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Question 1: (a) MnO_{4(aq)} + 8H^{+}_{(aq)} + 5Fe^{2+}_{(aq)} ==> Mn^{2+}_{(aq)} + 5Fe^{3+}_{(aq)} + 4H_2O_{(l)}
(b) (i) mol MnO<sub>4</sub> = 0.02 x 24.3 / 1000 = 0.000486, mol Fe<sup>2+</sup> = 5 x 0.000486 (1 : 5 in equation) =
0.00243 \text{ in } 20 \text{ cm}^3, so scaling up to 1 dm<sup>3</sup>, the molarity of Fe<sup>2+</sup> = 0.00243 \times 1000 / 20 = 0.122 \text{ mol}
dm<sup>-3</sup>.
(ii) The end point is the first faint permanent pink due to a trace excess of KMnO<sub>4</sub>.
(c) mol MnO<sub>4</sub> = 0.02 \times 25.45 / 1000 = 0.000509, mol Fe = 5 \times 0.000509 = 0.002545,
mass Fe = 0.002545 \times 55.9 = 0.1423 g,
total Fe in wire = 0.1423 \times 10 = 1.423 \text{ g} (^{1}/_{10}th of the made up solution used in titration),
so <u>% Fe</u> = 1.423 x 100 / 1.51 = <u>94.2 %</u>
(d) The choice of acid is fully discussed in Ex 6.4 of Advanced Redox Chemistry Part 2.
                                                                                                                           TOP
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Question 2:(a) 2S_2O_3^{2-}(aq) + I_{2(aq)} ==> S_4O_6^{2-}(aq) + 2I_{(aq)}^{2-}
(b) mol S_2O_3^{2-} = 0.012 \times 23.5 / 1000 = 0.000282, mole iodine as I_2 = \text{mol } S_2O_3^{2-} / 2 (1 : 2 in equation) =
0.000141.
mass of iodine = 0.000141 \times 126.9 \times 2 = 0.0358 q
(c) mol S_2O_3^{2-} = 0.095 \times 26.5 / 1000 = 0.002518,
mol of iodine = mole 'thio' / 2 = 0.002518 / 2 = 0.001259 in 25 cm<sup>3</sup>,
scaling up to 1 dm<sup>3</sup> gives 0.001259 \times 1000 / 25 = 0.0504 \text{ mol dm}^3 of molecular iodine I_2.
mass concentration of I_2 = 0.0504 \times 2 \times 126.9 = 12.8 \text{ g dm}^3 \text{ of iodine}
                                                                                                                           TOP
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Question 3: (a) (i) Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} ==> Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}
(ii) Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6Fe^{2+}(aq) ==> 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O_{(1)}
(b) for a 25cm<sup>3</sup> aliquot titrated, mol Cr_2O_7^{2-} = 0.02 \times 26.4 / 1000 = 0.000528,
mol Fe<sup>2+</sup> titrated = 6 x Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> = 0.003168 (1 : 6 in equation),
mol Fe_2O_3 = mol Fe / 2 = 0.003168 / 2 = 0.001584,
Mr(Fe_2O_3) = 159.8, mass Fe_2O_3 = 0.001584 \times 159.8 = 0.2531 g.
Total mass of Fe<sub>2</sub>O<sub>3</sub> = 0.2531 x 10 (^{1}/<sub>10</sub>th titrated) = 2.531 g. % Fe<sub>2</sub>O<sub>3</sub> = 2.531 x 100 / 2.83 = 89.4%
(c) Potassium manganate(VII) isn't used for this titration because it is strong enough to oxidise
chloride ions (from the hydrochloric acid) to form chlorine, giving a completely false titration.
                                                                                                                           TOP
                                                                                                                          index
Question 4: mol Fe<sup>2+</sup> = 0.1 \times 25 / 1000 = 0.0025,
mol MnO<sub>4</sub> = mol Fe<sup>2+</sup> / 5 (from equation 1:5) = 0.0005 in 24.15 cm<sup>3</sup>,
scaling up to 1 dm<sup>3</sup>, molarity of MnO<sub>4</sub> = 0.0005 x 1000 / 24.15 = 0.0207 mol dm<sup>-3</sup>.
                                                                                                                           TOP
                                                                                                                          index
Question 5: mol Cr_2O_7^{2-} = 0.02 \times 21.25 / 1000 = 0.000425,
mol of Fe salt = mol Fe<sup>2+</sup> titrated = 6 \times Cr_2O_7^{2-} = 6 \times 0.000425 = 0.00255,
BUT only <sup>1</sup>/<sub>10</sub>th of Fe<sup>2+</sup> salt used in titration,
so 1 g of FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> .xH<sub>2</sub>O is equal to 0.00255 mol.
Scaling up to 1 mol gives a molar mass for the salt in g mol<sup>-1</sup> of 1 x 1 /0.00255 = 392.2.
So the formula mass for FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.\mathbf{x}H<sub>2</sub>O is 392.2.
Now the formula mass of FeSO<sub>4</sub>.(NH_4)<sub>2</sub>SO<sub>4</sub> = 284.1, this leaves 392.2 - 284.1 = 108.1 mass units.
M_1(H_2O) = 18, so 108.1 / 18 = 6.005 mol of water, so x = 6 in the salt formula, FeSO<sub>4</sub>.
(NH_4)_2SO_4.6H_2O.
                                                                                                                           TOP
                                                                                                                          index
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Question 6: (a) $2MnO_4$ (aq) + $16H^+$ (aq) + $5C_2O_4^2$ (aq) ==> $2Mn^{2+}$ (aq) + $8H_2O_{(1)}$ + $10CO_{2(g)}$ or $2MnO_4$ (aq) + $6H^+$ (aq) + $5H_2C_2O_4$ (aq) ==> $2Mn^{2+}$ (aq) + $8H_2O_{(1)}$ + $10CO_{2(g)}$ (b) $M_r(H_2C_2O_4.2H_2O)$ = 126.0, total mol $H_2C_2O_4.2H_2O$ (or $C_2O_4^{2-}$) = 1.52 / 126 = 0.01206, but mol of $C_2O_4^{2-}$ in titration = 0.001206 ($^1/_{10}$ th used, 25 of 250 cm 3), mol MnO_4^- = mol of $C_2O_4^{2-}/2.5$ (2:5 or 1:2.5 ratio),

mol MnO₄⁻ = 0.001206 / 2.5 = 0.0004824 (in 24.55 cm³), scaling up to 1 dm³ the **molarity of MnO**₄⁻ = 0.0004824 x 1000 / 24.55 = **0.0196 mol dm**⁻³. M₁(KMnO₄) = 158, so in terms of mass **concentration** = 0.0196 x 158 = **3.1 g dm**⁻³

TOP index

Question 7: mol KHC₂O₄.H₂C₂O₄.2H₂O (M_r = 254.1) = 0.15 / 254.1 = 0.0005903, ratio of tetroxalate to manganate(VII) is 2:2.5 or 1:1.25 (note equiv of 2 C₂O₄²⁻ in salt), so mol MnO₄⁻ in titration = 0.0005903 / 1.25 = 0.0004723 in 23.2 cm³, scaling up to 1 dm³ gives for **[MnO₄]** = 0.0004723 x 1000 / 23.2 = **0.0204 mol dm**⁻³.

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Question 8: (a) $2MnO_4^{-}_{(aq)} + 6H^+_{(aq)} + 5H_2O_{2(aq)} ==> 2Mn^{2+}_{(aq)} + 8H_2O_{(l)} + 5O_{2(g)}$ (b) in titration mol MnO₄⁻ = 0.02 x 20.25 / 1000 = 0.000405,

 MnO_4 : H_2O_2 ratio is 2:5 or 1:2.5, so mol H_2O_2 in titration = 0.000405 x 2.5 = 0.0010125, scaling up for total mol H_2O_2 in diluted solution (of 1 dm³ or 1000 cm³) = 0.0010125 x 1000 / 25 = 0.0405 mol.

but in the original 50 cm³ solution,

therefore scaling up to 1 dm³, the original molarity of H_2O_2 is 0.0405 x 1000 / 50 = 0.81 mol dm⁻³.

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Question 9: (a) $Zn_{(s)} + 2Fe^{3+}_{(aq)} ==> Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$ (b) mol MnO₄ in titration = 0.01 x 26.5 / 1000 = 0.000265, mol Fe (Fe²⁺) = mol MnO₄ x 5 = 0.001325 in 20 cm³ of the alum solution, scaling up gives total mol Fe = 0.001325 x 500 / 20 = 0.033125, total mass Fe in the 13.2 g of alum = 0.033125 x 55.9 = 1.852, so % **Fe** = 1.852 x 100 / 13.2 = **14.0**%

> TOP index

Question 10: mol MnO₄ in titration = $0.05 \times 24.5 / 1000 = 0.001225$, ratio MnO₄: Na₂C₂O₄ is 2:5 or 1:2.5, so mol Na₂C₂O₄ titrated = $0.001225 \times 2.5 = 0.003063$ in 5 cm³, scaling up to 1 dm³, **molarity Na₂C₂O₄** = $0.003063 \times 1000 / 5 =$ **0.613 mol dm**³ M_f(Na₂C₂O₄) = 134, so **concentration** = $0.613 \times 134 =$ **82.1 g dm**³

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Question 11: mol KMnO₄ = 0.01 x 43.85 / 1000 = 0.0004385, mol Fe (Fe²⁺) = mol KMnO₄ x 5, mol Fe = 0.0004385 x 5 = 0.0021925, so mol FeSO₄.**x**H₂O is also 0.0021925, in the titration 1 /₂₀th of the salt was used (25 /₅₀₀), so 1 /₂₀th of 12.18 g = 0.0021925 mol of the salt = 0.609 g,

scaling up the mass of 1 mole of the salt is $0.609 \times 1 / 0.0021925 = 277.8$, so formula mass of FeSO₄.xH₂O is 277.8, now the formula mass of FeSO₄ is 152.0, so the formula mass of xH₂O = 277.8 - 152.0 = 125.8, M₁(H₂O) = 18, so x = 125.8 / 18 = 6.989,

so x = 7 and the formula of the salt is FeSO₄.7H₂O₂, i.e. seven molecules of water of crystallisation.

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Question 12: (a) $2MnO_4^-(aq) + 6H^+(aq) + 5NO_2^-(aq) ==> Mn^{2+}(aq) + 5NO_3^-(aq) + 3H_2O_{(1)}$ (b) mol KMnO₄ in titration = 0.025 x 25 / 1000 = 0.000625, mol ratio MnO₄⁻:NO₂⁻ is 2:5 or 1:2.5, so mol NO₂⁻ in titration = 0.000625 x 2.5 = 0.0015625 in 24.2 cm³, scaling up to 1 dm³ gives a **molar concentration of NaNO**₂ of 0.0015625 x 1000 / 24.2 = 0.0646 mol dm³

 $M_r(NaNO_2) = 69$, so in terms of mass **concentration** = 0.0646 x 69 = **4.46 g dm**⁻³

TOP index **Question 13**: $M_r(FeC_2O_4) = 143.9$, mol FeC_2O_4 in original solution = 2.68 / 143.9 = 0.01862, scaling down the mol FeC_2O_4 in the titration = 0.01862 x 25 / 500 = 0.000931, mol $KMnO_4$ in titration = 0.02 x 28.0 / 1000 = 0.00056,

so ratio $KMnO_4$: FeC_2O_4 is 0.00056: 0.000931 = giving the 'not so easy to spot' **3:5 the reacting mole ratio**.

FeC₂O₄ is made up of a Fe²⁺ ion and a C₂O₄²⁻ ion, and the full redox equation is: $3MnO_{4^-(aq)} + 5FeC_2O_{4(aq)} + 24H^+_{(aq)} ==> 3Mn^{2^+}_{(aq)} + 5Fe^{3^+}_{(aq)} + 12H_2O_{(l)} + 10CO_{2(g)}$ or $3MnO_{4^-(aq)} + 5Fe^{2^+}_{(aq)} + 5C_2O_4^{2^-}_{(aq)} + 24H^+_{(aq)} ==> 3Mn^{2^+}_{(aq)} + 5Fe^{3^+}_{(aq)} + 12H_2O_{(l)} + 10CO_{2(g)}$

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Question 14: (a) $IO_{3(aq)} + 5I_{(aq)} + 6H_{(aq)}^{+} ==> 3I_{2(aq)} + 3H_{2}O_{(l)}$

(b) mol I titrated = $0.100 \times 20 / 1000 = 0.002$, mole ratio IO_3 : I is 1:5,

so mole IO_3^- reacted = 0.002 / 5 = 0.0004,

so 0.0004 = 0.012 x (volume IO_3^- required) / 1000,

volume IO_3 required = 0.0004 x 1000 / 0.012 = 33.3 cm³

(c)(i) mole $S_2O_3^{2-}$ ('thio') = 0.05 x 24.1 / 1000 = 0.001205,

 I_2 : $S_2O_3^2$ ratio is 1:2 in the titration reaction, so mol I_2 = mole $S_2O_3^2$ / 2 = 0.001205 / 2 = 0.0006025, now the IO_3 : I_2 reaction ratio is 1:3,

so mol IO_3 reacting to give iodine = mole I_2 formed / 3 = 0.0006025 / 3 = 0.000201 in 25 cm³, so scaling up to 1 dm³ the <u>molarity of the KIO₃</u> (IO_3) = 0.000201 x 1000 / 25 = <u>0.00804 mol dm</u>³, $M_r(KIO_3)$ = 214.0, so in terms of mass, <u>concentration</u> = 0.00804 x 214 = <u>0.043 g dm</u>³.

A quicker approach if confident! - ratios from all equations involved are: $2S_2O_3^2$: I_2 : I_3IO_3 , means that the overall mole iodate(V) = mole thiosulphate I 6, so you can 'jump' from line '1' to the last 'few' lines. However in exams these days all the stages (i.e., to,!) are often 'broken down' for you.

(ii) **Starch indicator** is used for the titration, when the last of the iodine reacts with the thiosulphate, the blue colour from the starch-iodine 'complex' is discharged and the solution becomes colourless.

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Question 15: (i) mol KMnO₄ = $0.02 \times 22.5 / 1000 = 0.00045$,

mol Fe²⁺ = mol KMnO₄ x 5 = 0.00225 in 25 cm³,

scaling up to 1 dm³, molarity of the original Fe^{2+} = 0.00225 x 1000 / 25 = 0.090 mol dm³

(ii) the 2nd titration gives the total concentration of $Fe^{2+} + Fe^{3+}$ because any Fe^{3+} has been reduced to Fe^{2+} .

 $mol\ KMnO_4 = 0.02\ x\ 37.6\ /\ 1000 = 0.000752$, total $mol\ Fe^{2+}$ titrated = $mol\ KMnO_4\ x\ 5 = 0.00376$ in 25 cm³.

scaling up to 1 dm³, total molarity of $Fe^{2+} + Fe^{3+}$ in original solution = 0.00376 x 1000 / 25 = 0.150 mol dm⁻³,

so using the result from (a) the $\frac{\text{Fe}^{3+} \text{ concentration}}{\text{3}}$ = 'Fe' total - Fe²⁺ = 0.150 - 0.090 = 0.060 mol dm⁻

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Question 16: you can ignore the 25 cm³ of the solution because you use the same volume in each titration and you can work on the ratio of the moles of 'Fe' out of the (a) and (b) titration calculations. (a) $\underline{\text{mol Fe}^{2+}} = 5 \times \text{MnO}_4^- = 5 \times 0.02 \times 16.9 / 1000 = \underline{0.00169 \text{ mol}} = \text{unreacted iron (which dissolved in the acid to form Fe}^{2+}$).

(b) $mol Fe^{3+} = EDTA^4 = 0.10 \times 17.6 / 1000 = 0.00176 mol = total mol iron in the sample titrated.$

(c) calculation (a) gives the relative moles of unreacted iron Fe, as it dissolved to form the titratable Fe^{2+} .

Calculation (b) gives the total of unreacted Fe + the rust i.e. Fe^{3+} , because any Fe^{2+} formed from Fe has been oxidised to Fe^{3+} .

So from the original mixture (in terms of the 25 cm^3 sample), mol unreacted Fe = 0.00169, mol of reacted iron = 0.00176 - 0.00169 = 0.00007.

Therefore the % rusted iron = $0.00007 \times 100 / 0.00176 = 3.98 \%$ rusted iron.

TOP index Question 17: (a) $I_{2(aq)} + 2S_2O_3^{2-}(aq) ==> S_4O_6^{2-}(aq) + 2I_{(aq)}^{-}$

or $I_{2(aq)} + 2Na_2S_2O_{3(aq)} ==> Na_2S_4O_{6(aq)} + 2NaI_{(aq)}$

- (b) **Starch indicator** is used, starch gives a blue/black colour with iodine, this colour disappears when the last of the iodine is titrated, so a **blue to colourless** sharp end-point is observed.
- (c) mole 'thio' = $0.1 \times 17.6/1000 = 0.00176$,

mol $I_2 = 0.00176 \div 2 = 0.00088$ in 25 cm³,

scaling up gives $0.00088 \times 1000 \div 25 = 0.0352 \text{ mol dm}^{-3}$ for molarity of iodine,

formula mass $I_2 = 2 \times 127 = 254$, so **concentration** = 0.0352 x 254 = 8.94 g dm⁻³



Question 18: (a) $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6I^-(aq) = = > 2Cr^{3+}(aq) + 3I_{2(aq)} + 7H_2O_{(1)}$

- (b) $2S_2O_3^{2-}(aq) + I_{2(aq)} = > S_4O_6^{2-}(aq) + 2I_{(aq)}^{-}$
- (c) mol 'thio' = $20 \times 0.1/1000 = 0.002$,

therefore from equation (b), **mol iodine** = mol 'thio'/2 = 0.001

- (d) From equation (a) mol dichromate(VI) reacting = mol iodine liberated/3 = 0.000333 (3sf)
- (e) $M_r(K_2Cr_2O_7) = 294.2$

mass $K_2Cr_2O_7$ titrated = 0.000333 x 294.2 = 0.0980 g (3 sf)

(f) Since the aliquot of 25 cm3 is 1/10th of the total solution in the flask, the total mass of the K₂Cr₂O₁ in original sample dissolved in the flask solution = 10×0.0980 g = 0.98g

and the % purity of the $K_2Cr_2O_7 = 0.98 \times 100/1.01 = 97.0 \%$ (3 sf)