.31 g weight is lost by $NaHCO_3$ and remaining 0.44 g by $CaCO_3$

Therefore, 5.0 g mixture contain 0.01 mol $CaCO_3$, **m% $CaCO_3$ = 20**

Moles of Na_2CO_3/g of mixture $= (4.265 - 2) \times 10^{-3} = 2.265 \times 10^{-3}$

$\Rightarrow$ $$m\% \text{ of } Na_2CO_3 = \mathbf{24} \Rightarrow m\% \text{ of } NaCl = \mathbf{39.2}$$

72. Let the original sample contained '*a*' m mol of $CaCO_3$ and *b* m mol of $NaHCO_3$. Therefore,

$$CaCO_3 \longrightarrow CaO + CO_2$$

$$2NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

m mol of CO_2 produced $= a + \dfrac{b}{2}$

$$\underset{a+\frac{b}{2}}{CO_2} + NaOH \longrightarrow \underset{a+\frac{b}{2}}{NaHCO_3}$$

$$\underset{a+\frac{b}{2}-x}{NaHCO_3} + NaOH \longrightarrow \underset{x}{Na_2CO_3}$$

Till phenolphthalein end point m mol of HCl = 5 = *x*

After phenolphthalein end point m mol of $NaHCO_3$ present in solution $= a + \dfrac{b}{2}$

$\Rightarrow$ $$a + \frac{b}{2} = 15 \qquad \text{...(i)}$$

Also, from precipitation information:

$$\frac{b}{2} = \frac{0.985 \times 1000}{197} = 5 \quad \Rightarrow \quad a = 10, b = 10$$

$\Rightarrow$ mass of $CaCO_3 = 1\,g$, mass of $NaHCO_3 = 0.84\,g$

$m\%$: $CaCO_3 = 50$, $NaHCO_3 = 42$, **Impurity = 8%**

73. In presence of methyl orange, the whole NaOH and Na_2CO_3 are neutralized.

$\Rightarrow$ meq of $HCl = 16 \times 0.25 = 4 =$ meq of $(NaOH + Na_2CO_3) =$ meq. of NaOH original

$\Rightarrow$ Total meq of NaOH in original 1.0 g sample $= 4 \times 5 = 20$

$$\Rightarrow \quad \text{mass \% of NaOH (original)} = \frac{20 \times 40 \times 100}{1000} = 80$$

Now, let us assume that in 20 mL, x m mol of NaOH has got converted to Na_2CO_3

$\Rightarrow$ In 20 mL, m mol of NaOH $= 4 - x$

m mol of $Na_2CO_3 = \dfrac{x}{2}$

In 2nd titration, HCl used in titration of $NaOH + Na_2CO_3 = 5 \times 0.1 - 9 \times 0.2 = 3.2$

$\Rightarrow$ upto phenolphthalein end point, m mol of HCl required $= 4 - x + \dfrac{x}{2} = 4 - \dfrac{x}{2} = 3.2$

$$\Rightarrow \quad x = 1.6$$

$$\Rightarrow \quad \text{Total } Na_2CO_3 \text{ formed} = \frac{x}{2} \times 5 = \frac{5x}{2} = 4$$

m mol of NaOH left unreacted $= 20 - 4 \times 2 = 12$

$\Rightarrow$ weight of 1.0 g of exposed sample $= 1 - \dfrac{8 \times 40}{1000} + \dfrac{4 \times (106 + 18)}{1000} = 1.176\,g$

$\Rightarrow$ weight % of Na_2CO_3 in exposed sample $= \dfrac{4 \times 106}{1000 \times 1.176} \times 100 = 36.05\%$

74. Molarity (M) of NH_4SCN solution $= \dfrac{50 \times 0.0452}{22.98}$

$\Rightarrow$ m mol of $ClCH_2COOH$ present in beverage $= 50 \times 0.0452 - 10.43 \times \dfrac{50 \times 0.0452}{22.98} = 1.234$

$\Rightarrow$ mass of $ClCH_2COOH = 1.234 \times 94.5 =$ **116.6 mg**

75. Let 20 mL stock solution contain x m mol $Na_2C_2O_4$ and y m mol $H_2C_2O_4$

$$\Rightarrow \quad 2x + 2y = 23.34 \times 0.04 \times 5 = 4.668$$

and $\quad 2y = 26.67 \times 0.1 = 2.667 \quad \Rightarrow \quad x = 1 \quad$ and $\quad y = 1.3335$

Therefore, $\quad m\%$ of $Na_2C_2O_4 = \dfrac{5 \times 10^{-3} \times 134}{2} \times 100 =$ **33.5**

$m\%$ of $H_2C_2O_4{\cdot}2H_2O = \dfrac{1.3335 \times 5 \times 10^{-3} \times 126}{2} \times 100 =$ **42**

76. Let the sample contain x m mol $(NH_4)_2SO_4$ and y m mol NH_4NO_3.

$$\text{In 20 mL, m mol of } NH_4^+ \text{ ion } = \frac{1}{5}(2x + y)$$

$$\text{m mol of NaOH reacted with } NH_4^+ = 5 - 9 \times \frac{1}{14} \times \frac{70}{30} = 3.5$$

$$\Rightarrow \qquad \frac{1}{5}(2x + y) = 3.5 \qquad \ldots\text{(i)}$$

Also $\quad x = \dfrac{466}{233} \times \dfrac{100}{32} = 6.25 \;\Rightarrow\;$ From Eq. (i) $\quad y = 5$

$$\Rightarrow \quad \text{mass \% of } (NH_4)_2SO_4 = \frac{6.25 \times 10^{-3} \times 132}{1.5} \times 100 = 55$$

$$\text{mass \% of } NH_4NO_3 = \frac{5 \times 10^{-3} \times 80}{1.5} \times 100 = \mathbf{26.67}$$

77. The reaction involved is:

$$[Zn(NH_3)_4]Cl_2 + 4NaOH \longrightarrow Na_2[Zn(OH)_4] + 4NH_3 + 2NaCl$$

$$\text{m mol of NaOH consumed} = 15 - \frac{10}{6} = 13.33$$

$$\Rightarrow \quad \text{m mol of complex present} = \frac{13.33}{4} = 3.33$$

$$\Rightarrow \quad \text{mass \%} = 3.33 \times 10^{-3} \times 204 \times 100 = \mathbf{68}$$

Also total m mol of Cl^- ions present in final solution $= 3.33 \times 2 + \dfrac{10}{6} = 8.33$

$\Rightarrow$ mass of AgCl formed $= 8.33 \times 10^{-3} \times 143.5 =$ **1.195 g**

78. From charge balance: $\quad x + y = 2z \qquad \ldots$(i)

Also if M be empirical formula weight then

$$\frac{1.2}{M} \times \frac{1}{5} \times 1000x = 1.1 \qquad \ldots\text{(ii)}$$

$$\frac{1.2}{M} \times \frac{15}{50} \times 1000y = 4.95 \qquad \ldots\text{(iii)}$$

Dividing Eq. (iii) by (ii): $\quad 3x = y$

Now, substituting $x = 1, \; y = 3, \; z = 2$

Empirical formula: $\quad \mathbf{KH_3(C_2O_4)_2}$

79. Normality of original H_2SO_4 solution $= \dfrac{50 \times 0.04}{20} = 0.1$

In 20 mL, meq. of H_2SO_4 left unreacted $= 40 \times 0.02 = 0.8$

$\Rightarrow$ meq. of $Ca_3(PO_4)$ in 20 mL $= 20 \times 0.1 - 0.8 = 1.2$

$\Rightarrow$ Total meq. of $Ca_3(PO_4)_2 = 1.2 \times 5 = 6$

$$\Rightarrow \text{mass \% of } Ca_3(PO_4)_2 = \frac{6 \times 10^{-3}}{2} \times \frac{310}{6} \times 100 = \mathbf{15.5\%}$$

80. The chemical reaction involved is:

$$6NH_4ClO_4 + 10Al \longrightarrow 5Al_2O_3 + 3N_2 + 6HCl + 9H_2O$$

$$\text{mole of Al reacted} = \frac{3}{27} = \frac{1}{9}$$

$$\text{mole of } NH_4ClO_4 \text{ present} = \frac{1}{9} \times \frac{6}{10} = \frac{1}{15}$$

$$\Rightarrow \quad \text{mass \% of } NH_4ClO_4 = \frac{117.5}{15} \times \frac{100}{10} = 78.33$$

$$\text{Also moles of HCl produced} = \frac{1}{15}$$

$$\text{moles of NaOH taken initially} = 0.1$$

$$\Rightarrow \quad \text{moles of HCl required to neutralize left over NaOH} = 0.1 - \frac{1}{15} = 0.033$$

$$\text{Vol. of HCl required} = \frac{33}{0.5} = \mathbf{66\ mL}$$

81. Volume of room $= 150\text{m}^3 = 150 \times 10^3$ L

$\Rightarrow$ Total mole of CO_2 in the room $= \dfrac{150 \times 10^3}{0.082 \times 300} \times 0.01 = 60.9756$

Reaction: $$4KO_2 + 2H_2O \longrightarrow 3O_2 + 4KOH$$

$$KOH + CO_2 \longrightarrow KHCO_3$$

$\Rightarrow$ moles of KO_2 in original sample $= 60.9756$

Reaction of KO_2 with H_2SO_4 is:

$$2KO_2 + H_2SO_4 \longrightarrow K_2SO_4 + H_2O + \tfrac{3}{2}O_2$$

moles of KO_2 required to neutralize $H_2SO_4 = 2 \times 100 \times 0.1 \times 10^{-3} = 0.02$

$$\text{mass of } KO_2 \text{ required} = \frac{5000}{60.9756} \times 0.02 = 1.64\text{ g}$$

82. Equivalent weight of acid $= \dfrac{3.25 \times 1000}{68.4 \times 0.75} = 63.35 \quad \Rightarrow \quad$ Molar mass $= 190$

$$\text{Formula of acid} = C_nH_{2n-1}(COOH)_3 \quad \Rightarrow \quad 14n - 1 + 135 = 190 \qquad \Rightarrow \quad n = 4$$

$$\text{Formula} = \mathbf{C_7H_{10}O_6}$$