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)  $\Delta S$ 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
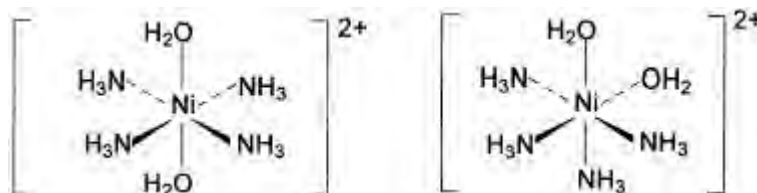
                 

                 Octahedral structure **(1)**
                 ALLOW the word octahedral to explain diagram's shape                                2

                                                                                                 **[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)**
*2$^{nd}$ mark is dependent on 1$^{st}$*　　　　　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) $1 \times –6 = –6,$　　$3 \times +2 = +6$　　*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) $\dfrac{24.0}{1000} \times 2.4(0) \times 10^{-4}$　　*OR* 0.00024 (mol)

*The mark is for the answer*　　　　　1

(iv) $\dfrac{2.40 \times 10^{-4}}{2} = 1.2(0) \times 10^{-4}$ (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$^{-3}$)
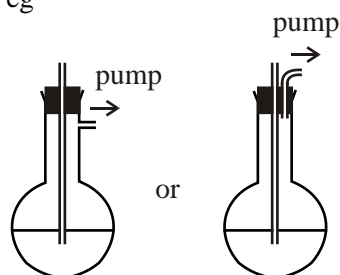
ALLOW TE from (iv)
*The mark is for the answer*     1
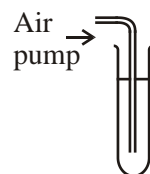
**[12]**

**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
$= 5 \times 0.00040 = 0.002(0) \; (\mathbf{1})$

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

*4*

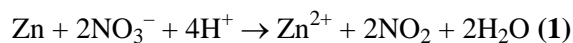(iv)   It is a powerful oxidising agent, $E^{\ominus} = +1.51$ V

*OR*
It is self-indicating                                                                    1

**[7]**

**5.**   (a)   (i)   uses $E^{\ominus}$ values to find $E_{\text{reaction}} = (+) 1.57$ (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)   $E_{\text{reaction}}$ 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 $E^{\ominus}$ $H^+/\frac{1}{2} H_2$ **(1)**

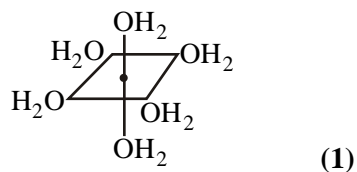is a stronger oxidising agent than $H^+$ **(1)**                                2

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



OR

                                            **(1)**
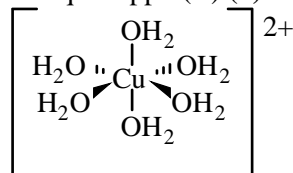
Both marks stand alone
[IGNORE charge]                                                                              2
[IGNORE how $H_2O$ ligand is bonded to central cation]

*Accept hexaaquacopper(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* $\rightarrow$
>
> *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 = $0.01655 \text{ dm}^3 \times 0.1 \text{ mol dm}^{-3}$ **(1)**

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

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

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

% Cu in brass $= 1.051 \times 100/1.5 = 70 \text{ %}$ **(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 $2^{nd}$ 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] $3d^54s^1$
Cu: [Ar] $3d^{10}4s^1$
**Both needed for the mark** 1

*Accept $4s^13d^5$*
*Accept $4s^13d^{10}$*
*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
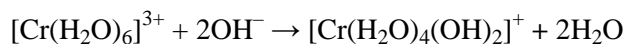(of the water molecule) to the ion

This could be shown on a diagram 1

*Accept a clear description of the dative bond*
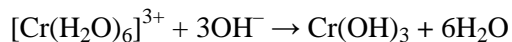
*Reject 'dative' alone or from water*
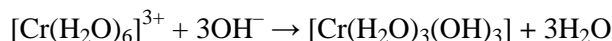
*Reject just "dative bond formed from oxygen"*

(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

$[Cr(H_2O)_6]^{3+} + 3OH^- \rightarrow [Cr(H_2O)_3(OH)_3] + 3H_2O$
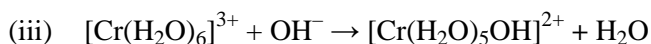
**First mark** is for the correct Cr product
**Second mark** is conditional on the first and is for the rest
of the equation correct and balanced                2


(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*

$2^{nd}$ 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 $2^{nd}$ mark and not multiplying by 2 for $4^{th}$ mark**
amount thiosulphate in titre $= 0.0372\ dm^3 \times 0.100\ mol\ dm^{-3}$
$= 3.72 \times 10^{-3}\ mol$ **(1)**

amount $I_2 = \dfrac{3.72 \times 10^{-3}}{2}$ **(1)** $= 1.86 \times 10^{-3}\ mol$

$2^{nd}$ mark cq on amount thiosulphate

amount dichromate in 25 cm$^3$

$= \dfrac{1.86 \times 10^3}{3}$ **(1)** $= 6.2 \times 10^{-4}\ mol$

$3^{rd}$ 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)**
$= 0.645\ g$
$4^{th}$ 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$^3$ × 0.100 mol dm$^{-3}$ × 10
= 3.72 × 10$^{-2}$ mol **(1)**

amount I$_2$ = 1.86 × 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$_2$O$_7^{2-}$/orange*

**[16]**


**8.**    (a)    B                                              1
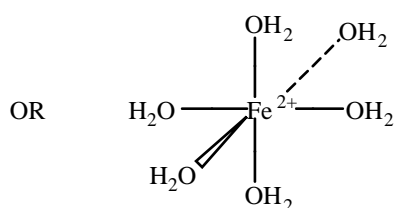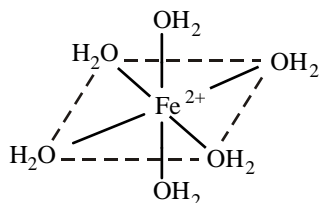
    (b)    C                                              1

**[2]**


**9.**    C

**[1]**


**10.**    D

**[1]**


**11.**    D

**[1]**

**12.** (a) (i) Fe[Ar] $3d^64s^2$ in either order, allowing superscripts to be subscripts
Fe[Ar] $3d^6$ or $3d^64s^0$ in either order, allowing
superscripts to be subscripts
Letter d must be lower case                                     1
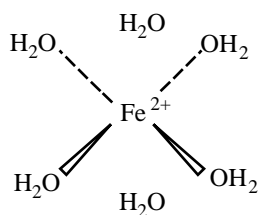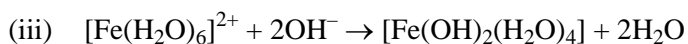
*Reject any other letters*
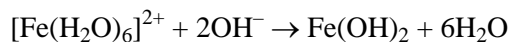
(ii)



OR



OR



 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 $\rightarrow$ 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]**