Redox Titration

PROBLEM 83 A sample of chrome-vanadium steel weighing 2.0 g was dissolved in a mixture of sulphuric acid and just sufficient oxidant was added to raise the oxidation state of iron to Fe³⁺, the chromium to $Cr_2O_7^{2^-}$, vanadium to VO_3^- and Mn to MnO_4^- . The solution was then treated with HCl and resulting solution still containing Fe³⁺, $Cr_2O_7^{2^-}$ and VO_3^- then treated with 25 mL of 0.101 M FeSO₄. This resulted in reduction of dichromate and VO_3^- to Cr^{3+} and VO^{2+} in the solution respectively. Fe²⁺ and VO^{2+} in the solution was then titrated with 0.02236 M KMnO₄ and required 12.6 mL to reach the equivalence point. A small amount of Fe²⁺ was then added to again reduce the VO_3^- produced by KMnO₄ back to VO^{2+} and this then titrated directly with 0.02236 M KMnO₄, a process requiring 0.86 mL to reach the equivalence point. Calculate the following quantities:

- (a) Moles of Fe^{2+} in 25 mL sample of standard $FeSO_4$ solution.
- (b) Moles of Fe^{$^{2+}$} titrated with 12.6 mL of standard KMnO₄.
- (c) Moles of Fe²⁺ consumed by $Cr_2O_7^{2-}$.
- (d) Percentage of V and Cr in the steel [Atomic weight of V = 51, Cr = 52]

PROBLEM 84 A sample of crude uranium oxide is known to be contaminated with iron. To determine the extent of contamination, the crude oxide were dissolved and reduced with Zn to yield a solution containing U^{4+} and Fe²⁺. A 20 mL aliquot of this solution was treated with cupferron which precipitated all uranium and the resulting precipitate on ignition yielded 423.3 mg of U_3O_8 . A further 20 mL sample was treated with 0.024 M KMnO₄ solution and consumed 27.23 mL. Calculate mass percentage of contamination if the iron were present as Fe₂O₃ in a sample of crude oxide containing 100 g of U_3O_8 . KMnO₄ solution oxidised Fe²⁺ to Fe³⁺ and U⁴⁺ to UO_2^{2+} . Atomic mass of U = 238.

PROBLEM 85 A 5.0 g sample containing Pb_3O_4 , PbO_2 and some inert impurity is dissolved in 250 mL dil. HNO₃ solution and 2.7 g of $Na_2C_2O_4$ was added so that all lead converted into Pb^{2+} . A 10 mL portion of this solution required 8.0 mL 0.02 M KMnO₄ for titration of excess of oxalate. In an another experiment, 25 mL of solution was taken and excess oxalate was removed by extraction, this required 10 mL of a permanganate solution for oxidation of Pb^{2+} to Pb^{4+} . 10 mL this permanganate solution is equivalent to 4.48 mL 5 V H₂O₂ solution. Calculate mass percentage of PbO_2 and Pb_3O_4 in the original sample.

[Atomic mass of Pb = 207]

PROBLEM 86 An unknown cupric salt with formula $Cu_x (CO_3)_y (OH)_z$ is analyzed to determine the exact formula. A 1.7225 g sample of salt was dissolved in 100 mL of pure water. A 50 mL portion of this solution required 10 mL 1.0 N H₂SO₄ solution to reach the equivalence point if phenolphthalein was used as indicator. Another 50 mL portion was titrated using methyl orange as indicator and 15 mL acid of same strength was required. Deduce the formula of the salt.

PROBLEM 87 Both CaCl₂ and NaCl are used to melt ice and snow on roads in winter. A certain company was marketing a mixture of these two compounds for this purpose. A chemist, wishing to analyze the mixture, dissolved 1 g of it in water and precipitated the calcium by adding sodium oxalate. The calcium oxalate was then carefully filtered, dissolved in dilute sulphuric acid, and titrated with 0.1 M KMnO₄ solution. The titration required 22 mL of the KMnO₄ solution. Calculate freezing point of an aqueous solution which is 5% (*w/V*) of the above mixture. K_f of water is 1.86 K kg mol⁻¹.

PROBLEM 88 A 4.25 g sample containing CaC_2O_4 , $Na_2C_2O_4$ and some inert impurity is heated gently so that CaC_2O_4 decomposed as:

$$CaC_2O_4 \longrightarrow CaO + CO(g) + CO_2(g)$$

All gaseous products were passed through a NaOH solution where following reaction occurred quantitatively:

$$2\text{NaOH} + \text{CO}_2(g) \longrightarrow \text{Na}_2\text{CO}_3$$

The resulting solution is separated into two equal part (by volume) and one part required 30 mL 0.5 M HCl to reach the phenolphthalein end point while the other half solution required 50 mL 0.5 M HCl solution to reach the methyl orange end point. In a separate experiment same mass of the same sample is dissolved into 100 mL dilute HCl solution and its 10 mL portion required 10 mL 0.1 M $K_2Cr_2O_7$ solution. Determine the mass percentage of Na $_2C_2O_4$ in the original sample.

PROBLEM 89 In acidic solution, 45 mL KMnO₄ solution is required to react with 50 mL 0.25 N $Na_2C_2O_4$ solution. How many mL of this same KMnO₄ solution would be required to oxidise 25 mL 0.1 N $K_2C_2O_4$ solution in alkaline medium where KMnO₄ is reduced to MnO₂.

PROBLEM 90 A sample weighing 0.3 g containing $K_3[Fe(C_2O_4)_3] \cdot 3H_2O,FeCl_3 \cdot 6H_2O$ and inert impurity is dissolved in dilute sulphuric acid and volume made up to 100 mL. A 20 mL portion of this solution required 3.75 mL of 0.005 M acidified KMnO₄ solution to reach the equivalence point. In an another experiment, 50 mL sample of the same stock solution is treated with Zn-amalgum and the resulting solution required 17.5 mL of permanganate solution of same strength. Determine mass percentage of FeCl₃ · 6H₂O in the original sample.

PROBLEM 91 A 6.1 g sample containing oxalic acid dihydrate, sodium oxalate and $NaHC_2O_4$ and is dissolved in 100 mL of water and its 10.0 mL portion required 16 mL 0.25 M HCl to reach the equivalence point. In another experiment 10.0 mL portion of the same stock solution required 24 mL 0.25 M NaOH to reach the equivalence point. Determine the mass percentage of all components in the original mixture.

PROBLEM 92 A 0.127 g of an unsaturated oil was treated with 25 mL of 0.1 M ICl solution. The unreacted ICl was then treated with excess of KI. Liberated iodine required 40 mL 0.1 M hypo solution. Determine mass of I_2 that would have been required with 100.0 g oil if I_2 were used in place of ICl.

PROBLEM 93 Alkali metal nitrate on heating decomposes to metal nitrite and oxygen whereas alkaline earth metal on heating decomposes into metal oxide, NO₂ and oxygen. In an experiment 15 g mixture of NaNO₃ and Mg(NO₃)₂ was heated until no more gas were evolved. The water soluble part of residue was used for analysis and dissolved in 1.0 litre water. 10 mL portion of this solution was reacted with 20 mL 0.02 M acidified KMnO₄ solution. The excess reagent required 10.00 mL 0.05 M oxalic acid solution. Determine mass percentage of each nitrate in the mixture. Also determine the molar ratio of oxygen to NO₂ in the gaseous products given off.

PROBLEM 94 The mass percentage of MnO_2 in a sample of mineral is determined by reacting with As_2O_3 in acid solution. A 0.225 g sample of mineral is ground and boiled with 75 mL 0.0125 M As_2O_3 solution. After the reaction is complete, the solution is cooled and titrated with 2.28×10^{-3} M acidified KMnO₄ solution. 16.34 mL of the oxidizing agent solution was required to reach the end point. Determine mass percentage of MnO₂ in the sample.

PROBLEM 95 A driver is arrested and asked to pass "breath analyzer" test. A sample consisting 56.5 mL of exhaled air is then bubbled into a spectrometer cell containing 3 mL 0.025% (w/V) K₂Cr₂O₇ solution. The transmittance of the solution was 41.5% initially and 43.4% after bubbling the sample through the reaction cell. It is known that the alcohol content in blood stream is 2300 times higher than in exhaled air and that the legal limit is 80 mg of alcohol per 100 mL of blood. Determine the concentration of alcohol in the blood and state whether or not the driver should be charged with drunk driving.

PROBLEM 96 A sample of 0.3657 g powder containing only Ba(NO₃)₂ and Ca(NO₃)₂ are dissolved in 50 mL water. Ammonia is added to the solution to raise the pH than an excess of Na₂C₂O₄ is added to precipitate the metals. The precipitate is then filtered, washed with 1.0 L of water and transferred to a beaker containing 50 mL H₂O. The solution is acidified to solublise the precipitate and finally titrated with 0.05 M KMnO₄ solution. A total of 13.94 mL of oxidizing agent solution was required to reach the end point. Find the composition of the initial mixture. $K_{sp.}$ of BaC₂O₄ = 1.5×10⁻⁸ and of CaC₂O₄ = 2.34×10⁻⁹.

PROBLEM 97 1.0 g sample containing KO₂ and some inert impurity is dissolved in excess of aqueous HI solution and finally diluted to 100 mL. The solution is filtered off and 20 mL of filtrate required 15 mL 0.4 M Na₂S₂O₃ solution to reduce the liberated iodine. Determine mass % of KO₂ in the original sample.

PROBLEM 98 Cuprous ion is known to disproportionate quantitatively in acid medium. A 3.0 g sample of Cu₂O is dissolved in dilute H_2SO_4 solution. The solution is filtered off and 8.3 g pure KI crystal is added to filtrate. This caused precipitation of CuI with evolution of I₂. The solution is filtered off and filtrate is boiled till all I₂ is expelled off. Now, excess of an oxidizing agent is added to filtrate and liberated iodine required 10 mL 1.0 N Na₂S₂O₃ solution. Calculate mass percentage of Cu₂O in the original sample.

PROBLEM 99 To a 10 mL 1.0 M aqueous solution of Br_2 , excess of NaOH is added so that all Br_2 disproportionated to Br^- and BrO_3^- . The resulting solution is freed from bromide ion by extraction and excess of OH⁻ neutralized by acidifying the solution. The resulting solution is just sufficient to react with 1.5 g of an impure CaC₂O₄ sample. Calculate percentage purity of oxalate sample.

PROBLEM 100 One gram of an impure sample of NaCl was dissolved in water and treated with excess of $AgNO_3$ solution. The precipitate AgCl thus, formed undergo decomposition into Ag and $Cl_2(g)$ and latter disproportionate into chlorate (V) and chloride ions and chloride is re-precipitated due to presence of excess of AgNO₃. If the original precipitate was 60% decomposed and final precipitate weigh 1.5 gram, determine mass percentage of NaCl in original sample.

PROBLEM 101 0.4 g of a sample containing $CuCO_3$ and some inert impurity was dissolved in diute sulphuric acid and volume made up to 50 mL. To this solution was added 50 mL 0.04 M KI solution where copper precipitate as CuI and iodide ion is oxidized into I_3^- . A 10 mL portion of this solution is taken for analysis, filtered, made free from I_3^- and treated with excess of acidic permanganate solution. Liberated iodine required 20 mL 2.5 m M sodium thiosulphate solution to reach the end point. Determine mass percentage of CuCO₃ in the original sample.

PROBLEM 102 One gram of an unknown sample of NaCN is dissolved in 50 mL 0.33 M alkaline solution of $KMnO_4$ and refluxed so that all cyanide is converted into cyanate (OCN⁻). The reaction mixture was cooled and its 5.0 mL portion was acidified by adding excess of sulphuric acid solution and finally titrated with 19.0 mL 0.1 M FeSO₄ solution. Determine mass percentage of NaCN in the original sample.

PROBLEM 103 5.0 mL of a pure liquid toluene is dissolved in 100 mL of dilute alkaline KMnO₄ solution and refluxed so that all toluene is oxidized into benzoic acid and a dark brown precipitate of MnO_2 is formed. Solution is filtered off and filtrate and precipitate were analyzed separately. Precipitate

was re-dissolved into 100 mL 1.0 M acidified solution of Na ${}_{2}C_{2}O_{4}$ and excess of oxalate required 50.73 mL 0.1 M acidic dichromate solution for back titration. On the other hand 10.5 mL of filtrate was acidified by adding excess of sulphuric acid and titrated with 0.1 M acidified solution of Na ${}_{2}C_{2}O_{4}$. A 38 mL of oxalate solution was required to reach the end point. Determine density of liquid toluene and molarity of original permanganate solution.

PROBLEM 104 A 2.0 g sample containing $CaOCl_2$ and NaOCl is dissolved in 100 mL water and its 10 mL portion was titrated against 0.15 M acidified solution of $Na_2C_2O_4$. 10 mL of oxalate solution was required to reach the end point. Titrated solution was then treated with excess of aqueous solution of AgNO₃ where all chloride precipitates as AgCl and weighed to be 0.287 g. Determine mass percentage of CaOCl₂ and NaOCl in original sample.

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83. (a) 2.525×10^{-3} mol (b) meq of VO²⁺ = meq of MnO₄⁻ consumed in last step = $0.86 \times 0.02236 \times 5 = 9.6148 \times 10^{-2}$ Total meq of permanganate taken against Fe²⁺ and VO²⁺ =1.4087 \Rightarrow meq of KMnO₄ used up by Fe²⁺ = 1.4087 - 9.6148 × 10⁻² = 1.3125 \Rightarrow Moles of Fe²⁺ titrated with KMnO₄ = 1.3125 × 10⁻³ (c) meq of Fe²⁺ consumed with $Cr_2O_7^{2-} = 2.525 - 9.6148 \times 10^{-2} = 2.428$ \Rightarrow Moles of Fe²⁺ consumed with Cr₂O₇²⁻ = 2.428 × 10⁻³ (d) Mass of V = $9.6148 \times 10^{-2} \times 51 \times 10^{-3}$ $m\% V = \frac{9.6148 \times 51 \times 10^{-5}}{2} \times 100 = 0.25$ \Rightarrow moles of Cr = $\frac{2.428 \times 10^{-3}}{3}$ \Rightarrow m% of Cr = $\frac{2.428 \times 10^{-3}}{3 \times 2} \times 52 \times 100 = 2.1$ 84. In 20.00 mL solution moles of $U_3O_8 = \frac{423.3 \times 10^{-3}}{842} = 5.027 \times 10^{-4}$ Moles of U^{4+} in 20 mL = 1.508×10^{-3} \Rightarrow meq of U^{4+} in 20 mL = 3.016 \Rightarrow meq of MnO_4^- require for 20 mL = $0.024 \times 27.23 \times 5 = 3.2676$ meq of Fe²⁺ = 3.2676 - 3.016 = 0.2516 \Rightarrow Mass of Fe₂O₃ = $\frac{0.2516}{2} \times 160 \times 10^{-3} = 20.128 \times 10^{-3} \text{ g}$ \Rightarrow ⇒ Mass of Fe₂O₃ associated with 100 g U₃O₈ = $\frac{20.128 \times 10^{-3}}{423.3 \times 10^{-3}} \times 100 = 4.755$ m% of Fe₂O₃ = $\frac{4.755}{104.755} \times 100 = 4.54$ \Rightarrow **85.** Let sample contain $x \mod Pb_3O_4$ and $y \mod of PbO_2$ $2x + 2y = \frac{2.7}{134} \times 2 \times 1000 - 8 \times 0.02 \times 5 \times 25 = 20$ \Rightarrow x + y = 10...(i) \Rightarrow $N(\text{KMnO}_4)$ in 2nd titration $=\frac{5 \times 4.48}{5.6 \times 10} = 0.4$ Also, $(3x + y) \times 2 = 0.4 \times 10 \times 10 \implies 3x + y = 20$ \Rightarrow ... (ii)

Solving, Eqs. (i) and (ii)

$$x = 5 = y \implies m(Pb_3O_4) = 3.425 \text{ g}, m(PbO_2) = 1.195 \text{ g}$$

 $m\% Pb_3O_4 = 68.5 \quad m\% PbO_2 = 23.9$
 $2x = 2y + z$

86.

 \Rightarrow

Also,

$$\frac{1.7225}{M}y + \frac{1.7225}{M}z = 10 \times 2 \times 10^{-3} \qquad \dots (i)$$

$$\frac{1.7225}{M} 2y + \frac{1.7225}{M} z = 15 \times 2 \times 10^{-3} \qquad \dots (ii)$$

Solving Eqs. (i) and (ii) gives $y = z \implies x = 1.5 y$

Now, substituting y = 1, gives $Cu_3(CO_3)_2(OH)_2$

87. meq. of KMnO₄ = 0.1×22×5=11= meq. of CaC₂O₄ ⇒ m mol of CaCl₂ = 5.5
Mass of CaCl₂ per gram of mixture = 5.5×111×10⁻³ = 0.61g
Mass of NaCl per gram of mixture = 0.39 g
⇒
$$-\Delta T_f = K_f \left(3 \times 5.5 \times 5 \times 10^{-3} \times \frac{1000}{95} + 2 \times 6.67 \times 5 \times 10^{-3} \times \frac{1000}{95} \right) = 2.92$$

⇒ $T_f = -2.92^{\circ}$ C
88. Let half solution contain 'a' m mol Na₂CO₃ and 'b' m mol NaOH
⇒ $a + b = 15$ and $2a + b = 25$ ⇒ $a = 10 = m$ mol of Na₂CO₃
⇒ Total m mol of CaC₂O₄ = 20
Also, $20 \times 2 + x = 10 \times 0.6 \times 10$ ⇒ $x = 20$ meq of Na₂C₂O₄
 m° Na₂C₂O₄ = $20 \times 10^{-3} \times \frac{134}{2} \times \frac{100}{4.25} = 31.53\%$
89. $M(KMnO_4) = \frac{50 \times 0.25}{45 \times 5} = 0.055$
⇒ Normality of KMnO₄ in alkaline medium = 0.167 N
⇒ $V = \frac{25 \times 0.1}{0.167} = 15.00$ mL
90. I. meq of KMnO₄ = 3.75 × 0.005 × 5 = 93.75 × 10⁻³
⇒ Total meq. of $C_2O_4^2 = 93.75 \times 10^{-3} \times 5 = 0.46875$
⇒ m mol of K₃ [Fe(C₂O₄)₃].³H₂O = 78.125 × 10⁻³
II. meq of MnO₄ = 17.5 × 0.005 × 5 = 0.4375
⇒ Total meq. of E^{2+} ion = 0.875 = m mol of Fe²⁺
⇒ m mol of Fe²⁺ form FeCl₃. 6H₂O = $\frac{0.2155}{0.300} \times 100 = 71.84$
91. Let mixture contain x m mol H₂C₂O₄ · 2H₂O₄ ym mol Na₂C₂O₄ and z m mol NaHC₂O₄
⇒ $2y + z = 40$...(i)
and $2x + z = 60$...(ii)
Also, $126x + 134y + 112z = 6100$...(iii)
Also, $126x + 134y + 112z = 6100$...(iii)
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Also, $126x +$

92. meq of hypo = $4 = \text{meq of } I_2$

⇒ 2 m mol of I₂ is produced from unreacted ICl as ICl + KI → KCl + I₂ ⇒ m mol of ICl combined with oil = 0.5 Also, 0.127 g oil = 0.5 m mol of ICl. ⇒ 100 g oil = $\frac{0.5}{0.127} \times 100$ m mol of ICl or $\frac{0.5 \times 100}{0.127}$ m mol of I₂ ⇒ Mass of I₂ required for 100 g oil = $\frac{100 \times 0.5}{0.127} \times 254 \times 10^{-3}$ = **100 g 93.** meq of KMnO₄ reacted with nitrite in 10 mL solution = 2 - 1 = 1 ⇒ Total meq of NO₂⁻ = 100 = m mol of NaNO₃ ⇒ m% of NaNO₃ = $\frac{100 \times 85 \times 10^{-3}}{15} \times 100$ = **56.67** m% of Mg(NO₃)₂ = **43.33** Total m moles of O₂ = 100 + 44 = 144 m mol of NO₂ = 44 × 4 = 176 ⇒ Molar ratio $\left(\frac{NO_2}{O_2}\right)$ = **1.22 94.** meq of As₂O₃ taken = 75 × 0.0125 × 4 = 3.75

94. meq of As_2O_3 taken = $75 \times 0.0125 \times 4 = 3.75$ meq of MnO_4^- used up in back titration = 0.1862

$$\Rightarrow$$
 meq of MnO₂ = 3.5638 \Rightarrow m% of MnO₂ = 3.5638 $\times \frac{67}{2} \times 10^{-3} \times \frac{100}{0.225} = 68.9$

07

100

95. Molarity of original $K_2Cr_2O_7$ solution = 0.85×10^{-3} M

$$\Rightarrow$$
 m mol of K₂Cr₂O₇ initially = 2.25 × 10⁻¹

$$T_{\text{initial}} = 41.5 \implies (\text{Absorbance})_{\text{initial}} = 58.5$$

 $T_{\text{final}} = 43.5 \implies (\text{Absorbance})_{\text{final}} = 56.6$

- \therefore Absorbance \propto [concentration] or amount.
- :. 56.6% absorbance correspond to

$$\frac{2.25 \times 10^{-3}}{58.5} \times 56.6 = 2.177 \times 10^{-3} \text{ m mol } \text{K}_2 \text{Cr}_2 \text{O}_7$$

 \Rightarrow m mol of K₂Cr₂O₇ reacted with alcohol = 7.3 × 10⁻⁵

meq of alcohol in air =
$$7.3 \times 10^{-5} \times 6 = 4.38 \times 10^{-4}$$

meq of alcohol in 56.5 mL of blood = $4.38 \times 10^{-4} \times 2300 = 1.0074$

 \Rightarrow meq of alcohol in 100 mL blood = 1.783

 $m(C_2H_5OH) = 1.783 \times \frac{46}{4} = 20.5$ mg alcohol content is within the legal limit.

96. m moles of BaC₂O₄ lost in washing = 1000
$$\sqrt{1.5 \times 10^{-8}}$$
 = 0.1224
m moles of CaC₂O₄ lost in washing = 1000 $\sqrt{2.34 \times 10^{-9}}$ =0.0483
meq of MnO₄ used up for oxidising oxalate = 0.05 × 13.94 × 5 = 3.485
 \Rightarrow m mol of oxalate tirtated = $\frac{3.485}{2}$ = 1.7425
 \Rightarrow Total m moles of oxalate produced during precipitation
= 1.7425 + 0.1224 + 0.0483 = 1.9132
Let mixture contain x g Ba(NO₃)₂ :
 $\Rightarrow \frac{x}{261} + \frac{0.3657 - x}{164} = 1.9132 \times 10^{-3} \Rightarrow x = 0.1397 \Rightarrow m\%$ Ba(NO₃)₂ = 38.2
97. The balanced redox reaction is: 2KO₂ + 6HI → 2KOH + 2H₂O + 3I₂
meq of hypo = 15 × 0.4 = 6 = meq of I₂ ⇒ Total I₂ liberated = 15 m mol
 \Rightarrow m mol of KO₂ in original sample = 10 \Rightarrow m% = 10 × 10⁻³ × 71 × 100 = 71%
98. 2Cu⁺ → Cu²⁺ + Cu, Cu²⁺ + 2I⁻ → Cul + $\frac{1}{2}$ I₂
m mol of KI taken initially = $\frac{8.3}{166} \times 1000 = 50$
meq. of I₂ produced from excess KI = 10
 \Rightarrow m mol of KI reacted with Cu²⁺ = 40 \Rightarrow m mol of Cu²⁺ = 20 = m mol of Cu₂O
m% Cu₂O = 20 × 142 × 10⁻³ × $\frac{100}{3}$ = 94.67
99. 3Br₂ + 6OH⁻ → 5Br⁻ + BrO₃ = 43H₂O
 \Rightarrow m mol of BrO₃ = $\frac{10}{3}$
 \Rightarrow meq of BrO₃ = $\frac{10}{3} \times 6 = 20$ = meq of CaC₂O₄
 \Rightarrow mass of CaC₂O₄ = 20 × 10⁻³ × 64 = 1.28 g
 \Rightarrow m⁹/₀ = 85.33
100. Let sample contain x m mol NaCl.
 \Rightarrow Initially x m mol of AgCl formed.
Now, 2AgCl → 2Ag + Cl₂
0.6x 0.3x
and 3Cl₂ → 5Cl⁻ + ClO₃ → 5AgCl
0.3x 0.5x 0.5x 0.5x
 \Rightarrow Final AgCl = 0.4x + 0.5x + 0.9x m mol
 \Rightarrow 0.9x × 143.5 × 10⁻³ = 1.5 \Rightarrow x = 11.614
 \Rightarrow %NaCl = 11.614 × 10⁻³ × 58.5 × 100 = 67.94

101. m mol of KI taken = 2meq of hypo $50 \times 10^{-3} \implies$ meq of I⁻ left unreacted = $50 \times 10^{-3} \times 10 = 0.5$ \Rightarrow m mol of I⁻ used up with CuCO₃ = 1.5 Reaction of I^- with Cu^{2+} is : $2Cu^{2+} + 5I^- \longrightarrow 2CuI + I_3^ \Rightarrow$ m mol of Cu²⁺ = $\frac{2}{5} \times 1.5 = 0.6$ \Rightarrow mass % of CuCO₃ = 0.6 × 10⁻³ × 123 × $\frac{100}{0.4}$ = 18.45 **102.** meq. of Fe²⁺ required for excess MnO₄⁻ = $19 \times 0.1 \times 10$ \Rightarrow m mol of excess MnO₄⁻ = 3.8m mol of MnO_4^- reacted with $CN^- = 16.5 - 3.8 = 12.7$ meq of $MnO_4^- = 12.7 \times 3 = 38.1 = meq of CN^$ m mol of NaCN = 19.05 \Rightarrow m % NaCN = $19.05 \times 10^{-3} \times 49 \times 100 = 93.345$ \Rightarrow **103.** meq of oxalate reacted with $MnO_2 = 200 - 50.73 \times 0.6 = 169.562$ \Rightarrow m mol of MnO₂ produced = $\frac{169.562}{2}$ = 84.781 \Rightarrow meq of KMnO₄ used for oxidation of toluene = 84.781 × 3 \Rightarrow m mol of toluene oxidised = $\frac{84.781 \times 3}{6}$ = 42.39 Mass of toluene = $42.39 \times 10^{-3} \times 92 = 3.8998$ g density (ρ) = 0.78 g / mL \Rightarrow meq of KMnO₄ left unreacted = $38 \times 0.2 \times \frac{100}{10.5} = 72.38$ \Rightarrow m mol of KMnO₄ left unreacted = 14.476 Hence, total m mol of $KMnO_4$ present in original solution = 99.257 \Rightarrow Molarity of original KMnO₄ solution = $\frac{99.257}{100} \approx 1.0 \text{ M}$ **104.** Let mixture contain x m mol CaOCl₂ and y m mol NaOCl $2x + 2y = 0.15 \times 2 \times 10 \times 10 \implies x + y = 15$ \Rightarrow ...(i) $2x + y = \frac{0.287 \times 10 \times 10^3}{143.5} = 20$ Also, ...(ii) Solving, Eqs. (i) and (ii) gives x = 5, y = 10m% CaOCl₂ = 5×10⁻³×127× $\frac{100}{2}$ = 31.75 \Rightarrow

$$m\%$$
 NaOCl = 10×10⁻³ × 74.5× $\frac{100}{2}$ = 37.25