

H2 P1 REVIEW

1	2	3	4	5	6	7	8	9	10
A	C	B	B	C	B	D	B	B	C
11	12	13	14	15	16	17	18	19	20
D	A	D	A	B	B	C	C	D	C
21	22	23	24	25	26	27	28	29	30
A	B	B	C	D	C	D	A	A	B

1 Answer: A

Angle of deflection α charge/mass

Option A : $2/4 = 0.5$

Option B : $1/19 = 0.05$

Option C : $1/28 = 0.036$

Option D : $2/32 = 0.06$

2 Answer: C

Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Mn: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Fe: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Fe²⁺: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

3 Answer: B

Option A : [F --- H - F]. There is hydrogen bond formed between H in HF and F--as indicated by ---.

Option B : Both compounds have hydrogen bonding between molecules. However, volatility depends on the electron cloud size (inferred from M_r) which affects the strength of H-bond.

Option C : 2-nitrophenol can form intramolecular hydrogen bonding giving rise to less extensive H bonding between molecules and lower melting point.

Option D : Ethanoic acid can dimerise in benzene by forming two H bonds between two acid molecules.

4 Answer: B

A simple molecular solid should have a lower melting point (due to weak intermolecular forces) and does not conduct electricity (due to lack of mobile charge carriers - ions or free electrons). It may be soluble or insoluble in water depending on the type of intermolecular forces that it can form with water.

Since the unknown compound is a solid at room temperature, the answer cannot be A due to the melting point.

5 Answer: C

Option 1 has a dative bond from O to C while option 3 has a dative bond from N to O. Option 2 has no dative bond present.

6 Answer: B

Vol of original gas mixture = $10 + 50 \text{ cm}^3$

Vol of residual gas = $\frac{1}{4} \times 60 = 15 \text{ cm}^3$

Vol of unreacted O₂ = 15 cm^3

Vol of reacted O₂ = $50 - 15 = 35 \text{ cm}^3$

$$\text{C}_x\text{H}_y + (x + y/4)\text{O}_2 \longrightarrow x\text{CO}_2 + y/2 \text{H}_2\text{O}$$

10 35

$x + y/4 = 35/10$

$4x + y = 14$

$x = 2, y = 6$

7 Answer: D

A: $17 + 4(8) + 1 = 50 \text{ e}$

B: $2 + 16 + 4(8) = 50 \text{ e}$

C: $16 + 4(8) + 2 = 50 \text{ e}$

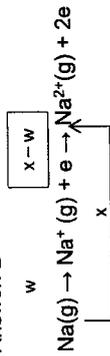
D: $50 - 2 = 48 \text{ e}$

8 Answer: B

During thermal decomposition, heat is absorbed to the reaction, so the reaction is endothermic (option A or B).

The activation energy is twice that of the enthalpy change, so option A is incorrect.

9 Answer: B



10 Answer: C

$$\text{Rate} = k[\text{L}][\text{N}] = k[\text{L}]^2[\text{M}]$$

1: incorrect as Units for $k = \text{mol dm}^{-3} \text{s}^{-1} / (\text{mol dm}^{-3})^3 = \text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$.2: correct as adding up the 3 elementary steps gives $2\text{L} + \text{N} \rightarrow 2\text{P}$

3: correct. Catalyst is consumed first then regenerated at the end of the reaction while an intermediate is produced and consumed at the end of the reaction.

11 Answer: D

$$\text{Rate} = k[\text{W}][\text{X}]^2$$

$$\text{Using run 1 data, } 0.0064 = k(0.02)(0.015)^2,$$

$$k = 1420$$

12 Answer: A

$$\text{Using } pV = nRT$$

$$101000(400 \times 10^{-6}) = n(8.31)(300)$$

$$n = 0.0162 \text{ mol}$$

$$\text{Ar of gas} = 40:1 (\text{Ar})$$

13 Answer: D

Option D: By Le Chatelier's principle, when the experiment is conducted at a lower temperature, the position of equilibrium will shift to the right to release heat as forward reaction is exothermic (mole fraction of $\text{I}_2(\text{g})$ should be lower).Option A: Incorrect as catalyst only speeds up the reaction (equilibrium reached in shorter time), there should not be changes in composition (mole fraction of $\text{I}_2(\text{g})$ should remain the same).Option B: Incorrect as the mole fraction of $\text{I}_2(\text{g})$ at time = 0 is the same (0.5) as the first experiment.

Option C: Incorrect as change in pressure does not affect the equilibrium position.

14 Answer: A

Options C and D: Incorrect as first IE of X is greater than that of Y, X should be above Y in the Periodic Table.

Option B: Incorrect. Since phosphorus has simple molecular structure, the melting point of P is lesser than aluminium which has giant metallic structure.

15 Answer: B

$$E^\ominus(\text{Cl}_2/\text{Cl}^-) = +1.36 \text{ V}$$

$$E^\ominus(\text{Br}_2/\text{Br}^-) = +1.07 \text{ V}$$

$$E^\ominus(\text{I}_2/\text{I}^-) = +0.54 \text{ V}$$

Option A: Chloride ion is less readily oxidised and thus chloride ions are weaker reducing agent.

Option B: $E_{\text{cell}}^\ominus = E_{\text{red}}^\ominus - E_{\text{ox}}^\ominus = +1.07 - 1.36 < 0 \Rightarrow$ reaction is not feasible

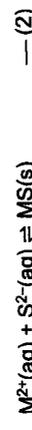
Option C: A yellow precipitate that is insoluble (not partially soluble) in aqueous ammonia is formed when iodide (not iodine) is added to silver nitrate solution.

Option D: Incorrect. When one drop of manganate(VII) is added to bromide, manganate(VII) decolourises and orange aqueous bromine is formed.

16 Answer: B

$$\text{Ionic product of ZnS} = \text{Ionic product of CuS} = [\text{M}^{2+}][\text{S}^{2-}]$$

$$= (0.1)(10^{-35}) = 10^{-36} \text{ mol}^2 \text{ dm}^{-6}$$

For ZnS, ionic product $< K_{\text{sp}} \Rightarrow$ No ppt observedFor CuS, ionic product $> K_{\text{sp}} \Rightarrow$ Ppt observed (Option B is correct)When pH is lowered, $[\text{H}^+]$ is increased, by LCP, position of equilibrium (1) shifts to the left. $[\text{S}^{2-}]$ decreases. Thus position of equilibrium (2) shifts to the left and $\text{MS}(\text{s})$ dissolves (less ppt formed).

17 Answer: C

As the equivalence pH is less than 7, this is a reaction between strong acid (HCl) and weak base (NH_3).

$$[\text{NH}_3] = \frac{20 \times 0.1}{10} = 0.2 \text{ mol dm}^{-3}$$

18 Answer: C

At 25 °C, $[H^+] = [OH^-] = 10^{-7} \text{ mol dm}^{-3}$

$pH = -\log [H^+] = 7$

$K_w = [H^+][OH^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-3}$

$pK_w = -\lg K_w = 14$

$K_a \text{ of H}_2\text{O} = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-14}}{55.6} = 1.80 \times 10^{-16} \text{ mol dm}^{-3}$

$pK_a = -\lg K_a = 15.7$ (Statement 1 is incorrect)

$pH < pK_w < pK_a$ (Statement 2 is correct)

When temperature increases, by Le Chatelier's Principle, position of equilibrium shifts right to absorb heat since forward reaction is endothermic. $[H^+]$ and $[OH^-]$ will increase and K_w will increase and pK_w will decrease. (Statement 3 is correct)

19 Answer: D

A $\text{CH}_2=\text{C}=\text{CHCH}_3$ contains one sp hybridised and one sp^3 hybridised C atoms.

B $\text{CH}_2=\text{CHCN}$ contains one sp hybridised C atom but no sp^3 hybridised C atoms.

C $\text{HOCH}_2\text{C}\equiv\text{CH}$ contains two sp hybridised and one sp^3 hybridised C atoms.

D $\text{CH}_3\text{CCH}_2\text{C}=\text{CHCN}$ contains one sp hybridised and two sp^3 hybridised C atoms.

20 Answer: C

The reaction involves breaking of C-X bond to release free X^- ions which can then combine with Ag^+ ions to form a precipitate of AgX .

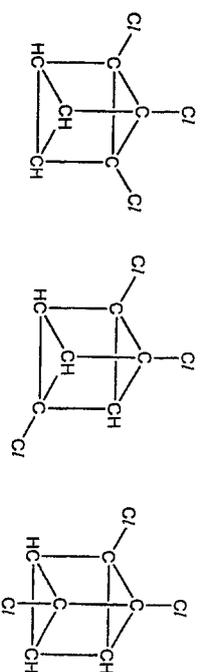
The rate of reaction depends on the strength of C-X bond.

The time taken to observe precipitate for compound 1, 2 and 3 depends on strength of C-Cl, C-Br and C-I respectively and independent of C-F bond.

Since C-I bond is the weakest of the three bonds, it is the easiest to break and will take the shortest time for the formation of precipitate.

Since C-Cl bond is the strongest of the three bonds, it is the hardest to break and will take the longest time for the formation of precipitate.

21 Answer: A



22 Answer: B

Step 1 is electrophilic substitution (Friedel Crafts alkylation) using halogenoalkane, $(\text{CH}_3)_2\text{CCl}$.

Step 2 involves converting benzene to cycloalkane hence this is reduction (inferred from gain of H).

Step 3 involves formation of ester from either the use of CH_3COOH , warm with conc. H_2SO_4 or CH_3COCl .

23 Answer: B

1. The ring contains more than 8 carbon atoms hence the C=C bond in the ring can exhibit cis-trans isomerism.

Statement 1 is correct. 2.

The alkene functional group can react with Br_2 via electrophilic addition reaction. However, the molecular formula of the product should be $\text{C}_{17}\text{H}_{30}\text{OBr}_2$ not $\text{C}_{17}\text{H}_{32}\text{OBr}_2$ as only Br atoms are added across the C=C bond and there should be no change in number of H atoms.

Statement 2 is incorrect.

3. Civetone does not exhibit intermolecular hydrogen bonding since there are no H atoms directly bonded to F, O or N atoms in the molecule.

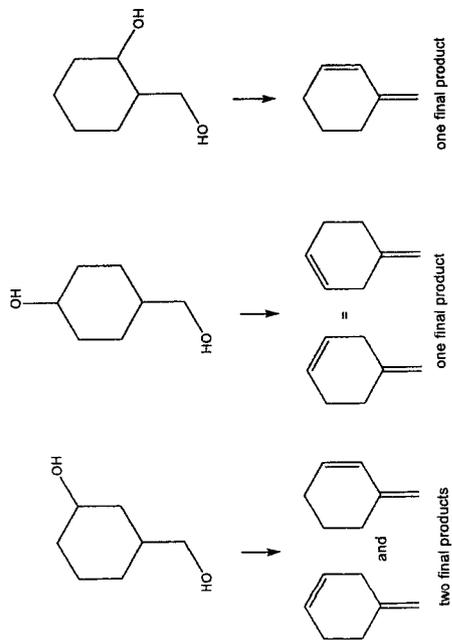
The dominant type of intermolecular forces should be permanent dipole-permanent dipole and instantaneous dipole-induced dipole attractions.

Note: the presence of O atom in civetone can still allow it to form hydrogen bonding with other types of molecules.

Statement 3 is correct.

24 Answer: C

The three compounds undergo elimination to form alkenes.



Only one of the compounds can form two final products with molecular formula C_7H_{10} .

25 Answer: D

A: Incorrect. $-NH_2$ group is 2- and/or 4- directing and polysubstitution will occur with $Br_2(aq)$ to give 2,4,6-tribromophenylamine instead.

B: Incorrect as $-Br$ is 2- and/or 4- directing. Hence in the first step, the NO_2^+ will be directed to the 2nd or 4th position with respect to the $-Br$ group, instead of the 3rd position.

C: Incorrect. While $-NO_2$ is 3-directing, the $LiAlH_4$ will reduce the nitrobenzene to other compounds (not phenylamine) instead.

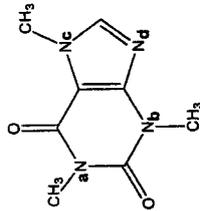
26 Answer: C

A: Incorrect. $NaBH_4$ only reduces ketones and aldehydes but there is no carbonyl functional group in the caffeine molecule. The amides in the caffeine molecule can only be reduced by $LiAlH_4$ in dry ether.

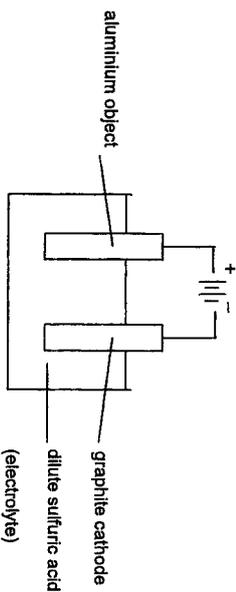
B: Incorrect. The amides and tertiary amine do not undergo condensation with ethanoyl chloride. Hence HCl gas is not formed.

C: Correct. The amide groups in the caffeine molecule can undergo alkaline hydrolysis to give CH_3NH_2 which is an alkaline gas.

D: Incorrect. 1 mole of caffeine reacts with 1 mole of $HCl(aq)$ at room temperature via an acid-base reaction. The amide groups in the caffeine molecule are neutral as the lone pair of electrons on Na and Nb are delocalised over the O-C-O bond and not available to form a dative covalent bond with a proton. The lone pair of electrons on Nc are delocalised in the ring and not available to form a dative covalent bond with a proton. Only Nd is basic and can react with $HCl(aq)$ as the lone pair of electrons on Nd is not delocalised and available for donation to a proton.



27 Answer: D



Option A: Incorrect. The aluminium object to be coated is placed at the anode.

Option B: Incorrect. At the graphite cathode:



Option C: Incorrect. Anodising is the process of increasing the thickness of the Al_2O_3 layer of aluminium objects through electrolysis.

Option D: Correct.



0.01 mol of Al_2O_3 formed would require 0.06 mol of electrons.

$$Q = It = n_e F$$

$$I = \frac{0.06 \times 96500}{30 \times 60} = 3.2 \text{ A}$$

28 Answer: A



$$E^\ominus_{\text{cell}} = E^\ominus(\text{O}_2/\text{H}_2\text{O}) - E^\ominus(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-}) = (+1.23) - (+0.09) = +1.14 \text{ V}$$

Option 1: Correct. Adding water will decrease both the $[\text{S}_4\text{O}_6^{2-}(\text{aq})]$ and $[\text{S}_2\text{O}_3^{2-}(\text{aq})]$. By LCP, equilibrium position of (2) will shift to the right to increase total ion concentration as there are more ions on the right hand side of the equation. Hence $E(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-})$ will be more positive than +0.09 V and E_{cell} will be less positive.

Option 2: Correct. Iodine will react with $\text{S}_2\text{O}_3^{2-}$, decreasing $[\text{S}_2\text{O}_3^{2-}(\text{aq})]$. By LCP, equilibrium position of (2) will shift to the right to increase $[\text{S}_2\text{O}_3^{2-}(\text{aq})]$. Hence $E(\text{S}_4\text{O}_6^{2-}/\text{S}_2\text{O}_3^{2-})$ will be more positive than +0.09 V and E_{cell} will be less positive.

Option 3: Correct. Using a lower pressure than 1 bar (standard conditions) will cause equilibrium position (1) to shift left. Hence $E(\text{O}_2/\text{H}_2\text{O})$ will be less positive than +1.23 V and E_{cell} will be less positive.

29 Answer: A

A solution containing $\text{Fe}^{3+}(\text{aq})$ ions is yellow.

When $\text{NaCN}(\text{aq})$ is added to this solution, CN^- replaces the H_2O ligands in $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ via a ligand exchange and orange red $[\text{Fe}(\text{CN})_6]^{3-}$ ions are formed. Hence the solution turns from yellow to orange red.

$[\text{FeF}_6]^{3-}$ has a smaller K_{stab} than $[\text{Fe}(\text{CN})_6]^{3-}$. Hence, F^- will not be able to replace CN^- in a ligand exchange. Thus, the orange red solution remains orange red.

30 Answer: B

Option A: Incorrect. Reaction I is a redox reaction but reaction II is a hydrolysis reaction of $\text{Fe}^{3+}(\text{aq})$ ions to give H^+ ions, followed by acid-base reaction between H^+ and CO_3^{2-} ions.

Option B: Correct. Cr^{3+} has a high charge density. $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ can undergo hydrolysis in water to produce H^+ ions, forming effervescence of CO_2 and a grey-green ppt of $\text{Cr}(\text{OH})_3$ when CO_3^{2-} ions are added.

Option C: Incorrect. The orange solution contains $\text{Cr}_2\text{O}_7^{2-}$ ions. Hence Cr^{3+} is oxidised to $\text{Cr}_2\text{O}_7^{2-}$, and reagent **R** should be an oxidising agent such as H_2O_2 . Zn is a reducing agent.

Option D: Incorrect. EDTA^{4-} is a hexadentate ligand. Reaction IV is a ligand exchange where one EDTA^{4-} ligand exchanges for six H_2O molecules. Hence, the number of particles increases and the disorder of the system increases. Thus, ΔS should be positive.



2025 JC2 Prelims H2 P2 (Review)

1

In 1932, the American chemist Linus Pauling developed the most common scale of relative electronegativity (EN) values for the elements. The Pauling EN values of elements can be used to predict the chemical properties of compounds. The EN values of four Period 3 elements are given in Table 1.1.

Table 1.1

Element	Sodium	Aluminium	Phosphorus	Chlorine
Pauling EN value	0.93	1.61	2.19	3.16

- (a) (i) Explain the difference in the Pauling electronegativity values of Na and Cl. [2]

Comparing sodium and chlorine, [✓] chlorine has a higher nuclear charge due to larger number of protons, [✓] screening effect remains approximately constant as electrons are added to the same electronic shell.

[✓] As there is stronger attraction between the nucleus and the bonding electrons in the outer shell, chlorine has higher [✓] electronegativity, resulting in a larger EN value.

2[✓] = [1]

The ionic character of a bond is directly related to the electronegativity difference (ΔEN) between the bonded atoms. Fig. 1.1 shows the plot of percent ionic character against ΔEN for NaCl.

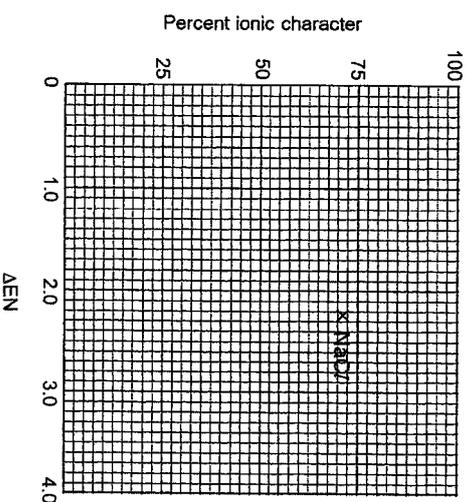


Fig. 1.1

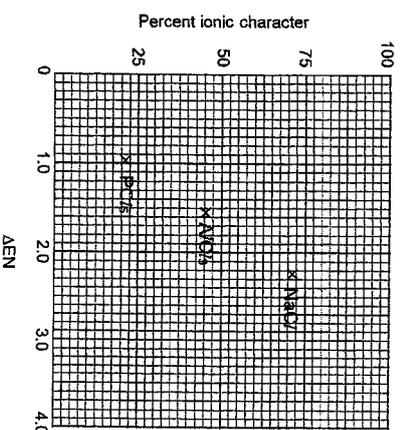
- (ii) Using the values in Table 1.1, calculate ΔEN for $AlCl_3$ and PCl_5 respectively. Hence plot the percent ionic character of $AlCl_3$ and PCl_5 on Fig. 1.1. Label your points clearly. [2]

ΔEN for $AlCl_3 = 3.16 - 1.61 = 1.55$ [✓]

ΔEN for $PCl_5 = 3.16 - 2.19 = 0.970$ [✓]

2[✓] = [1]

[1] Correct relative order for percent ionic character for the three compounds



- (iii) Explain the difference in bonding for $NaCl$ and PCl_5 in terms of electronegativity. [2]

[1] Ionic bonds exist in $NaCl$ due to large ΔEN (or large difference in electronegativities) between Na and Cl.

[1] Covalent bonds exist in PCl_5 due to small ΔEN (or small difference in electronegativities) between P and Cl.

- (b) (i)

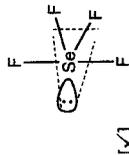
The polarity of bonds in covalent molecules is also affected by ΔEN . SeF_4 and BF_3 are two fluorine-containing molecules. State whether SeF_4 or BF_3 contains covalent bonds with a higher ionic character. [1]

[1] $SeF_4 > BF_3$

- (ii)

Using VSEPR theory, predict and explain the shape and bond angles of SeF_4 . Illustrate the shape of SeF_4 with an appropriate diagram. [3]

There are [✓] 4 bond pairs and 1 lone pair in the valence shell of Se atom. [✓] To minimise repulsion and maximise stability, the shape of SeF_4 is [✓] see-saw.



Since [✓] lone pair – bond pair repulsion > bond pair repulsion, the [✓] bond angles are 88° and 118° (accept other bond angles $< 90^\circ$ and $< 120^\circ$).

$$2[\checkmark] = [1]$$

[Total: 10]

2 PCl_5 is a Period 3 chloride commonly used as a chlorinating agent and catalyst in making organic compounds. Industrial production of PCl_5 involves the reaction of Cl_2 with PCl_3 .



(a) Suggest, with an explanation, how the position of equilibrium and the composition of the equilibrium mixture might change when chlorine is added to the equilibrium system. [2]

By Le Chatelier's Principle, the [✓] position of equilibrium will shift right to [✓] decrease the concentration of Cl_2 . The equilibrium mixture will contain [✓] more PCl_5 , less PCl_3 and [✓] more Cl_2 .

$$2[\checkmark] = [1]$$

x mol of Cl_2 gas is added to a 2 dm^3 vessel containing an equilibrium system of 0.4 mol of PCl_3 , 0.25 mol of Cl_2 gas and 1.2 mol of PCl_5 . The new equilibrium amount of PCl_5 is 1.28 mol.

(b) (i) Write the K_c expression for reaction (1), giving its units. [1]

$$[1] K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}, \text{ mol}^{-1} \text{ dm}^3$$

(ii) Using the information given above, calculate K_c . [1]

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{\left(\frac{1.2}{2}\right)}{\left(\frac{0.4}{2}\right)\left(\frac{0.25}{2}\right)} = \underline{24.0} \text{ mol}^{-1} \text{ dm}^3 [1]$$

(iii) Hence calculate x , the amount of Cl_2 added. [2]

	$\text{PCl}_3(\text{g})$	$+$	$\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{PCl}_5(\text{g})$
Initial amount /mol	0.4		0.25 + x		1.2
Change in amount /mol	- y		- y		+ y
Equilibrium amount /mol	0.4 - y		0.25 + $x - y$		1.28
			= 0.32		= 0.17 + x

[1] ICE Table Working

$$y = 1.28 - 1.2 = 0.08$$

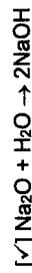
$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{\left(\frac{1.28}{2}\right)}{\left(\frac{0.32}{2}\right)\left(\frac{0.17+x}{2}\right)} = 24$$

$$x = 0.163 \text{ mol [1]}$$

(c) Period 3 oxides follow a similar trend in bonding as the Period 3 chlorides.

Describe the action of water on the oxides of sodium, aluminium and phosphorus, write equations for any reactions that occur, and suggest the pH of each solution formed. [3]

Na_2O [✓] reacts vigorously with water to give a strongly alkaline solution of $\text{NaOH}(\text{aq})$ with a [✓] pH = 13.



P_4O_{10} [✓] reacts vigorously with water to give a strongly acidic solution of

(b) Figure 3.1 shows the second ionisation energies of nine consecutive elements **A** to **I** with atomic numbers below 20 in the Periodic Table. Labels **A** to **I** are not the atomic symbols of the elements.

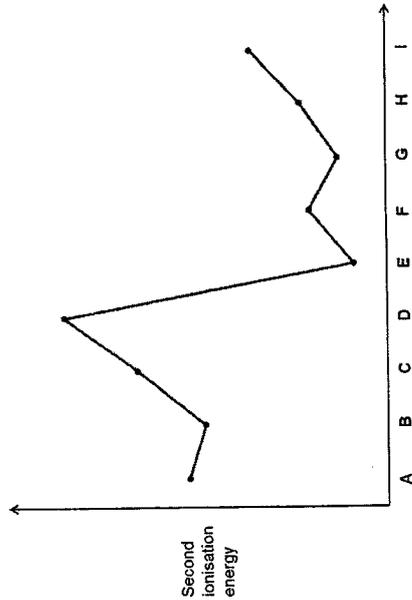
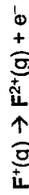


Fig. 3.1

(i) Define the second ionisation energy of element **F**. [1]

[1] The second ionisation energy of element **F** is the minimum energy required to completely remove one mole of electrons from one mole of ground-state gaseous F^+ ions to form 1 mole of gaseous F^{2+} ions.



(ii) Suggest the identity of **B**. Explain how you arrived at your answer. [2]

[1] Large decrease in 2nd ionisation energy from **D** to **E** implies that the 2nd electron in **E** is removed from the outer electron shell.

E belongs to Group 2 and **B** belongs to group 17.

[1] **B** is fluorine

(iii) Explain the difference in second ionisation energy between element **A** and element **B**. [1]

A: s^2p^4 **A**⁺: s^2p^3

B: s^2p^5 **B**⁺: s^2p^4

[1] The 2nd electron removed in **B** is a paired electron which experiences interelectronic repulsion, so less energy is needed to remove the paired electron than the unpaired electron removed in **A**.

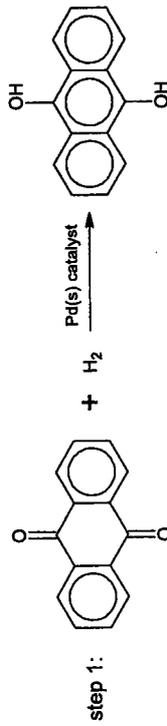
[Total: 9]

4 Hydrogen peroxide, H_2O_2 , finds its applications in a diversity of fields as it is considered an environmentally-friendly oxidising agent.

(a) (i) Suggest why it is environmentally-friendly to use H_2O_2 as an oxidising agent. [1]

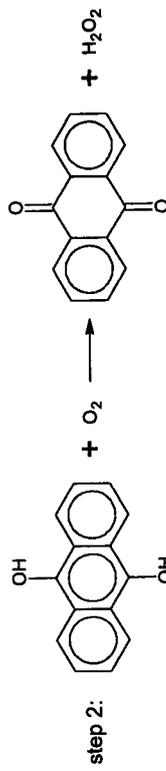
[1] The product of reduction of H_2O_2 is water which is clean / non-pollutant / environmentally friendly.

Today, most of the world's hydrogen peroxide is manufactured by the anthraquinone, $C_{14}H_{10}O_2$ process. This process involves the two steps shown below.



Anthraquinone

Anthrahydroquinone



Anthrahydroquinone

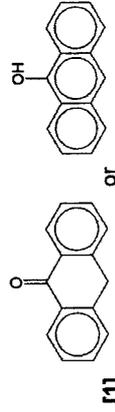
Anthraquinone

(ii) State the type of reaction in step 1. [1]

[1] Reduction

(iii) In step 1, if Sn is used instead of Pd, compound **P**, $C_{14}H_{10}O$ is obtained. Suggest the structure of **P**. [1]

Analysis: from $C_{14}H_{10}O_2$ to $C_{14}H_{10}O$, gain of 2 H and loss of 1 O = reduction



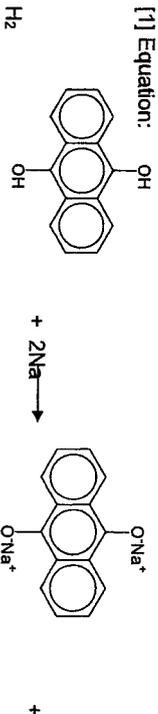
[1]

- (iv) Describe a chemical test that can be used to distinguish anthraquinone from anthrahydroquinone. State the observations and write a balanced equation for the reaction that occurred. [2]

Add Na metal.	
Anthrahydroquinone	<u>effervescence of hydrogen gas</u>
Anthraquinone	<u>No effervescence</u>
Add Brady's reagent / 2,4-DNPH.	
Anthrahydroquinone	<u>No orange ppt / solid</u>
Anthraquinone	<u>Orange ppt / solid formed</u>

[1] reagent + obs for BOTH cpds

[1] Equation:



Other possible tests: Brady's reagent

At the end of step 2, only anthraquinone and H_2O_2 remain in the reaction mixture. H_2O_2 can be separated out from the reaction mixture by adding water to the reaction mixture.

- (b) With reference to the interactions between relevant molecules, explain how the addition of water separates H_2O_2 from the reaction mixture. [2]

[✓] Sufficient energy is released from the formation of [✓] hydrogen bonds between water and H_2O_2 to overcome the [✓] hydrogen bonds between water molecules and hydrogen bonds between H_2O_2 molecules.

[✓] Insufficient energy is released from the formation of [✓] instantaneous dipole-induced dipole interactions between anthraquinone and water to overcome the hydrogen bonds between water molecules.

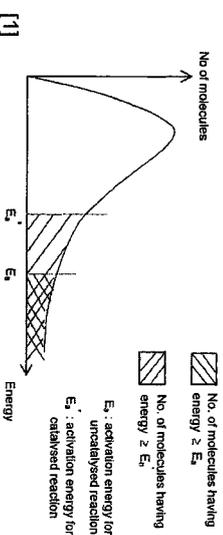
[✓] H_2O_2 dissolve in water / anthraquinone cannot dissolve in water.
3[✓] = [1]

- (c) (i) Palladium metal is often used as a heterogeneous catalyst.

Explain what is meant by a heterogeneous catalyst. [1]

[1] A catalyst which is not in the same phase / state as the reactants.

- (ii) Explain how a heterogeneous catalyst increases the rate of reaction. Include a sketch of the Maxwell-Boltzmann distribution and use it to illustrate your answer. [4]



[1] The reactant molecules are [✓] adsorbed onto the surface of the solid catalyst.

Alternative pathway has [✓] lower activation energy due to [✓] higher surface concentration of reactant molecules and [✓] covalent bonds are weakened.

[✓] Number of particles with energy $\geq E_a'$ / lower activation energy increases. [✓] Frequency of effective collisions increases. [✓] Rate constant increases.

After the reaction, [✓] desorption of product molecules occurs and the molecules eventually [✓] diffuse away from the catalyst surface.

3[✓] = [1]

- (d) Nanoparticles are particles with all its dimensions from 1 to 100 nm on the nanoscale. It is observed that the catalytic activity of palladium is vastly increased when the catalyst is finely divided into nanoparticles. These nanoparticles are usually deposited onto the surface of inert metal particles such as gold. This prevents the nanoparticles from being a health hazard.

- (i) Explain why catalytic activity is vastly increased when nanoparticles of palladium are used. [1]

[1] Finely dividing the palladium into nanoparticles increases its surface area to volume ratio, providing more active sites for adsorption of reactants.

- (ii) Predict how nanoparticles could present a risk to human health. [1]

[1] Due to their small size, nanoparticles can enter human body through pores on skin, breathing/respiratory system, or ingestion (by digestive system).

These particles can travel around the body via the circulatory system, get deposited in body tissues / cells / organs and cause the latter to be damaged / inflamed / develop cancer / cause immune response.

(iii) Explain how the deposition of palladium nanoparticles on gold particles prevents them from being a health hazard. [1]

[1] Gold particles are larger and the deposition of the nanoparticles decreases the chances / prevents them from being inhaled or ingested.

[Total: 15]

5 Copper is a first-row transition metal which has two stable isotopes, ^{63}Cu and ^{65}Cu , that exist naturally in mineral ores.

(a) Explain the trend of first ionisation energy of first-row transition metals. [2]

[✓] Across the period, nuclear charge increases due to increasing number of protons.

[✓] Screening effect increases as electrons are added to the penultimate / second outermost 3d subshell, providing a shield between nucleus and outer 4s electrons.

[✓] The increase in nuclear charge is only slightly more significant than the increase in screening effect.

[✓] Small increase in first IE / relatively invariant

2[✓] = [1]

(b) A sample of mineral ore containing the two isotopes of copper is run in a mass spectrometer to determine their relative amounts. The following mass spectrum is obtained.

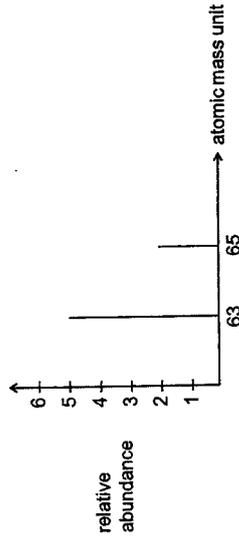


Fig. 5.1

(i) Define the term isotope. [1]

[1] Atoms of same element with the same number of protons but different number of neutrons.

(ii) Using Fig. 5.1, determine the relative atomic mass, A_r , of copper. Give your answer to 4 decimal places. [1]

[1] A_r of copper = $[5(63)+2(65)]/7 = 63.5714$

Chlorine and bromine each has two naturally occurring isotopes. Their relative abundance are shown below.

Table 5.1

Element	Isotope	relative abundance
Chlorine	^{35}Cl	75%
	^{37}Cl	25%
Bromine	^{79}Br	50%
	^{81}Br	50%

The following *incomplete* mass spectrum is obtained from a sample of BrCl where only the abundance for atomic mass unit of 116 is shown.

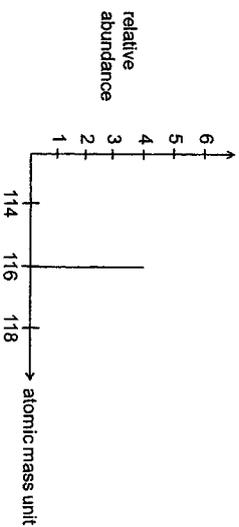


Fig. 5.2

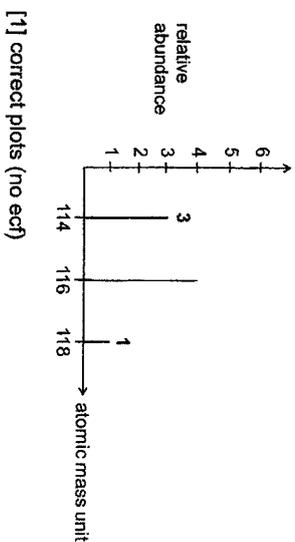
(iii) Identify the species responsible for the atomic mass unit of 114, 116 and 118, taking into consideration the various isotopes. [2]

atomic mass unit of 114 $[\checkmark] ^{79}\text{Br}^{35}\text{Cl}$
 atomic mass unit of 116 $[\checkmark] ^{79}\text{Br}^{37}\text{Cl}$ and $[\checkmark] ^{81}\text{Br}^{35}\text{Cl}$
 atomic mass unit of 118 $[\checkmark] ^{81}\text{Br}^{37}\text{Cl}$
 2[\checkmark] = [1]

(iv) Hence, calculate the relative abundance of BrCl with atomic mass unit of 114 and 118, and complete Fig 5.2. [2]

Percentage of sample with $^{79}\text{Br}^{35}\text{Cl} = (1/2)(3/4) = 3/8 = 0.375 = 37.5\%$
 Percentage of sample with $^{81}\text{Br}^{37}\text{Cl} = (1/2)(1/4) = 1/8 = 0.125 = 12.5\%$
 Percentage of sample with $^{79}\text{Br}^{37}\text{Cl}$ and $^{81}\text{Br}^{35}\text{Cl} = (1/2)(1/4) + (1/2)(3/4) = 4/8 = 50\%$

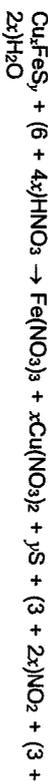
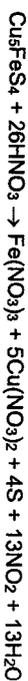
[1] correct working and answer



[1] correct plots (no eq)

(c) Most of the world's copper comes from the mining of copper-containing minerals. Two such minerals are bornite, Cu_5FeS_4 , and chalcopyrite, Cu_2FeS_3 , where x and y are integer values to be determined.

Bornite and chalcopyrite react with concentrated HNO_3 as follows.



(i) Explain the role of HNO_3 in the above reactions. [1]

[1] Oxidising agent. Oxidation state nitrogen decreases from +5 in HNO_3 to +4 in NO_2 .

(ii) When 1 mole each of bornite and chalcopyrite were fully reacted with HNO_3 , bornite produced 64.2 g more sulfur precipitate and 182 dm³ more nitrogen dioxide than chalcopyrite, at standard temperature and pressure. Determine the values of x and y . [2]

$$[\text{1}] \text{ Sulfur precipitate: } 4 - y = \frac{64.2}{32.1} \therefore y = 2$$

$$[\text{1}] \text{ NO}_2 \text{ gas: } 13 - (3 + 2x) = \frac{182}{22.7} \therefore x = 1$$

[Total: 11]

6 Polymers are macromolecules which consist of chains built up from small molecules known as monomers, with at least 100 repeating units. In general, polymers can be made via addition or condensation reactions.

The characteristic properties exhibited by polymers are the result of their unique structure and bonding. Not all polymers are biodegradable, which poses difficulty in recycling them.

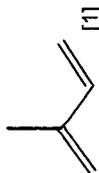
The monomers and biodegradability of addition and condensation polymers are shown in Table 6.1.

Table 6.1

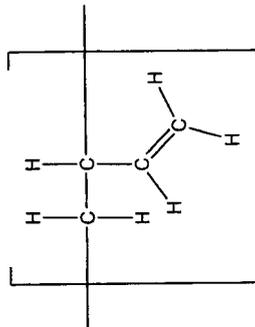
monomers	addition polymer	condensation polymer
	molecules containing C=C bonds	molecules containing two functional groups
biodegradability of polymer	generally difficult to biodegrade	generally biodegradable

(a) The outer layers of some golf balls are made from a polymer called polyisoprene. The isoprene monomer is a non-cyclic branched hydrocarbon with five carbon atoms. One mole of isoprene reacts with two moles of Br₂ in CCl₄.

Suggest a possible structure of isoprene. [1]



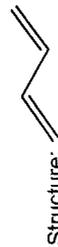
(b) The insides of some golf balls are made from a mixture of three other polymers, X, Y and Z. The repeating unit for polymer X is shown.



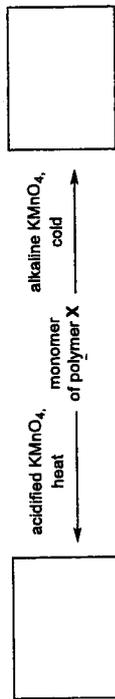
(i) The molecular formula of the monomer of X is C₄H₆.

Give the systematic name of the monomer used to make X. [1]

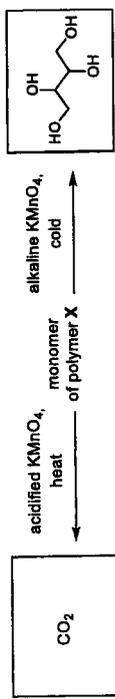
buta-1,3-diene or butadiene [✓]



(ii) Draw the carbon-containing products formed when the monomer undergoes the reactions below.

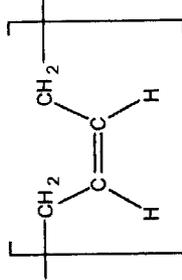


[2]



[1]

(c) (i) Polymers Y and Z are stereoisomers. One of the polymers has a repeating unit with the structure shown.

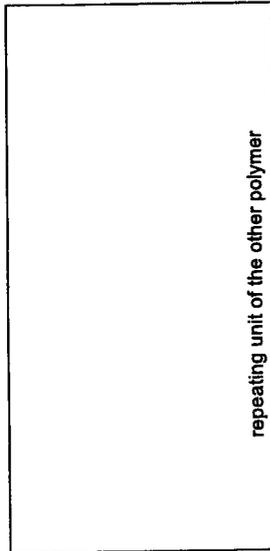


State the type of stereoisomerism and explain why it arises. [2]

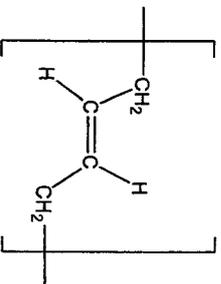
Cis-trans isomerism. [1]

There is restricted rotation about the C=C bond and each carbon of the C=C bond is bonded to two different groups. [1]

(ii) Draw the structure of the repeating unit of the other polymer. [1]



repeating unit of the other polymer



Structure of polymer Y (trans isomer) [1]

Table 6.2 shows some properties of polymers Y and Z.

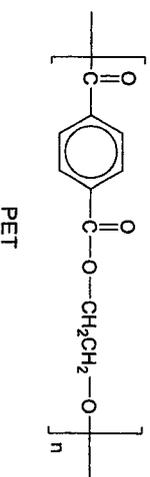
	polymer Y	polymer Z
arrangement of polymer chains	crystalline with regular repeating pattern	amorphous with random arrangement
rigidity	high	low
melting point	75 to 135 °C	-25 to 12 °C

Table 6.2

- (iii) By referring to the information in Table 6.2, identify whether polymer Y or Z has the repeating unit in (c)(i). [1]
 polymer Z (cis isomer) [1]

- (d) Golf balls recovered from lakes and ponds can be used again even after being in water for several years. Suggest why these golf balls do not biodegrade. [1]
Carbon-carbon bonds are non-polar / too strong / not attacked by nucleophiles / cannot be hydrolysed. [1] with explanation

- (e) Another polymer, poly(ethylene terephthalate), PET, is commonly used to make shirts worn by golfers. The structure of PET is shown below where n is the number of repeating units in the polymer chain. One of the two monomers used to synthesise PET is benzene-1,4-dicarboxylic acid.



Atom economy is a measure of the amount of starting materials which are in the final desired product.

$$\text{percentage atom economy} = \frac{M_r \text{ of the final desired product}}{\text{total } M_r \text{ of all reactants}} \times 100\%$$

- (i) Suggest why chemists usually aim to design production methods with a high percentage atom economy. [1]
 Reactions with a high percentage atom economy are more efficient and less wasteful/maximises the use of resources/reduce by-products. [1]

- (ii) Explain how the percentage atom economy of the reaction to form PET compares with that of polymer X. [1]

The percentage atom economy of the reaction to form PET is lower than that to form polymer X as H_2O / another molecule is also formed during the condensation while all the monomers are used to form polymer X. [1]

- (i) Figure 6.1 shows a two-step synthesis of benzene-1,4-dicarboxylic acid from methylbenzene. State the reagents and conditions for each step and draw the structure of the intermediate. [2]

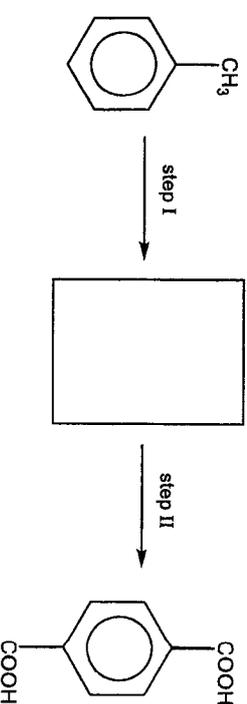
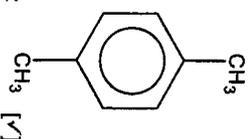


Fig. 6.1

- step I: CH_3Cl , anhydrous AlCl_3 [✓] BOD if didn't write 'anhydrous', as long as didn't write aqueous [2]
 step II: $\text{KMnO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$, heat [✓] accept: acidified KMnO_4 , heat



Intermediate: [✓]
 3[✓] = 2 marks
 2[✓] = 1 mark

(g) Benzene-1,2-dicarboxylic acid molecules can also be found in the product mixture in (f).

Table 6.3

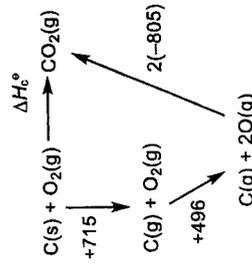
	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
standard enthalpy change of formation of $\text{H}_2\text{O}(\text{l})$	-286
standard enthalpy change of combustion of benzene-1,2-dicarboxylic acid, $\text{C}_6\text{H}_4(\text{COOH})_2(\text{s})$	-3220
standard enthalpy change of combustion of benzene-1,4-dicarboxylic acid, $\text{C}_6\text{H}_4(\text{COOH})_2(\text{s})$	-3190

(i) Use relevant data from Table 6.3 to deduce whether benzene-1,2-dicarboxylic acid or benzene-1,4-dicarboxylic acid is more energetically stable under standard conditions. Explain your answer. [1]

Benzene-1,4-dicarboxylic acid is more energetically stable as it has a less exothermic standard enthalpy change of combustion. [1]

Note: Benzene-1,4-dicarboxylic acid is more stable than benzene-1,2-dicarboxylic acid due to less steric repulsion between the -COOH groups as they are further apart.

(ii) The standard enthalpy change of atomisation of carbon is +715 kJ mol⁻¹. Use this information and the Data Booklet to calculate a value for the standard enthalpy change of combustion of carbon. [2]

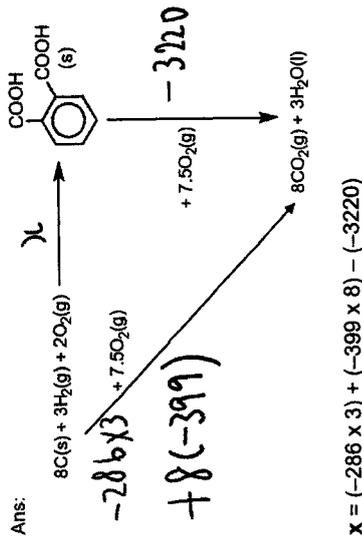


[1] use of standard enthalpy change of atomisation of carbon

$$\Delta H_c^\circ = 715 + 496 + 2(-805) = -399 \text{ kJ mol}^{-1} \text{ [1] (no need cycle)}$$

(iii) The standard enthalpy change of formation of benzene-1,2-dicarboxylic acid, x, cannot be determined via direct experiment. Using relevant data from Table 6.3 and your answer to (g)(ii), draw an energy cycle to determine a value for x. Show your working clearly.

If you were unable to calculate a value for the standard enthalpy change of combustion of carbon in (g)(ii), you should use -450 kJ mol⁻¹. This is not the correct answer. [2]



x = (-286 x 3) + (-399 x 8) - (-3220) = -830 kJ mol⁻¹

[1] Correct cycle (including balanced equations with correct state symbols)
[1] Correct use of values and correct final answer

(h) (i) Define the term **standard enthalpy change of neutralisation**. [1]
The **standard enthalpy change of neutralisation**, ΔH_n° , is the **enthalpy change when an acid and a base react under infinitely dilute conditions to form one mole of water at 298 K and 1 bar**. [1]

The molarity of a buffer is defined as the **total number of moles of buffering solutes in 1 dm³ of solution**. For example, a 1 dm³ buffer solution containing 0.3 mol of CH_3COOH and 0.2 mol of CH_3COO^- will have a molarity of 0.5 mol dm⁻³. Potassium hydrogen phthalate is a salt that contains the monoanion of benzene-1,2-dicarboxylic acid, HA^- .

(ii) 250 cm³ of buffer solution at pH 5.0 is prepared by adding 0.1 mol dm⁻³ $\text{NaOH}(\text{aq})$ to solid potassium hydrogen phthalate and the resulting solution is made up to 250 cm³. The molarity of this buffer is 0.1 mol dm⁻³.

Given that the $\text{p}K_a$ of the monoanion of benzene-1,2-dicarboxylic acid, HA^- , is 5.40, calculate the volume of $\text{NaOH}(\text{aq})$ required.

After adding $\text{NaOH}(\text{aq})$ to solid potassium hydrogen phthalate, the buffer contains A^{2-} and HA^- .

$$5.0 = 5.40 + \lg \left(\frac{[A^{2-}]}{[HA^{-}]}\right)$$

$$\frac{[A^{2-}]}{[HA^{-}]} = 0.398 \quad (1)$$

$$[A^{2-}] + [HA^{-}] = 0.1 \quad (2)$$

Solving (1) and (2), $[HA^{-}] = 0.07153 \text{ mol dm}^{-3}$ [1]

$$[A^{2-}] = 0.1 - 0.07153 = 0.02847 \text{ mol dm}^{-3}$$



Amount of NaOH needed = amount of $A^{2-} = 0.02847 \times \frac{250}{1000} = 0.007118$
mol

$$\text{Volume of NaOH needed} = \frac{0.007118}{0.1} \times 1000 = 71.2 \text{ cm}^3 \quad [1]$$

[Total: 21]

H2 P3 Review

1 Schweizer's reagent is used in purifying cellulose. This dark blue compound has the formula $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2](\text{OH})_2$ and contains the tetraamminediaquacopper(II) cation, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

(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 $\sqrt{d-d}$ with partially filled d-subshell, when a d-electron from lower energy group is promoted to the higher energy group (d-d transition), $\sqrt{\text{radiation corresponding to } \Delta E, \text{ orange light, is absorbed. } \sqrt{\text{Light of wavelengths not absorbed (blue light) will be seen as the colour of the complex.}}$

$5\gamma = 3$ marks, $3.4\gamma = 2$ marks, $2\gamma = 1$ mark

(b) When a solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ was gently heated, NH_3 gas was released. A precipitate of $\text{Cu}(\text{OH})_2$ and NH_4^+ ions were also obtained as products.

The $\text{Cu}(\text{OH})_2$ 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 $\text{Cu}(\text{OH})_2$ was added to dilute sulfuric acid, forming blue complex ion Y.

$[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, X and Y are of different colours.

When $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ was strongly heated, a black solid Z is formed.

(i) Write an equation for the reaction when a solution of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ was gently heated. [1]



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



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



(iv) Explain why $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ and X are of different colours. [1]

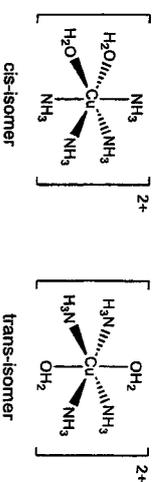
The $\sqrt{\text{ligands, datively bonded to Cu(II) are different, resulting in } \sqrt{\text{different energy gaps between the d orbitals in the complexes. This will affect the}}$

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

$2\gamma = 1$ mark, with clear explanation

(c) Tetraamminediaquacopper(II) cation, $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$, has two possible stereoisomers.

Draw the two stereoisomers. [2]



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 nanoparticles like $\text{Cu}(\text{OH})_2$ and CuO , have been used to protect crops from bacteria induced diseases.

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

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



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

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

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

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

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

(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}

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

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

Since the $\sqrt{[Cu^{2+}]}$ is lesser than minimum effective concentration of Cu^{2+} ion ($6.35 \times 10^{-5} \text{ g dm}^{-3}$), 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.

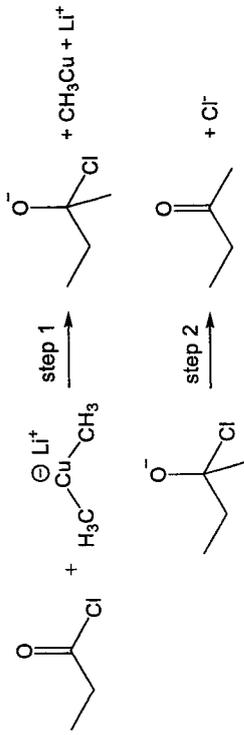
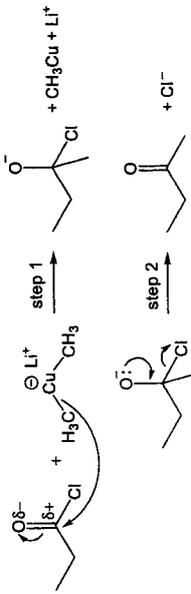


Fig. 1.1

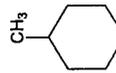
- (i) Draw four curly arrows on Fig. 1.1 to complete the mechanism. Include relevant lone pairs and partial charges. [2]



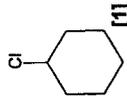
✓✓✓✓ 4 arrows, ✓ lone pair, ✓ partial charge

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]

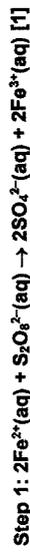


[1]

- (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]



[Total: 19]

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.



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	$[\text{C}_6\text{H}_5\text{CHClCH}_3] / \text{mol dm}^{-3}$	$[\text{OH}^-] / \text{mol dm}^{-3}$	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, $[\text{OH}^-]$ kept constant, $[\text{C}_6\text{H}_5\text{CHClCH}_3]$ 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 $\text{C}_6\text{H}_5\text{CHClCH}_3$ [1]

Comparing experiments 1 & 2, $[\text{C}_6\text{H}_5\text{CHClCH}_3]$ doubled from 0.05 mol dm⁻³ to 0.10 mol dm⁻³ and $[\text{OH}^-]$ 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 $[\text{C}_6\text{H}_5\text{CHClCH}_3]$, so zero order wrt $[\text{OH}^-]$. [1]

Hence, overall order = 1 + 0 = 1

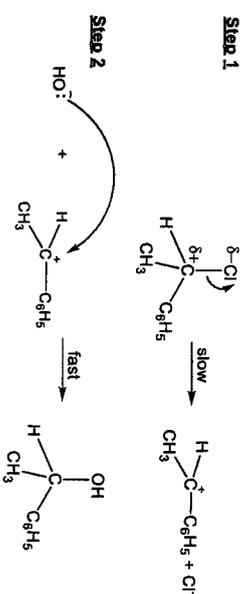
(ii) Write the rate equation for this reaction. [1]

$$\text{Rate} = k[\text{C}_6\text{H}_5\text{CHClCH}_3] \quad [1]$$

(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 $\text{C}_6\text{H}_5\text{CHClCH}_3$, concentration of $\text{C}_6\text{H}_5\text{CHClCH}_3$ 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]

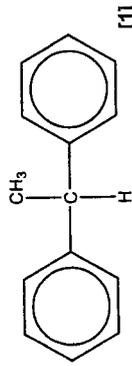
The positive charge on the C of the intermediate is dispersed into the benzene ring, resulting in the formation of a stable carbocation. [1]

- (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]

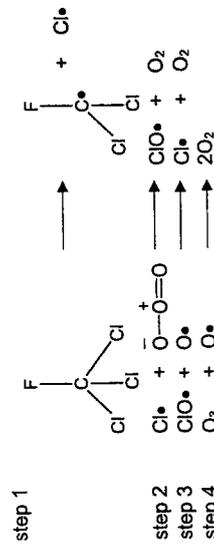
The intermediate is a carbocation which is trigonal planar about the positively charged C. The nucleophile OH⁻ can attack from the top and bottom of the plane with equal probability resulting in a racemic mixture. Hence product will be optically inactive.

2✓ = 1 mark

- (vii) The reaction was contaminated with a small amount of benzene to give a side product, C₁₄H₁₄. Suggest the structure of the side product. [1]



- (c) Chlorofluorocarbons, CFCs, such as CFC₁₂, 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.



- (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 CF₃CH₂F. 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 CF₃CH₂F 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]



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



Thermal stability decreases down the group: HCl > 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: HCl, 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]

$$E^\ominus_{\text{Fe}^{2+}/\text{Fe}} = +1.36 \text{ V}, E^\ominus_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.54 \text{ V}$$

$$E^\ominus_{\text{Fe}^{3+}/\text{Fe}} = -0.44 \text{ V}, E^\ominus_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.77 \text{ V}$$

$$\text{Fe to Fe}^{2+}: E^\ominus_{\text{cell}} = +0.54 - (-0.44) = +0.98 \text{ V} \checkmark$$

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

Iodine is only able to oxidise Fe to Fe²⁺ but not Fe³⁺. FeI₂ ✓ is formed.

$$\text{Fe to Fe}^{2+}: E^\ominus_{\text{cell}} = +1.36 - (-0.44) = +1.80 \text{ V} \checkmark$$

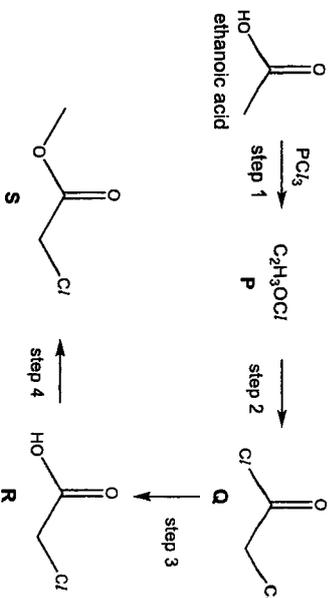
$$\text{Fe}^{2+} \text{ to Fe}^{3+}: E^\ominus_{\text{cell}} = +1.36 - (+0.77) = +0.59 \text{ V} \checkmark$$

Chlorine can further oxidise Fe²⁺ to Fe³⁺. FeCl₃ ✓/is formed as Cl₂ 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]



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

CH₃OH, concentrated H₂SO₄, heat [1]

(iii) Compare and explain the relative acidity of aqueous solutions of ethanoic acid, Q and R. [1]

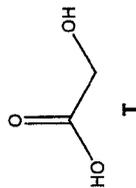
[1] Q > R > ethanoic acid

[✓] electronnegative / electron-withdrawing Cl disperses the negative charge on the anion of R (CH₂ClCOO⁻), [✓] stabilising the anion of R

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

[✓] Q hydrolyses / reacts in water to form a strong acid / HCl
2[✓] = [1]

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

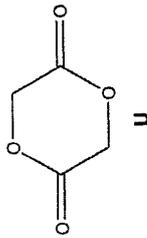
Use the *Data Booklet* to identify the chemical bonds responsible for the absorption at these wavenumbers and deduce the functional group present in **U**. Hence, state the type of reaction that has taken place to form **U**. [2]

[✓] 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.

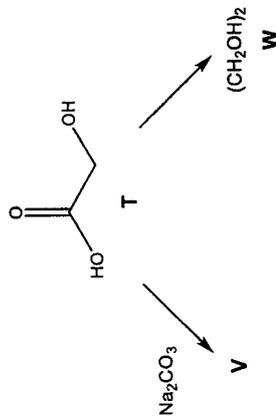
$2[\checkmark] = [1]$

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

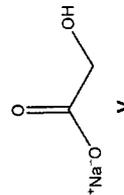


For information:

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



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



[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**, $\text{C}_6\text{H}_5\text{C/O}$, is optically active. Upon heating with excess sodium metal, **K** produces effervescence and compound **L**, $\text{C}_6\text{H}_5\text{O}$. 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 $\text{C}_2\text{H}_2\text{O}_4$ 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 $\text{Br}_2(\text{aq})$ and does not produce an orange solid with Brady's reagent	[✓] No electrophilic addition with $\text{Br}_2(\text{aq})$ [✓] 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 $\text{C}_2\text{H}_2\text{O}_4$ after acidifying the mixture.	[✓] Nucleophilic substitution with alkaline medium (NaOH) [✓] Oxidation with alkaline aqueous iodine [✓] Acid-base reaction	[✓] K has $\text{CH}_2\text{CH}(\text{OH})$ - group (cannot have CH_3CO - as part of ans as K can only have 1 OH group based on molecular formula)

$13[\checkmark]$ in total, $2[\checkmark] = 1$, max [6] for deductions

K is	L is	M is
		$-\text{OOC}-\text{COO}^-$ [1] Note: M is the salt BEFORE acidifying to form $\text{HOOC}-\text{COOH}$.

[3] for structures

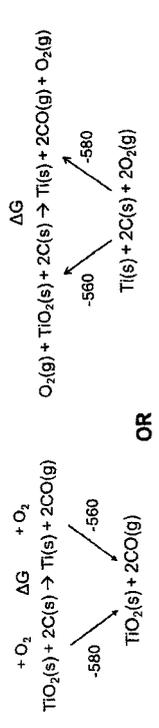
Reaction scheme (for info)

(b) Titanium can be obtained by the reduction of TiO₂ with carbon, via the reaction below.



(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, $\Delta G = -580 - (-560) = -20 \text{ kJ mol}^{-1}$ [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 ($\Delta G < 0$) once $\Delta G_{\text{reaction}(2)}$ becomes more negative than $\Delta G_{\text{reaction}(1)}$. [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 = 10⁵ 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).

$\Delta G = -RT \ln K_p$
 $-20000 = -(8.31)(2000) \ln K_p$
 $\ln K_p = 1.2033$
 $K_p = 3.33$ (or 2.47 using $\Delta G = -15 \text{ kJ mol}^{-1}$) [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 TiO₂ with carbon has a volume of 100 dm³.
 (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 = $\sqrt{3.33} = 1.82 \text{ bar} = 182000 \text{ Pa}$ (to 3sf) [1]

(v) Hence, calculate the equilibrium mass of titanium produced at 2000 K. [2]
 Applying ideal gas eqn for CO: $n = \frac{pV}{RT} = \frac{(1.82 \times 10^5)(100 \times 10^{-3})}{(8.31)(2000)} = 1.0980 \text{ mol}$ [1]

From reaction (4): $Ti(s) \equiv 2CO$
 Mass of Ti produced = $\frac{1.0980}{2} \times 47.9 = 26.3 \text{ g}$ (or 22.6 g if $\Delta G = -15 \text{ kJ mol}^{-1}$) [1]

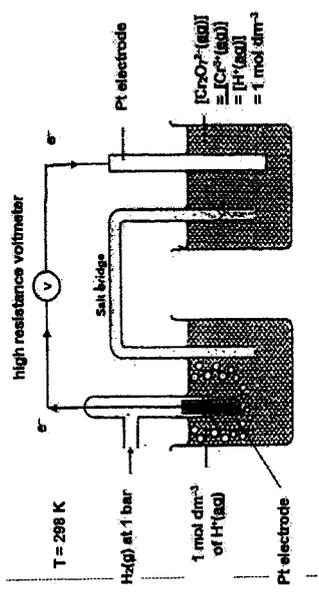
(d) The chemistry of carboxylic acids involves a range of reactions from their formation via oxidation to their conversion into other useful derivatives.

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]



(iii) The E_{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. [2]

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

$$E_{cell}^{\circ} = E_{red}^{\circ} - E_{ox}^{\circ}$$

$$+2.27 V = +1.33 - U$$

$$U = -0.94 V \quad [1] \text{ with working shown}$$

(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]



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_{cell}^o~~ 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

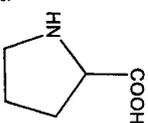
amino acid	abbreviation	formula of side chain
aspartic acid	asp	—CH ₂ CO ₂ H
glutamine	gln	—CH ₂ CH ₂ CONH ₂
phenylalanine	phe	—CH ₂ — 

(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

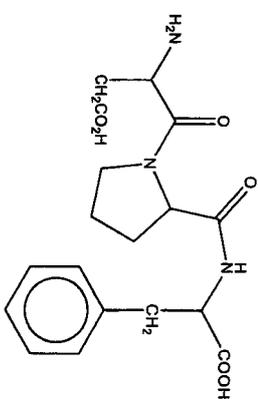
(b) (i)



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

[1]

Draw the structural formula of the tripeptide, asp-pro-phe.



[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 hydrolysis of J gave the following eight amino acids:
 - ala, arg, asp, gln, pro, tyr, 2 x 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

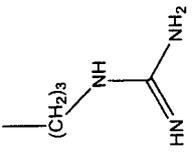
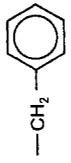
[1] : some working showing using enzyme hydrolysis

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

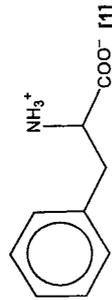
A mixture of arginine, aspartic acid and phenylalanine was placed at the center of the electrophoresis plate in a buffer solution of pH 6.0. A potential difference was then applied across the plate.

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 ₂ CO ₂ H	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]



(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]

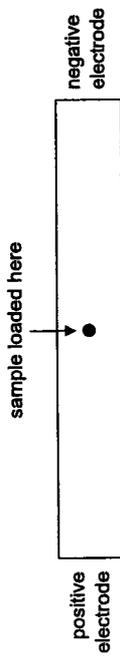


Fig. 5.1

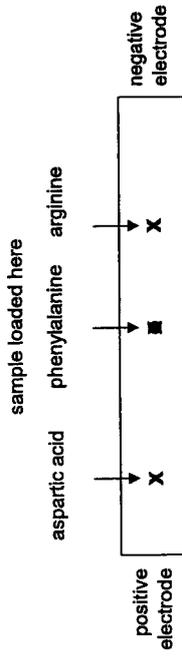
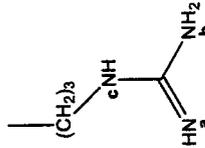


Fig. 5.1

- ✓ 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

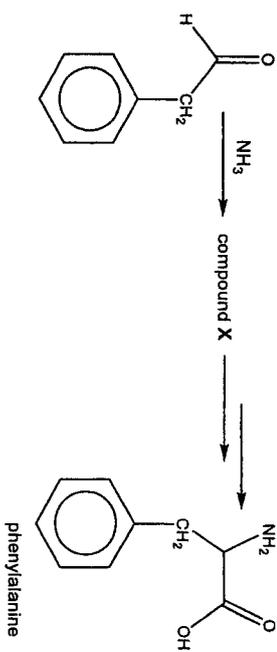
(iii) The side chain of arginine is shown.



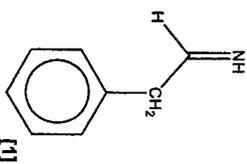
Nitrogen atoms, a, b and c, are all sp^2 hybridised. Only one of the nitrogen atoms will be protonated in an acidic medium. Identify which nitrogen atom would be protonated. Explain your answer. [1]

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. [1]

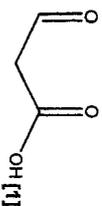
- (d) The Strecker method is a series of chemical reactions which synthesises an amino acid from an aldehyde as a starting material.



- (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]



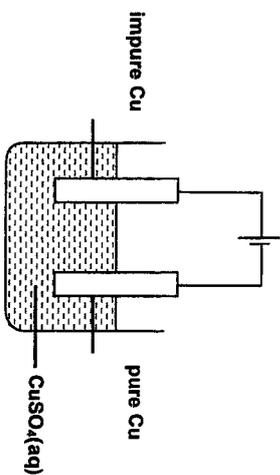
- (ii) A starting material, compound Y, can be used to prepare aspartic acid via the Strecker method. Suggest the structure of Y. [1]



- (e) Group 2 carbonates decompose when heated. Describe and explain the trend in the thermal stability of the Group 2 carbonates. [2]
 Hence, charge density of the cation decreases. ✓
Polarising power of cation decreases / resulting in less polarisation of the C-O bond in CO₃²⁻ 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 Cu²⁺ 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]

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

At the anode, Cu was oxidised over H₂O and Cu dissolved to form Cu²⁺ ions, which enter the electrolyte. ✓

Or

Oxidation at anode: Cu(s) → Cu²⁺(aq) + 2e⁻ (must mention oxidation at anode)

As E[⊖](Co²⁺/Co) is more negative/less positive than E[⊖](Cu²⁺/Cu), the cobalt impurity at the anode oxidised to form Co²⁺ ions, ✓ which entered the electrolyte/Co²⁺ ions not reduced at the cathode. ✓

M was not oxidised as its E[⊖] is more positive than E[⊖](Cu²⁺/Cu) and dropped to the bottom of the anode as 'anode sludge'. ✓

At the cathode, reduction of Cu²⁺ ions to Cu occurred due to more positive E[⊖](Cu²⁺/Cu) compared to E[⊖](H₂O/H₂) and E[⊖](Co²⁺/Co). ✓

or

Reduction at cathode: Cu²⁺(aq) + 2e⁻ → 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]



Amount of Cu deposited at cathode = $0.680 / 63.5 = 0.0107 \text{ mol}$

Amount of electrons, $n_e = 0.0107 \times 2 = 0.0214 \text{ mol}$

$$Q = It = n_e F$$

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

- (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]

$$F = Le$$

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

$$= 5.96 \times 10^{23} \text{ mol}^{-1} \text{ [1]}$$

- (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)

$$= 4.62 \times 10^{-4} \text{ mol}$$

$$\text{Mass of Co} = 4.62 \times 10^{-4} \times 58.9 = 0.0272 \text{ g } \checkmark$$

$$\text{Amount of Cu oxidised} = \frac{0.680}{63.5} - 4.62 \times 10^{-4} = 0.0102 \text{ mol } \checkmark$$

$$\text{Mass of Cu} = 0.0102 \times 63.5 = 0.648 \text{ g } \checkmark$$

$$\text{Mass of M} = 0.714 - 0.0272 - 0.648 = 0.0388 \text{ g } \checkmark$$

$$2 \checkmark = 1 \text{ mark}$$

[Total: 20]