1. (a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2/4s^2\ 3d^6$ *OR* $3d^8$ $(4s^0)$ **(1)**
Incomplete d shell (in the ion) **(1)** 2

(b) (i) $Ni(CO)_4$ 1

(ii) 0 1

(c) (i) $Ni(H_2O)_6^{2+}(aq) + NH_3(aq) \rightarrow Ni(H_2O)_5(NH_3)^{2+}(aq) + H_2O(I)$ 1

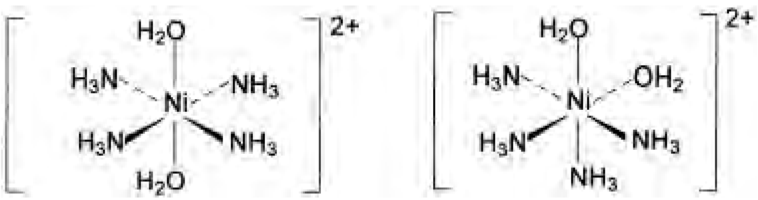
QWC* (ii) ΔS is likely to be small / close to zero **(1)** – *No TE*
Same number of moles/molecules/particles in the **same states** on both sides of the equation **(1)** 2

(d) (i) $Ag^+(aq) + Cl^-(aq) \rightarrow Ag^{(+)}Cl^{(-)}(s)$ 1

(ii) 1 mole of AgCl has a mass of 143.5/(108+35.5) **(1)**
OR 143.3 from Data Book (or 143.4)
Number of moles of AgCl = 6.133/143.5 = 0.0427(4) 0.04280 **(1)**
Number of moles of complex = 0.04274/2 = 0.02137
Therefore mass of 1 mole = 5.000/0.02137 = 234/234.4 **(1)**
3SF sufficient but not 2SF 3

(iii) $59 + 18 \times x + 17 \times (6 - x) + 71 = 234$
$232 + x = 234$
$x = 2$ 1
($[Ni(H_2O)_2(NH_3)_4]Cl_2$) Formula NOT needed for mark

(iv) The two water molecules could be at 180° or 90° to one another



Octahedral structure **(1)**
ALLOW the word octahedral to explain diagram's shape 2

[14]

2. (a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
OR
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$ 1

QWC*(ii) V and Mn have two 4s electrons / filled 4s (orbital) Cr has one **(1)**
due to stability of half-filled shell/4s and 3d levels have similar energies **(1)** 2

QWC*(b)	Cr^{3+}(aq), Cr^{2+}(aq)(IPt) –0.41(V) **(1)** [O_2(g) + 2H_2O(l)], 4OH^-(aq)(IPt) +0.4(0) (V) **(1)** *ALLOW a state symbol omission in each.* *ALLOW half equations* *Can be given in a cell diagram* by application of the anti-clockwise rule oxygen will oxidise Cr^{2+} *OR* E^0 cell = (+) 0.81(V) and this is **greater** than (+) 0.6 (V) *OR* Cr^{2+} has more negative electrode potential so will reduce oxygen / oxygen more positive etc. **(1)**		3
QWC*(c)	(i)	Water acts as a ligand by a non-bonding pair (of electrons on the oxygen atom) **(1)** Making a dative (covalent)/co-ordinate bond (to the chromium ion) **(1)**	2
	(ii)	Bidentate/chelate/bridging	1
	QWC*(iii)	Two peaks in the NMR spectrum **(1)** Due to two different environments of hydrogen atoms / H in H_2O and H in CH_3 **(1)** *Mark independently*	2
	QWC*(iv)	**Any two**: C-H just below 3000 / 2962-2853 / 1485-1365 O-H 3200-3800 C=O 1700-1750 C-O 1230 - 1250 *ALLOW values or ranges within these ranges* *If more than two given, –1 for each incorrect*	2
(d)	(i)	3C_2H_6O to 3C_2H_4O <u>provided</u> 1 $Na_2Cr_2O_7$ **(1)** 4H_2SO_4 and 7H_2O **(1)** *ACCEPT multiples*	2
	(ii)	Orange to green *ALLOW qualified green e.g. blue-green* *NOT green to orange*	1
	(iii)	(Sodium dichromate(VI)) is a carcinogen / toxic / irritant *In any combination* *Lose mark for anything else with these.*	1

[17]

3. (a) (i) Add silver nitrate (solution) **(1)** *ACCEPT correct formula*
(pale) yellow **precipitate**/solid**(1)**

OR
Add chlorine (solution)/bromine (solution) **and** hydrocarbon solvent **(1)**
Solvent goes purple/pink/violet **(1)**
2nd mark is dependent on 1st — 2

(ii) Iodine /I <u>and</u> sulphur / S identified **(1)** -*NOT* I_2 /I^-/iodide
Iodine
initial (+)5 final –1 **(1)**
Sulphur
initial (+)4 final (+)6 **(1)**
ACCEPT as roman numerals
ACCEPT +/– on either side/sub or superscript
ACCEPT as words — 3

(iii) 1 × –6 = –6, 3 × +2 = +6 *ALLOW TE from (ii)*

OR total change in oxidation number of +6 for S, –6 for I

ACCEPT justification in terms of electrons — 1

(b) (i) pipette
ALLOW burette
NOT measuring cylinder — 1

(ii) Starch (solution) **(1)**

blue/dark blue/blue-black/black to colourless **(1)**
ALLOW **max 1** *if candidate states* "no indicator needed/self-indicating" with colour change brown/yellow to colourless
If no indicator given but correct colour change **1 (out of 2)** — 2

(iii) $\frac{24.0}{1000} \times 2.4(0) \times 10^{-4}$ *OR* 0.00024 (mol)

The mark is for the answer — 1

(iv) $\frac{2.40 \times 10^{-4}}{2} = 1.2(0) \times 10^{-4}$ (mol) *OR* 0.00012 (mol)

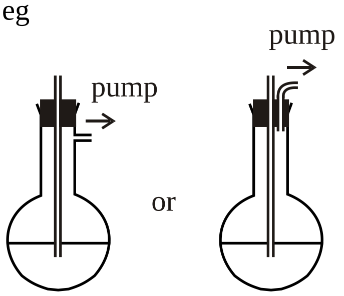
ALLOW TE from (iii)
The mark is for the answer — 1

(v) $1.2 \times 10^{-4} \times 100 = 0.012(0)$ (mol dm^{-3})

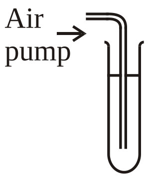
ALLOW TE from (iv)
The mark is for the answer 1

[12]

4. (i) (Buchner) flask / boiling tube connected to pump, glass tube through stopper into solution
eg



ACCEPT



But must be a test tube and tube to bottom as shown 1

(ii) $8H^+$ $4H_2O$
ACCEPT multiples 1

(iii) Number of moles of manganate(VII) ion

$$= \frac{20 \times 0.020}{1000} = 0.0004(0)\ \mathbf{(1)}$$

Number of moles of electrons
= 5 × 0.00040 = 0.002(0) **(1)**

Number of moles of vanadium ions

$$= \frac{10 \times 0.10}{1000} = 0.001\ \mathbf{(1)}$$

(as vanadium(V) is formed by loss of 2 moles of electrons)
Oxidation number of vanadium in aerated solution is +3 **(1)** 4

(iv) It is a powerful oxidising agent, $E^{\ominus}$ = +1.51 V

OR

It is self-indicating 1

[7]

5. (a) (i) uses $E^{\ominus}$ values to find $E_{reaction}$ = (+) 1.57 (V) **(1)**

Reject – 1.57

$Zn + 2NO_3^- + 4H^+ \rightarrow Zn^{2+} + 2NO_2 + 2H_2O$ **(1)** 2

Accept equation with equilibrium sign

Rejection equation with Zn on the right

(ii) $E_{reaction}$ for the production of hydrogen is (+) 0.76 (V) **(1)**

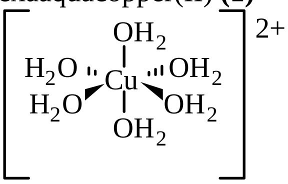
smaller than reaction in (i) so is less likely **(1)**

OR

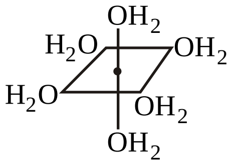
NO_3^- being the oxidised form of a redox couple with a more positive $E^{\ominus}$ than $E^{\ominus}$ $H^+/½ H_2$ **(1)**

is a stronger oxidising agent than H^+ **(1)** 2

(iii) hexaaquacopper(II) **(1)**



OR



(1)

Both marks stand alone

[IGNORE charge] 2

[IGNORE how H_2O ligand is bonded to central cation]

Accept hexaquacopper(II)

Reject formula

(iv) **ligand** exchange/replacement/substitution **(1)**

$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons CuCl_4^{2-} + 6H_2O$ **(1)**
OR
$[Cu(H_2O)_6]^{2+} + 4HCl \rightleftharpoons CuCl_4^{2-} + 4H^+ + 6H_2O$ **(1)** 2

ALLOW →

Accept $H_2CuCl_4 + 2H^+$ for $CuCl_4^{2-} + 4H^+$

(b) (i) $E^\ominus$ for the reaction is **–** 0.39 (V) (so not feasible) [value is required]. 1

Accept Cu^{2+} being the oxidised form of the redox couple with the more negative $E^\ominus$, will not oxidise I^-

(ii) CuI is a solid (so conditions are not standard) **(1)**

Equilibrium is pulled over/moves to favour the r.h.s. **(1)** 2

Reject just 'conditions not standard'

(iii) $[Cu(NH_3)_4]^+$

OR $[Cu(NH_3)_4(H_2O)_2]^+$ 1

Accept $[Cu(NH_3)_2]^+$

Reject $[Cu(NH_3)_6]^+$

Reject any 2+ complex

(iv) (atmospheric) oxygen **(1)**

oxidises Cu^+ to Cu^{2+} **(1)** 2

Reject air for oxygen

(c) (i) starch **(1)**
blue-black/blue/black to colourless **(1)** 2

Reject clear for colourless

(ii) (If added too early) insoluble complex/black solid formed, making titre too low

OR (If added too early) insoluble complex/black solid formed, removes iodine from solution

OR (If added too early) insoluble complex/black solid formed, causes inaccurate titre.

OR (If added too early) insoluble complex/black solid formed, not all the iodine is titrated. 1

(iii) Amount thiosulphate = 0.01655 dm^3 × 0.1 mol dm^{-3} **(1)**

= amount Cu^{2+} in 25.0 cm^3 = 1.655 × 10^{-3} mol **(1)**

amount of Cu^{2+} in 250 cm^3 = 1.655 × 10^{-3} × 10 **(1)**

mass of Cu (in sample) = 1.655 × 10^{-2} × 63.5 **(1)** = 1.051 g

% Cu in brass = 1.051 × 100/1.5 = 70 % **(1)**
[IGNORE sf]

[mass of 1.051g with working scores **(4)**;
correct answer with no working scores **(3)**.]
Mark consequentially 5

[22]

6. (a) $3d^{10}4s^1$ and $3d^{10}$ 1

Accept $4s^1 3d^{10}$

(b) (i) QWC*

the (3)*d* sub–shell is full **(1)**

*Accept orbital<u>**s**</u> (it must be plural) for sub-shell*

Reject comments on partially filled sub-shell

so no d-d transitions are possible
OR no transitions in the right energy range are possible **(1)**
(and no light is absorbed**)**
Any mention of light emission loses 2nd mark 2

(ii) combine the half–reactions to get $2Cu^+ \rightarrow Cu^{2+} + Cu$ **(1)**
IGNORE state symbols

and show that $E^{\ominus}$ for this is (+) 0.37 (V) (and as it is positive it is feasible) **(1)**
conditional on correct reaction 2

Reject just '> 0.3 (V)'

(iii) activation energy (for the disproportionation) is high
OR
Cu^+ is kinetically stable 1

Reject activation energy for one of the half-equations is too high

(c) (i) divides each by atomic mass **(1)**

divides by smallest to obtain $Cu_2SO_6H_2$ **(1)** 2

Division by atomic number scores zero

(ii) $CuSO_4.Cu(OH)_2$ **(2)**

If formula wrong but sulphate/ SO4 is present scores 1 (out of 2) 2

Accept $Cu_2SO_4(OH)_2$
Accept $Cu_2(OH)_2SO_4$
Accept $(CuOH)_2SO_4$

Reject HSO_4 instead of SO_4

(iii) $[Cu(NH_3)_4(H_2O)_2]^{2+}$ 1

Accept $[Cu(NH_3)_4]^{2+}$

Reject $[Cu(NH_3)_6]^{2+}$

(iv) ligand exchange / ligand substitution 1

(d) (i) QWC

(add aldehyde to 2,4–DNP) to obtain precipitate/ppt/solid/crystals **(1)**

recrystallise derivative **(1)**

determine melting temperature of derivative **(1)**

compare with data tables **(1)** 4th mark conditional on melting temperature of a derivative being measured 4

Reject any identification method based on IR, NMR or mass for last 2 marks

(ii) the aldehyde is distilled off as it is formed 1

Reject any mention of reflux

Reject just 'the aldehyde is distilled off'

(iii) propanoic acid OR CH_3CH_2COOH OR $CH_3CH_2CO_2H$ 1

Accept C_2H_5 for CH_3CH_2

(iv) No (extra) oxygen present
OR catalyst specific to formation of aldehyde / only lowers E_a of first oxidation
OR presence of hydrogen gives reducing conditions
OR copper is not an oxidising agent
OR aldehydes rapidly leave catalyst surface 1

(v) (At high pressure) all active sites are occupied/full

OR
(At higher pressures) rate controlled by availability of sites. 1

Accept reverse argument for low pressure

[20]

7. (a) (i) Cr: [Ar] $3d^5 4s^1$
Cu: [Ar] $3d^{10} 4s^1$
Both needed for the mark 1

Accept $4s^1 3d^5$
Accept $4s^1 3d^{10}$
Accept [Ar] written in full

(ii) all the others are $4s^2$ / have full 4s orbital **(1)**

Accept Cr and Cu/they do not have a full 4s orbital

Reject just 'only have one electron in 4s'
OR
Have incomplete 4s orbital

The d subshell is more stable when either half or fully filled
OR
A specific example of chromium having half-filled or
copper having filled d sub-shell/**set** of d orbitals which
is more stable **(1)** 2

Accept sub-energy levels d shell

Reject half-filled or filled d ***orbital(s)***

(b) (i) Octahedral drawn must be 3-D
IGNORE any or no charge 1

Accept –H_2O (bond to H) except on water molecules on left of Cr

(ii) Dative bond formed from electron pair/lone pair on oxygen
(of the water molecule) to the ion

This could be shown on a diagram 1

Accept a clear description of the dative bond

Reject 'dative' alone or from water

Reject just "dative bond formed from oxygen"

(iii) $[Cr(H_2O)_6]^{3+} + OH^- \rightarrow [Cr(H_2O)_5OH]^{2+} + H_2O$

OR

$[Cr(H_2O)_6]^{3+} + 2OH^- \rightarrow [Cr(H_2O)_4(OH)_2]^+ + 2H_2O$

OR

$[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow Cr(OH)_3 + 6H_2O$

OR

$[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow [Cr(H_2O)_3(OH)_3] + 3H_2O$

First mark is for the correct Cr product
Second mark is conditional on the first and is for the rest of the equation correct and balanced 2

(iv) Forms a green precipitate **(1)**
IGNORE initial colour of solution

(which reacts or dissolves or changes to)
a **green solution** (with excess reagent) **(1)**

Accept any shade of green

2nd mark is conditional on an initial ppt 2

(v) acid / acidic 1

Accept amphoteric/able to be deprotonated

Reject coloured ions/ligand exchange/ deprotonation /partially filled d orbitals

(c) (i) **Check working – correct answer can be obtained by not dividing by 2 for 2nd mark and not multiplying by 2 for 4th mark**
amount thiosulphate in titre = $0.0372\ dm^3 \times 0.100\ mol\ dm^{-3}$
$= 3.72 \times 10^{-3}$ mol **(1)**

amount $I_2 = \dfrac{3.72\times10^{-3}}{2}$ **(1)** $= 1.86 \times 10^{-3}$ mol
2nd mark cq on amount thiosulphate

amount dichromate in 25 cm^3
$= \dfrac{1.86\times10^{3}}{3}$ **(1)** $= 6.2 \times 10^{-4}$ mol
3rd mark cq on amount I_2

Total mass Cr = $6.2 \times 10^{-4}\ mol \times 2 \times 10 \times 52\ g\ mol^{-1}$ **(1)**
= 0.645 g
4th mark cq on amount dichromate

% of Cr = 64.5 % **(1)**
IGNORE SF unless rounded to 1 SF cq on mass Cr, provided less than 1 g

Accept 64.48 %

OR
amount thiosulphate for whole sample
$= 0.0372\ dm^3 \times 0.100\ mol\ dm^{-3} \times 10$
$= 3.72 \times 10^{-2}$ mol **(1)**

amount $I_2 = 1.86 \times 10^{-2}$ mol **(1)**

amount dichromate = 6.2×10^{-3} mol **(1)**

mass Cr = 6.2×10^{-3} mol × 2 × 52 g mol^{-1} **(1)**
= 0.645 g

% of Cr = 64.5% **(1)**
IGNORE SF unless rounded to 1sf Mark consequentially, as above

Note:
Correct answer with no working **(3)** 5

(ii) Colour at the end point would be green which would prevent the loss of iodine colour being seen
OR
colour change at end point would be disguised by the colour of Cr^{3+} 1

Accept chromium instead of Cr^{3+}

Reject end point disguised by colour of $Cr_2O_7^{2-}$/orange

[16]

8. (a) B 1

(b) C 1

[2]

9. C

[1]

10. D

[1]

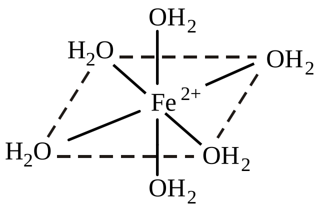
11. D

[1]

12. (a) (i) Fe[Ar] $3d^6 4s^2$ in either order, allowing superscripts to be subscripts
Fe[Ar] $3d^6$ or $3d^6 4s^0$ in either order, allowing
superscripts to be subscripts
Letter d must be lower case 1

Reject any other letters

(ii)



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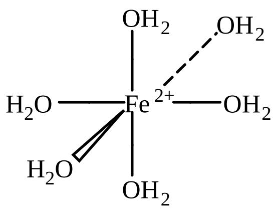

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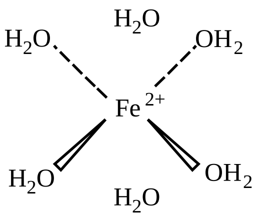

 Instead of dotted line

ALLOW bond to H of H_2O (accept 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

$[Fe(H_2O)_6]^{2+} + 2OH^- \rightarrow Fe(OH)_2 + 6H_2O$ 1

(iv) Green precipitate/solid → Foxy-red/red-brown/
brown/orange
Both colours **and** precipitate/solid needed 1

Reject just "Darkens"

(b) (i) QWC

Emf of cell/ potential difference of cell containing Fe **(1)**

dipping into a 1 mol dm^{-3} Fe^{2+} solution **(1)**

And standard hydrogen electrode/half cell
OR hydrogen electrode and 1 mol dm^{-3} H^+ and 1 atm H_2
OR description of standard hydrogen electrode **(1)**
IGNORE temperature — 3

Reject'SHE'

(ii) QWC

Emf of hydrogen electrode is zero – *stated or implied*
e.g. if calculate E_{cell} = +0.44 V **(1)**

Potential for the reaction is positive so reaction is feasible
OR Fe half cell has more negative electrode potential
OR H^+ and (½)H_2 has a more positive electrode potential **(1)** — 2

(iii) High E_a so slow reaction / reactants are kinetically stable
IGNORE any mention of non-standard conditions — 1

[10]