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) $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe^{2+}(aq) + 4OH^{-}(aq)$ or multiples

OR

$2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe(OH)_2(s)$

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) $\Delta E^{\ominus}_{react} = (+)\ 0.84\ (V)$ **(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"*

$E^{\ominus}$ Zn^{2+} / Zn more negative than for Fe
OR

$E^{\ominus}$ Zn / Zn^{2+} more positive than for Fe
OR
E^{θ}_{cell} for Zn being oxidised by O_2 is more positive than for Fe being oxidised by O_2
OR

similar $E^{\ominus}$ arguments related to preferential oxidation with Sn **(1)** 3
disallow "higher" or "bigger" for more negative or more positive

[10]

2. (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

(ii) no. moles $S_2O_3^{2-}$ used = 12.5 × 0. 1 / 1000 = 1. 25 × 10^{-3} **(1)**

no. moles I_2 = 1.25 × 10^{-3} / 2 = 6.25 × 10^{-4} **(1)**

no. moles ClO^- = no. moles 1_2 **(1)**

no. moles ClO^- in original 10 cm^3 = 10 × 6.25 × 10^{-4}

= 6.25 × 10^{-3} **(1)**

no. moles ClO^- in 1 dm^3 = 100 × 6.25 × 10^{-3} **(1)** = 0.625 5

(iii) mass Cl_2 = 0.625 × 71
= 44.4 (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 l_2 oxidises S from (+)2 to (+)2.50 **(1)** 2

QWC (d) O_2 oxidises KI / iodide to l_2. or balanced equation **(1)**
ll_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” 1

(c) (i) <u>Reagent</u>
2-chloropropane **(1)**
ALLOW 1-chloropropane *OR* other halogenopropanes
NOT chloropropane
NOT bromo-2-propane

ALLOW formula with or without non-systematic name
ALLOW $ClCH(CH_3)_2$ *OR* $(CH_3)_2CHCl$ *OR* $C(CH_3)_2HCl$ *OR* $ClC(CH_3)_2H$

<u>Catalyst</u>
aluminium chloride / $AlCl_3/Al_2Cl_6$
OR aluminium bromide / $AlBr_3$
OR iron(III) chloride/$FeCl_3$ **(1)**
NOT $AlCl_4^{(-)}$
NOT ”iron” *on its own*

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

(ii) electrophilic **(1)**
substitution **(1)**
Can be given in any order
Mark independently 2

[9]

4. (a) (i) **EITHER**

ΔE^{θ} = (+) 0.15 (V) OR E^{θ} $(MnO_4^{-}/\ Mn^{2+})$ more positive or
greater than E^{θ}
(Cl_2 / Cl^{-}); accept reverse argument **(1)**
(so) MnO_4^{-} reacts with Cl^{-} OR Cl^{-} ions form Cl_2
OR $KMnO_4$ reacts with HCl **(1)**
OR
$2MnO_4^{-} + 16H^{+} + 10Cl^{-} \rightarrow^{-} 2Mn^{2+} + 8H_2O + 5Cl_2$ **(1)**
E^{θ} = (+) 0.15(V) **(1)** 2

(ii) stated colour change of colourless to (pale) pink NOT purple OR
stays (pale) pink
OR pink to colourless
OR first excess of (coloured) manganate((VII))
IGNORE “self-indicating”
IGNORE references to Mn^{2+} 1

(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 × 0.000402
= 0.00201 mol Fe^{2+} **(1)**

Moles Fe^{2+} per 200 cm^3 = 0.00201 × $\frac{200}{25}$ mol Fe^{2+}
= 0.01608 mol Fe^{2+} **(1)**

Mass of $FeSO_4 . 7H_2O$ = 0.01608 × 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 $\frac{6.00}{278}$, 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) $E^\theta = +1.46 - (-0.13) = (+)$ **1.59** (V)
Correct answer alone **(1)** 1

(ii) $PbSO_4$ precipitated **(1)**
$[H^+_{(aq)}]$ not 1 mol dm^{-3} **(1)**
$[Pb^{2+}_{(aq)}]$ not 1 mol dm^{-3} **(1)**
the conditions (in the car battery) are not standard **(1)**
} *any of these*

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

[11]

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

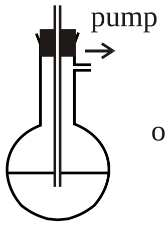
(v) $1.2 \times 10^{-4} \times 100 = 0.012(0)$ (mol dm^{-3})

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

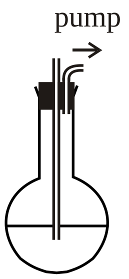
[12]

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

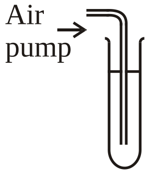
eg



or



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]

7. (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)**

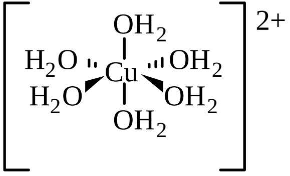
smaller than reaction in (i) so is less likely **(1)**

OR

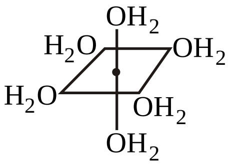
NO_3^- being the oxidised form of a redox couple with a more positive $E^\ominus$ than $E^\ominus$ $H^+/\frac{1}{2} H_2$ **(1)**

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 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 = $1.655 \times 10^{-3} \times 10$ **(1)**

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

% Cu in brass = 1.051 × 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]

8. (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**s** (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]

9. (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}
= 3.72×10^{-3} mol **(1)**

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

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

Total mass Cr = 6.2×10^{-4} mol × 2 × 10 × 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 $dm^{-3} \times 10$
= 3.72×10^{-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 $Cr_2O_7^{2-}$/orange

[16]

10. (a) MnO_4^- needs acid to be reduced to Mn^{2+} 1

(b) 5 1

(c) (i) 1.79×10^{-4} 1

(ii) 1.79×10^{-4} mols of Fe^{2+} in one tablet

$\therefore$ mols of $MnO_4^- = \frac{1}{5} \times 1.79 \times 10^{-4}$ **(1)**

0.01 mol in 1000 cm^3

$\therefore \frac{1}{5} \times 1.79 \times 10^{-4}$ in $\frac{1000}{0.01} \times \frac{1.79 \times 10^{-4}}{5}$

= 3.58

= 3.6 cm^3 **(1)** 2

(iii) No, titration value too low
Either: use more tablets
Or: use more dilute solution of $KMnO_4$ 1

(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)** 2

[8]