

Answer Key

B	A	A	B	D	D	C	B	C	D
D	C	C	B	A	A	A	C	D	B
D	C	D	B	A	A	C	B	C	D

✓	3	$[PCl_4]^+$ Bond angle 109.5°
✗	4	SF_6 Bond angle 90°

1	B	Given: angle of deflection $\propto \frac{q}{m}$ $+15^\circ = k\left(\frac{q}{m}\right)$ $k = +15$ $-5^\circ = +15\left(\frac{q}{m}\right)$ $\frac{q}{m} = -\frac{1}{3}$
✗	A	$q = 0$ $m = +2 = 3$ $\frac{q}{m} \neq -\frac{1}{3}$
✓	B	$q = +3 = -2$ $m = 3+3 = 6$ $\frac{q}{m} = -\frac{2}{3}$
✗	C	$q = +4 = +3$ $m = 4+5 = 9$ $\frac{q}{m} \neq -\frac{1}{3}$
✗	D	$q = +4 = -3 = +1$ $m = 4+5 = 9$ $\frac{q}{m} \neq -\frac{1}{3}$

2	A	Interpretation of the graph: C is likely to be in Group 1 since it has the lowest r_1 . E, since the four elements are consecutive, B is in Group 18 and A is in Group 17.
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3	A	Os Bond angle <120°
✗	2	PF_5 Bond angles 90°, 120°

4	B	 This hydrocarbon is a non-polar molecule.
✗	A	 This hydrocarbon is a non-polar molecule.
✓	B	The C=O bond has a relatively large dipole moment (due to the large difference in the electronegativities of carbon and oxygen) and there are no other significantly polar bonds to offset the dipole moment of the C=O bond. Thus, the molecule has the largest overall dipole moment among the four options.
✗	C	 C-C bond is polar but the dipole moments cancel out.
✗	D	C=O bond is more polar than C-C bond as O is more electronegative than C, but since both bonds are polar, there will be some degree of offset of dipole moments of the bonds, hence this molecule does not have the largest overall dipole moment among the four options.

5	D	Both CO_2 and C_2 are non-polar molecules with weaker instantaneous dipole-induced dipole interactions (I-d-I) as compared to CH_3OH and N_2H_4 , which have stronger intermolecular hydrogen bonding. N_2H_4 has more extensive hydrogen bonds (an average of 2 H-bonds per molecule), hence CH_3OH (an average of 1 H-bond per molecule), than N_2H_4 exhibit greatest deviation from ideal gas behaviour.
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	Per molecule	$CH_3-C(=O)-H$	$H-N(=O)-N(=O)-H$
	Total no. of H atoms bonded to O/N	1	4
	No. of lone pairs on atom(s)	2	2
	Average no. of H bonds possible	1	2

6	D	Possible identities of X: $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ Possible identities of Y: Al_2O_3 is insoluble in water but is amphoteric, however one mole of Al_2O_3 requires 6 moles of H^+ for neutralisation. $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$ hence, options A and B are incorrect as they do not match the required mole ratio stated in the question with both given options for X. $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ Since, one mol of H_2SO_4 is completely neutralised by two mol of $NaOH$, oxide X is SO_3 and oxide Y is Na_2O .
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7	C	Polarizability pertains to ease of distortion of the anion's electron cloud and since the anion is the same, i.e. CO_3^{2-} , in both compounds, the polarisability factor is the same in both. Melting is not the same as thermal decomposition/thermal stability. Melting point involves change in states, not chemical composition. Since ionic radius of Ca^{2+} is smaller than that of Ba^{2+} , the charge density of Ca^{2+} is higher. charge density $\propto \left \frac{q}{r_1} \right $
✓	C	Ca^{2+} has a greater polarising power and distorts the electron cloud of CO_3^{2-} anion to a greater extent. The C-O covalent bond within the CO_3^{2-} anions in $CaCO_3$ is weakened to a greater extent as compared to that in $BaCO_3$. Hence $CaCO_3$ decomposes at a lower temperature. Lattice energy is a measure of the ionic bond strength in metal carbonates and is not a measure of their thermal stability.
✗	D	Lattice energy is a measure of the ionic bond strength in metal carbonates and is not a measure of their thermal stability.

8	B	Volatility is defined as the tendency of a substance to vapourise. Since the halogens exist as non-polar simple covalent molecules, the volatility of the halogens depends on the strength of the instantaneous dipole-induced dipole (I-d-I) interactions between molecules. Both bond length and bond strength are about the same for Cl_2 and I_2 . The covalent bond between the atoms in the halogen molecule. Thus, these factors do not affect volatility. Each halogen molecule is comprised of two identical elements from Group 17. Since the elements present in each molecule is identical, the resultant halogen molecule is non-polar. Hence the electronegativity of the halogen atom has no effect on the strength of the I-d-I interactions. Strength of I-d-I interactions increases when number of electrons in the molecule increases due to greater ease of distortion of the larger electron cloud. Hence, this statement is correct.
✗	4	Strength of I-d-I interactions increases when number of electrons in the molecule increases due to greater ease of distortion of the larger electron cloud. Hence, this statement is correct.

9	C	$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ $n(H_2SO_4) = \frac{30}{1000} \times 0.1 = 0.003 \text{ mol}$ $n(NaOH) = \frac{40}{1000} \times 0.2 = 0.008 \text{ mol}$ H_2SO_4 is the limiting reagent. $n(H_2O) = 2 \times n(H_2SO_4) = 2 \times 0.003 = 0.006 \text{ mol}$ Heat released from the reaction = $n(H_2O) \times \Delta H_{mol} = 0.006 \times 57.3 \times 1000 = 343.8 \text{ J}$ = heat absorbed by the solution $343.8 = 70 \times 1 \times 4.2 \times \Delta T $ $ \Delta T = 1.2^\circ C$ Since heat is absorbed by the solution, $\Delta T = +1.2^\circ C$.
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10	D	ΔH ΔS ΔG - when temperature is high enough such that $ \Delta S > \Delta H $ - at all temperatures not just at low T - when temperature is high enough such that $ \Delta S > \Delta H $ - at all temperatures
✗	A	- when temperature is high enough such that $ \Delta S > \Delta H $
✗	B	- at all temperatures not just at low T
✗	C	- when temperature is high enough such that $ \Delta S > \Delta H $
✓	D	- at all temperatures

10	D	From the Data Booklet, $\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}$ $\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}$ $E_{\text{cell}} = +1.77 - (+0.68)$ $= +1.09 \text{ V} > 0$ Overall equation: $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ H_2O_2 undergoes disproportionation where the oxidation state of O increases from -1 in H_2O_2 to 0 in O_2 and decreases from -1 in H_2O_2 to -2 in H_2O . Both MnO_4^- and Fe^{3+} are oxidising agents and will not react. From the Data Booklet, both species are on the left-hand side of the equation and show tendency to undergo reduction. $\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^- \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O}$ $\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+}$ E^\ominus / V $+1.52$ $+0.77$	✓
11	1	From the Data Booklet, $\text{I}_2 + 2\text{e}^- \rightleftharpoons 2\text{I}^-$ $\text{S}_2\text{O}_8^{2-} + 2\text{e}^- \rightleftharpoons \text{S}_2\text{O}_8^{2-}$ $E_{\text{cell}} = +0.54 - (+0.09)$ $= +0.45 \text{ V} > 0$ Overall equation: $\text{I}_2 + \text{S}_2\text{O}_8^{2-} \rightarrow 2\text{I}^- + \text{S}_2\text{O}_8^{2-}$ I_2 oxidises $\text{S}_2\text{O}_8^{2-}$ to give $\text{S}_2\text{O}_8^{2-}$ while $\text{S}_2\text{O}_8^{2-}$ reduces I_2 to give I^- . Let the oxidation state of C in HC_2O_4^- be x . $(+1) + 2x + 4(-2) = -1$ $\Rightarrow x = +3$ Note: The oxidation state of both C atoms in HC_2O_4^- can be determined by the calculation above since they are bonded to O atoms in the same way. The oxidation state of each atom is indicated below. $\begin{array}{c} \text{O} \\ \parallel \\ \text{H} - \text{C} - \text{C} - \text{O}^- \\ \parallel \quad \parallel \\ \text{O} \quad \text{O} \end{array}$	✓
12	C	The proposed reaction mechanism must fulfill two criteria: 1. Given that rate = $k[\text{NO}]^2[\text{H}_2]$, the slow step should involve two NO molecules and one H_2 molecule. 2. The overall equation should contain the products N_2 and H_2O only, as given in the question.	✓

Mathematically,
 $\text{rate}_2 = k[\text{K}]_{\text{impact}}^x [\text{L}]_{\text{impact}}^y [\text{M}]_{\text{impact}}^z$
 $\text{rate}_3 = k[\text{K}]_{\text{impact}}^x [\text{L}]_{\text{impact}}^y [\text{M}]_{\text{impact}}^z$
 $0.25 = k(0.0050)^x (0.08)^y (0.40)^z$
 $0.50 = k(0.0050)^x (0.04)^y (0.80)^z$
 $\frac{1}{2} = \frac{(0.08)^y (0.40)^z}{(0.04)^y (0.80)^z}$
 $\frac{1}{2} = (2)^y \left(\frac{1}{4}\right)^z$
 $2^1 = (2)^y$
 $y = 1$
 $\therefore \text{rate} = k[\text{K}]^1[\text{M}]^2$

14 B
 $K_c = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2}$

	$2\text{NO}_2(\text{g})$	\rightleftharpoons	$2\text{NO}(\text{g})$	+	$\text{O}_2(\text{g})$
Initial n / mol	2.50		0		0
Change in n / mol	-1.056		+1.056		+0.528
Eqm n / mol	1.444		1.056		0.528

 $K_c = \frac{(1.056)^2 (0.528)}{(1.444)^2 (0.8)} = 0.35296 = 0.353 \text{ dm}^3 \text{ mol}^{-1}$

15 A
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$
 $K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$
 * 1 If the stoichiometric coefficients are halved, $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$
 $K_c' = \frac{[\text{SO}_3]}{[\text{SO}_2][\text{O}_2]^{1/2}} = K_c^{1/2} = \frac{1}{\sqrt{2}} K_c$
 * 2 At dynamic equilibrium, the rates of the forward and backward reactions are equal but not zero.
 By Le Chatelier's Principle, when pressure increases, the position of equilibrium shifts to the right to produce less moles of gas, favouring the forward reaction. Hence, more moles of SO_3 will be produced.
 By Le Chatelier's Principle, when temperature is reduced, position of equilibrium shifts to the right to favour the forward exothermic reaction to produce heat. Rates of the forward and backward reaction will decrease but the rate of the forward reaction is decreased to a smaller extent.
 * 3
 * 4

16 A
 In order for end-point to be determined, the transition range of the indicator should fall within the region of sharp pH change.
 For the first end-point, the sharp pH change occurs between 5.33 and 9.73. Hence, a suitable indicator would be bromothymol blue. Thymolphthalein will not be suitable as its colour would have changed before the first equivalence point is reached.
 For the second end-point, the ethyl orange would be a suitable indicator as its pH range is below 5.33. Methyl red will not be suitable since its colour would have changed before the second equivalence point is reached.

17 A
 The colours of the silver halides and their solubilities in concentrated aqueous ammonia are shown below.

AgX	colour	solubility in concentrated NH_3
AgCl	white	soluble
AgBr	cream	soluble
AgI	yellow	insoluble

Hence, beaker 1 should be colourless. Yellow precipitates should be observed for beakers 2 and 3.

18 C
 * A Half (or fish-hook) arrows should be used to represent homolytic fission and the movement of the lone electron in the chlorine radical.
 A full arrow should be used to represent the bond formation between OH^- and electrophilic carbon atom. Similarly, the heterolytic fission of C-Br bond should be represented by a full arrow to indicate the transfer of an electron pair to Br.
 * B Electron movement is represented correctly using half arrows.
 * C Electron move from regions of high electron density to low electron density. The full arrow should point from the lone pair of electrons on OH^- to the electrophilic carbon.
 * D The transfer of electrons to electrophilic C from heterolytic fission of C-Br bond is incorrect as a bromide ion, Br^- , is formed. This is indicative that the electron pair of the C-Br bond was transferred to Br.

19 D
 * A A racemic mixture contains equal proportions of each enantiomer. They cancel out each other's rotation of plane-polarised light and hence there is no overall effect. It is therefore optically inactive.
 * B Enantiomers have identical physical properties except that in the way they rotate plane-polarised light. Hence, they have the same melting points.
 * C Enantiomers have different biological behaviour in the human body.

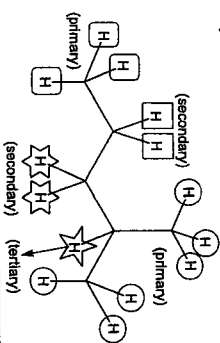
Does not fulfil both criteria:
 * Only two NO molecules involved in the slow step, missing one H_2 molecule.
 * Final products are N_2O and H_2O , not N_2 and H_2O .
 Does not fulfill criterion (1):
 * Only one NO molecule and one H_2 molecule involved in slow step, missing one NO molecule.
 Fulfills both criteria.
 Does not fulfill (2):
 * Products of the reaction are N_2 and H_2O_2 , not N_2 and H_2O .

13 C
 Let the orders of reaction with respect to K, L and M be x, y and z respectively.
 $\text{rate} = k[\text{K}]^x[\text{L}]^y[\text{M}]^z$
 Comparing experiments 1 and 2, keeping [L] and [M] constant, when [K] is decreased by a factor of 2.5, relative rate decreases by a factor of 2.5. Hence, reaction is 1st order with respect to K (i.e. x = 1).
 Comparing experiments 2 and 3, keeping [L] constant, when [K] is increased by a factor of 5 while [M] is halved, relative rate increased by a net factor of 1.25. Since the reaction is first order with respect to K, relative rate should have increased by a factor of 5. Hence, halving [M] have increased the relative rate to decrease by a factor of 4 (i.e. $5 \div 1.25 = 4$). Reaction is second order with respect to M, i.e. z = 2.

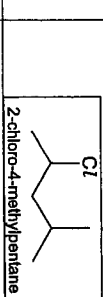
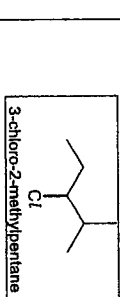
Mathematically,
 $\text{rate}_2 = k[\text{K}]_{\text{impact}}^x [\text{L}]_{\text{impact}}^y [\text{M}]_{\text{impact}}^z$
 $\text{rate}_3 = k[\text{K}]_{\text{impact}}^x [\text{L}]_{\text{impact}}^y [\text{M}]_{\text{impact}}^z$
 $0.20 = k(0.0010)^x (0.08)^y (0.80)^z$
 $0.25 = k(0.0050)^x (0.08)^y (0.40)^z$
 $\frac{4}{5} = \frac{1(0.8)^z}{5(0.4)^z}$
 $4 = (2)^z$
 $z = 2$
 Comparing experiments 3 and 4, keeping [K] constant, when [L] is halved while [M] is doubled, relative rate increased by a net factor of 2. Since reaction is second order with respect to M, rate should have increased by a factor of 4. Hence, halving [L] have resulted the relative rate to decrease by a factor of 2 (i.e. $4 \div 2 = 2$). Reaction is first order with respect to L, i.e. y = 1.

D Enantiomers have identical physical properties except that they rotate plane polarised light in opposite directions. Hence, they have the same solubility in the same solvent.

20 B The hydrogen atoms can be classified based on the carbon atom i.e. whether it is primary, secondary or tertiary.

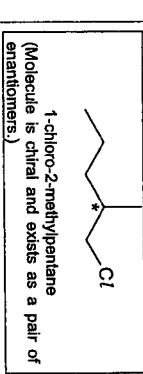
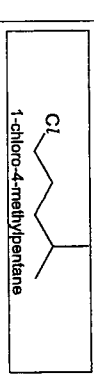


There are two distinct groups of secondary hydrogen atoms as the secondary carbon atoms are bonded to different groups. The monosubstituted chloroalkanes formed by free radical substitution are isomers.



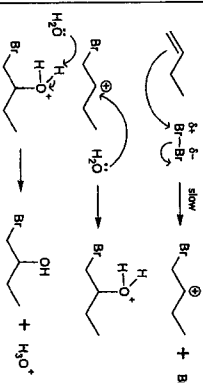
Since there exists only one tertiary hydrogen atom, the relative proportion of tertiary monochloroalkane will be the smallest.

There are three isomeric primary monochloroalkane products. Their structures are shown below.



He radicals are not formed during free radical substitution. Only Cl• and alkyl radicals are formed in the propagation step.

21 D

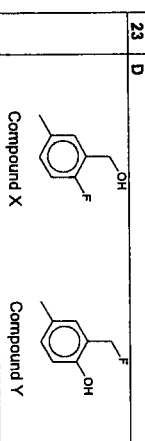


1 Two molecules are involved in the slow step. Overall order of reaction is 2.
2 See step 2. Water is a nucleophile as it donates its lone pair of electrons on O to the positively charged C atom of the carbocation.
3 See step 1. The intermediate formed is a trigonal planar carbocation.
4 See step 1 which forms the more stable secondary carbocation as compared to the primary carbocation shown below.

Also, water is in excess as compared to the Br⁻ formed in step 1. As such, water participates in step 2 to generate the major product, not Br⁻.

22 C A Lewis acid catalyst is required to generate a stronger electrophile. For example, $FbBr_3 + Br_2 \rightarrow FbBr_2^+ + Br^-$

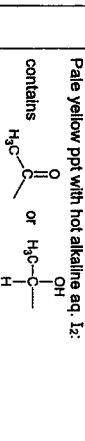
The electrophile Br⁺ reacts with the nucleophilic aromatic ring to form 5 atoms with sp² hybridisation (with five p orbitals overlapping) and 1 atom with sp³ hybridisation (which contains 4 σ bonds including the newly formed σ bond with the Br). Hence, the 'U-shape' should have its opening pointing to the sp³ hybridised atom.



A Add Br₂ in CCl₄. Compound X: No decolourisation of orange-red Br₂ (due to presence of phenol).
B Compound X: No violet complex formed (due to presence of phenol).
C Warm with K₂Cr₂O₇(aq) and H₂SO₄(aq). Compound X: orange solution turns green (due to oxidation of primary alcohol).
D Compound Y: orange solution remains (phenols and alkyl side chains do not undergo oxidation with K₂Cr₂O₇).

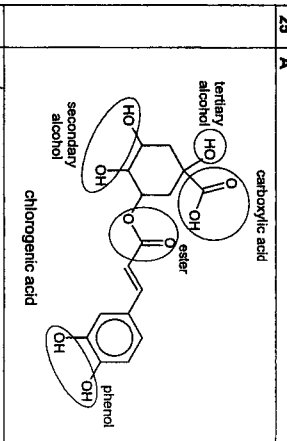
D Warm with KOH(aq), then add excess HNO₃(aq) followed by AgNO₃(aq). C-F bonds are considered inert (due to their high bond strength) and hence the F atoms in both compounds do not get substituted by the OH⁻ ions in KOH.

24 B No reddish-brown ppt with Fehling's solution. No aliphatic aldehyde.



The C=O belongs to the ester functional group and will not give a positive iodoform test. In the presence of hot alkali, the hydrolysis of the ester can occur. This forms a carboxylate ion and an alcohol. Both do not give a positive iodoform test too.

A Structure does not contain an aliphatic aldehyde. The secondary alcohol has the appropriate structure which will give a positive iodoform test.
B Aliphatic aldehyde is present. A reddish-brown ppt. will be formed with Fehling's solution.
C Benzaldehyde. Gives no reddish-brown ppt with Fehling's solution but will also not give a positive iodoform test.
D

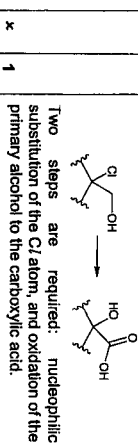


Heating in the presence of a dilute acid will result in acid hydrolysis of the ester to give two organic products.

A Note: In addition to acid hydrolysis, there will be oxidation of the secondary alcohol groups on the organic product with the cyclohexane ring. Only 1 mol of carboxylic acid functional group is present, per mol of chlorogenic acid. Only 0.5 mol of CO₂ is produced.
B RCOOH + ½Na₂CO₃ → RCOO⁻Na⁺ + ½CO₂ + ½H₂O
 Only the 2 phenolic groups and the carboxylic acid will undergo neutralisation with NaOH. The alcohols remain unreacted. Hence, 1 mol of chlorogenic acid only reacts with 3 mol of NaOH(aq) at room temperature.

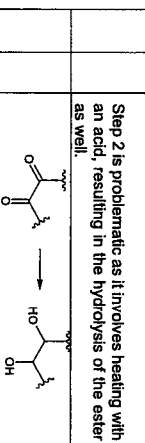
D Note: the ester functional group will react with NaOH(aq) via alkaline hydrolysis if heating is involved. Only the 2 phenolic groups and the 3 alcohol groups will undergo condensation with ethanoyl chloride. Hence, 1 mol of chlorogenic acid only reacts with 5 mol of ethanoyl chloride.

26 A The diagrams below show the isolated part of starting reagent that needs to react for the synthesis of chlorogenic acid to happen. For the synthesis to be feasible, the other parts of the molecule need to remain unreacted.



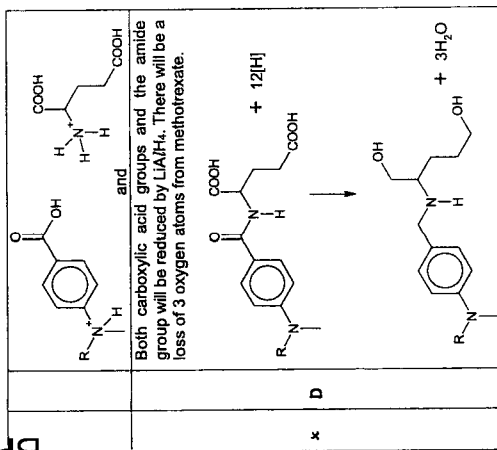
1 Two steps are required: nucleophilic substitution of the Cl atom, and oxidation of the primary alcohol to the carboxylic acid.
2 These two steps are problematic as both involve heating with a base or an acid. This will result in the hydrolysis of the ester group as well. In addition, the oxidation process will also oxidise the secondary alcohol groups on the six-membered carbon ring.

2 Two steps are required: nucleophilic addition (adding HCN to the ketone), and acid hydrolysis to convert the nitrile to the carboxylic acid.
3 Step 2 is problematic as it involves heating with an acid, resulting in the hydrolysis of the ester as well.



One step required: reduction of ketones to secondary alcohols
3 The use of LiAlH₄ is problematic as it will result in the reduction of the carboxylic acid (and the ester). However, we can use NaBH₄ in this synthesis. It will allow for the selective reduction of the ketones only, as it is not strong enough to reduce the carboxylic acid (and the ester).

27 C The amine containing N1 is a tertiary amine. It cannot undergo condensation with ethanoyl chloride.
A No belongs to an amide functional group. Amides are neutral due to the unavailability of the lone pair of electrons for donation.
B Heating with aq. H₂SO₄ involves two reactions: acid hydrolysis of the amide group and neutralization of any basic groups.
C Both products are cationic.



28 B Before the addition of NaCN(s)
 $E_{\text{Ag}^+/\text{Ag}}^\ominus = +0.80 \text{ V}$
 $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\ominus = +0.77 \text{ V}$

Since $E_{\text{Ag}^+/\text{Ag}}^\ominus$ is more positive than $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\ominus$, reduction happens in half-cell 1 and oxidation happens in half-cell 2.

$E_{\text{cell}}^\ominus = +0.80 - (+0.77) = +0.03 \text{ V}$

Electrons flow from half-cell 2 to half-cell 1. The cathode increases in mass as $\text{Ag}^+(\text{aq})$ is reduced to Ag(s) and is deposited onto the cathode.

After the addition of excess NaCN(s)
 $E_{\text{Ag}^+/\text{Ag}}^\ominus = +0.80 \text{ V}$
 $E_{\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}}^\ominus = +0.36 \text{ V}$

Since $E_{\text{Ag}^+/\text{Ag}}^\ominus$ is more positive than $E_{\text{Fe(CN)}_6^{3-}/\text{Fe(CN)}_6^{4-}}^\ominus$, reduction still happens in half-cell 1 and oxidation still happens in half-cell 2 (i.e. no change in polarity of electrodes).

$E_{\text{cell}}^\ominus = +0.80 - (+0.36) = +0.44 \text{ V}$
 (cell potential becomes more positive)

Electrons still flows from half-cell 2 to half-cell 1. The cathode continues to increase in mass as $\text{Ag}^+(\text{aq})$ is reduced to Ag(s) and is deposited onto the cathode.

29 C	At the anode: $E_{\text{Zn}^{2+}/\text{Zn}}^\ominus = -0.76 \text{ V}$ $E_{\text{Cu}^{2+}/\text{Cu}}^\ominus = +0.34 \text{ V}$ $E_{\text{Ag}^+/\text{Ag}}^\ominus = +0.80 \text{ V}$	At the cathode: $E_{\text{Cu}^{2+}/\text{Cu}}^\ominus = +0.34 \text{ V}$ $E_{\text{Zn}^{2+}/\text{Zn}}^\ominus = -0.76 \text{ V}$ $E_{\text{H}_2\text{O}/\text{H}_2}^\ominus = -0.83 \text{ V}$
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✓	1	Since $E_{\text{Cu}^{2+}/\text{Cu}}^\ominus$ is the most positive, Cu^{2+} will be preferentially reduced at the cathode.
✓	2	Since $E_{\text{Zn}^{2+}/\text{Zn}}^\ominus$ is the most negative, Zn will be preferentially oxidised at the anode, followed by Cu.
x	3	The cell voltage must be adjusted such that Ag does not get oxidised i.e. only copper and metals with less positive E^\ominus than $E_{\text{Cu}^{2+}/\text{Cu}}^\ominus$ are preferentially oxidised.

30	D	Electronic configuration of Fe^{3+} : $[\text{Ar}]3d^5$
x	A	Arrangement of electrons in 3d orbitals: $\uparrow \uparrow \uparrow \uparrow \uparrow$
x	B	Electronic configuration of Cu^{2+} : $[\text{Ar}]3d^9$
x	C	Arrangement of electrons in 3d orbitals: $\uparrow \uparrow \uparrow \uparrow \uparrow$
✓	D	Electronic configuration of Ni^{2+} : $[\text{Ar}]3d^8$
		Arrangement of electrons in 3d orbitals: $\uparrow \uparrow \uparrow \uparrow \uparrow$



DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

Suggested Solutions

H2 CHEMISTRY

Paper 2 Structured Questions

9729/02

13 September 2022

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer all questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

A Data Booklet is provided.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
1	12
2	12
3	14
4	16
5	21
Total	75

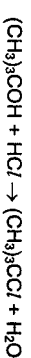
Answer all the questions in the spaces provided.

- 1 (a) Describe the thermal decomposition of the hydrogen halides HCl, HBr and HI and explain any variation in their thermal stabilities. [3]

Hydrogen halides thermally decompose to give its constituent elements / show equation: $2HX \rightarrow H_2 + X_2$.
HCl does not decompose even on strong heating. HBr decomposes on strong heating while HI decomposes readily in the presence of a hot rod.

Thermal stability decreases in the order $HCl > HBr > HI$ as bond energy / bond strength of the H-X bond decreases from HCl to HBr to HI. As such, decreasing amount of energy is required to decompose the hydrogen halide from HCl to HI.

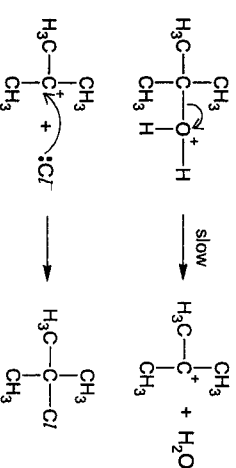
- (b) Tert-butyl alcohol reacts with hydrogen chloride according to the equation shown.



This reaction occurs in three steps.

- step 1 protonation of -OH group in $(CH_3)_3COH$ to produce $(CH_3)_3COH_2^+$ cation
step 2 loss of H_2O molecule from $(CH_3)_3COH_2^+$ to produce a carbocation
step 3 chloride ion reacts with carbocation to produce $(CH_3)_3CCl$

- (i) Describe the mechanisms which occur in steps 2 and 3. Use curly arrows to show the movement of electrons and label the slow step. [3]



- (ii) An enantiomerically pure alcohol, where the carbon atom bonded to the -OH group is chiral, was used for the reaction in (b).
Use your answer in (b)(i) to deduce the stereochemical outcome of this reaction. Explain your reasoning. [2]

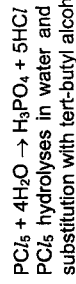
The reaction will produce a racemic mixture / the product will be formed as a 50 : 50 mixture of enantiomers.

This document consists of 18 printed pages.

The carbocation intermediate is (trigonal) planar around the positively charged C atom. The chloride ion can attack the positively charged C atom from the top and bottom of the plane with equal probability.

Tert-butyl alcohol also reacts with solid phosphorus pentachloride, PCl_5 , to produce $(\text{CH}_3)_3\text{CCl}$.

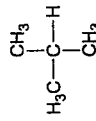
(iii) With the aid of a suitable equation, explain why the reaction is not carried out in aqueous medium. [2]



(c) $(\text{CH}_3)_3\text{CCl}$ is one of the two monochlorinated products of the reaction between an alkane, **X**, and chlorine gas in the presence of UV light.

(i) Draw the structure of the alkane, **X**, and state the IUPAC name of the other monochlorinated product. [1]

Structure of Alkane, **X**:



Name of the other monochlorinated product:
1-chloro-2-methylpropane

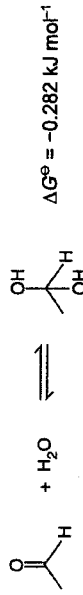
(ii) The rate of formation of $(\text{CH}_3)_3\text{CCl}$ is faster than that of the other monochlorinated product.

Suggest an explanation for the different rates of reaction. [1]

$(\text{CH}_3)_3\text{CCl}$ is formed from a tertiary radical intermediate, $(\text{CH}_3)_3\text{C}^\bullet$, which is more stable than the primary radical intermediate, $(\text{CH}_3)_2\text{CHCH}_2^\bullet$, that forms the other monochlorinated product, $(\text{CH}_3)_2\text{CHCH}_2\text{Cl}$.

[Total: 12]

2 (a) The following equilibrium occurs when ethanal is mixed with water.



Use relevant data from the *Data Booklet* to calculate the equilibrium constant, K , for the reaction. [2]

$$\Delta G^\ominus = -RT \ln K$$

$$(-0.282 \times 10^3) = -(8.31)(298) \ln K$$

$$\ln K = 0.11388$$

$$K = e^{0.11388} = \underline{1.12}$$

(b) The aldol reaction is a useful reaction that forms a carbon-carbon bond between two carbonyl compounds. For example, two ethanal molecules can be combined using the aldol reaction.

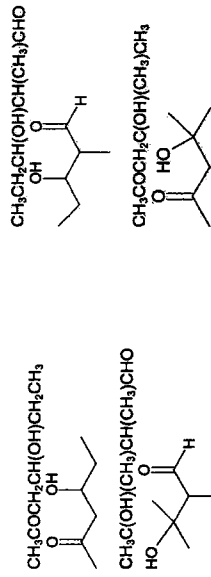
The carbonyl carbon, **a**, of one ethanal molecule forms a covalent bond with a carbon atom, **b**, of another ethanal molecule. Carbon atom, **b**, must be adjacent to carbonyl carbon, **c**.



(i) When different carbonyl compounds are used in an aldol reaction, a mixture of structural isomers is formed.

Suggest two possible structural isomers that can be formed if propanone, CH_3COCH_3 , and propanal, $\text{CH}_3\text{CH}_2\text{CHO}$, are mixed. [2]

Any two of the following:



(ii) Both propanal and propanoic acid can be formed from propan-1-ol in the same reaction.

Describe the reagents and conditions needed to ensure that the reaction yields propanal as the major product. [2]

Heat propan-1-ol with $K_2Cr_2O_7$, $H_2SO_4(aq)$ with immediate distillation to collect mainly propanal as distillate.

- (g) Some tin reagents are useful in organic chemistry.

Tin forms two chlorides, $SnCl_2$ and $SnCl_4$.

- (i) A mixture of these chlorides was found to contain 50.0% by mass of tin. Calculate the percentage by mass of $SnCl_2$ in the mixture. [3]

Relative formula mass of $SnCl_2 = 189.7$

Relative formula mass of $SnCl_4 = 260.7$

Percentage by mass of Sn in $SnCl_2 = \frac{118.7}{189.7} \times 100 = 62.572\%$

Percentage by mass of Sn in $SnCl_4 = \frac{118.7}{260.7} \times 100 = 45.531\%$

Let y be the fraction of mass of $SnCl_2$ in the sample.

$$y \left(\frac{62.572}{100} \right) + (1-y) \left(\frac{45.531}{100} \right) = \frac{50}{100}$$

$$y = 0.26229$$

percentage by mass of $SnCl_2$ in the sample = $0.26229 \times 100 = 26.2\%$

- (ii) Tin exists in +2 or +4 oxidation states in many of its compounds. Great care must be taken to ensure the correct oxidation state of tin is formed.

A student proposed the following preparation methods to prepare the two chlorides, $SnCl_2$ and $SnCl_4$.

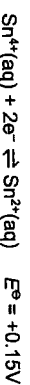
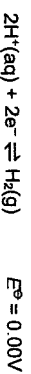
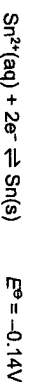
Preparation method for $SnCl_2$

Heating tin with hydrochloric acid produces hydrogen gas. Careful evaporation of the water and dehydration produces white solid $SnCl_2$.

Preparation method for $SnCl_4$

Passing chlorine gas over heated tin produces colourless liquid $SnCl_4$ as the only product.

Explain if the preparation methods proposed above are feasible without reference to any calculation. Use relevant standard electrode potentials from the *Data Booklet*. [3]



The preparation method of $SnCl_2$ proposed is feasible.

$E^\ominus_{H^+/H_2}$ is more positive than $E^\ominus_{Sn^{2+}/Sn}$ but less positive than for $E^\ominus_{Sn^{4+}/Sn^{2+}}$. Hence H^+ can oxidise Sn to Sn^{2+} to form $SnCl_2$ but cannot oxidise Sn^{2+} to Sn^{4+} .



The preparation method of $SnCl_4$ proposed is feasible.

$E^\ominus_{Cl_2/Cl^-}$ is more positive than both $E^\ominus_{Sn^{2+}/Sn}$ and $E^\ominus_{Sn^{4+}/Sn^{2+}}$. Hence Cl_2 can oxidise Sn to Sn^{4+} to form $SnCl_4$.

[Total: 12]

- 3 (a) Compound **N**, $C_3H_4O_3$, liberates a gas when treated with aqueous sodium carbonate.
(i) Identify the gas and state the functional group that is present in compound **N**. [1]

Gas is carbon dioxide.

Functional group: carboxylic acid / -COOH group

When 0.10 cm^3 of liquid compound **N** was dissolved in an inert solvent and an excess of sodium metal added, 15 cm^3 of gas was produced at 303 K and 1 atm.
[Density of compound **N** = 1.093 g cm^{-3}]

- (ii) Calculate the ratio of the amount of compound **N** reacted to the amount of gas that is produced. [1]

mass of **N** = $0.10 \times 1.093 = 0.1093 \text{ g}$
moles of **N** = $0.1093/88 = 0.0012420 \text{ mol}$

moles of gas = $\frac{(101325)(15 \times 10^{-6})}{(8.31)(303)} = 0.00060362 \text{ mol}$

mole ratio of **N** : gas = $0.0012420 : 0.00060362 \approx 2 : 1$

- (iii) Use your answers in (a)(i) and (a)(ii) to suggest **two** possible structures of compound **N**. Explain your reasoning. [3]

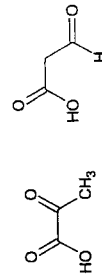
From (a)(ii),

since mole ratio of **N** : H_2 gas $\approx 2 : 1$, one mole of **N** undergoes redox / acid-metal reaction to produce 0.5 mole of H_2 gas. Hence, **N** contains one carboxylic acid (or one alcohol) group.

From (a)(i),

Since **N** already contains a carboxylic acid functional group, **N** must contain either a ketone or an aldehyde functional group to satisfy the molecular formula of $C_3H_4O_3$.

The two possible structures of **N** are:



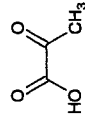
Compound **N**, $C_3H_4O_3$, is formed as the only organic product when a neutral organic compound **M**, $C_4H_6O_3$, is heated with acidified $KMnO_4$. **M** does not decolourise aqueous bromine.

- (iv) Use the information provided and your answer in (a)(iii) to

- identify the structure of **N** and
- deduce the structure of **M**.

Explain your reasoning and the chemistry of the reactions involved. [3]

Since **N** is an oxidation product of **M**, **N** cannot contain an aldehyde group and thus **N** is:

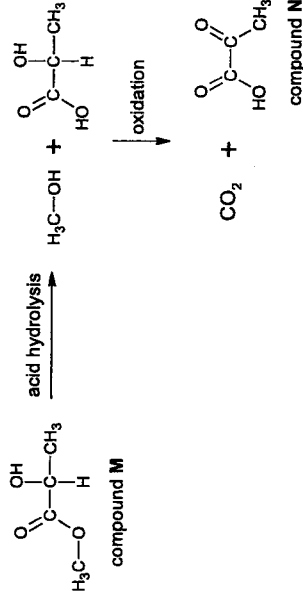


Since **M** is a neutral organic compound, it cannot contain the carboxylic group and is likely to contain an ester functional group given that there are three oxygen atoms in its molecular formula.

Since **N** already contains three carbon atoms, **M** is a methyl ester and the remaining oxygen atom could be attributed to a ketone or secondary alcohol functional group.

Possible structures of M	Molecular formula
	$C_4H_6O_3$
	$C_4H_6O_3$

M has to contain a secondary alcohol functional group to satisfy the molecular formula of $C_4H_6O_3$. Therefore, **M** has undergone acid hydrolysis (of ester), followed by oxidation (of methanol and the secondary alcohol) to produce **N** (as the only organic product) with the liberation of CO_2 gas when **M** is heated with acidified $KMnO_4$.



- (b) Phenylethene, $C_6H_5CH=CH_2$, can be used to synthesise three different aromatic compounds **R**, **S** and **T** as shown in Fig. 3.1.

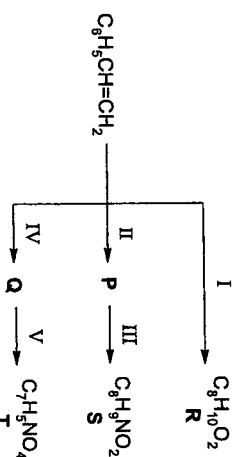


Fig. 3.1

(i) State the reagents and conditions required for reaction I.

$KMnO_4(aq)$, $NaOH(aq)$, cold

[1]

Compounds S and T have the following features.

- Each compound contains a disubstituted benzene ring.
- They have an identical substituent on their benzene rings.
- S has its substituents at positions 1 and 2 on the benzene ring.
- T has its substituents at positions 1 and 3 on the benzene ring.

(ii) Using the information provided and given that the same type of reaction is occurring in III and V, suggest structures for the intermediates P and Q.

Hence state the reagent and conditions required for reaction II.

[3]

P	Q

Reagent and conditions required for reaction II: H_2 , Mn , heat

(iii) Suggest and explain how the conditions for reactions III and V would differ despite the same type of reaction occurring.

[2]

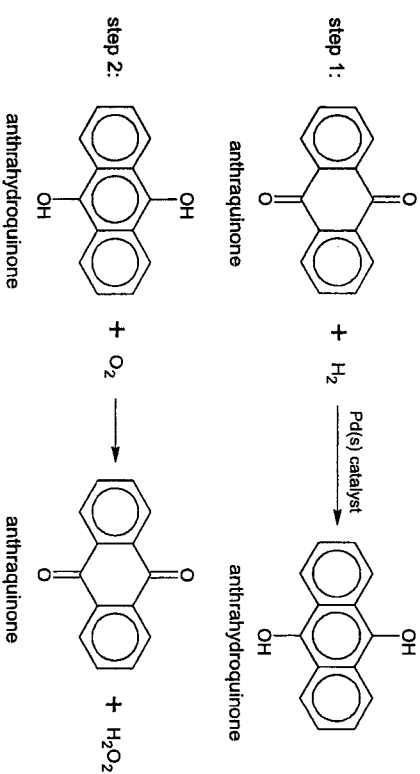
A higher temperature is required for reaction V than III.

The $-CO_2H$ group is deactivating while the $-CH_2CH_3$ group is activating. The benzene ring in benzoic acid has a lower electron density and is a weaker nucleophile / less susceptible to electrophilic substitution compared to that in ethylbenzene.

[Total: 14]

4 Hydrogen peroxide, H_2O_2 , finds its applications in a diversity of fields. Amongst many uses, it is an important precursor for the synthesis of organic peroxides and polymers. As such the manufacture of hydrogen peroxide has been an important industrial process since the 20th century.

Today, most of the world's hydrogen peroxide is manufactured by the anthraquinone process. This process involves the two steps shown below.



(a) Step 1 involves the adsorption of H_2 gas onto the surface of the palladium metal catalyst.

(i) State the property that palladium possesses that allows it to act as a catalyst in step 1, and explain how the adsorption of H_2 gas onto palladium increases the rate of reaction.

[2]

Palladium has low-lying vacant / partially filled d orbitals.

The adsorption of H_2 weakens the H-H bond, and allows it to break more readily, lowering the activation energy. Hence, rate of reaction increases.

(ii) A study of the kinetics of step 1 revealed that at low pressures, the rate of reaction increases with increasing pressure of H₂. However, at high pressures, increasing the pressure of H₂ has no effect on the rate of reaction.

Explain these observations. [2]

At low pressures, the surface of palladium has available active sites for H₂ to adsorb as it is not saturated. Hence, the rate of reaction increases when the pressure of H₂ is increased.

In contrast, at high pressures, the surface of palladium is saturated with H₂ and there are no active sites for adsorption to occur / active sites are fully occupied with H₂. Hence, the rate of reaction is no longer affected by the increase in H₂ pressure.

Although palladium and nickel belong to Group 10 of the Periodic Table, both elements have different ways of filling up their d orbitals. For palladium, it has a fully filled 4d subshell.

(iii) Draw, on the Cartesian axes provided in Fig. 4.1, the orbital from which the first electron of palladium is removed. Label the axes and orbitals clearly. [1]

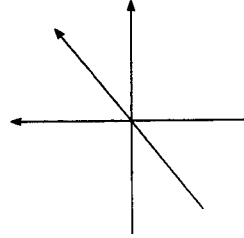
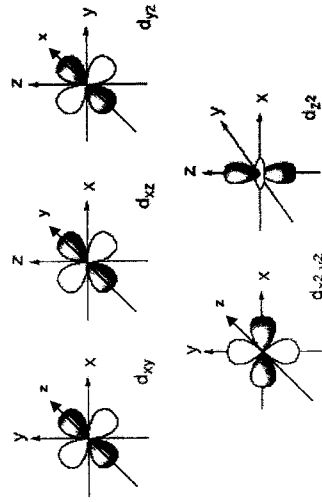


Fig. 4.1

Any one the following with correctly labelled axes and orbitals:



(iv) It is observed that the first ionisation energies of the Period 4 transition elements remain relatively invariant. Explain this observation. [2]

- The first ionisation energy of Period 4 transition elements involves the removal of an electron from the 4s orbital.
- Across the transition elements, electrons are added to the penultimate 3d orbitals.
- As such, the increase in nuclear charge is cancelled out by the increase in shielding effect.
- Effective nuclear charge remains relatively constant. Hence, the energy required to remove the 4s electron remains relatively invariant.

(b) At the end of step 1, anthrahydroquinone is extracted from the reaction mixture before reacting it with O₂ in step 2.
It is observed that step 2 follows the rate equation below.

$$\text{rate} = k[\text{anthrahydroquinone}][\text{O}_2]$$

In this step, a large excess of O₂ is required to ensure that anthrahydroquinone is completely oxidised back to anthraquinone, producing hydrogen peroxide.

(i) Explain why the rate equation for step 2 can be rewritten as rate = k' [anthrahydroquinone]. [1]

This is because O₂ is in large excess and hence the concentration / pressure of O₂ remains relatively constant throughout the reaction. As such, the rate equation can be rewritten as rate = k' [anthrahydroquinone] where k' = k[O₂] is a constant.

(ii) Hence sketch, on Fig 4.2, a labelled graph to show how the concentration of H₂O₂ in step 2 will vary over time. [2]

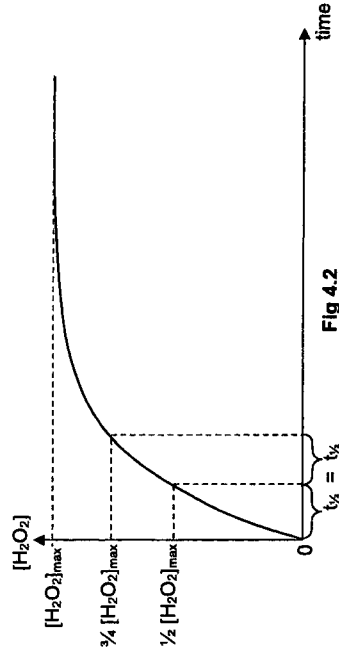


Fig 4.2

(iii) Step 2 was repeated with different initial pressures of O₂ and different initial concentrations of anthrahydroquinone.

Table 4.1 shows the initial quantities of reactants used for each experiment and the time required for the initial concentration of anthrahydroquinone to be halved for experiment 1.

Table 4.1

expt	initial pressure of O ₂ (g) / Pa	initial [anthrahydroquinone] / mol dm ⁻³	time required for initial [anthrahydroquinone] to be halved / min
1	4 × 10 ⁵	1.00	12.0
2	4 × 10 ⁵	0.50	
3	8 × 10 ⁵	1.00	

Complete Table 4.1 and explain your answer.

[2]

Table 4.1

expt	initial pressure of O ₂ (g) / Pa	initial [anthrahydroquinone] / mol dm ⁻³	time required for initial [anthrahydroquinone] to be halved / min
1	4 × 10 ⁵	1.00	12.0
2	4 × 10 ⁵	0.50	12.0
3	8 × 10 ⁵	1.00	6.0

Since $t_{1/2} = \frac{\ln 2}{k'}'$, where $k' = k[\text{O}_2]$, changes in the concentration of anthrahydroquinone has no effect on the half-life of the reaction. Instead, doubling the initial pressure of O₂ would halve the half-life of the reaction.

- (c) At the end of step 2, the reaction mixture contains only anthraquinone and H₂O₂. H₂O₂ can be separated out from the reaction mixture by adding water to the reaction mixture.

With reference to the bonding between relevant molecules, explain how the addition of water allows this to happen.

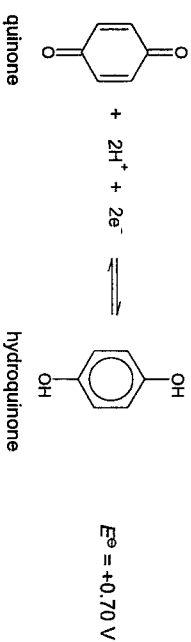
[2]

H₂O₂ can form hydrogen bonding with the water molecules. Hence, H₂O₂ will dissolve in water.

In contrast, anthraquinone has large non-polar benzene rings which will interfere with the hydrogen bonding it forms with water. Hence, anthraquinone will not dissolve in water but remain in the reaction mixture.

- (d) Quinone and hydroquinone have similar structures to anthraquinone and anthrahydroquinone respectively.

The standard reduction potential of the quinone–hydroquinone system is +0.70 V.

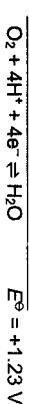


An electrolytic cell was set up under standard conditions with a mixture of aqueous quinone and dilute sulfuric acid as the electrolyte and platinum rods as electrodes.

State the products formed at the anode and the cathode.

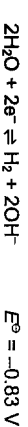
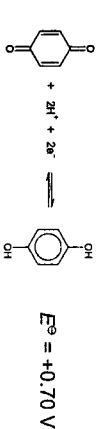
[2]

Possible oxidations at the anode:



Since $E^\ominus(\text{O}_2/\text{H}_2\text{O})$ is less positive than $E^\ominus(\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-})$, H₂O will be preferentially oxidised to oxygen gas at the anode.

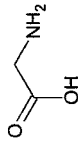
Possible reductions at the cathode:



Since $E^\ominus_{\text{quinone/hydroquinone}}$ is most positive, quinone will be preferentially reduced to hydroquinone at the cathode.

[Total: 16]

- 5 (a) Glycine has the following structure.



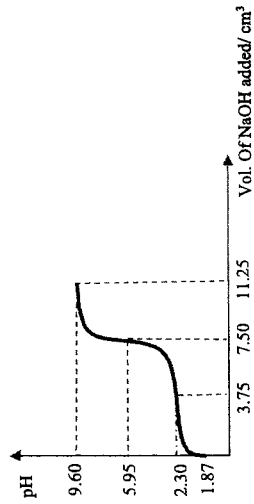
The pK_a values of glycine are shown in Table 5.1.

Table 5.1

pK_a of α -carboxyl group	pK_a of α -amino group
2.30	9.60

- (i) Glycine exists as a zwitterion at pH 5.95.
State what is meant by the term *zwitterion*. [1]
- A zwitterion is a species which is dipolar with no overall electrical charge.
- (ii) A 15 cm³ solution of 0.05 mol dm⁻³ glycine is prepared in which glycine is fully protonated. The initial pH of this solution is 1.87.
- Sketch the pH–volume added curve you would expect to obtain when 11.25 cm³ of 0.10 mol dm⁻³ NaOH is added to this solution.
- Use the information provided, and data from (a)(i) and Table 5.1 to label the various key points on the curve.

Show your working. [3]

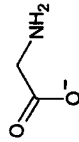


- (iii) Write an equation to show the reaction occurring when 1.75 cm³ of 0.10 mol dm⁻³ NaOH is further added to the resulting solution in (a)(ii). [2]
- Hence calculate the pH of the solution obtained.
- Resulting solution in (a)(ii) is a buffer solution at maximum buffering capacity, containing equal concentrations of H₂NCH₂CO₂⁻ and H₃N⁺CH₂CO₂.

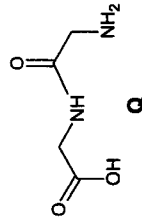
When NaOH is added,
H₃N⁺CH₂CO₂⁻ + OH⁻ → H₂NCH₂CO₂⁻ + H₂O

$$\begin{aligned} \text{New moles of salt, H}_2\text{NCH}_2\text{CO}_2^- &= 0.000375 + \left(\frac{1.75}{1000} \times 0.1\right) = 0.00055 \text{ mol} \\ \text{New moles of acid, H}_3\text{N}^+\text{CH}_2\text{CO}_2^- &= 0.000375 - \left(\frac{1.75}{1000} \times 0.1\right) = 0.0002 \text{ mol} \\ \text{pH} &= 9.60 + \log_{10}\left(\frac{0.00055/0.028}{0.0002/0.028}\right) = \underline{10.0} \text{ (3 sf)} \end{aligned}$$

- (iv) Draw the structure of the predominant species of glycine at pH 10.0. [1]



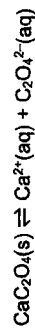
- (v) Name the type of reaction occurring when **Q** is formed from two glycine molecules. [1]



Condensation [1]

- (b) The presence of some amino acids has been linked to the precipitation of calcium ethanedioate (CaC₂O₄), a component of kidney stones, in the body. Research studies have been performed to better understand the effect of pH on the solubility of CaC₂O₄.
- (i) Predict and explain the effect of pH on the solubility of CaC₂O₄. [2]

When the pH decrease, the [H⁺] increases. C₂O₄²⁻(aq) will react with H⁺ causing the [C₂O₄²⁻] to decrease.



By Le Chatelier's Principle, the position of the equilibrium will shift to the right to increase the [C₂O₄²⁻].

Hence, the solubility of CaC₂O₄ will increase with decreasing pH.

One research study on the effect of pH on the solubility of CaC_2O_4 involves adding excess powdered CaC_2O_4 to water that has its pH value adjusted. The suspension was filtered and the filtrate was titrated against acidified potassium manganate(VII) of a known concentration. The results are shown in Table 5.2.

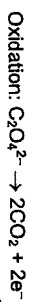
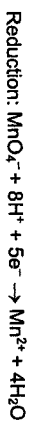
Table 5.2

experiment	pH of filtrate	volume of KMnO_4 added / cm^3
1	1.56	30.00
2	1.76	24.55
3	2.45	13.40
4	3.20	8.00
5	5.37	3.70
6	6.16	3.50

- (ii) Construct balanced ion-electron equations for the reaction between CaC_2O_4 and potassium manganate(VII) which produces a gas.

Hence write the overall equation for the reaction.

[2]



- (iii) Using the data in Table 5.2, comment on your prediction in (b)(i).

[2]

The prediction in (b)(i) is consistent with the data with the solubility of CaC_2O_4 increasing with decreasing pH.

The data shows that as pH decreases, the volume of KMnO_4 required to fully titrate ethanedioate increases. Since the ethanedioate ions originated from the dissolution of CaC_2O_4 , the greater volume of KMnO_4 required is indicative that more CaC_2O_4 has dissolved.

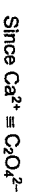
- (iv) In experiment 1, 200 cm^3 of the filtered solution was titrated against 0.00100 mol dm^{-3} potassium manganate(VII).

Calculate the mass of Ca^{2+} in mg, present in the filtrate.

[2]

$$\text{No. of moles of } \text{MnO}_4^- = \frac{30}{1000} \times 0.001 = 3.00 \times 10^{-5} \text{ mol}$$

$$\text{No. of moles of } \text{C}_2\text{O}_4^{2-} = \frac{5}{2} \times 3.00 \times 10^{-5} = 7.50 \times 10^{-5} \text{ mol}$$



$$\Rightarrow \text{No. of moles of } \text{Ca}^{2+} = 7.50 \times 10^{-5} \text{ mol}$$

$$\text{Mass of } \text{Ca}^{2+} = 7.50 \times 10^{-5} \times 40.1 = 3.0075 \times 10^{-3} \text{ g}$$

$$= 3.01 \text{ mg (3 s.f.)}$$

- (e) Thermogravimetric analysis is an analytical technique used to determine a substance's thermal stability by monitoring the change in mass that occurs as a sample is heated at a constant rate.

- (i) Calcium ethanedioate monohydrate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, has been used to calibrate equipment that performs thermogravimetric analysis because of its well-defined three-step decomposition process.

Complete the following equations which describe the decomposition process of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Include state symbols. [2]



- (ii) A thermogram from a thermogravimetric analysis plots mass of carbonate against temperature.

Given the same initial mass of carbonate, state and explain how the thermogram of magnesium carbonate will differ from that of calcium carbonate in terms of

- the final mass of carbonate obtained,
- the temperature at which the mass of carbonate starts to change significantly.

[3]

Since both carbonates are of the same mass, the number of moles of magnesium carbonate (with a smaller relative formula mass) is greater than that of calcium carbonate. Hence, more moles and mass of carbon dioxide will be lost from magnesium carbonate, leading to a smaller final mass for magnesium carbonate.

Since the thermal stability of magnesium carbonate is lower than that of calcium carbonate due to Mg^{2+} having a higher charge density / polarising power than Ca^{2+} , less energy and a lower temperature is required for the thermal decomposition of magnesium carbonate to occur.

[Total: 21]



DUNMAN HIGH SCHOOL
Preliminary Examination
Year 6

H2 CHEMISTRY

Paper 3 Free Response Questions

9729/03**21 September 2022****2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer all questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

Section A

Answer all questions.

Section B

Answer one question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

The number of marks is given in brackets [] at the end of each question or part question.

For Examiner's Use	
Section A	
1	20
2	20
3	20
Section B	
4 / 5	20
Total	80

Section A

Answer all the questions from this section.

- 1 (a) Alkynes is a class of organic compounds with the general formula, C_nH_{2n-2} .

(i) Describe what is meant by sp hybridisation with reference to one carbon atom in ethyne, C_2H_2 . Draw the hybrid orbitals of the carbon atom. [2]

One 2s and one 2p atomic orbitals are mixed to form two 2sp hybrid orbitals that are degenerate / of equal energy.



internuclear axis

(ii) Use relevant radius values from the *Data Booklet* to calculate the bond length of a single carbon-hydrogen bond. Show your working clearly. [1]

From the *Data Booklet*,
 single covalent radius of hydrogen = 0.037 nm
 single covalent radius of carbon = 0.077 nm

Bond length = sum of covalent radii
 = 0.037 nm + 0.077 nm = 0.114 nm

(iii) Table 1.1 shows the carbon-hydrogen bond length in ethene and ethyne.

Table 1.1

molecule	carbon-hydrogen bond length/ nm
ethene	0.109
ethyne	0.106

With reference to Table 1.1, state which carbon-hydrogen bond is stronger. Use the concept of hybridisation to explain the difference in bond length of the carbon-hydrogen bond between these two molecules. [2]

The carbon-hydrogen bond of ethyne is stronger.

The sp hybridised carbon atom in ethyne has a higher percentage s character than the sp² hybridised carbon atom in ethene. Hence, the extent of orbital overlap between the sp hybridised carbon atom and H atom is greater, resulting in a shorter bond length.

(iv) Write a balanced equation for the complete combustion of propyne, C_3H_4 . [1]



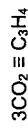
(v) A sample of propyne was burned in excess oxygen. When the remaining gases were passed through aqueous sodium hydroxide, the gas volume was reduced by 0.450 dm³. Calculate the mass of propyne in the sample.

9729/03

This document consists of 23 printed pages.

Assume all gas volumes were measured at r.t.p. [2]

Since carbon dioxide is the only acidic gas, volume of $\text{CO}_2 = 0.450 \text{ dm}^3$



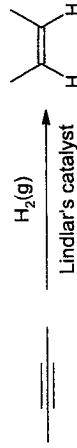
By volume ratio, volume of $\text{C}_3\text{H}_4 = 0.150 \text{ dm}^3$

$$\text{Moles of C}_3\text{H}_4 = \frac{0.15}{24} = 0.00625 \text{ mol}$$

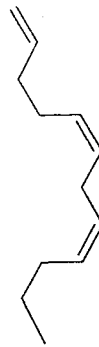
$$\text{Mass of C}_3\text{H}_4 = 0.00625 \times ((4 \times 1.0) + (3 \times 12.0)) = 0.250 \text{ g}$$

(b) The use of hydrogen gas with Lindlar's catalyst is a selective method which reduces alkynes to form the *cis*-isomer of alkenes.

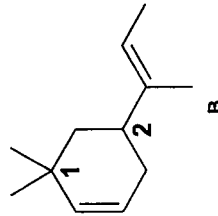
As an example, but-2-yne, C_4H_6 , can be reduced to give *cis*-but-2-ene only.



Suggest the structure of the alkene formed when compound **A** is reduced with the use of Lindlar's catalyst. [1]



(c) Compound **B** has the following structure.



(i) State the isomeric relationship between **B** and your answer in (b). [1]

Chain / constitutional isomers

(ii) A student made the following deductions about compound **B**.

"Since carbon atoms labelled **1** and **2** are chiral and there are two carbon-carbon double bonds, compound **B** has 16 possible stereoisomers."

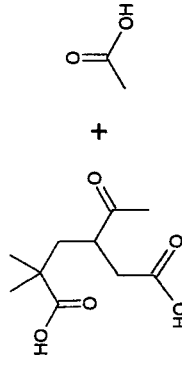
Explain where the student has gone wrong in his deductions. [3]

Carbon 1 is not chiral as it is bonded to two identical methyl groups.

For the C=C bond in the ring, only the *cis*-isomer exists. In the presence of a small six-membered ring, the *trans*-isomer will be highly strained and unstable.

With one chiral centre and one C=C bond not located in a ring, there is a total of $2^2 = 4$ possible stereoisomers for compound **B**.

(iii) Draw all the organic products that are formed when compound **B** is heated with acidified potassium manganate(VII). [1]

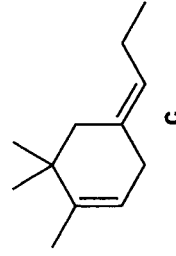


Marker's Comments

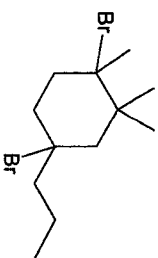
Typical mistakes include:

- Oxidation of the C=C bond to aldehyde functional group instead of carboxylic acid functional group
- Missing ethanoic acid as one of the organic products
- Missing methyl groups or carbon atoms
- Five bonds around carbon in C=O of the ketone functional group

(d) Compound **C** is an isomer of compound **B**.



Draw the structure of the major product formed when compound **C** is reacted with excess HBr(g) . Explain your answer. [2]



The tertiary carbocation is more stable than the secondary carbocation formed as there are more electron-donating alkyl groups to disperse the positive charge on each carbon atom.

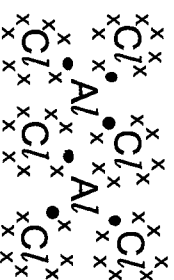
(e) Lithium aluminium hydride, LiAlH_4 , is a reducing agent commonly used in organic chemistry.

(i) Assuming LiAlH_4 as a source of hydride (H^-) ions, suggest why the reduction of alkynes using LiAlH_4 is likely not a suitable method. [1]

The π electrons / triple bond / $\text{C}\equiv\text{C}$ bond in alkynes will repel the negatively charged H^- .

(ii) LiAlH_4 can be synthesised from aluminium chloride, which exists as a dimer, Al_2Cl_6 , at room temperature.

Draw a dot-and-cross diagram to illustrate the bonding present in Al_2Cl_6 . [1]



(iii) When heated, LiAlH_4 decomposes to LiAl(s) as one of its products. LiAl(s) has a melting point of 718°C . It can conduct electricity when in solid and molten states.

Suggest the structure of LiAl(s) and describe the bonding present. [2]

Giant metallic structure.
Strong electrostatic forces of attraction between lattice of Li^+ and Al^{3+} positively-charged ions and the sea of delocalised electrons.

[Total: 20]

2 (a) 1,2-diols are common precursors used in many pharmaceuticals, agrochemicals, and natural products.

Fig. 2.1 shows a pinacol coupling reaction which involves the homo-coupling* of a carbonyl compound to produce a symmetrically substituted 1,2-diol.

*Two identical molecules react to form a different one.

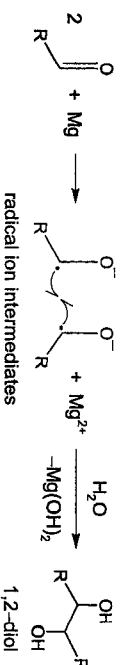


Fig. 2.1

The first step is single electron transfer involving the carbonyl group, which generates radical ion intermediates that couple via carbon-carbon bond formation to give a 1,2-diol.

(i) State the role of magnesium in the first step of Fig. 2.1 and give a reason for its suitability in this reaction. [2]

Magnesium is functioning as a reducing agent in the first step. It is suitable due to its relatively low ionisation energies/ low electronegativity.

(ii) It is possible to synthesise a desired unsymmetrical diol using methods similar to the pinacol coupling reaction but a mixture of diols will be obtained.

Explain why a mixture of diols is formed. Suggest why this is unfavourable other than a low yield of the desired diol. [2]

Two different carbonyl compounds have to be used to synthesise an unsymmetrical diol. In the process, two different radical ion intermediates will be formed and different combinations of these radicals will couple to form a mixture of (three) diols.

Obtaining a mixture of diols is unfavourable as the separation of the diols to yield the desired one would be complex.

The pinacol coupling can be followed up by a pinacol rearrangement to convert the 1,2-diol to a carbonyl compound.

Pinacolone is a carbonyl compound that can be produced via the pinacol rearrangement and it has the following structure.

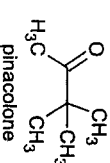


Fig. 2.2 shows the first step of the pinacol rearrangement to form pinacolone using pinacol as the starting reactant.

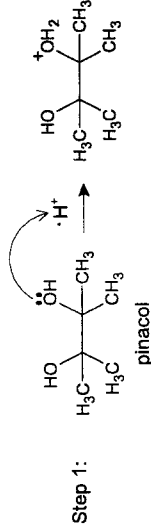


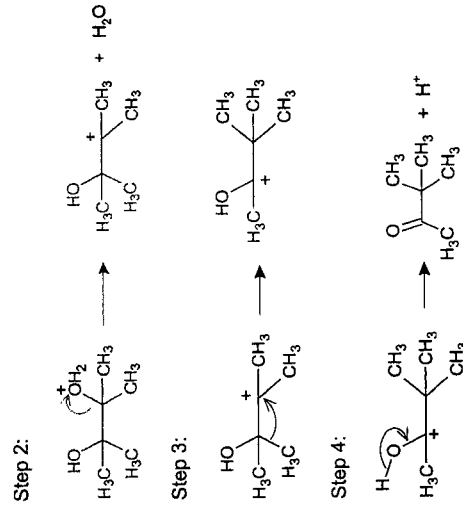
Fig. 2.2

(iii) Below describes the remaining three steps of the *pinacol rearrangement* to form pinacolone.

- Step 2 involves the removal of water from the intermediate in Step 1 in Fig. 2.2 to form a carbocation.
- Step 3 involves the shifting of an adjacent methyl group to the positively charged carbon to form another carbocation.
- Step 4 involves the deprotonation of the -OH group in the carbocation in Step 3 to form pinacolone.

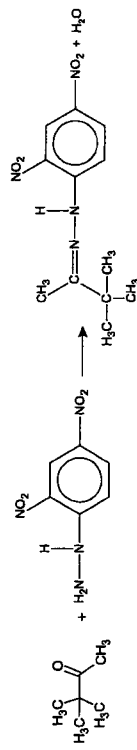
Using the information provided, draw Steps 2 to 4 of the mechanism for the formation of pinacolone via *pinacol rearrangement*.

Show all charges and show the movement of electron pairs by using curly arrows. [3]

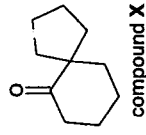


(iv) Suggest a simple chemical test that you could carry out to confirm the formation of pinacolone from pinacol. State the observations you would make and write a balanced equation for the reaction. [2]

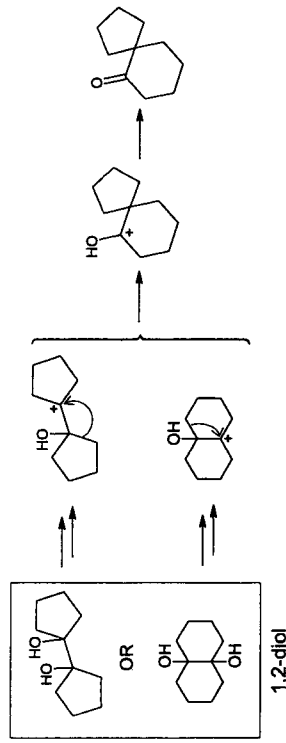
Add 2,4-DNPH to the reaction mixture.
The formation of an orange ppt indicates the formation of pinacolone.



(v) Compound X is a product formed from *pinacol rearrangement*.



Draw the structure of the 1,2-diol responsible for producing X. [1]



(b) A research team in Kanazawa University was successful in selectively synthesising one species of 1,2-diol from an aldehyde and a ketone as the starting materials. The key to the success was a newly developed copper catalyst that could distinguish between the two different carbonyl compounds.

Fig. 2.3 shows the structure of the copper catalyst with N-heterocyclic carbene (NHC) as one of the ligands.

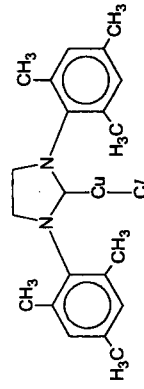


Fig. 2.3

Bases can be used to prepare the NHC ligand, as shown in Fig. 2.4.

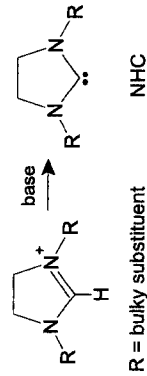


Fig. 2.4

(i) Define the term *ligand*. [1]

A ligand is a neutral molecule or an anion containing at least one atom with a lone pair of electrons that can be donated into low lying vacant orbital of metal atom/ion to form a coordinate bond.

(ii) State the oxidation number of Cu in Fig. 2.3. [1]
+1

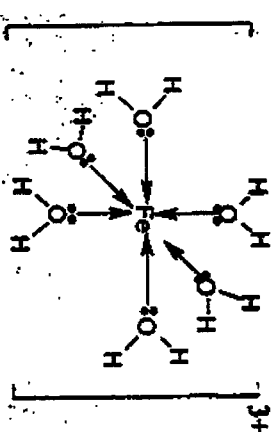
(iii) Coordination number is defined as the number of dative bonds formed between ligands and the central metal atom or ion.

State the coordination number of Cu in Fig. 2.3. [1]

2

(c) (i) Hexaquaaliron(III) ions, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, are pale violet.

Draw the structure of hexaquaaliron(III) ion, showing the arrangement of the ligands in the structure. [1]



(ii) Explain why hexaquaaliron(III) ions are coloured. [3]

In the presence of water ligands in the hexaquaaliron(III) ions, the d orbitals of the Fe^{3+} ion are split into two groups of different energy levels.

When white light shines on the complex, a d electron is promoted to a higher energy vacant or partially filled d orbital.

During the transition, the d electron absorbs wavelength of light from the visible spectrum.

The light energy not absorbed/transmitted, which is complementary to the wavelength of light absorbed, gives the transition metal complex its colour.

(iii) When a few drops of $\text{KSCN}(\text{aq})$ are added to 5 cm^3 of $\text{Fe}^{3+}(\text{aq})$, followed by a few drops of $\text{KF}(\text{aq})$, the solution changes colour from violet to deep-red to colourless.

Identify the type of reaction occurring and explain the sequence of colour changes observed. [3]

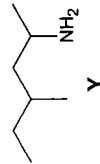
In both reactions, ligand exchange has taken place.

When a few drops of KSCN are added to Fe^{3+} , the stronger SCN^- ligand replaces the weaker H_2O ligand, and hence the colour of the solution changes from violet to deep red.

When a few drops of KF are added to the resultant solution from the first part, the solution changes colour from deep red to colourless as the stronger F^- ligand replace the weaker SCN^- ligands.

[Total: 20]

- 3 (a) Compound Y is a banned performance-enhancing stimulant. Usain Bolt lost one of his three gold medals from the 2008 Olympics because one of his relay team members tested positive for this drug.



Compound Y may be prepared by the three-step synthesis shown in Fig. 3.1. Other products of each step are not shown.

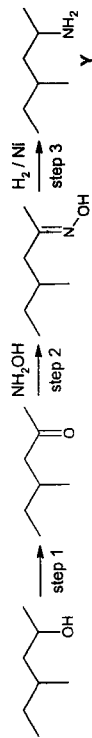


Fig. 3.1

- (i) Name the starting organic material in step 1 of Fig. 3.1. [1]
4-methylhexan-2-ol

- (ii) Deduce the identity of the other product formed in step 2 of Fig. 3.1. [1]
H₂O

- (b) A student suggested that compound Y could be prepared directly from the starting material in step 1 by reacting it with phosphorus pentachloride, PCl₅, followed by ammonia, NH₃.

- (i) State the property of ammonia that makes this a possible synthesis route for compound Y. [1]

There is a lone pair of electrons on the nitrogen atom which allows NH₃ to act as a nucleophile.

- (ii) A second student suggested that the first student's proposal might work better if the reaction with ammonia was carried out in the presence of acid. [1]

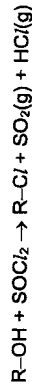
Explain if the second student's suggestion is correct.

The second student is wrong. The lone pair of electrons on the nitrogen atom will not be available as it would have been used to form dative bond with the acid in the acid-base reaction.

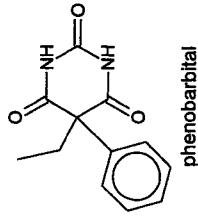
- (iii) Thionyl chloride, SOCl₂, can be used as a replacement for PCl₅ in the reaction mentioned in (b). SOCl₂ is difficult to handle safely and is similar to PCl₅ in terms of reactivity and cost.

Suggest an advantage of using SOCl₂ instead of PCl₅. [1]

Both the by-products, SO₂ and HCl, are gases hence are easily separated from the chloroalkane product.



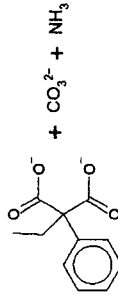
- (c) Phenobarbital is a drug used in the treatment of seizures.



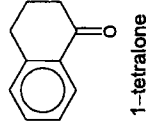
- (i) Comment on the basicity of phenobarbital. [1]

In each -CONH group, the lone pair of electrons on the nitrogen atom is not available to form a dative bond with a proton as it is delocalised into the adjacent C=O bond. Therefore, phenobarbital is not a basic (or is a neutral) drug.

- (ii) Predict the products of the alkaline hydrolysis of phenobarbital. [2]



- (d) 1-tetralone is used in the synthesis of propranolol, a drug used in the treatment of high blood pressure.



Benzene can be used to make 1-tetralone.

- (i) Suggest the structure of an organic reagent that could form 1-tetralone from benzene in a single step. [1]



- (ii) Explain why benzene does not undergo addition reactions. [1]

The extra stability associated with the delocalisation of six π electrons in the continuous overlapping p-orbitals is destroyed if benzene undergoes addition reactions.

- (e) Organic drug synthesis processes often involve alkali metals.

Alkali metals react with water as shown in the equation, where M represents the alkali metal.



For each of the alkali metals, Table 3.1 shows:

- the standard enthalpy change of atomisation, ΔH_{at}^\ominus ,
- the standard enthalpy change of hydration, ΔH_{hyd}^\ominus ,
- the first ionisation energy, $1^{st}IE_1$,
- the standard enthalpy change of reaction between alkali metal and water, ΔH_f^\ominus .

Table 3.1

alkali metal	ΔH_{at}^\ominus (M) / kJ mol ⁻¹	ΔH_{hyd}^\ominus (M ⁺) / kJ mol ⁻¹	1 st IE (M) / kJ mol ⁻¹	ΔH_f^\ominus (M) / kJ mol ⁻¹
Li	+160	-519	+519	-222
Na	+109	-406	+495	-184
K	+90	-322	+418	-196
Rb	+86	-301	+402	-195
Cs	+79	-276	+376	-203

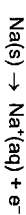
- (i) Define the term
- standard enthalpy change of hydration*
- . [1]

Standard enthalpy change of hydration of an ion is the energy released when one mole of the gaseous ion is hydrated at standard conditions / 298 K and 1 bar.

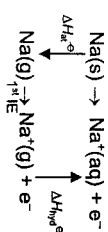
- (ii) Explain the trend in the standard enthalpy change of hydration,
- ΔH_{hyd}^\ominus
- , down the group. [2]

The magnitude of ΔH_{hyd}^\ominus of an ion depends on its charge density. The charge density of the ions decreases as the ionic radii increases down the group. The lower the charge density of the ion, the weaker the ion-dipole interactions formed between the ion and water molecules. Less energy will be evolved and hence, ΔH_{hyd}^\ominus will be less exothermic.

- (f) Use relevant data from Table 3.1 to calculate the enthalpy change for the following reaction. [1]



[1]



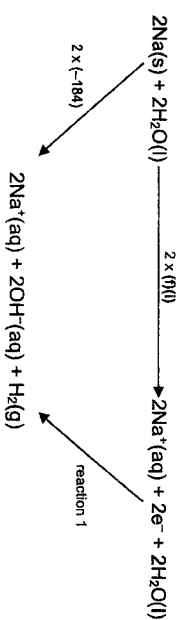
enthalpy change = $(+109) + (+495) + (-406) = +198$ kJ mol⁻¹

- (ii) Using relevant data from Table 3.1 and your answer in (f)(i), draw an energy cycle to determine the enthalpy change of reaction 1. [2]



Show your working clearly.

[2]



Enthalpy change of reaction 1 = $-(2 \times 198) + [2 \times (-184)]$
 $= -764$ kJ mol⁻¹

- (iii) There is particular interest in lithium as an energy source due to its low density.

Use relevant data from Table 3.1 to calculate the energy change per gram of lithium for the reaction between lithium and water. [1]

Energy change per gram of lithium = $-222 \div 6.9 = -32.2$ kJ g⁻¹

- (g) Lithium carbonate undergoes thermal decomposition in a similar way to Group 2 carbonates, though a much higher temperature is required.

Explain why the reaction occurs at high temperatures. Refer to the signs of ΔH , ΔS and ΔG in your answer. [2]

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

$\Delta H_{decomposition} > 0$ since heat is required to break the chemical bonds during decomposition.

$\Delta S_{decomposition} > 0$ since CO₂ gas is produced.

Production of CO₂ gas results in the products being more disordered than the reactants.

At high T, the negative $-T\Delta S$ outweighs the positive ΔH , hence $\Delta G < 0$.

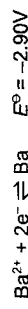
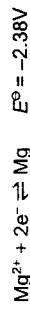
The decomposition reaction is spontaneous.

(h) Group 2 metals undergo reaction with water in a similar way to alkali metals.

However, magnesium and barium have different reactivities when added separately to water.

Use relevant E^\ominus values from the *Data Booklet* to explain the difference in the reactivity of magnesium and barium with water. [1]

Barium is more reactive than magnesium.



E^\ominus (Ba²⁺/Ba) is more negative than E^\ominus (Mg²⁺/Mg). Therefore, the reducing power of barium is greater compared to magnesium.

[Total: 20]

Section B

Answer one question from this section.

- 4 (a) Alcohol is widely used in the preparation of aldehydes and ketones. The electrolysis of alcohols to carbonyl compounds is reported. A simplified diagram of the cell set-up is shown in Fig. 4.1.

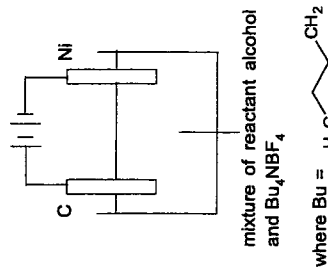


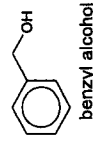
Fig. 4.1

The overall equation for the electrolysis of alcohol is shown.

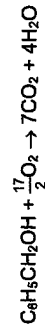


where R = alkyl or aryl
R' = H, alkyl or aryl

- (i) Write a balanced equation that shows the complete combustion of benzyl alcohol.

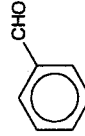


[1]



- (ii) Draw the structure of the product formed when benzyl alcohol is electrolysed.

[1]



- (iii) State and explain at which electrode does the conversion of the reactant alcohol take place. You should state the element that the electrode is made of. [2]

Carbon. Since the electrolysis of alcohol to form carbonyl compound is an oxidation process, it will occur at the anode.

- (iv) Suggest the role of Bu_4NBF_4 in the set-up in Fig. 4.1. [1]

Electrolyte.

- (v) A constant current of 800 mA is delivered at room temperature over 10 minutes. By considering the change in the oxidation state of the reactive carbon, calculate the number of moles of carbonyl compound formed from the electrolysis given that the yield of this conversion is 90%. [3]

$$Q = \frac{800}{1000} \times 10 \times 60 = 480 \text{ C}$$

Since no. of moles of alcohol: no. of moles of e^- is 1:2,

$$\begin{aligned} \text{No. of moles of alcohol used} &= \frac{Q}{2F} \\ &= \frac{480}{2 \times 96500} \\ &= 2.487 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{No. of moles of carbonyl formed} &= 0.9 \times 2.487 \times 10^{-3} \\ &= 2.24 \times 10^{-3} \text{ mol (3sf)} \end{aligned}$$

- (vi) Anodising aluminium is another useful application of electrochemical method. Describe how anodising of aluminium is achieved. [2]

An electrolytic cell with the aluminium that is to be anodised being the anode is set up. The electrolyte used is either H_2SO_4 or chromic acid. At the anode, H_2O is preferentially discharged to form O_2 . The discharged O_2 reacts with the aluminium anode to form a protective layer of Al_2O_3 .

- (b) Iodine-based reagents are commonly used in organic synthesis owing to their unique chemical properties which are linked to their physical properties such as ionic radius and ionisation energy.

- (i) State what is meant by the first ionisation energy of iodine. [1]

The first ionisation energy of iodine is the amount of energy absorbed by one mole of gaseous iodine atoms to remove one mole of electrons to form one mole of gaseous singly positively charged iodine cations.

- (ii) State and explain the variation of atomic radius down Group 17. [2]

Atomic radius increases down the group.

The number of electronic shells and shielding effect increase and each successive element has its valence electrons located in a shell with a higher principal quantum number, n . Hence, valence electrons are increasingly further away from the nucleus despite the increase in nuclear charge.

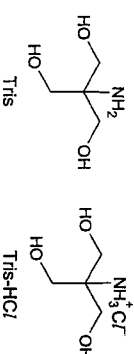
- (iii) Hydrofluoric acid and sodium fluoride can be used to form an acidic buffer. Explain how an acidic buffer controls the pH of a solution. [1]

A buffer resists pH changes when small amounts of acid or base is added to the solution. When a small amount of acid is added, the conjugate base will neutralise the added acid. When a small amount of base is added, the weak acid will neutralise the added base.

- (iv) Predict and explain if hydroiodic acid and sodium iodide can be used to form an acidic buffer. [1]

Since hydroiodic acid is a strong acid, it will not be able to form an acidic buffer with sodium iodide.

- (c) Tris buffer is a biochemical buffer used in COVID-19 vaccines. The structure of Tris and Tris-HCl is shown below. The K_a of Tris is 1.05×10^{-6} mol dm^{-3} .



A Tris buffer is formed by mixing 200 cm^3 of 1.50 mol dm^{-3} Tris with 200 cm^3 of 1.66 mol dm^{-3} Tris-HCl.

- (i) Calculate the pH of the Tris buffer. [2]

$$K_a \text{ of Tris-HCl} = \frac{1 \times 10^{-14}}{1.05 \times 10^{-6}} = 9.523 \times 10^{-9} \text{ mol dm}^{-3}$$

Since equal volume of Tris and Tris-HCl is added,

$$[\text{Tris}] = 0.75 \text{ mol dm}^{-3}$$

$$[\text{Tris-HCl}] = 0.83 \text{ mol dm}^{-3}$$

$$\begin{aligned} \text{pH} &= -\log_{10}(9.523 \times 10^{-9}) + \log_{10} \frac{0.75}{0.83} \\ &= 7.98 \text{ (3sf)} \end{aligned}$$

- (ii) 25.0 cm^3 of 0.500 mol dm^{-3} HNO_3 is added to 75.0 cm^3 of the Tris buffer prepared.

Calculate the pH of this solution. [3]

$$\text{moles of HNO}_3 \text{ added} = \frac{25}{1000} \times 0.500 = 1.25 \times 10^{-2} \text{ mol}$$

$$\text{New moles of Tris} = \left(\frac{75}{1000} \times 0.75\right) - 1.25 \times 10^{-2} = 0.04375 \text{ mol}$$

$$\text{New moles of Tris-HCl} = \left(\frac{75}{1000} \times 0.83\right) + 1.25 \times 10^{-2} = 0.07475 \text{ mol}$$

$$\text{pH} = -\log_{10}(9.523 \times 10^{-9}) + \log_{10} \frac{0.04375/0.10}{0.07475/0.10} = 7.79 \quad (3\text{sf})$$

[Total: 20]

- 5 (a) Fig. 5.1 shows a hydrogen-halogen fuel cell where H_2 gas is supplied to the anode while Br_2 , dissolved in an aqueous solution of HBr , is provided to the cathode.

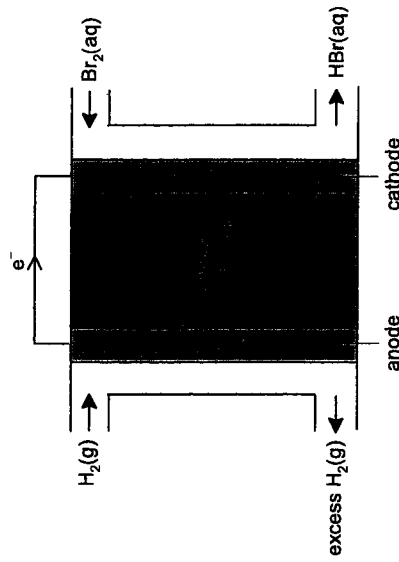


Fig. 5.1

- (i) The polymer electrolyte allows the transfer of a simple ion from the anode to the cathode. Use Fig. 5.1 to suggest the identity of the ion and hence construct balanced equations for the reactions occurring at the electrodes. [2]

Identity of ion: H^+ /hydrogen ion/proton

Anode: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$

Cathode: $\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$

- (ii) Use your answer in (a)(i) to write the overall equation when current flows and hence use the *Data Booklet* to calculate the standard cell potential, E_{cell}^\ominus , for this cell. [2]

Overall: $\text{H}_2 + \text{Br}_2 \rightarrow 2\text{HBr}$

$E_{\text{cell}}^\ominus = 1.07 - 0.00 = +1.07 \text{ V}$

- (iii) Use your answer to (a)(ii) to calculate the standard Gibbs free energy change, ΔG^\ominus , for this electrochemical reaction. [1]

$$\begin{aligned} \Delta G^\ominus &= -nFE_{\text{cell}}^\ominus = -2(96500)(1.07) \\ &= -206510 \text{ J mol}^{-1} = -207 \text{ kJ mol}^{-1} \end{aligned}$$

- (iv) A similar hydrogen-halogen fuel cell is set up where Cl_2 , dissolved in an aqueous solution of HCl , is supplied to the cathode.

How would you expect the standard Gibbs free energy change, ΔG^\ominus , for this electrochemical reaction to compare with your answer in (a)(iii)?

Explain your answer in terms of the difference in relative reactivity of the halogens. [2]

ΔG^\ominus will be more negative than that in (a)(iii).

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Cl_2 is a stronger oxidising agent than Br_2 so the reduction of Cl_2 will take place more readily at the cathode and the electrochemical reaction will be more spontaneous.

(b) The values of two solubility products are given.

$$K_{sp}(\text{PbBr}_2) = 1.9 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

$$K_{sp}(\text{AgBr}) = 5.4 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$$

(i) Solid PbBr_2 is shaken with water. The remaining solid is filtered off, leaving a saturated solution X. Calculate $[\text{Br}^-](\text{aq})$ in X. [1]

Let the solubility of PbBr_2 be $s \text{ mol dm}^{-3}$.

$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2 = (s)(2s)^2 = 1.9 \times 10^{-5}$$

$$4s^3 = 1.9 \times 10^{-5}$$

$$s = 0.016810$$

$$[\text{Br}^-] = 2s = 0.033620 = 0.0336 \text{ mol dm}^{-3}$$

(ii) Drops of dilute aqueous AgNO_3 are added to X until AgBr just precipitates. Calculate $[\text{Ag}^+(\text{aq})]$ in the resulting solution when AgBr just precipitates. [1]

$$\text{Ionic product} = K_{sp} = 5.4 \times 10^{-13}$$

$$[\text{Ag}^+][\text{Br}^-] = [\text{Ag}^+](0.033620) = 5.4 \times 10^{-13}$$

$$[\text{Ag}^+] = 1.6062 \times 10^{-11} = 1.61 \times 10^{-11} \text{ mol dm}^{-3}$$

(iii) HBr is a strong acid when dissolved in water.

Describe what you will observe if equal volumes of $0.100 \text{ mol dm}^{-3}$ solution of HBr and saturated solution of PbBr_2 were mixed. Explain your answer using appropriate calculations. [2]

Observation: Formation of (white) precipitate.

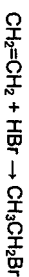
$$[\text{Br}^-] \text{ in mixture} = (0.033620 + 0.100)/2 = 0.06681 \text{ mol dm}^{-3}$$

$$\text{Ionic product} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

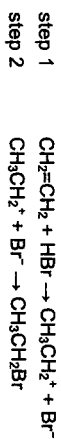
$$= (0.01681/2)(0.06681)^2 = 3.75 \times 10^{-5} > 1.9 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$$

Since ionic product of PbBr_2 will exceed its K_{sp} , white precipitate of PbBr_2 will be formed.

(c) Ethene reacts with hydrogen bromide exothermically to produce bromoethane.



The reaction mechanism has two steps as shown.



(i) State the slow step and hence write the rate equation for the reaction. [1]

$$\text{step 1 and rate} = k[\text{CH}_2=\text{CH}_2][\text{HBr}]$$

(ii) Use your answer in (c)(i) and the collision theory to explain the effect on the rate of reaction, if any, of

- decreasing the concentration of hydrogen bromide,
- increasing the temperature of the reaction.

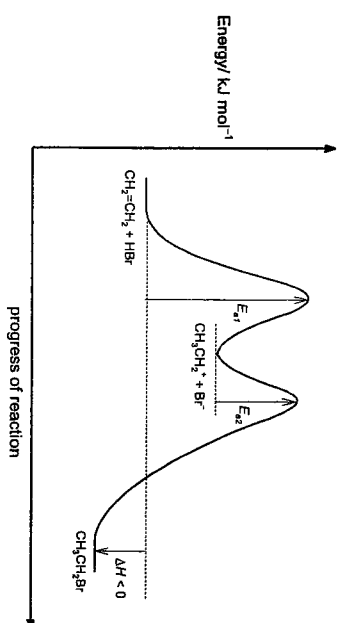
Rate depends on $[\text{HBr}]$ / reaction is first order or non-zero order with respect to HBr as shown by the rate equation. Decreasing the concentration of hydrogen bromide decreases the number of reactant particles per unit volume which decreases the frequency of effective collisions. Hence rate of reaction decreases. [2]

Increasing the temperature of the reaction increases the average kinetic energy of reactant particles. More particles have energy greater than or equal to the activation energy and frequency of effective collisions increases. Rate constant, k , increases and hence rate of reaction increases.

(iii) Use the mechanism to explain the role of CH_3CH_2^+ . [1]

CH_3CH_2^+ is an intermediate; it is formed in step 1 but consumed in step 2.

(iv) Draw the labelled energy profile diagram for the reaction. [2]



Note:

- Labelled axes, reactants, intermediate and products
- Two steps with $E_{a1} > E_{a2}$
- Energy level of intermediate higher than reactants
- Overall $\Delta H < 0$

(d) The strength of an acid is measured by its K_a value.

How would you expect the K_a values to compare for the following pairs of acids?

- HF and HCl
- CH_3COOH and CF_3COOH
- $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

Explain your answer, quoting relevant data from the Data Booklet where appropriate. [3]

- HF and HCl

K_a value of HCl is **larger** than that of HF .

Since $\text{BE}(\text{H}-\text{C}) = 431 \text{ kJ mol}^{-1} < \text{BE}(\text{H}-\text{F}) = 562 \text{ kJ mol}^{-1}$, the **H-C bond is weaker** and **requires less energy to break** than the H-F bond. HC/ donates H^+ more readily and is a stronger acid with a larger K_a value than HF.

- CH_3COOH and CF_3COOH

K_a value of CF_3COOH is **larger** than that of CH_3COOH .

The presence of three **electron-withdrawing F atoms disperses the negative charge** on the conjugate base of CF_3COOH , making **CF_3COO^- more stable than CH_3COO^-** . CF_3COOH dissociates to a greater extent and is a stronger acid with a larger K_a value than CH_3COOH .

- $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

K_a value of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ is **smaller** than that of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

Since Fe^{2+} has a **smaller charge and larger ionic radius (0.061 nm)** than Al^{3+} (ionic radius = **0.050 nm**), Fe^{2+} has a **smaller charge density** and polarising power than Al^{3+} . $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ hydrolyses to a smaller extent and is a weaker acid than $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$.

[Total: 20]



DUNMAN HIGH SCHOOL

Preliminary Examination

Year 6

H2 CHEMISTRY

Paper 4 Practical

9729/04

25 August 2022

2 hours 30 minutes

Candidates answer on the Question Paper.

READ THESE INSTRUCTIONS FIRST

Write your centre number, index number, name and class at the top of this page.

Give details of the practical shift and laboratory where appropriate, in the boxes provided.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer all questions in the spaces provided on the Question Paper.

The use of an approved scientific calculator is expected, where appropriate.

You may lose marks if you do not show your working or if you do not use appropriate units.

Qualitative Analysis Notes are printed on pages 21 and 22.

At the end of the examination, fasten all your work securely together. The number of marks is given in brackets [] at the end of each question or part question.

Shift
Laboratory

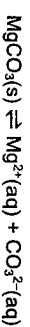
For Examiner's Use	
1	16
2	10
3	14
4	15
Total	55

This document consists of 16 printed pages.

Answer all questions in the spaces provided.

1 Determination of solubility product, K_{sp} , of magnesium carbonate

The solubility of solid magnesium carbonate, $MgCO_3$, in water is low. In this experiment, you will determine the solubility product, K_{sp} , of magnesium carbonate using volumetric analysis.



A saturated solution of magnesium carbonate was prepared by collecting the filtrate after mixing aqueous solutions of magnesium sulfate and sodium carbonate.

You will then determine the amount of carbonate ions left in the filtrate using hydrochloric acid.

FA 1 is a saturated solution of magnesium carbonate, $MgCO_3$.

FA 2 is $0.003 \text{ mol dm}^{-3}$ hydrochloric acid, HCl, methyl orange indicator

Note:

- Read the procedures given in part (a) and part (b)(i).
- Part (a) has been done for you. **You are not required to carry out part (a)**, but you will still need to read part (a) to know how FA 1 is prepared.

(a) Preparation of FA 1

1. Use a measuring cylinder to transfer 20 cm^3 of $0.100 \text{ mol dm}^{-3}$ magnesium sulfate to a clean and dry 250 cm^3 beaker.
2. Use a measuring cylinder to transfer 50 cm^3 of $0.0400 \text{ mol dm}^{-3}$ sodium carbonate to the same beaker. A white precipitate forms.
3. Stir the mixture thoroughly. Leave this mixture to stand for 15 minutes to allow equilibrium to be reached.
4. Filter the reaction mixture into a dry 250 cm^3 conical flask, using dry filter funnel and filter paper. The filtrate is labelled as FA 1. Do not wash the white precipitate with water.

(b) (i) Titration of FA 1 against FA 2

1. Fill a burette with FA 2.
2. Pipette 10.0 cm^3 of FA 1 into a 100 cm^3 conical flask.
3. Add a few drops of methyl orange indicator to the conical flask.
4. Titrate the solution in the conical flask with FA 2. The end-point for this titration is reached when the solution changes colour from yellow to orange.
5. Record all burette readings, to an appropriate level of precision, in the space provided on page 3.
6. Repeat steps 1 to 5 until consistent results are obtained.

Titration results

Final burette reading / cm ³	17.00	34.00
Initial burette reading / cm ³	0.00	17.00
Volume of FA 2 used / cm ³	17.00	17.00

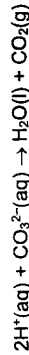
[3]

(ii) From your titrations, obtain a suitable volume of FA 2 to be used in your calculations. Show clearly how you obtained this volume.

$$\text{Average volume of FA 2 used} = \frac{17.00 + 17.00}{2} = 17.00 \text{ cm}^3$$

$$\text{volume of FA 2} = \dots\dots\dots \text{cm}^3 \quad [4]$$

(c) (i) The equation for the reaction in the titration is shown below.



Calculate the concentration of CO₃²⁻ ions in FA 1.

$$\text{Moles of HCl reacted} = \left(\frac{17.00}{1000}\right)(0.003) = 5.1 \times 10^{-5} \text{ mol}$$

$$2\text{H}^+ \equiv \text{CO}_3^{2-}$$

$$\text{Moles of CO}_3^{2-} \text{ in } 10.0 \text{ cm}^3 \text{ of FA 1} = \left(\frac{1}{2}\right)(5.1 \times 10^{-5}) = 2.55 \times 10^{-5} \text{ mol}$$

$$\text{Concentration of CO}_3^{2-} = \frac{2.55 \times 10^{-5}}{0.01} = 2.55 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{concentration of CO}_3^{2-} \text{ ions} = \dots\dots\dots \text{mol dm}^{-3} \quad [1]$$

(ii) Calculate the total amount of CO₃²⁻ ions present in the total volume of filtrate prepared in (a).

$$\begin{aligned} \text{Total moles of CO}_3^{2-} \text{ in } 70.0 \text{ cm}^3 \text{ of FA 1} &= \left(\frac{20}{10}\right)(2.55 \times 10^{-5}) \\ &= 1.785 \times 10^{-4} \\ &= 1.79 \times 10^{-4} \text{ mol} \end{aligned}$$

$$\text{total amount of CO}_3^{2-} \text{ ions} = \dots\dots\dots \text{mol} \quad [1]$$

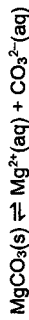
(iii) Hence, calculate the amount of CO₃²⁻ ions precipitated as MgCO₃.

$$\text{Initial moles of CO}_3^{2-} = \left(\frac{50}{1000}\right)(0.04) = 2 \times 10^{-3} \text{ mol}$$

$$\begin{aligned} \text{Total moles of CO}_3^{2-} \text{ precipitated as MgCO}_3 &= 2 \times 10^{-3} - 1.785 \times 10^{-4} \\ &= 1.8215 \times 10^{-3} \\ &= 1.82 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{amount of CO}_3^{2-} \text{ ions precipitated as MgCO}_3 = \dots\dots\dots \text{mol} \quad [2]$$

(iv) Deduce the amount of Mg²⁺ ions removed by precipitation, in step 3 of the procedure in (a). Hence, calculate the amount of Mg²⁺ ions left in FA 1.



$$\text{Moles of Mg}^{2+} \text{ removed by precipitation} = 1.82 \times 10^{-3} \text{ mol}$$

$$\text{Initial moles of Mg}^{2+} = \left(\frac{20}{1000}\right)(0.1) = 2 \times 10^{-3} \text{ mol}$$

$$\begin{aligned} \text{Moles of Mg}^{2+} \text{ left in FA 1} &= 2 \times 10^{-3} - 1.8215 \times 10^{-3} \\ &= 1.785 \times 10^{-4} \\ &= 1.79 \times 10^{-4} \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{amount of Mg}^{2+} \text{ ions removed by precipitation} &= \dots\dots\dots \text{mol} \\ \text{amount of Mg}^{2+} \text{ ions left} &= \dots\dots\dots \text{mol} \quad [2] \end{aligned}$$

(v) Write an expression for the solubility product, K_{sp}, of magnesium carbonate. Include units in your answer.

$$K_{sp} \text{ of MgCO}_3 = [\text{Mg}^{2+}][\text{CO}_3^{2-}] \text{ mol}^2 \text{ dm}^{-6}$$

[1]

(vi) Calculate a value for the solubility product, K_{sp}, of magnesium carbonate.

$$K_{sp} \text{ of MgCO}_3 = \left(\frac{1.785 \times 10^{-4}}{1000}\right) \left(\frac{1.785 \times 10^{-4}}{1000}\right) = 6.50 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$$

$$K_{sp} = \dots\dots\dots [1]$$

(d) A student follows the procedures described and obtained a higher K_{sp} value compared to the literature value of 6.82 × 10⁻⁶ at 25 °C.

Give a possible explanation for the higher K_{sp} value obtained.

The student did not carry out the experiment at 25 °C. He probably carried out the experiment at a temperature at which the equilibrium position of the reaction lies more towards the Mg²⁺ and CO₃²⁻ ions / the forward reaction is favoured. Hence, the K_{sp} value obtained was higher.

[1]

[Total: 16]

2 Planning

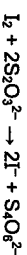
Avogadro's constant, L , is defined as the number of particles in one mole of a substance. The currently accepted value is $6.02 \times 10^{23} \text{ mol}^{-1}$.

The Avogadro's constant, L , can be determined through the electrolysis of acidified aqueous potassium iodide.

During electrolysis, the amount of material discharged at each of the electrodes depends solely on the amount of current that has passed through the system.

A student conducted the electrolysis experiment. When a current was passed through a solution of acidified aqueous potassium iodide, hydrogen gas was produced at one electrode, while iodine was produced at the other electrode.

The amount of hydrogen produced can be determined from the volume of hydrogen gas collected by downward displacement of water. The amount of iodine produced can be determined by titration of a portion of the resultant solution with aqueous sodium thiosulfate.



- (a) Explain why the volume of gas collected was higher than the theoretical volume of hydrogen gas that can be produced in the electrolysis. [1]

The volume of the hydrogen gas that is measured using the downward displacement of water also includes the volume of water vapour.

- (b) (i) Plan an investigation to determine the amount of iodine produced in the electrolysis of acidified aqueous potassium iodide, if a current of 0.50 A is passed for 10 minutes, and hence determine a value for the Avogadro's constant, L .

You may assume that you are provided with:

- 500 cm³ of 0.500 mol dm⁻³ acidified aqueous potassium iodide,
- 0.0100 mol dm⁻³ aqueous sodium thiosulfate,
- ammeter (instrument used to measure current)
- wires and crocodile clips
- adjustable DC power source (battery)
- graphite rods
- the equipment normally found in a school or college laboratory.

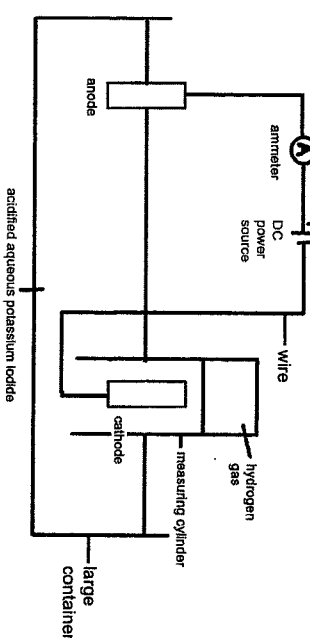
In your plan you should include brief details of:

- a fully labelled diagram of the electrolytic set-up, showing how you would collect and measure the volume of hydrogen gas,
- the apparatus you would use,
- the procedure you would follow for the electrolysis of aqueous potassium iodide.

You need **not** include details of:

- the adjustment of the current setting of the power source to 0.50 A,
- the titration of the resultant solution with aqueous sodium thiosulfate.

Diagram:



1. Assemble the apparatus as shown in the diagram above.
2. Record the initial reading of the measuring cylinder / burette.
3. Switch on the power supply. Adjust current setting to 0.50 A. Start the stopwatch when the current reading is 0.50 A.
4. At the end of 10 minutes, stop the stopwatch.
5. Switch off the power supply and record the final reading of the measuring cylinder / burette.

[5]

- (ii) Table 2.1 gives information about the titration of the resultant solution with aqueous sodium thiosulfate.

Table 2.1

total volume of resultant solution after electrolysis / cm ³	500
volume of portion of resultant solution used in titration / cm ³	25.0
volume of sodium thiosulfate used to reach end-point / cm ³	V

By means of calculations, show how you would use the information in Table 2.1 to determine the Avogadro's constant, L , in terms of V . Show your working clearly.

[electronic charge, $e = -1.60 \times 10^{-19} \text{ C}$]

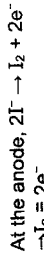
[3]

titre = V/cm^3

Moles of $S_2O_3^{2-} = \frac{V}{1000} \times 0.01 = 1 \times 10^{-5} V \text{ mol}$

$I_2 \equiv 2S_2O_3^{2-}$

$$\text{Moles of } I_2 = 1 \times 10^{-5} V \times \frac{1}{2} = 5 \times 10^{-6} V \text{ mol}$$



$$\text{Moles of electrons, } n_e, \text{ transferred for } 25 \text{ cm}^3 = 2 \times 5 \times 10^{-6} V \\ = 1 \times 10^{-5} V \text{ mol}$$

$$\text{Moles of electrons, } n_e, \text{ transferred for } 500 \text{ cm}^3 = 1 \times 10^{-5} V \times \frac{500}{25} \\ = 2 \times 10^{-4} V \text{ mol}$$

$$Q = It = 0.50 \times (10 \times 60) = 300 \text{ C}$$

$$Q = n_e F$$

$$F = \frac{Q}{n_e} = \frac{300}{2 \times 10^{-4} V}$$

$$F = Le$$

$$L = \frac{F}{e} = \frac{300}{2 \times 10^{-4} V} \times \frac{1}{1.60 \times 10^{-19}} \\ = \frac{9.38 \times 10^{24}}{V} \text{ mol}^{-1}$$

- (c) A student suggested that the percentage error in titre value can be reduced if 0.0500 mol dm⁻³ aqueous sodium thiosulfate was used instead.

Do you agree with this student? Explain your answer.

I do not agree.

With a higher concentration of sodium thiosulfate, the titre value will be lower, resulting in a higher percentage error associated with it.

[1]
 [Total: 10]

3 Determination of a value for the enthalpy change of reaction between CO₂ and KOH via Hess' Law

The reaction between KHCO₃(s) and HCl(aq) is an endothermic process.



Using ΔH_1 and the standard enthalpy change of neutralisation, you will be able to determine the enthalpy change, ΔH_2 , of the following reaction between CO₂ and KOH via Hess' Law.



FA 3 is solid potassium bicarbonate, KHCO₃.
 FA 4 is 2.00 mol dm⁻³ hydrochloric acid, HCl.

(a) Determination of ΔH_1

In this experiment, you will be adding KHCO₃(s) to HCl(aq) in a Styrofoam cup. You will then measure the temperature of the reaction mixture over time. Plotting an appropriate graph using the data obtained will allow you to determine ΔH_1 .

In an appropriate format in the space provided on page 11, prepare tables in which to record for your experiment:

- all weighings to an appropriate level of precision,
- all values of temperature, T , to an appropriate level of precision,
- all values of time, t , recorded to 0.5 min.

It is important that you measure each temperature at the specified time.

Procedure

1. Weigh the capped bottle containing solid FA 3.
2. Place a clean dry Styrofoam cup inside a second Styrofoam cup, then place these in a glass beaker.
3. Using a measuring cylinder, add 40 cm³ of FA 4 into the first Styrofoam cup.
4. Stir the solution in the cup with the thermometer. Read and record its temperature, T (time, $t = 0.0$ min).
5. Continue to stir the solution. Read and record T every 0.5 min.
6. At exactly 2.0 minutes, transfer all the solid FA 3 into the Styrofoam cup in three portions, taking extra care that the mixture that does not overflow. Stir the mixture but do not read T .
7. Continue to stir the mixture. Read and record T at $t = 2.5$ min.
8. Continue stirring and reading T every 0.5 min until $t = 7.0$ min.
9. Reweigh the emptied bottle and its cap.

(i) Results

Mass of capped bottle containing solid FA 3 / g	8.455
Mass of emptied bottle and cap / g	5.423
Mass of FA 3 used / g	3.032

t / min	T / °C
0.0	29.8
0.5	29.8
1.0	29.8
1.5	29.8
2.0	-
2.5	24.6
3.0	24.6
3.5	24.6
4.0	24.7
4.5	24.8
5.0	24.9
5.5	24.9
6.0	25.0
6.5	25.1
7.0	25.2

[3]

(ii) Plot a graph of temperature, T , on the y-axis, against time, t , on the x-axis, on the grid in Fig. 3.1.

Draw a best-fit straight line taking into account all of the points before $t = 2.0$ min.

Draw another best-fit straight line taking into account all of the points after the temperature of the mixture has started to increase steadily.

Extrapolate both lines to $t = 2.0$ min.

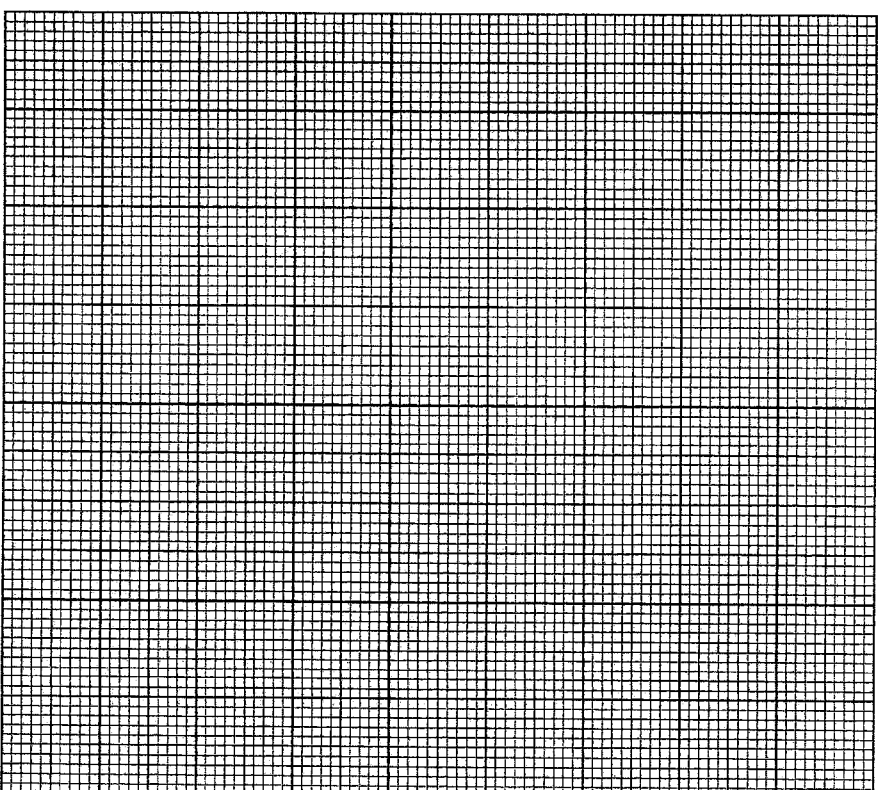
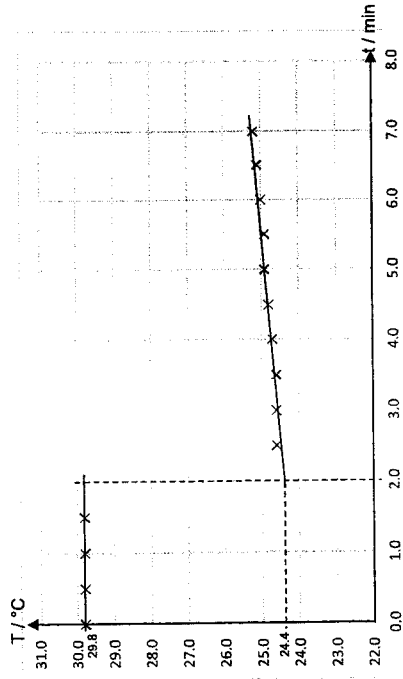


Fig 3.1

[3]



(iii) From your graph, read the minimum temperature, T_{\min} , and the maximum temperature T_{\max} , at 2.0 min. Record these values in the spaces provided below. Deduce the temperature change, ΔT , at $t = 2.0$ min.

$T_{\min} = \dots\dots\dots$
 $T_{\max} = \dots\dots\dots$
 $\Delta T = \dots\dots\dots$

$T_{\min} = 24.4 \text{ }^\circ\text{C}$
 $T_{\max} = 29.8 \text{ }^\circ\text{C}$
 $\Delta T = -5.4 \text{ }^\circ\text{C}$

[1]

(iv) Calculate the heat change, q , using the values you deduced in (a)(iii).

You should assume that the specific heat capacity of the solution is $4.18 \text{ J g}^{-1} \text{ K}^{-1}$, and that the density of the solution is 1.00 g cm^{-3} .

$q = mc|\Delta T| = (40)(4.18)(-5.4) = 902.88 = 903 \text{ J (3sf)}$

$q = \dots\dots\dots$ [1]

(v) Hence, determine the enthalpy change of reaction, ΔH_1 .

[A: K, 39.1; H, 1.0; C, 12.0; O, 16.0]

Moles of KHCO_3 used = $\frac{3.032}{39.1+1+12+16 \times 3} = 0.030290 \text{ mol}$

Moles of HCl used = $\frac{4.0}{1000} \times 2.00 = 0.08 \text{ mol}$

$\text{KHCO}_3 \equiv \text{HCl}$

Hence, KHCO_3 is the limiting reagent.

$\Delta H_1 = + \frac{902.88}{0.030290} \times 10^{-3} = +29.808 = \underline{\underline{+29.8 \text{ kJ mol}^{-1}}}$

$\Delta H_1 = \dots\dots\dots$ [2]

[Turn over

(vi) Calculate the percentage error associated with the measurement of the volume of FA 4.

$\% \text{ error} = \frac{\pm 0.5}{40} \times 100 \% = \pm 1.25 \%$ [1]

(vii) Suggest the effect that using 80 cm^3 , rather than 40 cm^3 , of HCl , would have on the value for ΔT . Hence, deduce and explain the effect this will have on the value for ΔH_1 .

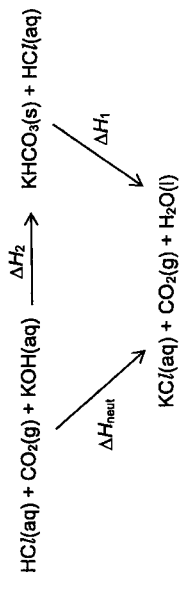
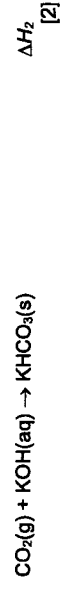
Since HCl was in excess, the amount of heat produced only depends on the number of moles of KHCO_3 present. Hence, ΔT should be halved as the same amount of heat is dissipated over double the volume.

There should be no change in ΔH_1 , as the amount of heat produced and the number of moles of KHCO_3 used is the same. [1]

(b) Determination of ΔH_2

The enthalpy change of neutralisation between a strong acid and a strong base is $-57.3 \text{ kJ mol}^{-1}$.

Using this information and your answer in (a)(v), draw an appropriate energy cycle to determine ΔH_2 , the enthalpy change of following reaction.



By Hess' Law,

$\Delta H_2 = \Delta H_{\text{heat}} - \Delta H_1$

$\Delta H_2 = -57.3 - (+29.808) = -87.108 = -87.1 \text{ kJ mol}^{-1}$

[Total: 14]

4 Inorganic Analysis

- (a) FA 5 contains two cations and two anions.
FA 6 is a solution of ammonium vanadate(V), NH_4VO_3 .

You are to perform the tests described in Table 4.1 and record your observations in the table. Unless otherwise stated, the volumes given below are approximate and should be estimated rather than measured.

In all tests, the reagents should be added gradually until no further change is observed unless you are instructed otherwise.

- You should indicate clearly at which stage in a test a change occurs, recording your observations alongside the relevant tests. Your answers should include
- details of colour changes and precipitates formed,
 - the identities of gases evolved and details of the test used to identify each gas, **except tests (a)(iv), (vi) and (vii).**

If there is no observable change, write **no observable change**.

Table 4.1

test	observations
(i) Using a measuring cylinder, add 2 cm ³ of FA 5 into a boiling tube. Add aqueous sodium hydroxide slowly, with shaking, until no further change is seen.	Grey-green ppt soluble in excess NaOH giving dark green solution Off-white ppt insoluble in excess
Filter the mixture. Retain the filtrate for tests (ii) and (iii). Retain the residue for test (iv).	Off-white residue rapidly turned brown on contact with air / brown residue observed. Filtrate is green.
(ii) Add 1 cm depth of the filtrate from test (i) into a boiling tube. Add one piece of aluminium foil and warm gently.	Gas evolved turns damp red litmus paper blue. Gas is ammonia.
(iii) Add 1 cm depth of filtrate from test (i) into a test-tube. Add an equal volume of barium nitrate followed by excess dilute nitric acid.	White ppt seen insoluble in excess
(iv) Add 1 cm ³ of hydrogen peroxide to the residue from test (i).	Efferescence observed. Black ppt/ dark brown ppt observed.

test	observations
(v) Using a measuring cylinder, transfer 2 cm ³ of FA 6 into a boiling tube. Add 10 cm ³ of dilute sulfuric acid and swirl the mixture gently. The resultant yellow solution is FA 7, which is an acidified solution of VO_2^+ .	Yellow solution turns green.
(vi) Using a spatula, add a very small quantity of zinc powder to the boiling tube containing FA 7 solution from test (v). Swirl the mixture gently and record your observations. Continue to add more zinc powder in small quantities with swirling, until no further colour change is observed. Record all colour changes observed.	Green solution turns blue. Blue solution turns green. Green solution turns violet/purple. Efferescence observed. Gas extinguished lighted splint with a pop sound. Gas is H_2 .
Filter the mixture and retain the filtrate for test (vii). (vii) To 1 cm depth of the filtrate from test (vi), add an equal volume of aqueous hydrogen peroxide.	Violet solution turns red brown/brown/orange/orange-brown. Efferescence observed. Gas relighted glowing splint. Gas is O_2 .

- (b) (i) Using the results in Table 4.1, deduce the identity of the two cations and two anions present in FA 5.

cations

anions

[2]

cations: Cr^{3+} and Mn^{2+}
anions: NO_3^- and SO_4^{2-}

- (ii) Table 4.2 shows some standard electrode potentials.

Table 4.2

electrode reaction	E^\ominus / V
$\text{VO}_2^+ + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}$	+1.00

$\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightleftharpoons \text{V}^{3+} + \text{H}_2\text{O}$	+0.34
$\text{V}^{3+} + \text{e}^- \rightleftharpoons \text{V}^{2+}$	-0.26
$\text{V}^{2+} + 2\text{e}^- \rightleftharpoons \text{V}$	-1.20
$\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$	-0.76

State and explain which ion is responsible for the final colour of the filtrate in test (a)(vi). [2]

The E^\ominus value for Zn^{2+}/Zn of -0.76 V is more negative than all of the above vanadium redox couples except $E^\ominus(\text{V}^{2+}/\text{V})$. Hence, VO_2^+ will be reduced to V^{2+} .

OR

V^{2+} : Zn will not further reduce V^{2+} to V as $E^\ominus_{\text{cell}} < 0$.

$E^\ominus_{\text{cell}} = (-1.20) - (-0.76) = -0.44 \text{ V} < 0$.

Since $E^\ominus_{\text{cell}} < 0$, reaction is not spontaneous.

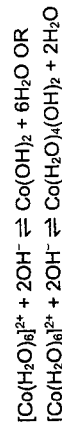
(c) A student performed an analysis using aqueous cobalt(II) chloride, CoCl_2 . The test and observations are recorded in Table 4.3.

Table 4.3

test	observations
To 1 cm depth of $\text{CoCl}_2(\text{aq})$ in a test-tube, add aqueous ammonia dropwise, with shaking, until no further change is seen.	Blue-green ppt formed is partially soluble in excess $\text{NH}_3(\text{aq})$ to form a pale brown solution.
Then add about 1 cm depth of aqueous hydrogen peroxide and shake the mixture thoroughly.	Blue-green ppt turned brown. Effervescence observed. Gas relights glowing splint. Gas is O_2 .

(i) Aqueous CoCl_2 contains $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions.

Write an equation for the formation of the blue-green precipitate. [1]



(ii) Using your answer in (c)(i), account for the partial dissolution of the blue-green precipitate to form a pale brown solution when aqueous ammonia was added in excess. [2]

Ligand exchange occurs where stronger NH_3 ligands displace the weaker H_2O ligands in $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ to form pale brown $[\text{Co}(\text{NH}_3)_6]^{2+}$ complex.

By Le Chatelier's Principle, the decrease in concentration of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ results in position of equilibrium in (c)(i) to shift left, resulting in partial dissolution of $\text{Co}(\text{OH})_2$.

(iii) With reference to changes in oxidation state, explain the formation of the brown precipitate upon the addition of aqueous hydrogen peroxide. [1]

$\text{Co}(\text{OH})_2$ is oxidised to $\text{Co}(\text{OH})_3$ as the oxidation state of Co increases from +2 (in $\text{Co}(\text{OH})_2$) to +3 (in $\text{Co}(\text{OH})_3$).

[Total: 15]