1. (a) The emf of a half-cell measured relative to the standard hydrogen electrode (1) all solutions at 1 mol dm\(^{-3}\) concentration and gases at 1 atm pressure / 101 kPa and at a stated temperature / 298K (1) Standalone mark ALLOW pressure of 100 kPa 2

(b) Introducing another metal wire would set up its own p.d. / can only measure a potential difference / need source and sink for electrons / voltmeter requires two connections 1

(c) (i) \(2\text{Fe}(s) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Fe}^{2+}(aq) + 4\text{OH}^-(aq)\) or multiples

\(\text{OR}\)

\(2\text{Fe}(s) + \text{O}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{Fe(OH)}_2(s)\)

Species (1)
balancing (1)

Do not allow species mark if electrons still in equation, but allow balancing mark if 4e on both sides 2

(ii) \(\Delta E^\circ_{\text{react}} = (+) 0.84\) (V) (1)

Greater than zero therefore feasible (1) 2

QWC (iii) Zn oxidises preferentially to Fe / Zinc acts as sacrificial (anode) (1)

If Sn used (and damaged), Fe oxidises; preferentially (1)

Disallow “oxidises more readily”

\(E^\circ_{\text{Zn}^{2+}/\text{Zn}}\) more negative than for Fe

\(\text{OR}\)

\(E^\circ_{\text{Zn}/\text{Zn}^{2+}}\) more positive than for Fe

\(\text{OR}\)

\(E^\circ_{\text{cell}}\) for Zn being oxidised by O\(_2\) is more positive than for Fe being oxidised by O\(_2\)

\(\text{OR}\)

similar \(E^\circ\) arguments related to preferential oxidation with Sn (1) 3

\(\text{disallow “higher” or “bigger” for more negative or more positive}\) 10

2. (a) \(3\text{OCl}^- \rightarrow 2\text{Cl}^- + \text{ClO}_3^-\) (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
(ii) no. moles $S_2O_3^{2-}$ used = $12.5 \times 0.1 / 1000 = 1.25 \times 10^{-3}$ (1)
no. moles $I_2 = 1.25 \times 10^{-3} / 2 = 6.25 \times 10^{-4}$ (1)
no. moles $ClO^- = $ no. moles $I_2$ (1)
no. moles $ClO^-$ in original $10 \text{ cm}^3 = 10 \times 6.25 \times 10^{-4}$
     $= 6.25 \times 10^{-3}$ (1)
no. moles $ClO^-$ in $1 \text{ dm}^3 = 100 \times 6.25 \times 10^{-3}$ (1) $= 0.625$  5

(iii) mass $Cl_2 = 0.625 \times 71$
     $= 44.4 \text{ (g)}$
     mark consequentially on (ii)
     must be 3s.f. in final answer  1

(c) $Cl_2$ is the stronger oxidising agent because $Cl_2$ oxidises $S$ from
     (+)2 to (+)6 (1)
     but $I_2$ oxidises $S$ from (+)2 to (+)2.50 (1)  2

QWC (d) $O_2$ oxidises $KI$ / iodide to $I_2$. or balanced equation (1)
     $I_2$ reacts with starch / paper to give blue / black (1)  2  [14]

3. (a) $C_{10}H_8$
     $ALLOW (C_5H_4)_2$
     $NOT (C_6H_4)_2$  1

(b) (i) $-600$
     $NOT + 600$
     $NOT 600$  1

(ii) Naphthalene is more/very stable than double bonds suggest (1)
     Must be a comparison for the 1st mark
     Therefore the electrons/bonds may be/are delocalised
     (over the ring system)
     OR it is a delocalised system (1)
     No TE from (i)
     Delocalised mark can be given if delocalisation mentioned in (iii)  2
(iii) No because it is likely to react like benzene / delocalised structure / no double bonds

OR bromine not a strong enough electrophile without a catalyst

OR “yes but only if bromine [NOT bromine solution] and a catalyst”

(c) (i) Reagent
2-chloropropane (1)
ALLOW 1-chloropropane OR other halogenopropanes
NOT chloropropene
NOT bromo-2-propane

ALLOW formula with or without non-systematic name
ALLOW ClCH(CH₃)₂ OR (CH₃)₂CHCl OR C(CH₃)₂HCl OR ClC(CH₃)₂H

Catalyst
aluminium chloride / AlCl₃/Al₂Cl₆
OR aluminium bromide / AlBr₃
OR iron(III) chloride/FeCl₃

NOT AlCl₄⁻
NOT ”iron” on its own

If both correct but wrong way round 1 (out of 2)

(ii) electrophilic (1)
substitution (1)
Can be given in any order
Mark independently

4. (a) (i) EITHER

$\Delta E^0 = (+) 0.15$ (V) OR $E^0$ (MnO₄⁻ / Mn²⁺) more positive or greater than $E^0$

(Cl₂ / Cl⁻): accept reverse argument (1)

(so) MnO₄⁻ reacts with Cl⁻ OR Cl⁻ ions form Cl₂
OR KMnO₄ reacts with HCl (1)

OR

$2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Cl}^- \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 5\text{Cl}_2$ (1)

$E^0 = (+) 0.15$ (V) (1)

(ii) stated colour change of colourless to (pale) pink NOT purple OR stays (pale) pink
OR pink to colourless
OR first excess of (coloured) manganese(VII)

IGNORE “self-indicating”

IGNORE references to Mn²⁺
(b) (i) (Multiply iron half-equation by five to) cancel out electrons
OR balance electrons 1

(ii) Moles MnO$_4^-$ = $\frac{0.0200 \times 20.10}{1000}$
= 0.000402 mol MnO$_4^-$ (1)
Moles Fe$^{2+}$ per 25.0 cm$^3$ = 5 x 0.000402
= 0.00201 mol Fe$^{2+}$ (1)
Moles Fe$^{2+}$ per 200 cm$^3$ = 0.00201 $\times$ $\frac{200}{25}$ mol Fe$^{2+}$
= 0.01608 mol Fe$^{2+}$ (1)
Mass of FeSO$_4$.7H$_2$O = 0.01608 $\times$ 278
= 4.47g or via concentrations (1)
Percentage purity = $\frac{4.47}{6.00} \times 100$
= 74.5% (1) ALLOW 74.7% / 75%

Correct answer + working (5)
ALLOW 2 or more sig figs
If start by dividing 6.00 / 278 , and final answer is incorrect, candidate can access first three marks only.
If third step omitted, answer 9.3% OR 9.33% OR 9.4% 5

(c) (i) E$^0$ = + 1.46 – ( – 0.13) = (+) 1.59 (V)
Correct answer alone (1)

(ii) PbSO$_4$ precipitated (1)
[H$^+$] (aq) not 1 mol dm$^{-3}$ (1)
[Pb$^{2+}$] (aq) not 1 mol dm$^{-3}$ (1)
any of these
the conditions (in the car battery) are not standard (1)

“temperature non-standard” alone or “not 1 atm pressure” alone does not score 1

5. (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 and 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

(iii) \[ 1 \times -6 = -6, \quad 3 \times +2 = +6 \quad \text{ALLOW TE from (ii)} \]
OR total change in oxidation number of +6 for S, –6 for I
ACCEPT justification in terms of electrons

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

(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)

(iii) \[ \frac{24.0}{1000} \times 2.4(0) \times 10^{-4} \quad OR \quad 0.00024 \text{ (mol)} \]
The mark is for the answer

(iv) \[ \frac{2.40 \times 10^{-4}}{2} = 1.2(0) \times 10^{-4} \text{ (mol) OR 0.00012 (mol)} \]
ALLOW TE from (iii)
The mark is for the answer

(v) \[ 1.2 \times 10^{-4} \times 100 = 0.012(0) \text{ (mol dm}^{-3}) \]
ALLOW TE from (iv)
The mark is for the answer
6. (i) (Buchner) flask / boiling tube connected to pump, glass tube through stopper into solution

eg

\[ \text{pump} \]

or

\[ \text{pump} \]

\text{ACCEPT}

\[ \text{Air pump} \]

\text{But must be a test tube and tube to bottom as shown} \quad 1

(ii) \[ 8H^+ + 4H_2O \]

\text{ACCEPT multiples} \quad 1

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

\[ = \frac{20 \times 0.020}{1000} = 0.00040 \quad (1) \]

Number of moles of electrons

\[ = 5 \times 0.00040 = 0.002(0) \quad (1) \]

Number of moles of vanadium ions

\[ = \frac{10 \times 0.10}{1000} = 0.001 \quad (1) \]

(as vanadium(V) is formed by loss of 2 moles of electrons)

Oxidation number of vanadium in aerated solution is +3 \quad 4

(iv) It is a powerful oxidising agent, \( E^\circ = +1.51 \) V

\text{OR}

It is self-indicating \quad 1

[7]
7. (a) (i) uses $E^\circ$ values to find $E_{\text{reaction}} = (+) 1.57$ (V) (1)

Reject – 1.57

\[ \text{Zn} + 2\text{NO}_3^- + 4\text{H}^+ \rightarrow \text{Zn}^{2+} + 2\text{NO}_2 + 2\text{H}_2\text{O} \] (1)

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 $E^\circ$ than $E^\circ \text{H}^+/\text{H}_2$ (1)

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

(iii) hexaaquacopper(II) (1)

\[
\begin{array}{c}
\text{OH}_2 \\
\text{H}_2\text{O} \\
\text{Cu} \\
\text{OH}_2 \\
\text{H}_2\text{O} \\
\text{OH}_2 \\
\end{array}
\]

2+

OR

\[
\begin{array}{c}
\text{OH}_2 \\
\text{H}_2\text{O} \\
\text{OH}_2 \\
\text{H}_2\text{O} \\
\text{OH}_2 \\
\end{array}
\]

Both marks stand alone
[IGNORE charge] 2
[IGNORE how H$_2$O ligand is bonded to central cation]

Accept hexaaquacopper(II)

Reject formula

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

\[
[\text{Cu(H}_2\text{O)}_6]^{2+} + 4\text{Cl}^- \leftrightarrow \text{CuCl}_4^{2-} + 6\text{H}_2\text{O} \] (1)

OR

\[
[\text{Cu(H}_2\text{O)}_6]^{2+} + 4\text{HCl} \leftrightarrow \text{CuCl}_4^{2-} + 4\text{H}^+ + 6\text{H}_2\text{O} \] (1)

ALLOW →

Accept $\text{H}_2\text{CuCl}_4 + 2\text{H}^+$ for $\text{CuCl}_4^{2-} + 4\text{H}^+$ 2
(b) (i) \( E^\circ \) for the reaction is \(-0.39\) (V) (so not feasible) [value is required].

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

(ii) Cul is a solid (so conditions are not standard) (1)
Equilibrium is pulled over/moves to favour the r.h.s. (1)

\[ \text{Reject just 'conditions not standard'} \]

(iii) \([\text{Cu(NH}_3\text{)}_4]^+\]
OR \([\text{Cu(NH}_3\text{)}_4(\text{H}_2\text{O})_2]^+\)

\[ \text{Accept } [\text{Cu(NH}_3\text{)}_2]^+ \]
\[ \text{Reject } [\text{Cu(NH}_3\text{)}_6]^+ \]
\[ \text{Reject any 2+ complex} \]

(iv) (atmospheric) oxygen (1)
oxidises \( Cu^+ \) to \( Cu^{2+} \) (1)

\[ \text{Reject air for oxygen} \]

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

\[ \text{Reject clear for colourless} \]

(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.
(iii) Amount thiosulphate = 0.01655 dm$^3 \times 0.1$ mol dm$^{-3}$ (1)

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

amount of Cu$^{2+}$ in 250 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 g

% Cu in brass = 1.051 \times 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

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

Accept $4s^13d^{10}$

(b) (i) QWC*

the (3)d sub–shell is full (1)

Accept orbitals (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

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

IGNORE state symbols

and show that $E^*$ for this is (+) 0.37 (V) (and as it is positive it is feasible) (1)

conditional on correct reaction

Reject just ‘> 0.3 (V)’

(ii) activation energy (for the disproportionation) is high

OR

Cu$^+$ is kinetically stable

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$_2$SO$_4$H$_2$ (1)

Division by atomic number scores zero

(ii) CuSO$_4$.Cu(OH)$_2$ (2)
If formula wrong but sulphate/ SO$_4$ is present scores 1 (out of 2) 2

Accept Cu$_2$SO$_4$(OH)$_2$
Accept Cu$_2$(OH)$_2$SO$_4$
Accept (CuOH)$_2$SO$_4$
Reject HSO$_4$ instead of SO$_4$

(iii) [Cu(NH$_3$)$_4$(H$_2$O)$_2$]$^{2+}$ 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$_3$CH$_2$COOH OR CH$_3$CH$_2$CO$_2$H 1

Accept C$_2$H$_5$ for CH$_3$CH$_2$
(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

(v) (At high pressure) all active sites are occupied/full
OR
(At higher pressures) rate controlled by availability of sites.

Accept reverse argument for low pressure

9. (a) (i) Cr: $[\text{Ar}] 3d^54s^1$
Cu: $[\text{Ar}] 3d^{10}4s^1$
Both needed for the mark

Accept $4s^13d^6$
Accept $4s^13d^{10}$
Accept $[\text{Ar}]$ 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)

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

Accept $-\text{H}_2\text{O}$ (bond to $H$) except on water molecules on left of
$\text{Cr}$
(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

Accept a clear description of the dative bond
Reject ‘dative’ alone or from water
Reject just “dative bond formed from oxygen”

(iii) \[
\text{[Cr(H}_2\text{O)}_6\text{]}^{3+} + \text{OH}^- \rightarrow \text{[Cr(H}_2\text{O)}_5\text{OH}]^{2+} + \text{H}_2\text{O}
\]
OR
\[
\text{[Cr(H}_2\text{O)}_6\text{]}^{3+} + 2\text{OH}^- \rightarrow \text{[Cr(H}_2\text{O)}_4(\text{OH})_2]^+ + 2\text{H}_2\text{O}
\]
OR
\[
\text{[Cr(H}_2\text{O)}_6\text{]}^{3+} + 3\text{OH}^- \rightarrow \text{Cr(OH)}_3 + 6\text{H}_2\text{O}
\]
OR
\[
\text{[Cr(H}_2\text{O)}_6\text{]}^{3+} + 3\text{OH}^- \rightarrow \text{[Cr(H}_2\text{O)}_3(\text{OH})_3]^+ + 3\text{H}_2\text{O}
\]
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

(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

(v) acid / acidic
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\textsuperscript{nd} mark and not multiplying by 2 for 4\textsuperscript{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\(_2\) = \(\frac{3.72 \times 10^{-3}}{2}\) (1) = \(1.86 \times 10^{-3}\) mol

2\textsuperscript{nd} mark cq on amount thiosulphate

Amount dichromate in 25 cm\(^3\)
= \(\frac{1.86 \times 10^{-7}}{3}\) (1) = \(6.2 \times 10^{-4}\) mol

3\textsuperscript{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\textsuperscript{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\(^3\) \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 = \(6.2 \times 10^{-3}\) mol (1)

Mass Cr = \(6.2 \times 10^{-3}\) mol \times 2 \times 52 g mol\(^{-1}\) (1)
= 0.645 g

% of Cr = 64.5% (1)

Ignore SF unless rounded to 1 SF 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\(^{4+}\)

Reject end point disguised by colour of Cr\(_2\)O\(_7\)\(^{2-}\)/orange

[16]
10. (a) \( \text{MnO}_4^- \) needs acid to be reduced to \( \text{Mn}^{2+} \) 

(b) 5 

(c) (i) \( 1.79 \times 10^{-4} \) 

(ii) \( 1.79 \times 10^{-4} \) mols of \( \text{Fe}^{2+} \) in one tablet 
\[ \therefore \text{mols of MnO}_4^- = \frac{1}{5} \times 1.79 \times 10^{-4} \text{ (1)} \] 
\[ 0.01 \text{ mol in 1000 cm}^3 \] 
\[ \therefore \frac{1}{5} \times 1.79 \times 10^{-4} \times \frac{1000}{0.01} \times \frac{1.79 \times 10^{-4}}{5} \] 
\[ = 3.58 \] 
\[ = 3.6 \text{ cm}^3 \text{ (1)} \] 

(iii) No, titration value too low 
Either: use more tablets 
Or: use more dilute solution of \( \text{KMnO}_4 \) 

(d) QWC 
(It is acceptable because) well below the maximum safe limit (1) 
Not significantly different from recommended daily dose 
OR Variation in body mass means that different doses are acceptable 
OR only if max 1 tablet per day is written on the bottle (1) 

[8]