H2 P3 Review

1 Schweizer's reagent is used in purifying cellulose. This dark blue compound has the formula, $[Cu(NH_3)_4(H_2O)_2](OH)_2$ and contains the tetraamminediaquacopper(II) cation, $[Cu(NH_3)_4(H_2O)_2]^{2+}$.

(a) Explain the origin of the dark blue colour of the tetraamminediaquacopper(II) cation. [3]

In the gas-phase Cu^{2+} ion, the five 3d orbitals are degenerate. In the cation, due to the √ presence of ligands, the five 3d orbitals are split into two energy levels, with energy gap, ΔE, due to the repulsion between the Cu^{2+} ion and the ligands.

For √ Cu^{2+} with partially filled d-subshell, when a d-electron from lower energy group is √ promoted to the higher energy group (d-d transition), √ radiation corresponding to ΔE, orange light, is absorbed. √ Light of wavelengths not absorbed (blue light) will be seen as the colour of the complex.

5√ = 3 marks, 3-4√ = 2 marks, 2√ = 1 mark

(b) When a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ was gently heated, NH_3 gas was released. A precipitate of $Cu(OH)_2$ and NH_4^+ ions were also obtained as products.

The $Cu(OH)_2$ formed was purified and separated into two samples. One of the samples was added to concentrated hydrochloric acid, forming complex ion **X**.

The other sample of $Cu(OH)_2$ was added to dilute sulfuric acid, forming blue complex ion **Y**.

$[Cu(NH_3)_4(H_2O)_2]^{2+}$, **X** and **Y** are of different colours.

When $[Cu(NH_3)_4(H_2O)_2]^{2+}$ was strongly heated, a black solid **Z** is formed.

(i) Write an equation for the reaction when a solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$ was gently heated. [1]

$[Cu(NH_3)_4(H_2O)_2]^{2+} \rightarrow Cu(OH)_2 + 2NH_4^+ + 2NH_3$ [1]

(ii) Write an equation for the reaction of $Cu(OH)_2$ with concentrated hydrochloric acid, forming **X**. [1]

$Cu(OH)_2 + 4HCl \rightarrow [CuCl_4]^{2-} + 2H_2O + 2H^+$ [1]

OR $Cu(OH)_2 + 4HCl \rightarrow H_2CuCl_4 + 2H_2O$

OR $Cu(OH)_2 + 4HCl \rightarrow [CuCl_4]^{2-} + 2H_3O^+$

(iii) Suggest the identities of **Y** and **Z**. [2]

Y: $[Cu(H_2O)_6]^{2+}$ [1]

Z: CuO [1]

(iv) Explain why $[Cu(NH_3)_4(H_2O)_2]^{2+}$ and **X** are of different colours. [1]

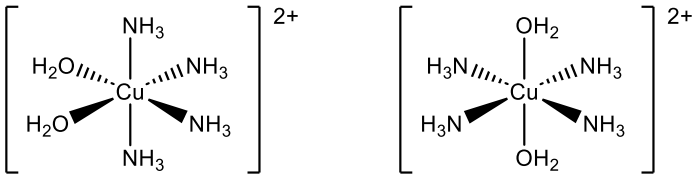
The √ ligands datively bonded to Cu(II) are different, resulting in √ different energy gaps between the d orbitals in the complexes. This will affect the

wavelength of visible light absorbed, and thus colour of transition metal complexes.

2√ = 1 mark, with clear explanation

(c) Tetraamminediaquacopper(II) cation, $[Cu(NH_3)_4(H_2O)_2]^{2+}$, has two possible stereoisomers.

Draw the two stereoisomers. [2]



cis-isomer trans-isomer

correct relative position of H_2O ligands for both isomers [1] only awarded if shape is correct

correct 3D shape, charge, ligands bonded correctly [1]

Note: Naming of isomers not required

(d) Copper based nanopesticides like $Cu(OH)_2$ and CuO, have been used to protect crops from bacteria induced diseases.

The minimum effective concentration for Cu^{2+} ion as a pesticide is 6.35×10^{-5} g dm^{-3}.

(i) Write the expression for the solubility product of $Cu(OH)_2$, giving its units. [1]

$K_{sp} = [Cu^{2+}][OH^-]^2$, $mol^3\ dm^{-9}$ [1]

(ii) A sample of solid $Cu(OH)_2$ is added to water. Given that the value of the solubility product of $Cu(OH)_2$ is 2.20×10^{-20}, calculate the solubility of $Cu(OH)_2$ in mol dm^{-3}. [1]

Let the solubility of $Cu(OH)_2$ be x mol dm^{-3}.

$K_{sp} = [Cu^{2+}]\ [OH^-]^2$

$2.20 \times 10^{-20} = x(2x)^2 = 4x^3$

$x = 1.77 \times 10^{-7}$ mol dm^{-3} [1]

(iii) Hence, deduce if the sample in part **(d)(ii)** is suitable for use as a pesticide. [2]

Concentration of Cu^{2+} ion in g dm^{-3}

$= 1.77 \times 10^{-7} \times 63.5$

$= 1.12 \times 10^{-5}$ g dm^{-3} [1]

Since the √ [Cu^{2+}] is lesser than minimum effective concentration of Cu^{2+} ion (6.35×10^{-5} g dm^{-3}), the sample is √ not suitable for use as a pesticide.

2√ = 1 mark

(e) Gilman reagent is an organometallic reagent containing two R groups (alkyl or aryl), copper, and lithium. The general formula of Gilman reagents can be expressed as R_2CuLi.

The Gilman reagent, lithium dimethylcopper, can react with an acyl chloride via nucleophilic reaction to form a ketone. The steps of the reaction are shown in Fig. 1.1.

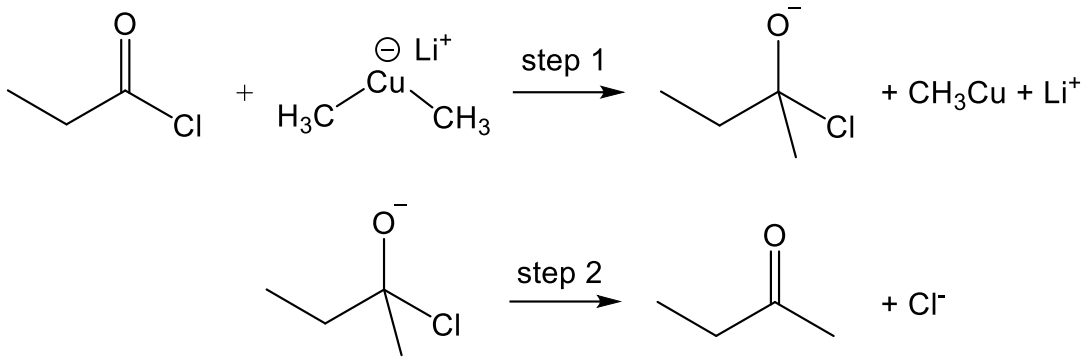
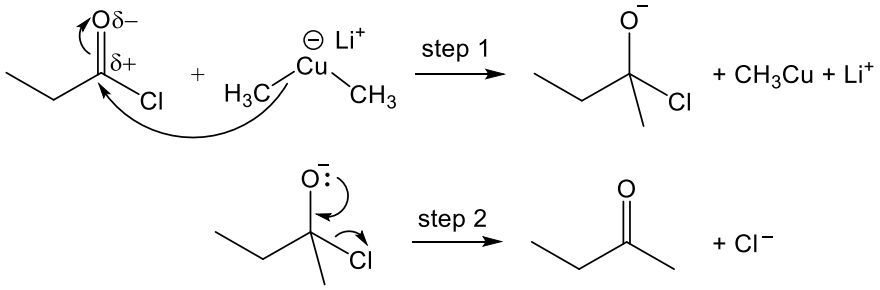


Fig. 1.1

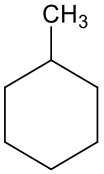
(i) Draw four curly arrows on Fig. 1.1 to complete the mechanism. Include relevant lone pairs and partial charges. [2]



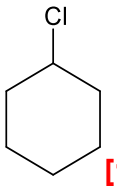
√√√√ 4 arrows, √ lone pair, √ partial charge

3√ = 1 mark

(ii) Lithium dimethylcopper can also react with alkyl halides. A product of this reaction is shown.



Suggest the structure of the alkyl halide that reacted with lithium dimethylcopper to give the product above. [1]



[1]

(f) Transition elements like copper and iron are commonly used as catalysts.

The reaction between $S_2O_8^{2-}$ ions and I^- ions is very slow. If a small amount of aqueous iron(II) ions is added to the mixture, the rate of reaction increases.

Write two equations to illustrate the catalytic role of Fe^{2+} in the $S_2O_8^{2-}$ / I^- reaction. [2]

Step 1: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2SO_4^{2-}(aq) + 2Fe^{3+}(aq)$ [1]

Step 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$ [1]

[Total: 19]

2 Chlorine-containing organic compounds are widely used in both industrial and laboratory settings due to their diverse chemical properties and applications.

One such compound is 1-chloro-1-phenylethane, an aromatic halogenoalkane, which exhibits reactivity typical of benzylic halides. A typical reaction is the reaction between 1-chloro-1-phenylethane and hydroxide ions to produce 1-phenylethanol.

$$C_6H_5CHClCH_3 + OH^- \rightarrow C_6H_5CH(OH)CH_3 + Cl^-$$

The rate of this reaction can be studied by measuring the amount of hydroxide ions that remained in the solution at a given time. The reaction can effectively be stopped if the solution is diluted with an ice-cold solvent.

(a) Briefly describe a suitable method for studying the rate of this reaction at a temperature of 40 °C. [3]

✓1 Ensure both reactant solutions are maintained at 40 °C using a thermostatically controlled water bath before mixing.

✓2 Mix known volumes of both reactants and start the stopwatch.

✓3 At known time, take out a sample and add it to ice-cold solvent for quenching

Method 1

✓4 titrate mixture against standard HCl solution.

✓5 repeat steps 3-4 to obtain volume of HCl at known time intervals.

✓6 plot graph of volume of HCl against time.

Method 2

✓4 Use a pH meter to record the pH.

✓5 repeat steps 3-4 to obtain pH readings at known time intervals.

✓6 plot graph of pH against time.

2✓ = 1 mark

(b) The reaction was studied by carrying out four experiments at different initial concentrations of the two reagents. Table 2.1 shows the results obtained.

Table 2.1

experiment	$[C_6H_5CHClCH_3]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	relative rate
1	0.05	0.10	0.5
2	0.10	0.20	1.0
3	0.15	0.10	1.5
4	*x*	0.15	2.0

(i) Show that the overall order of the reaction is 1. Explain your reasoning. [2]

Comparing experiments 1 & 3, [OH^-] kept constant, [C_6H_5CHC/CH_3] increases 3 times from 0.05 mol dm^{-3} to 0.15 mol dm^{-3}, relative rate increases 3 times from 0.5 to 1.5. First order wrt C_6H_5CHC/CH_3. [1]

Comparing experiments 1 & 2, [C_6H_5CHC/CH_3] doubled from 0.05 mol dm^{-3} to 0.10 mol dm^{-3} and [OH^-] doubled from 0.10 mol dm^{-3} to 0.20 mol dm^{-3}, relative rate doubled from 0.5 to 1.0. Doubling of rate is due to doubling of [C_6H_5CHC/CH_3], so zero order wrt [OH^-]. [1]

Hence, overall order = 1 + 0 = 1

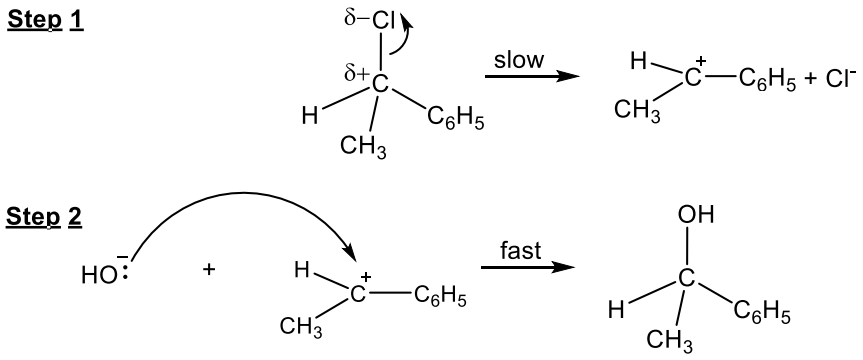
(ii) Write the rate equation for this reaction. [1]

Rate = k[C_6H_5CHC/CH_3] [1]

(iii) Deduce the value of *x* in Table 2.1. [1]

Comparing experiments 2 & 4, relative rate doubled from 1.0 to 2.0. Since zero order wrt to OH^- and first order wrt to C_6H_5CHC/CH_3, concentration of C_6H_5CHC/CH_3 will double to 0.2 mol dm^{-3}. [1] with explanation

(iv) Using your answer to **(b)(i)**, name and draw the mechanism for the reaction of 1-chloro-1-phenylethane with hydroxide ions. Include all relevant lone pairs, dipoles and curly arrows to show the movement of electron pairs. [3]



✓Mechanism : S_N1

✓C-Cl dipole and first curly arrow

✓slow step

✓ intermediate cation and Cl^-

✓OH^- with lone pair and curly arrow

✓correct product

2✓ = 1 mark

(v) With reference to the structure of relevant species in the mechanism, explain why the reaction would proceed via such a mechanism. [1]

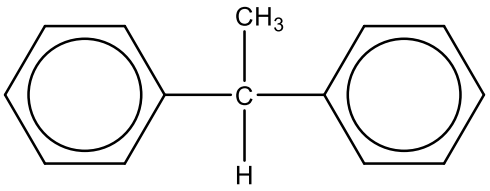
The positive charge on the C of the intermediate is dispersed into the benzene ring, resulting in the formation of a stable carbocation. [1]

(vi) This reaction was carried out using a single enantiomer of 1-chloro-1-phenylethane. Use your mechanism in **(b)(iv)** to predict whether the product will be optically active. Explain your answer. [2]

The intermediate is a carbocation which is ✓trigonal planar about the positively charged C. The nucleophile OH^- can attack from the ✓top and bottom of the plane with equal probability resulting in a ✓racemic mixture. Hence ✓product will be optically inactive.

2✓ = 1 mark

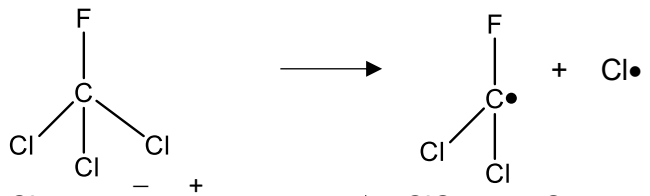
(vii) The reaction was contaminated with a small amount of benzene to give a side product, $C_{14}H_{14}$. Suggest the structure of the side product. [1]



[1]

(c) Chlorofluorocarbons, CFCs, such as $CFCl_3$, are extremely stable. This extreme stability allows CFCs to slowly make their way into the stratosphere. However, when the CFCs come into contact with ultraviolet light, they can cause extensive damage to the ozone layer. One such process of ozone destruction is believed to be the reaction shown below.

step 1



step 2 $Cl\bullet + O{-}O{=}O \rightarrow ClO\bullet + O_2$

step 3 $ClO\bullet + O\bullet \rightarrow Cl\bullet + O_2$

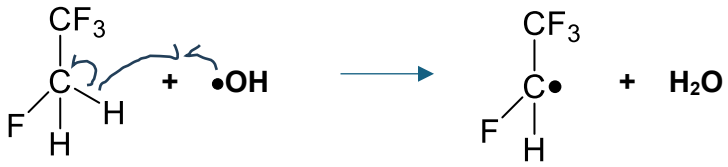
step 4 $O_3 + O\bullet \rightarrow 2O_2$

(i) State the role of Cl•. Explain your answer. [1]

Homogeneous catalyst. It is used up in step 2 and regenerated in step 3. [1]

To address the problem of ozone destruction, material chemists have developed new hydrofluorocarbons (HFCs) such as CF_3CH_2F. The HFCs contain carbon–hydrogen bonds which are susceptible to homolytic cleavage caused by small amounts of hydroxyl radicals present in the lower atmosphere. This degradation occurs before the HFCs molecules have a chance to drift higher up to the stratosphere and damage the ozone layer. The organic degradation products are unstable and can easily degrade to harmless by-products.

(ii) Write an equation for the reaction of CF_3CH_2F with hydroxyl radical. Draw three curly arrows to illustrate the mechanism for the reaction. [2]



[1] equation

[1] 3 curly arrows

[Total: 17]

3 **(a)** Aqueous halogens react with methanoic acid to form hydrogen halides and an acidic gas.

(i) Suggest the chemical equation for the reaction between bromine and methanoic acid. [1]

$Br_2(aq) + HCO_2H(aq) \rightarrow 2HBr(aq) + CO_2(g)$ [1] state symbols not required

(ii) With the use of relevant data from the *Data Booklet*, describe and explain the trend in the thermal stability of the hydrogen halides, HC*l*, HBr and HI. [2]

$2HX(g) \rightarrow H_2(g) + X_2(g)$ where X = C*l*, Br or I

Thermal stability decreases down the group: HC*l* > HBr > HI ✓

Atomic radius increases ✓ down the group resulting in less effective orbital overlap between hydrogen and halogen atom.✓

or

Covalent bond strength and hence bond energy of H–X decreases✓. Less energy is needed to break the H–X bond.

Bond energy / kJ mol^{-1}: HC*l*, 431; HBr, 366; HI, 299 ✓

2✓ = 1 mark

(b) When iron is heated separately with chlorine and iodine, the respective iron halide is formed but each containing iron of a different oxidation state.

Using $E^{\ominus}$ values from the *Data Booklet*, suggest the formula of the final iron halide formed for each reaction. [3]

$E^{\ominus}_{Cl_2/Cl^-}$ = +1.36 V, $E^{\ominus}_{I_2/I^-}$ = +0.54 V

$E^{\ominus}_{Fe^{2+}/Fe}$ = –0.44 V, $E^{\ominus}_{Fe^{3+}/Fe^{2+}}$ = +0.77 V

Fe to Fe^{2+}: $E^{\ominus}_{cell}$ = +0.54 – (–0.44) = +0.98 V ✓

Fe^{2+} to Fe^{3+}: $E^{\ominus}_{cell}$ = +0.54 – (+0.77) = –0.23 V ✓ (< 0; reaction is non-spontaneous)

Iodine is only able to oxidise Fe to Fe^{2+} but not Fe^{3+}. FeI_2 ✓ is formed.

Fe to Fe^{2+}: $E^{\ominus}_{cell}$ = +1.36 – (–0.44) = +1.80 V ✓

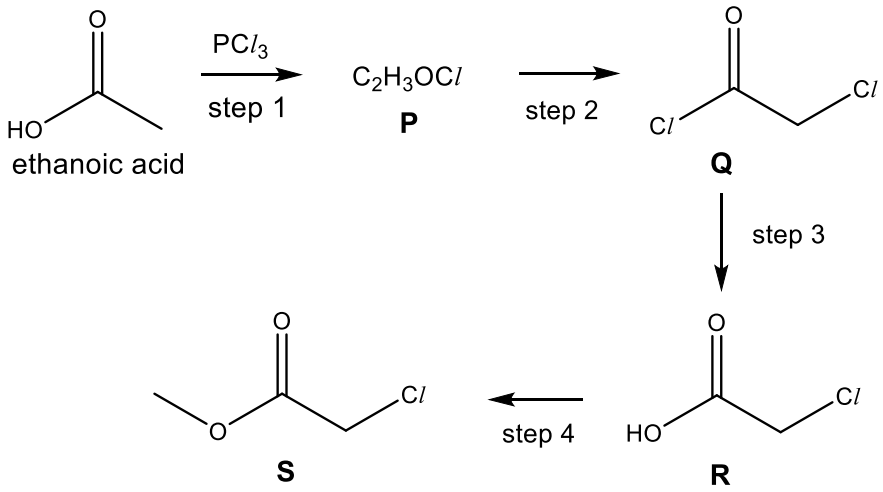
Fe^{2+} to Fe^{3+}: $E^{\ominus}_{cell}$ = +1.36 – (+0.77) = +0.59 V ✓

Chlorine can further oxidise Fe^{2+} to Fe^{3+}. $FeCl_3$ ✓is formed as Cl_2 is a stronger oxidising agent.

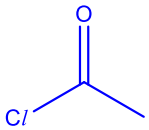
2✓ = 1 mark

(c) Halogenated esters are used as intermediates in pharmaceutical drugs.

The reaction scheme below shows how a chlorinated ester, **S**, can be made from ethanoic acid.



(i) Suggest the structure of intermediate **P** formed in step 1. [1]



P **[1]**

(ii) State the reagents and conditions for step 4. [1]

CH_3OH, concentrated H_2SO_4, heat [1]

(iii) Compare and explain the relative acidity of aqueous solutions of ethanoic acid, **Q** and **R**. [3]

[1] **Q** > **R** > ethanoic acid

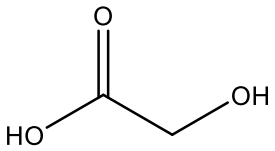
[✓] electronegative / electron-withdrawing C*l* disperses the negative charge on the anion of **R** (CH_2ClCOO^-), [✓] stabilising the anion of **R** more.

[✓] **R** has a higher tendency to dissociate to form H^+.

[✓] **Q** hydrolyses / reacts in water to form a strong acid / HC*l*

2[✓] = [1]

(iv) Steps 1 and 2 need to be carried out carefully to prevent the formation of compound **T**.



T

If **T** is present in the reaction mixture of step 3, a different compound **U** will also be formed in the final reaction mixture. Compound **U** has two identical functional groups.

The infrared spectrum of **U** shows strong absorptions at these wavenumbers, 1100 cm^{-1} and 1745 cm^{-1}, but no absorption due to O–H bonds.

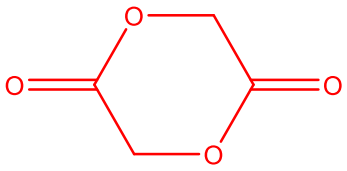
Use the *Data Booklet* to identify the chemical bonds responsible for the absorption at these wavenumbers and deduce the functional group present in **U**. Hence, state the type of reaction that has taken place to form **U**. [2]

[✓] Ester functional group

[✓] Strong absorptions at 1100 cm^{-1} and 1745 cm^{-1} indicates presence of C–O and C=O bond in esters respectively.

2[✓] = [1]

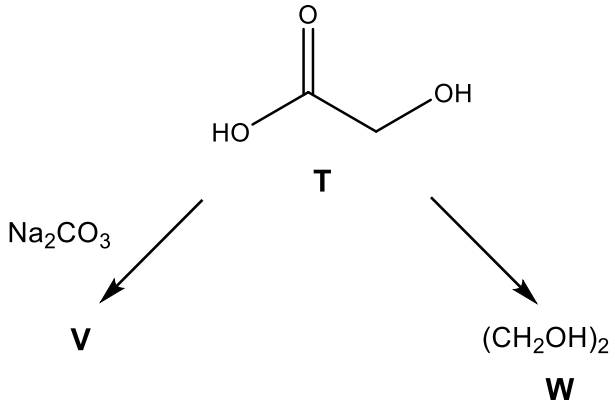
Two molecules of T undergo condensation [1] in the presence of conc. H_2SO_4 in step 4, to form two ester functional groups.



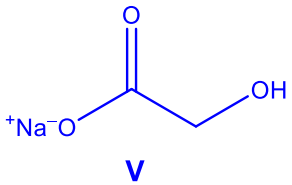
U

For information:

(d) Some further reactions of compound **T** are shown below.



(i) Draw the structure of compound **V**. [1]



V

[1]

(ii) Explain why $NaBH_4$ cannot be used in place of $LiAlH_4$ to form **W** from **T**. [1]

$NaBH_4$ is a weaker reducing agent which is not strong enough to reduce carboxylic acid.

[1] H in B-H bond is less nucleophilic / less electron rich / less reactive as B is more electronegative than Al / B-H bond has smaller electronegativity difference Al-H.

OR [1] B–H bond is stronger than Al–H bond hence B-H bond is less easily broken to form H^- / more energy needed to break B-H bond

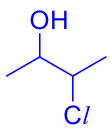
(e) Compound **K**, C_4H_9ClO, is optically active. Upon heating with excess sodium metal, **K** produces effervescence and compound **L**, C_4H_8O. Compound **L** is optically inactive and does not decolourise bromine water and does not produce an orange precipitate with 2,4-DNPH.

K gives a yellow precipitate with hot alkaline aqueous iodine and organic compound **M**, which produces $C_2H_2O_4$ after acidifying the mixture.

Deduce the structures of **K** to **M**, explaining clearly the reactions involved. [9]

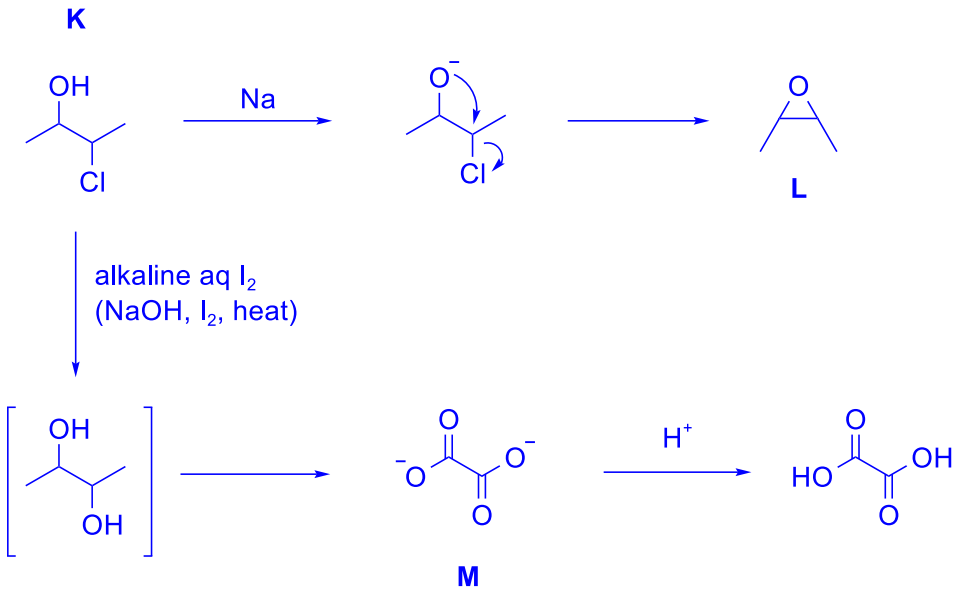
Observation	Type of reaction	Deduction
K is optically active or **L** is optically inactive	-	[✓] **K** has a chiral center Or **L** has a plane of symmetry
Upon heating with excess Na, **K** produces effervescence and **L**.	(not elimination) [✓] Redox reaction with Na *(not acid-metal, acid-base)* [✓] Nucleophilic substitution	[✓] **K** has -OH group *(loss of Cl atom)* [✓] **L** is an (cyclic) ether
L does not decolourise $Br_2(aq)$ and does not produce an orange solid with Brady's reagent	[✓] No electrophilic addition with $Br_2(aq)$ [✓] No condensation with Brady's reagent (must mention "no" for negative rxn)	[✓] Absence of alkene [✓] Absence of aldehyde or ketone .
K gives a yellow solid with hot alkaline aqueous iodine and organic **M**, which produces $C_2H_2O_4$ after acidifying the mixture.	[✓] Nucleophilic substitution with alkaline medium (NaOH) [✓] Oxidation with alkaline aqueous iodine [✓] Acid-base reaction	[✓] **K** has $CH_3CH(OH)$- group (cannot have CH_3CO- as part of ans as **K** can only have 1 OH group based on molecular formula)

13[✓] in total, 2[✓] = 1, max [6] for deductions

K is	**L** is	**M** is
 [1]	 [1]	$^-OOC–COO^-$ [1] **Note**: **M** is the salt BEFORE acidifying to form HOOC-COOH.

[3] for structures

Reaction scheme (for info)


K
OH
Cl
Na
O
Cl
O
L
alkaline aq I_2
(NaOH, I_2, heat)
OH
OH
O
O
O
O
M
H^+
HO
OH
O
O

[Total: 24]

4 The Gibbs free energy change, ΔG, is related to temperature, T, by the equation:

$$\Delta G = \Delta H - T\Delta S$$

Fig. 4.1 shows the Ellingham diagram which is a plot of ΔG against T and is used to evaluate the ease of reduction of oxides. The diagram shows how ΔG changes with T from 300 K to 2000 K for the following reactions.

reaction (1): $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

reaction (2): $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

reaction (3): $Ti(s) + O_2(g) \rightleftharpoons TiO_2(s)$

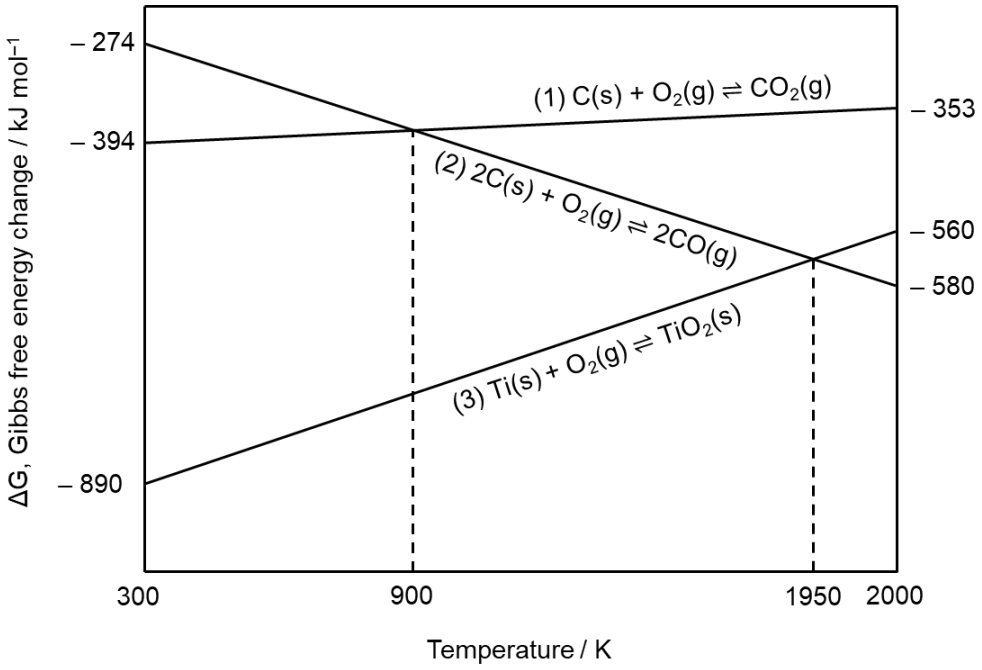


Fig. 4.1

Use Fig. 4.1 to answer parts **(a)** and **(b)**.

(a) **(i)** With reference to the ΔG equation, explain why the ΔG for reaction (1) is almost independent of temperature. [1]

$-\Delta S$ is the gradient of the ΔG vs T/ K graph.

In reaction (1), there is no change in the number of moles of gas after the reaction, so the entropy change is approximately 0. The gradient of the graph is almost horizontal and ΔG is almost independent of temperature. [1]

(ii) Calculate the entropy change for reaction (3), in J mol^{-1} K^{-1}. [1]

$-\Delta S$ = gradient of straight line of reaction (3) = ((– 560 – (– 890)) / (2000 – 300)

= 0.194 kJ mol^{-1} K^{-1} = 194 J mol^{-1} K^{-1}

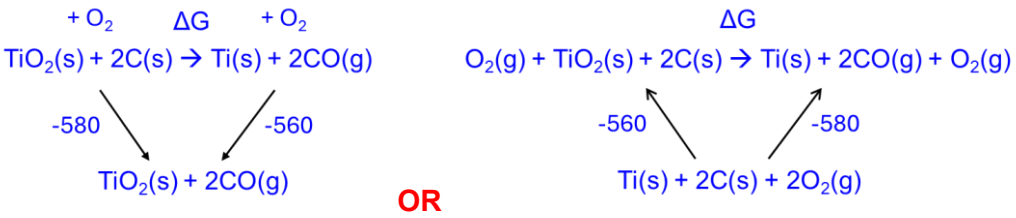
Hence ΔS = –194 J mol^{-1} K^{-1} [1]

(b) Titanium can be obtained by the reduction of TiO_2 with carbon, via the reaction below.

reaction (4): $TiO_2(s) + 2C(s) \rightleftharpoons Ti(s) + 2CO(g)$

(i) Similar to enthalpy change of reaction, the Gibbs free energy change of a reaction can be calculated using an energy cycle.

Using ΔG values at 2000 K from Fig. 4.1 and with the aid of a suitable energy cycle, calculate ΔG for reaction (4) at 2000 K. [2]



[1] for correct cycle

By Hess' Law, ΔG = – 580 – (–560) = – 20 kJ mol^{-1} [1]

(ii) State the temperature range for reaction (4) to be spontaneous. Explain your answer. [2]

Temperature > 1950 K [1] accept 1950-2000 K

From temperature > 1950 K, forward reaction becomes spontaneous (ΔG < 0) once $\Delta G_{reaction(2)}$ becomes more negative than $\Delta G_{reaction(3)}$. [1]

(c) **(i)** State two main assumptions of the kinetic theory as applied to an ideal gas. [2]

The gas consists of particles of negligible volume compared to the volume of the container it occupies. [1]

The gas particles exert no attractive forces on each other. [1]

(ii) The Gibbs free energy change of any reversible reaction can be expressed as a function of K_p given by:

$$\Delta G = - RT \ln K_p$$

where K_p is the equilibrium constant expressed in terms of partial pressures of gases in bar. [1 bar = 10^5 Pa]

Using your answer to **(b)(i)**, determine the value of K_p for reaction (4) at 2000 K. [1]

If you were unable to calculate a value for the ΔG in **(b)(i)**, you should use –15 kJ mol^{-1}. This is **not** the correct answer for **(b)(i)**.

ΔG = – RT ln K_p

– 20000 = – (8.31)(2000) ln K_p

ln K_p = 1.2033

K_p = 3.33 (or 2.47 using ΔG = –15 kJ mol^{-1}) [1]

(iii) Write an expression for the equilibrium constant, K_p, for reaction (4). [1]

$K_p = (P_{CO})^2$ [1]

A typical reaction vessel for the reduction of TiO_2 with carbon has a volume of 100 dm^3.

(iv) Determine the equilibrium partial pressure of CO at 2000 K, in Pa. [1]

You may assume that carbon monoxide behaves as an ideal gas under such conditions.

Partial pressure of CO at eqm = $\sqrt{3.33}$ = 1.82 bar = 182000 Pa (to 3sf) [1]

(v) Hence, calculate the equilibrium mass of titanium produced at 2000 K. [2]

Applying ideal gas eqn for CO: n = $\frac{pV}{RT} = \frac{(182482)(100\times10^{-3})}{(8.31)(2000)}$ = 1.0980 mol [1]

From reaction (4): Ti(s) ≡ 2CO

Mass of Ti produced = $\frac{1.0980}{2}$ × 47.9 = 26.3 g (or 22.6 g if ΔG = –15 kJ mol^{-1}) [1]

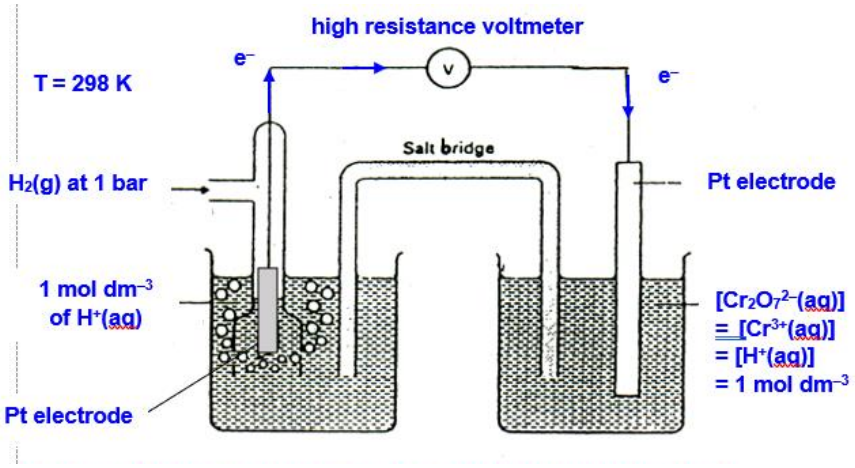
(d) The chemistry of carboxylic acids involves a range of reactions from their formation via oxidation to their conversion into other useful derivatives.

Two electrode reactions are shown in Table 4.1.

Table 4.1

electrode reaction	$E^\ominus$ / V
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$CH_3COOH + 2H^+ + 2e^- \rightleftharpoons CH_3CHO + H_2O$	**U**

(i) Draw a fully labelled diagram of the experimental set-up used to measure the standard electrode potential, $E^\ominus$, of the $Cr_2O_7^{2-}(aq)$ / $Cr^{3+}(aq)$ electrode. Include all necessary chemicals and show the direction of electron flow in the circuit. [3]



[1] correct set-up (electrodes, voltmeter, salt bridge, correct half-cell for SHE).

✓ **labelling (only awarded if set-up is correct)**

✓ **species**

✓ **conc and conditions**

✓ **electron flow**

2✓ = 1 mark

(ii) Construct the ionic equation for the reaction between ethanal and acidified potassium dichromate. [1]

[H] $Cr_2O_7^{2-}$ + $14H^+$ + $6e^-$ → $2Cr^{3+}$ + $7H_2O$

[O] CH_3CHO + H_2O → CH_3COOH + $2H^+$ + $2e^-$ (x 3)

$3CH_3CHO$ + $Cr_2O_7^{2-}$ + $8H^+$ → $3CH_3COOH$ + $2Cr^{3+}$ + $4H_2O$ [1]

(iii) The $E^{\ominus}_{cell}$ of an electrochemical cell consisting of a standard CH_3COOH / CH_3CHO electrode and a standard $Cr_2O_7^{2-}(aq)$ / $Cr^{3+}(aq)$ electrode is +2.27 V.

Calculate the value of the standard electrode potential, **U**, in Table 4.1. [1]

$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$

+2.27 V = +1.33 – U

U = –0.94 V [1] with working shown

(iv) Explain how the voltage of this cell would change when aqueous sodium hydroxide is added to the CH_3COOH / CH_3CHO half-cell. [2]

CH_3COOH + $2H^+$ + $2e^-$ ⇌ CH_3CHO + H_2O $E^{\ominus}_{ox}$ = –0.94 V

NaOH (or OH^-) added will react with H^+ causing a decrease in $[H^+]$. ✓ By Le Chatelier's Principle, equilibrium position will shift to the left ✓ to increase $[H^+]$, favouring oxidation reaction.

$E_{(CH3COOH/CH3CHO)}$ becomes more negative ✓ (or less positive) hence voltage will be more positive. (BOD increase) ✓

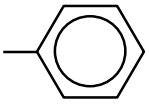
2✓ = 1 mark

[Total: 20]

5 Amino acids play central roles both as building blocks of proteins and as intermediates in metabolism.

Some amino acids found in proteins are shown in Table 5.1.

Table 5.1

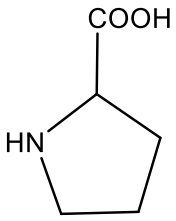
amino acid	abbreviation	formula of side chain
aspartic acid	asp	—CH_2CO_2H
glutamine	gln	—$CH_2CH_2CONH_2$
phenylalanine	phe	—CH_2 

(a) Blood plasma contains 90 % water. Suggest and explain which amino acids in Table 5.1 are likely to be found on the outer surface of proteins molecules in blood plasma at pH 7.4.

[2]

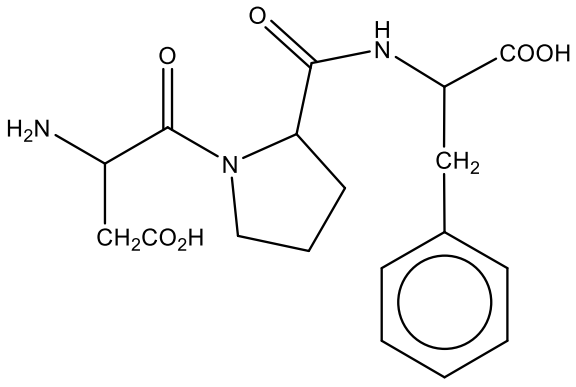
Aspartic acid ✓ and glutamine ✓. The side chain of aspartic acid can form ion-dipole interactions ✓ with water molecules while the side chain of glutamine can form hydrogen bonds ✓ with water molecules.

2✓ = 1 mark

(b) **(i)** The structure of another amino acid, proline (pro), is 

.

Draw the structural formula of the tripeptide, asp–pro–phe. [1]



[1]

(ii) The enzyme, chymotrypsin, selectively hydrolyses at the carboxyl end of phenylalanine (phe) and tyrosine (tyr) residues.

The enzyme, trypsin, selectively hydrolyses at the carboxyl end of arginine (arg) residues.

An octapeptide **J** was analysed and the results were as follows.

- **J** contains the partial sequence tyr–ala–pro.
- Complete hydroylsis of **J** gave the following eight amino acids:

  ala, arg, asp, gln, pro, tyr, 2 × phe
- On reaction with chymotrypsin, **J** gave tyr, gln and two different tripeptides.
- On reaction with trypsin, **J** gave arg and a heptapeptide only.

Determine the amino acid sequence of **J**. [2]

arg–asp–phe–tyr–ala–pro–phe–gln [1] correct ans

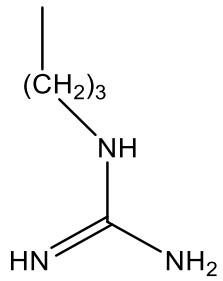
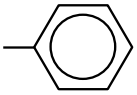
[1] : some working showing using enzyme hydrolysis

(c) Electrophoresis is a technique used to separate mixtures of amino acids based on the mobility of ions in an electric field.

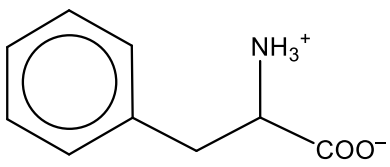
A mixture of arginine, aspartic acid and phenylalanine was placed at the center of the electrophoresis plate in a buffer solution of pH 6.0. A potential difference was then applied across the plate.

The pK_a values of the acidic groups of each amino acid are shown in Table 5.2.

Table 5.2

amino acid	formula of side chain	pK_a of α–carboxyl group	pK_a of α–amino group	pK_a of side chain
arginine		2.03	9.00	12.10
aspartic acid	—CH_2CO_2H	1.95	9.66	3.71
phenylalanine	—CH_2 	2.18	9.09	–

(i) Draw the structure of the major species in a phenylalanine solution at pH 6.0. [1]



[1]

(ii) On Fig. 5.1, use a 'x' to indicate the relative positions of each of the amino acid after the electrophoresis at pH 6.0. Label the amino acids clearly. [2]

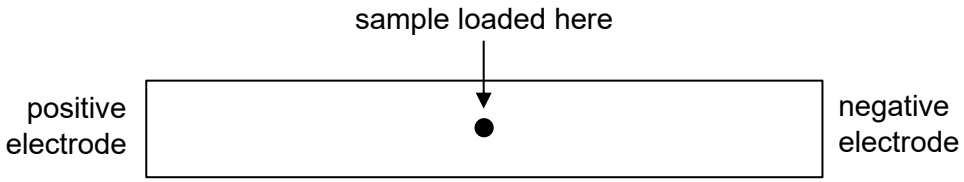


Fig. 5.1

sample loaded here

aspartic acid phenylalanine arginine

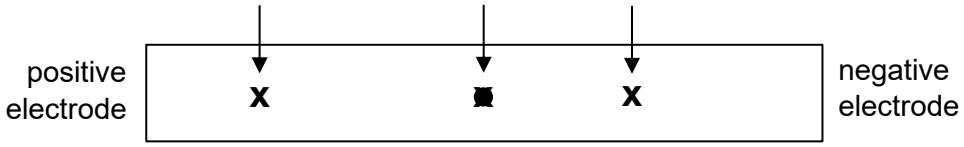
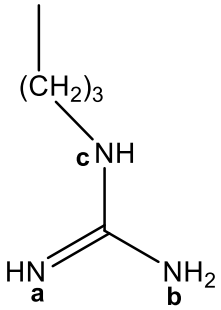


Fig. 5.1

✓ phenylalanine does not migrate as no net charge / zwitterion
✓ aspartic acid migrates to positive electrode as it exists as anion
✓ arginine migrates to negative electrode as it exists as cation
✓ relative distance between aspartic acid and arginine, ecf direction
2✓ = 1 mark

(iii) The side chain of arginine is shown.



Nitrogen atoms, **a**, **b** and **c**, are all sp^2 hybridised. Only one of the nitrogen atoms will be protonated in an acidic medium. Identify which nitrogen atom would be protonated. Explain your answer. [1]

Nitrogen atom a as its lone pair of electrons is not delocalised [1] and more available to form a dative covalent bond with a proton but the lone pair of electrons on b and c delocalise into the C=N group and are less available for donation to a proton.

(d) The Strecker method is a series of chemical reactions which synthesises an amino acid from an aldehyde as a starting material.

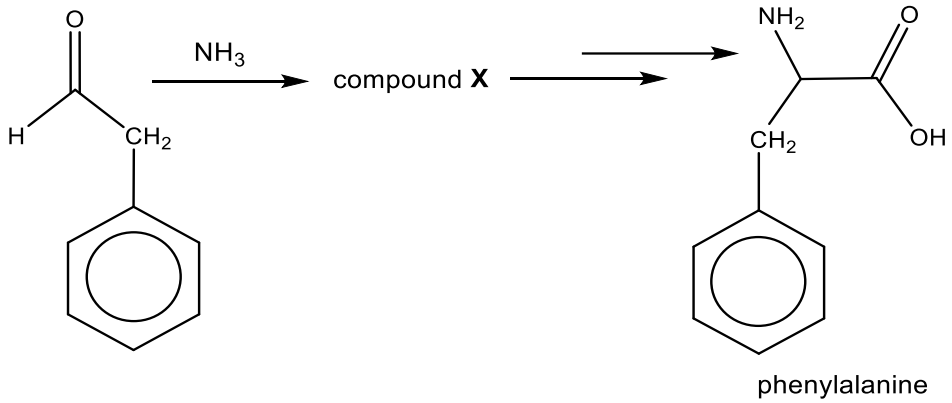
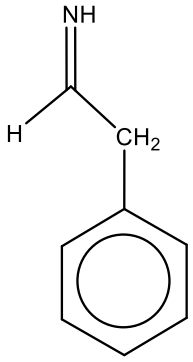


Fig. 5.2

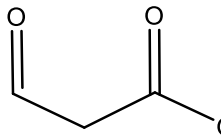
(i) In Fig. 5.2, the first stage involves ammonia acting as a nucleophile, followed by the elimination of a water molecule to form compound **X**. Suggest a structure for **X**. [1]



[1]

(ii) A starting material, compound **Y**, can be used to prepare aspartic acid via the Strecker method.

Suggest the structure of **Y**. [1]



[1]

(e) Group 2 carbonates decompose when heated.

Describe and explain the trend in the thermal stability of the Group 2 carbonates. [2]

Down the Group, charge of the cation remains constant but ionic radius increases ✓. Hence, charge density of the cation decreases. ✓

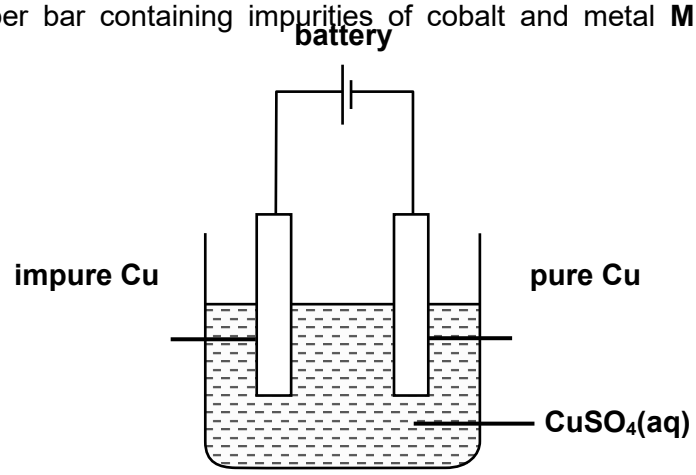
Polarising power of cation decreases / resulting in less polarisation of the C–O bond in CO_3^{2-} ion, ✓ weakening the C-O covalent bond to a lesser extent. ✓ ***must specify the C–O bond and the carbonate***

More energy/ higher temperature needed to decompose the carbonate. ✓

Thermal stability increases down the group. ✓

3✓ = 1 mark

(f) An impure copper bar containing impurities of cobalt and metal **M** was purified using electrolysis.



A current of 0.850 A was passed through the cell above. After 40.0 minutes, the mass of one electrode increased by 0.680 g and the mass of the other electrode decreased by 0.714 g. The electrolyte was further analysed and it was found that the amount of Cu^{2+} ions decreased by 4.62×10^{-4} mol.

M was found underneath one of the electrodes.

(i) Explain, in terms of electrode reactions, how each of the two impurity metals was removed from copper, using relevant data from the *Data Booklet*. [3]

$E^{\ominus}(Co^{2+}/Co) = -0.28V$ $E^{\ominus}(Cu^{2+}/Cu) = +0.34V$ ✓ both data quoted

At the anode, Cu was oxidised over H_2O and Cu dissolved to form Cu^{2+} ions, which enter the electrolyte. ✓
Or
Oxidation at anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ (must mention oxidation at anode)

As $E^{\ominus}(Co^{2+}/Co)$ is more negative/less positive than $E^{\ominus}(Cu^{2+}/Cu)$, the cobalt impurity at the anode oxidised to form Co^{2+} ions, ✓ which entered the electrolyte/Co^{2+} ions not reduced at the cathode. ✓

M was not oxidised as its $E^{\ominus}$ is more positive than $E^{\ominus}(Cu^{2+}/Cu)$ and dropped to the bottom of the anode as 'anode sludge'. ✓

At the cathode, reduction of Cu^{2+} ions to Cu occurred due to more positive $E^{\ominus}(Cu^{2+}/Cu)$ compared to $E^{\ominus}(H_2O/H_2)$ and $E^{\ominus}(Co^{2+}/Co)$. ✓
or
Reduction at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ + explanation

Hence, only pure Cu was formed at the cathode.

2✓ = 1 mark

(ii) Use the information in part **(f)** to calculate a value for the Faraday's constant obtained from this experiment. [1]

cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Amount of Cu deposited at cathode = 0.680 / 63.5 = 0.0107 mol

Amount of electrons, n_e = 0.0107 × 2 = 0.0214 mol

Q= It = n_eF

F = $\frac{0.85 \times 40.0 \times 60}{0.0214}$ = 95327 = 95300 C mol^{-1} [1]

(iii) Use your answer to **(f)(ii)** and the *Data Booklet* to calculate a value for the Avogadro's constant obtained from this experiment. [1]

F = Le

Hence, experimental Avogadro's constant, L = $\frac{95327}{1.60 \times 10^{-19}}$

= 5.96 × 10^{23} mol^{-1} [1]

(iv) Calculate the masses of copper, cobalt and **M** removed from the copper bar. [2]

Amount of Co oxidised and removed = change in amount of Cu^{2+} (electrolyte)

= 4.62 × 10^{-4} mol

Mass of Co = 4.62 × 10^{-4} × 58.9 = 0.0272 g ✓

Amount of Cu oxidised = $\frac{0.680}{63.5}$ – 4.62 × 10^{-4} = 0.0102 mol ✓

Mass of Cu = = 0.0102 × 63.5 = 0.648 g ✓

Mass of M = 0.714 – 0.0272 – 0.648 = 0.0388 g ✓

2✓ = 1 mark

[Total: 20]