

(iii) (Mn(II) is) oxidised / undergoes oxidation (1) to Mn(IV) / Mn(III) / to higher oxidation state/ will increase (1) Variable oxidation states (1) coloured compounds (1)
 (i) from +4 to +6/ up by 2 / +2
 (ii) Amount of KMnO₄ = 0.0228 × 0.0216 mol

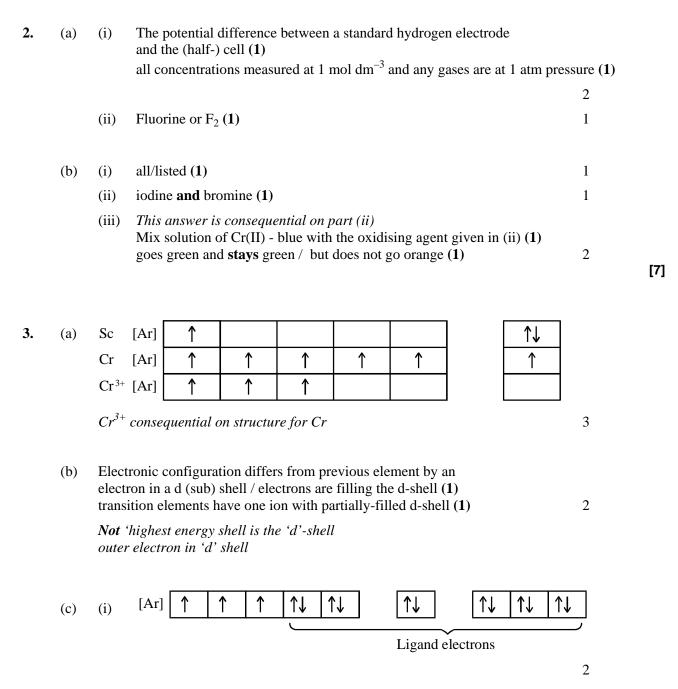
(c)

 $= 4.925 \times 10^{-4} \text{mol}$

- (iii) Amount of SO_3^{2-} in $25cm^3 = 5/2 \times 4.925 \times 10^{-4}$ mol $= 1.231 \times 10^{-3} \text{ mol}$
- (iv) Amount of SO_3^{2-} in $250cm^3 = 10 \times 1.231 \times 10^{-3}$ mol (1) = 1.231×10^{-2} mol Mass of pure $Na_2SO_3 = 126 \times 1.231 \times 10^{-2}$ g (1) = 1.551g
- (v) Purity of sample = (1.551g/ 1.75g) x 100% = 88.6%

[16]

2



Correct electron structure for complex ion (1) ligand electrons identified (1) 6 pairs identified stand alone mark *Consequential on structure of* Cr^{3+}

(ii)
$$\begin{bmatrix} OH_2 \\ H_2O & I \\ OH_2 \\ OH_2 \end{bmatrix} OH_2$$

There must be some attempt to show a 3-D structure 'Octahedral' could rescue a poor diagram

- (iii) d-orbitals split (in energy by ligands) / or diagram to illustrate electron transitions / jumps from **lower** to **higher** energy level (1) **absorbs** light in visible region (1)
- (d) (i) Green **precipitate** (1) (deep) green **solution** in excess sodium hydroxide (1) 2
 - (ii) Deprotonation / acid base (1) 1 [14]

3

3

2

1

[9]

- **4.** (a) (i) $[Ar]3d^6$ (1) 1 allow Is^2 etc
 - (b) (i) Zn / Iron (1) not the zinc ion or iron ion
 more negative potential than -0.28V (1)
 NB this mark must show evidence of use of the data
 gives +E for reduction reaction (1)
 consequential on second mark
 - (ii) rate too slow / activation energy too high / kinetically stable / allow oxide layer if metal electrode specified (1)
 non-standard conditions (1)
 - (c) (i) $Co(H_2O)_6^{2+}$ (1)
 - (ii) Example: $Co(H_2O)_6^{2+} + 4Cl^- \rightarrow CoCl_4^{2-} + 6 H_2O$ Any valid equation that shows a ligand exchange but begins with $Co(H_2O)_6^{2+} (1)$ ligand exchange correctly balanced (1) 2

5. (a) An element that has at least one of its ions has an incomplete d shell (1)

2 variable oxidation states (1) $Cr(H_2O)_6^{2+}$ / hexa aqua chromium (II) ion (1) (ii) Not Cr^{2+} or Cr(II). 1 Cr H_2O (c) 2 (i) 19.5 / 52 40 / 35.5 40.5 / 18 (1) 0.375 2.25 1.127/0.375 0.375/0.375 2.25/0.375 (1) 6 1 NB 2 method marks Violet $Cr(H_2O)_6^{3+}.3Cl^-$ (1) (ii) Green is $[Cr(H_2O)_5Cl]^{2+}2Cl^-.H_2O$ (1) 2 NB for 2 marks must make clear which is which and must be a salt which adds up to $Cr(H_2O)_6Cl_3$ 6. (a) (i) 1 1 1 (ii) 1 Allow single headed arrows or other suitable notation [Mark (ii) consequentially on (i)] (b) (i) Covalent (1) Coordinate or dative (1) 2 (ii) Deprotonation or acid-base 1 (iii) [Cr(H₂O)₃(OH)₃] or Cr(OH)₃Ligand exchange or ligand substitution (iv) $\left[\operatorname{Cr}(\operatorname{NH}_3)_6\right]^{3+}$ or $\left[\operatorname{Cr}(\operatorname{OH})_x (\operatorname{H}_2\operatorname{O})_v (\operatorname{NH}_3)_z\right]^{\operatorname{charge}}$ (v) 1 x + y + z = 6, z at least one, correct charge will be between 0 and +3, $x = \max 3$

[8]

Coloured ions / compounds/ complexes/ solutions (1)

(b)

(i)

- (c) ullet d orbitals/subshell/energy level split (in energy by ligands)/diagram to illustrate (1)
 - Electron transitions/jumps from **lower** to **higher** energy level (1)
 - **Absorbs** light in visible region/reference to white light (1) 3

If imply or state that emission is occurring, only the first marking point is available

[11]

7. (a) (i)
$$1s^22s^22p^63s^23p^63d^84s^2$$

(ii) $1s^22s^22p^63s^23p^63d^8$

1

(b)

$$\begin{bmatrix} H_2O_{\bullet,\bullet} & OH_2 \\ OH_2OH_2 & OH_2 \end{bmatrix}$$
(1)

Shape mark

Must be 3-D ie wedges or dashes

labelled dative covalent between O atom and ion (1)

3

(c) (i)
$$[Ni(H_2O)_4(OH)_2]$$

 $ALLOW Ni(OH)_2$

1

(ii) Deprotonation (1) two successive deprotonations / neutral species producing insoluble compound (1)

2

2

(iii) Ligand exchange (1) giving (soluble)
$$[Ni(H_2O)_0 \text{ or } 2(NH_3)_6 \text{ or } 4]^{2+}$$
 OR in words (1)

[10]

8. (a) (i) Use E $^{\theta}$ values for reduction of Fe³⁺ to Fe²⁺ by Zn (E $^{\theta}$ cell = + 1.53V) (1) and Fe²⁺ to Fe by Zn (E $^{\theta}$ cell = +0.32V)(1) They have positive E $^{\theta}$ so are feasible (1) *NOT* "will happen"

They have positive E^{θ} so are feasible (1) *NOT* "will happen" OR

ALLOW Zn^{2+}/Zn is more negative than both Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe (1) so zinc is a stronger reducing agent (1) so zinc reducing both is feasible (1)

3

- (ii) Reduction of Fe²⁺ has high activation energy / kinetically stable 1
- (b) (i) $\operatorname{Mn} \operatorname{O_4}^- + 5\operatorname{Fe}^{2+} + 8\operatorname{H}^+ \to \operatorname{Mn}^{2+} + 5\operatorname{Fe}^{3+} + 4\operatorname{H}_2\operatorname{O}$ Species (1) Balance (1) Any state symbols ignored.
 - (ii) purple colour of MnO₄⁻ lost (1) end point when yellow / colourless solution (1) becomes (permanently) pink (1) 3
- (c) Amount MnO_4^- in 1^{st} titration = 0.0182 dm³ × 0.0200 mol dm⁻³ = 3.64 × 10^{-4} mol (1)

Amount Fe²⁺ in original solution = $5 \times \text{above value} = 1.82 \times 10^{-3} \text{ mol } (1)$

Amount Fe^{2+} in 2^{nd} titration = amount of Fe^{2+} and Fe^{3+} original solution (1)

= $0.0253 \text{ dm}^3 \times 0.0200 \text{ mol dm}^3 \times 5 = 2.53 \times 10^{-3} \text{ mol}$

Amount of Fe^{3+} in original solution = $0.00253 - 0.00182 = 7.10 \times 10^{-4} \text{ mol (1)}$

Amount zinc needed to reduce $Fe^{3+} = \frac{1}{2} \times 0.000710 = 0.000355$ mol Mass of zinc = 0.000355 mol \times 65.4 g mol⁻¹ = 0.0232 g (1) 2,3 or 4 SF Consequential on their moles iron

The marks are for the following processes:

Either volume of MnO_4^- to moles of MnO_4^- (1)

Convert to moles of Fe^{2+} by multiplying either moles of MnO_4^- by 5 (1)

Realising that 2^{nd} titration measures total number of moles of iron (1))

Subtracting to get original moles Fe^{3+} (1)

Going to moles Zn then mass Zn (1)

1	n
	к

point

Volume MnO_4^- for Fe^{3+} , which has been reduced by zinc (1) 3^{rd} point = 25.3 cm³ – 18.2 cm³ = 0.0253 dm³ – 0.0182 dm³ = 0.0071 dm³ (1) 4^{th}

Amount of $MnO_4^- = 0.0071 \text{ dm}^3 \times 0.0200 \text{ mol dm}^{-3} = 1.42 \times 10^{-4} \text{ mol (1) } 1^{st}$

Amount Fe³⁺ reduced by zinc = $5 \times$ above value = 7.10×10^{-4} mol (1) 2^{nd} point

Amount zinc needed = $\frac{1}{2} \times 7.10 \times 10^{-4} = 3.55 \times 10^{-4} \text{ mol}$ mass of zinc needed = $3.55 \times 10^{-4} \text{ mol} \times 65.4 \text{ g mol}^{-1} = 0.00232 \text{ g (1) } 5^{th}$ point

5

3

1

4

[20]

- (d) (i) $[Fe(H_2O)_6]^{2^+} + H_2O \rightarrow [Fe(H_2O)_5OH]^+ + H_3O^+$ H_3O^+ in equation (1) other ion in equation (1) (Fe^{2^+}) polarises the O–H bond in ligand (1)
 - (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ more acidic than $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ (1) $[\text{Fe}^{3+}]$ higher charge density than $[\text{Fe}^{2+}]$ (1) $[\text{Fe}^{3+}]$ ion if more polarising (1)

9. (a) (i) $1s^22s^22p^63s^23p^63d^{10}4s^2$ accept any order

(ii) $1s^22s^22p^63s^23p^63d^{10}$ Conseq on (a) (i) 1

- (b) **d-block**: last (added) electron is in a d–(sub) shell / orbital (1) **Not transition**: does not form **ions** with partially filled d-(sub) shell / orbitals (1)
- (c) 3D-drawing e.g. wedges / hatches or perspective diagram (1)
 Labels covalent bond within water molecule (1). This must be drawn out /use of a key is acceptable.

Shows dative covalent bond from water to central Zn²⁺ (1) Labels a 90° angle (1) Ignore absence of charge on ion

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(d)
               White precipitate /solid /suspension (1) NOT powder
       (i)
               Colourless solution (in excess ammonia) NOT "clear" (1)
                                                                                                          2
               [Zn(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Zn(OH)_2(H_2O)_4] + 2NH_4^+
       (ii)
               [Zn(H_2O)_6]^{2+} + 2OH^- \rightarrow [Zn(OH)_2(H_2O)_4] + 2H_2O
               [Zn(H_2O)_6]^{2+} + 2OH^- \rightarrow Zn(OH)_2 + 6H_2O
               [Zn(H_2O)_6]^{2+} + 2NH_3 \rightarrow Zn(OH)_2 + 2NH_4^+ + 4H_2O (1)
               [Zn(OH)_2(H_2O)_4] + 4NH_3 \rightarrow [Zn(NH_3)_4(H_2O)_2]^{2+} + 2OH^- + 2H_2O
               Or
               Zn(OH)_2 + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + 2OH^-
               (1) for cation formed
               (1) for balancing equation with the correct species (2)
                                                                                                          3
               d-(sub) shell / orbitals are full / 3d<sup>10</sup> arrangement of electrons (1)
(e)
       (i)
               No jumps of d-electrons /no d-d transitions (1)
               Any mention of e<sup>-</sup> falling back down or "no splitting of d-orbitals" and
               second mark is not awarded
                                                                                                          2
               Cr is a transition metal / Cr can have d-d transitions /CrO<sub>4</sub><sup>2-</sup> is
       (ii)
               yellow / Cr(+6) or Cr(VI) is yellow
                                                                                                           1
                                                                                                                       [16]
               \frac{\text{Fe } [\text{Ar}]}{3\text{d}^6 4\text{s}^2}
(a)
       (i)
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2

10. (a) (i)
$$\frac{\text{Fe } [Ar]}{3d^64s^2}$$
or $3d_64s_2$
or $4s^23d^6$ (1)
$$\frac{\text{Fe}^{2+} [Ar]}{3d^6}$$
or $3d_6$
or $3d_6$
or $3d^64s^0$ (1)
$$\frac{\text{Letter } d \text{ must } be \text{ lower } case}{\text{Any additional letters of numbers } \textbf{(0)}$$

(ii) The mark is for the shape

$$H_2Q$$
 OH_2 OH_2 OH_2 OH_2 OH_2 OH_2

OR

$$H_2O_{M_2}$$
 H_2O
 H_2O
 H_2O
 H_2O
 H_2O
 H_2O
 H_2O
 H_2O
 H_2O

ALLOW bond to H of H_2O (except on left side if OH_2 is given) IGNORE charge unless incorrect

1

(iii)
$$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow [Fe(OH)_2(H_2O)_4] + 2H_2O$$

OR

 $[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(OH)_2 + 6H_2O$

OR equations with 2NaOH as reactant and 2Na $^+$ as product IGNORE state symbols

1

 (iv) Green precipitate / solid → foxy-red / red-brown / brown / orange Both colours and precipitate / solid needed NOT darkens

1

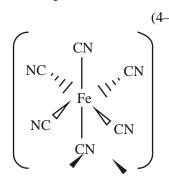
(v)
$$N_2 + 3H_2 \rightarrow / \rightleftharpoons 2NH^3$$

 $ALLOW \bigcirc + Br_2 \rightarrow \bigcirc - \stackrel{Br}{+} HBr$

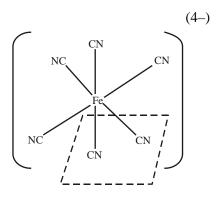
OR equation with Cl₂

	(b)	(i)	Emf of cell / potential difference of cell containing Fe ²⁺ and Fe (1) and standard hydrogen electrode / half cell <i>NOT</i> 'SHE' <i>OR</i> hydrogen electrode and 1 mol dm ⁻³ H ⁺ and 1 atm H ₂ (1) 1 mol dm ⁻³ Fe ²⁺ <i>IGNORE temperature</i>	3	
	QWo	C*(ii)	Emf of hydrogen electrode is zero – stated or implied (e.g. if calculate $E_{cell} = +0.44(V)$) (1) Fe + 2H ⁺ \rightarrow Fe ²⁺ + H ₂ (1) – equation stand alone Potential for the reaction is positive so reaction is feasible (1) OR H ⁺ and (½)H ₂ has a more +ve electrode potential than Fe ²⁺ and Fe (1) H ⁺ will oxidise Fe / H ⁺ is an oxidising agent / Fe is a reducing agent for H ⁺ / other correct redox statement (1) Fe + 2H ⁺ \rightarrow Fe ²⁺ + H ₂ (1) – stand alone	3	
		(iii)	High E_a so slow reaction / reactants are kinetically stable IGNORE any mention of non-standard conditions	1	
	(c) $2Fe^{3+} + 2\Gamma \rightarrow 2Fe^{2+} + I_2$ or words $E^0 = (+)$ 0.23 V (1) So Γ would reduce Fe^{3+} / Fe^{3+} would oxidise Γ / E^0 positive so reaction $L \rightarrow R$ (1) OR reverse argument (2) OR				
			and Fe^{2+} has a more positive electrode potential than I_2 and I^- (1) ll reduce Fe^{3+} / Fe^{3+} will oxidise I^- (1)	2	[15]
11.	(a)	(i)	Forms ions which have partially filled d -orbitals OR Forms ions which have a partially filled d -subshell	1	
		(ii)	Scandiurn / Sc and Zinc / Zn	1	
	(b)	(i)	Fe^{2+} [Ar] $3d^6$ Mn ²⁺ [Ar] $3d^5$ (1) for both correct	1	
		(ii)	Fe ³⁺ is $3d^5$ / half filled <i>d</i> -subshell which is more stable than $3d^6$ (1) Mn ²⁺ is (already) $3d^5$ (which is more stable than $3d^4$) (1)	2	

(c) Shape (1)
Bonding to correct atoms (1)



OR



(d) Two As atoms oxidised from +3 to +5 per mole of As_2O_3 (loss of $4e^-$) (1)

: if 5 moles oxidised, total $20e^{-}$ Lost / change in oxidation no. = 20 (1)

∴4 moles MnO₄ reduced, total 20e gained / change in oxidation no. 20

∴ each Mn(VII) gains 5e⁻ / change in oxidation no. 5 (1)

 \therefore Mn(11) / Mn²⁺ (1) NOT standalone mark

(e) (i)
$$VO_3^- + 2H^+ / 2H_3O^+ \rightarrow VO_2^+ + H_2O / 3H_2O$$

1

4

2

(ii) No because oxidation no. of V is +5 in VO_2^+ / Oxidation no. of V unchanged (at +5)

1

3

(iii) First green colour : VO_2^+ and VO^{2+} (1)

Second green colour: $V^{3+}/[V(H_2O)_6]^{3+}$ (1)

Violet colour : $V^{2+} / [V(H_2O)_6]^{2+}$, (1)

[16]

12. (a) $3OCl^- \rightarrow 2Cl^- + ClO_3^-$ (1)

chlorine (in OCl $^-$) is (simultaneously) oxidised from +1 to +5 (1) and reduced from +1 to -1 (1)

If only oxidation numbers given max 1 (out of 2)

If oxidation numbers omitted max 1 (out of 2)

3

(b) (i) blue / black to colourless

1

- no. moles $S_2O_3^{2-}$ used = $12.5 \times 0.1 / 1000 = 1.25 \times 10^{-3}$ (1) (ii) no. moles $I_2 = 1.25 \times 10^{-3} / 2 = 6.25 \times 10^{-4}$ (1) no. moles $ClO^- = no. moles 1_2$ (1) no. moles ClO⁻ in original 10 cm³ = $10 \times 6.25 \times 10^{-4}$ $=6.25\times10^{-3}$ (1) no. moles ClO⁻ in 1 dm³ = $100 \times 6.25 \times 10^{-3}$ (1) = 0.6255 mass $Cl_2 = 0.625 \times 71$ (iii) =44.4(g)mark consequentially on (ii) must be 3s.f. in final answer 1 Cl₂ is the stronger oxidising agent because Cl₂ oxidises S from (+)2 to (+)6 (1) 2 but l_2 oxidises S from (+)2 to (+)2.50 (1) O_2 oxidises KI / iodide to l_2 . or balanced equation (1) ll₂ reacts with starch / paper to give blue / black (1) 2 [14]

(c)

QWC (d)

(c) (i) Dative (covalent) OR co-ordinate (1)

Covalent (1) 2

		OR		
		$[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow Ni(OH)_2 + 4H_2O + 2NH_4^+$		
		OR		
		$[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow [Ni(OH)_2(H_2O_4)] + 2H_2O$ OR		
		$[Ni(H_2O)_6]^{2+} + 2OH^- \rightarrow Ni(OH)_2 + 6H_2O$		
		IGNORE state symbols		
		IGNORE missing square brackets in any formula	1	
	(iii)	H ⁺ removed (by NH ₃ OR OH ⁻) (1)		
		From (H ₂ O) ligands (1)		
		NOT just from "complex"	2	
	(iv)	Ligand exchange		
		OR ligand replacement OR ligand substitution	1	
		OK figalid substitution	1	
	(v)	$[Ni(OH)_2(H_2O)_4] + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 2OH^- + 4H_2O$		
		OR		
		$Ni(OH)_2 + 6NH_3 \rightarrow [Ni(NH_3)_6]^{2+} + 2OH^-$		
		Allow formation of $[Ni(NH_3)_4]^{2+}$ OR $[Ni(NH_3)_4(H_2O)_2]^{2+}$		
		cation formed (1)		
		balancing equation (1)	2	
QWC (d)		pital <u>s</u> split (in energy) by ligands (1) OW d-sublevel		
	absorbs light (in visible region) (1) NOT "uv light"			
	elect	ron is promoted OR electron moves to a higher energy level (1)		
	Any	mention of emission of light can only score 1st mark	3	
				[14]

 $[Ni(H_2O)_6]^{2+} + 2NH_3 \rightarrow [Ni(OH)_2(H_2O_4)] + 2NH_4^+$

(ii)