H2 Chemistry Prelim Exam Answers

Paper 1 Answer Key

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

Paper 1 Worked Solutions

1 **(A)**

Charge of nucleon A = (+⅔) + 2(-⅓) = 0
Charge of nucleon B = 2(+⅔) + (-⅓) = +1
Hence, A is a neutron, B is a proton. Statement 1 is correct.

Statement 2: A neutrino does not have a charge.
Hence the charge of C must be -1. C will be attracted to the positive plate.
Statement 2 is correct.

Statement 3: $^{22}_{10}Ne \rightarrow {}^{22}_{11}Na$ is correct.
When a neutron breaks up into a proton, mass number remains constant; proton number increase by 1.

2 **(B)**

The ratio of O_2: Cl^- is 3:2. In chlorates (or any oxoanions), O exist as oxides with OS -2. Hence each O is oxidised from -2 in chlorates to 0 in oxygen gas.

Total number of electrons lost by three O_2 molecules = 3 x 2 x 2 = 12
Total number of electrons gained by two Cl^- = 12
Number of electrons gained by each Cl^- = 6

Change in OS of Cl = -6
Final OS – Initial OS = -6
Initial OS = -1 – (-6) = +5

3 **(B)**

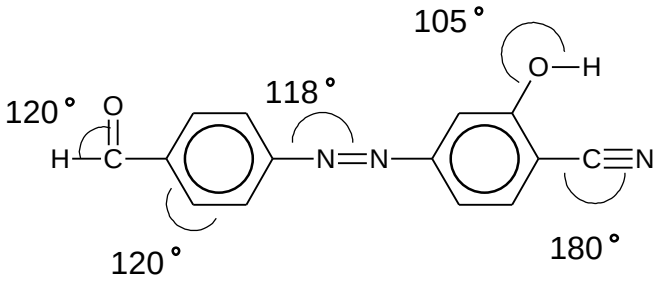
Cations with higher charge and smaller ionic radius have higher charge density, will polarise anion electron cloud more to form a more covalent bond.

For ionic compounds of Group 14 halides, we look for cation with smaller 2+ charge and larger ionic radius (further down the group), hence Pb^{2+} ($\therefore PbF_2$).

For covalent compounds, we look for cation with larger 4+ charge and smaller ionic radius (up the group), hence Sn^{4+} ($\therefore SnCl_4$).

(Note: Although not tested here, students should know that anions with larger electron cloud, are more easily polarised, form more covalent bonds. Hence chlorides form more covalent bonds than fluorides.)

4 **(B)**



There are no sp^3 hybridised carbon atom with 4 bond pairs and 0 lone pairs to give a 109° bond angle.

5 **(D)**

At constant temperature and pressure, V α n.

The initial 5 cm^3 is due to air particles. The final reading of 81 cm^3 includes the volume due to the air particles. After subtracting off 5 cm^3, the volume due to the volatile liquid only is 76 cm^3.

$$M_r = \frac{mRT}{pV}$$

$$M_r = \frac{0.253 \times 8.31 \times (273+97)}{101\,325 \times 76 \times 10^{-6}}$$

$M_r = 101.0$

6 **(C)**

This question test how well students know the definitions of the different enthalpy changes.

Statement 1:
$\Delta H_7 \equiv LE(CaCO_3)$ and $\Delta H_8 \equiv -\Delta H_{sol}(CaCO_3)$
From $\Delta H_{sol} = \sum \Delta H_{hyd} - LE$,
$LE = \sum \Delta H_{hyd} - \Delta Hsol$
$= \Delta H_{hyd}(Ca^{2+}) + \Delta H_{hyd}(CO_3^{2-}) - (-\Delta H_8)$
Hence statement 1 is wrong.

Statement 2:
$\Delta H_7 \equiv 1^{st} + 2^{nd}$ IE of Ca = 590 + 1150 = 1740
Hence statement 2 is correct.

Statement 3:
$\Delta H_2 \equiv \Delta H_{atm}(Ca)$
From Hess's law,
$\Delta H_1 = \Delta H_2 + (\Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7) - \Delta H_8$
rearrange, $\Delta H_2 = \Delta H_1 + \Delta H_8 - (\Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7)$
Hence statement 3 is correct.

7 **(A)**

Calibration methods account for heat loss by assuming a constant heat capacity C of the set-up.

In experiment 1, reaction is a neutralisation reaction.
Total amount of heat evolved depends on amount of water formed. n(water) = 2.0 x 50/1000

Using heat evolved = heat absorbed and letting C be heat capacity in kJ K^{-1}.
2.0 x 50/1000 x 57.4 = C x 10.0 -Eqn ①

For experiment 2, we calculate the enthalpy change of neutralisation for one mole of the weak acid $H_2C_2O_4$. n($H_2C_2O_4$) reacted = 2.0 x 50/1000 x ½ (as NaOH is limiting)

Using heat evolved = heat absorbed
2.0 x 50/1000 x ½ x $|\Delta H_{rxn}|$ = C x 8.5 -Eqn ②

Taking Eqn②/Eqn①, $\frac{2.0 \times 50/1000 \times ½ \times |\Delta H_{rxn}|}{2.0 \times 50/1000 \times 57.4} = \frac{C \times 8.5}{C \times 10.0}$

Hence $|\Delta H_{rxn}| = \frac{57.4 \times 8.5 \times 2}{10}$

8 **(D)**

Statement	Equation	$\Delta G^{\ominus}$	$\Delta S^{\ominus}$
1	$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$	–	+
2	$Cl_2(g) + 2I^-(aq) \rightarrow I_2(aq) + 2Cl^-(aq)$	–	–
3	$MgCO_3(s) \xrightarrow{\Delta} MgO(s) + CO_2(g)$	+	+

Statement 1 only is correct.

9 **(B)**

Graph of colour intensity against time shows 1st order characteristics with constant half-lives. Since NO was used in excess, the variable is $[Cl_2]$. As reaction proceeds, rate decreases proportionally (flatter gradient) with decreasing $[Cl_2]$. Reaction is 1st order wrt Cl_2.

Graph of rate against $[NO]^2$ shows a straight line with constant positive gradient passing through origin, rate is directly proportional to $[NO]^2$. Hence 2nd order wrt to NO.

Statement 1 is correct.

Statement 2 test whether students can draw the link between orders of reaction and stoichiometric coefficient in the mechanism. 1st order wrt to Cl_2 and 2nd order wrt NO tells us one molecule of Cl_2 and two molecule of NO takes part in the reaction up to and including the slow step of the reaction.
Hence, for the given mechanism, when the slow step is the second step, the mechanism will be consistent with the rate equation.

Statement 3 is wrong.

For an overall 3rd order reaction, units of k = $\frac{\text{mol dm}^{-3}\ \text{min}^{-1}}{\left[\text{mol dm}^{-3}\right]\left[\text{mol dm}^{-3}\right]^2} = \text{mol}^{-2}\ \text{dm}^6\ \text{min}^{-1}$.

10 **(D)**

At constant temperature, decomposition of hydrogen peroxide is a first order reaction, hence rate is directly proportional to $[H_2O_2]$. The time taken to use up 10% of initial amount remains constant. After 5 minutes, 90% of initial $[H_2O_2]$ will remain.

Prove:
rate = $k[H_2O_2]$
When $[H_2O_2]$=0.10 mol dm^{-3}, rate = 0.1k. 10% of 0.10 mol dm^{-3} is 0.01 mol dm^{-3}. At a rate of 0.1k, it takes 5 mins to use up 0.01 mol dm^{-3} of H_2O_2.
When $[H_2O_2]$=1.00 mol dm^{-3}, rate = k. 10% of 1.00 mol dm^{-3} is 0.10 mol dm^{-3}. When the amount to be used up increase by 10x and the rate also increase by 10x, the increases cancel out and the time taken will remain constant at 5 mins.

11 **(B)**

Human blood is buffered by the H_2CO_3, HCO_3^- system.
The weak base will react with and remove small amounts of $H^+(aq)$ in the blood to maintain a relatively constant pH of 7.4.
$HCO_3^- + H^+ \rightarrow H_2CO_3$

12 **(C)**

For precipitation, ionic product ≥ Ksp. Substitute $[IO_3^-] = 0.10$ mol dm^{-3}, $[CrO_4^{2-}] = 0.10$ mol dm^{-3}, $[AsO_4^{3-}] = 0.10$ mol dm^{-3} into the corresponding ionic products.

$AgIO_3$: $[Ag^+]\,[IO_3^-] \geq 3.2 \times 10^{-8}$ mol^2 dm^{-6}
$[Ag^+] \geq 3.2 \times 10^{-7}$ mol dm^{-3}

Ag_2CrO_4: $[Ag^+]^2\,[CrO_4^{2-}] \geq 9.0 \times 10^{-12}$ mol^3 dm^{-9}
$[Ag^+] \geq 9.5 \times 10^{-6}$ mol dm^{-3}

Ag_3AsO_4: $[Ag^+]^3\,[AsO_4^{3-}] \geq 1.0 \times 10^{-22}$ mol^4 dm^{-12}
$[Ag^+] \geq 1.0 \times 10^{-7}$ mol dm^{-3}

The first precipitate is Ag_3AsO_4 and it appears at the smallest $[Ag^+]$ of 1.0×10^{-7} mol dm^{-3}.

13 **(A)**

Rearranging $\Delta G^\ominus = -nFE^\ominus$, $-\Delta G^\ominus/F = nE^\ominus$

A quick calculation of $E^\ominus$ will give the more standard reduction potential values.

half-equation	$-\Delta G^\ominus/F$ (V)	$E^\ominus$ / V
$UO_2^{2+} + e^- \rightleftharpoons UO_2^+$	+0.16	+0.16
$UO_2^+ + 4H^+ + e^- \rightleftharpoons U^{4+} + 2H_2O$	+0.27	+0.27
$U^{4+} + e^- \rightleftharpoons U^{3+}$	−0.52	−0.52
$U^{3+} + 3e^- \rightleftharpoons U$	−4.98	−1.66
$Mg^{2+} + 2e^- \rightleftharpoons Mg$		−2.38

Mg metal is a reducing agent that will reduce UO_2^+ and itself oxidised to Mg^{2+}.

Using $E_{cell}^\ominus = E_{red}^\ominus - E_{oxd}^\ominus$, we can see $E_{cell}^\ominus > 0$ (and reaction will be spontaneous) when $E_{red}^\ominus > E_{Mg2+/Mg}^\ominus$.

Since $E_{UO2+/U4+}^\ominus > E_{U4+/U3+}^\ominus > E_{U3+/U}^\ominus > E_{Mg2+/Mg}^\ominus$, UO_2^+ will be reduced by Mg metal all the way to U.

14 **(B)**

Using the equations Q=It and Q=nzF,

where n = amount of Cu deposited, z = 2 for $Cu^{2+} + 2e \rightarrow Cu$

$$n = \frac{It}{zF}$$

The amount of charge supplied will affect the amount of Cu deposited. The amount of charge, Q, is affected by current used and the length of time for which the current is run.

15 **(C)**

The strongest reducing agent has the lowest $1^{st} + 2^{nd}$ ionisation energies.

IEs decrease down the group and increase across the period. Sr is in group 2, to the left of Cd, both in Period 4. Hence Sr should have lower $1^{st} + 2^{nd}$ IEs than Cd.

A glance at the data booklet should tell you that the first two IEs of Sr is lower than for both Ni and Zn.

16 **(D)**

Statement 1:

$2VO_3^- + 3Zn \rightarrow 2V^{2+} + 3Zn^{2+}$. Vanadium is reduced from +5 OS in VO_3^- to +2 in V^{2+}.

Statement 2:

$Cr(H_2O)_6^{3+} + SO_4^{2-} \rightarrow Cr(H_2O)_5(SO_4)^+ + H_2O$. Chromium undergoes ligand exchange reaction where a water ligand is replaced with a sulfate(VI) ligand. Cr remains +3 cation.

Statement 3:

Tartrate anion $^-OOCCH_2(OH)CH_2(OH)COO^-$ has a charge of -2.

In $[Co(tartrate)_3]^{3-}$, the oxidation state of Co is +3. Hence Co has been oxidised by hydrogen peroxide from Co(II) to Co(III). Once $[Co(tartrate)_3]^{3-}$ is formed, it will be reduced back to Co(II) by hydrogen peroxide. $[Co(II)(tartrate)_3]^{4-}$ is acting as a homogeneous catalyst for the disproportionation of hydrogen peroxide.

17 **(A)**

Steps	Cl^-	I^-
add $AgNO_3(aq)$	AgCl ppt	AgI ppt
Filter + wash with H_2O	Residue	Residue
add $NH_3(aq)$	soluble to form Cl^- and $Ag(NH_3)_2^+$ complex	insoluble AgI ppt
Filter	Cl^- and $Ag(NH_3)_2^+$ in filtrate	AgI ppt in residue
Note: All the K^+ ions should have been washed off in the first filtration		

18 **(C)**

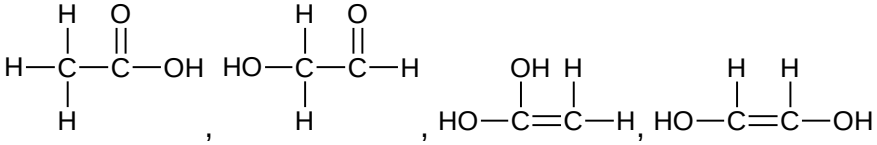
Element	C	H	O
% mass	40	6.7	53.3
Amt	3.33	6.7	3.33
Ratio	1	2	1

Empirical Formula is CH_2O.

Consider Molecular Formula (MF) in increasing number of carbon atoms.

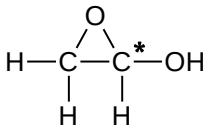
MF is CH_2O:
The C atom is unsaturated, no chiral carbon possible.

MF is $C_2H_4O_2$:

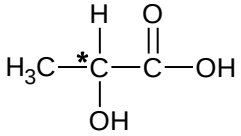


All straight chain structures are not chiral.

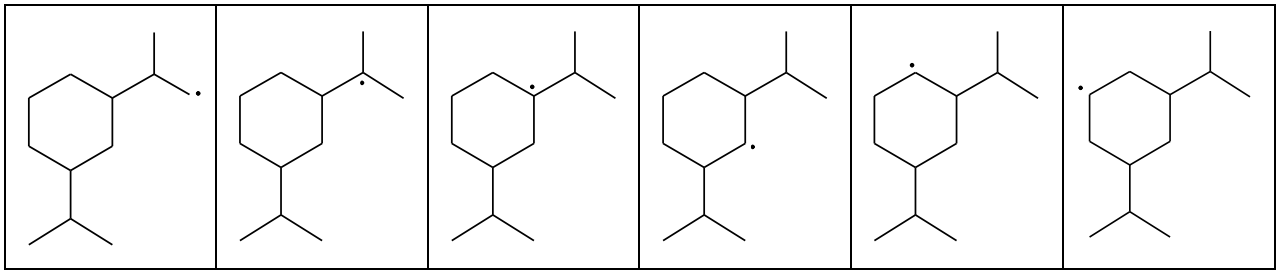
Only a cyclic structure can give a chiral carbon.



Hence, the smallest number of C atoms must be 3, MF is $C_3H_6O_3$:



19 **(A)**



20 **(C)**

A: Correct. Graphene sheet is one layer of carbon atoms in graphite structure. It is non-polar with delocalised π electrons above and below the plane of carbon atoms that repel water. Hence a graphene sheet is insoluble in water.

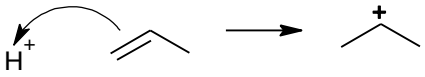
B: Correct. Each C atom of a graphene sheet (graphite layer) is sp^2 hybridised with p-orbitals that overlap with p-orbitals of adjacent carbon atoms. The partial double bond formed strengthens the C-C bond.

C: Incorrect. There are sp^3 hybridised carbon atoms in the graphene oxide layer which have tetrahedral shape. This caused the carbon layer to become "puckered", with some carbon atoms above and below the plane.

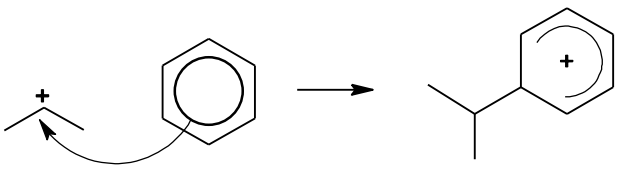
D: Correct. There are σ bonds between sp^3 hybridised carbon and/or oxygen atoms.

21 **(D)**

H_3PO_4 is used as a strong acid catalyst in the EA of H_2O to propene.

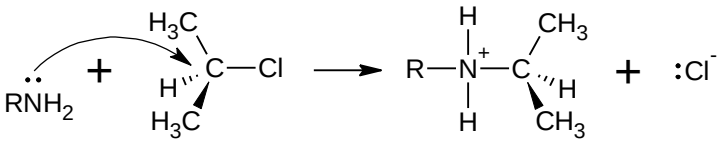


Once the strong electrophile (a carbocation) is formed, it will undergo ES with the benzene.



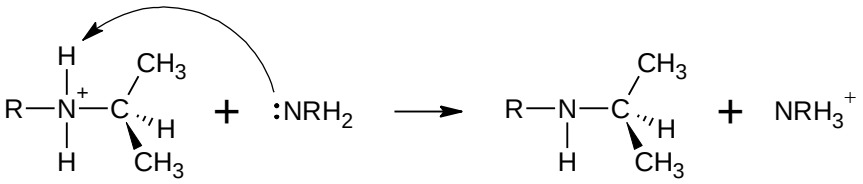
22 **(B)**

Step 1:



RNH_2 is acting as a nucleophile to attack the electron deficient carbon of the C-Cl bond.

Step 2:

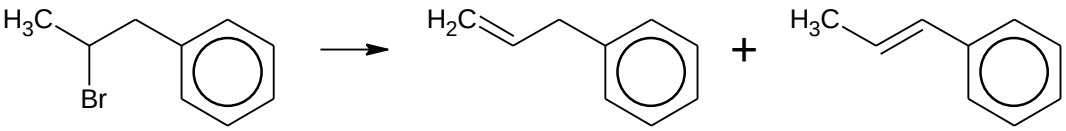


RNH_2 is acting as a Bronsted base. RNH_2 accepts a H^+ from the intermediate to form its conjugate acid RNH_3^+.

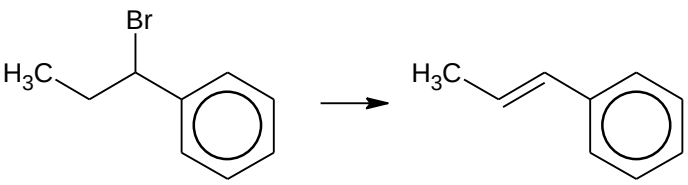
There are no changes in oxidation states for any element in these reactions.

23 **(A)**

In alcohol solvent, the OH^- negative charge is not well dispersed, hence OH^- acts as a base to remove a H^+ from the bromoalkane, Br^- will leave at the same time. Net result is elimination of HBr to form alkene using NaOH in alcohol.

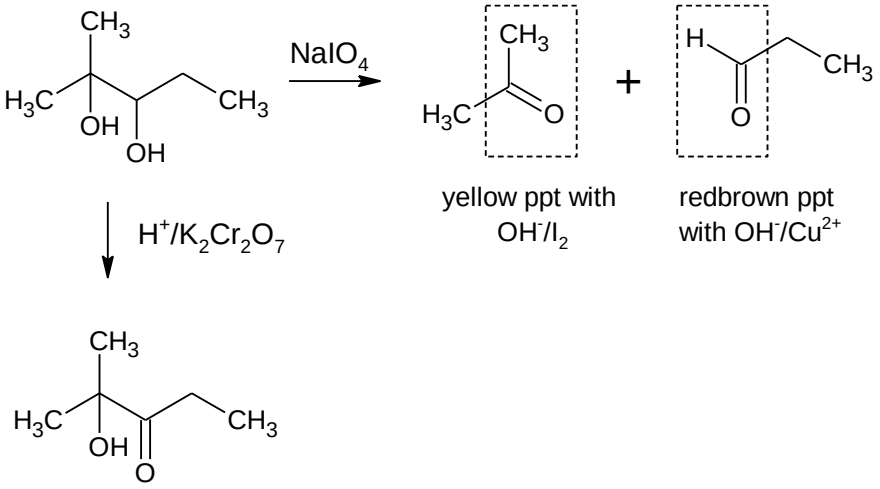


(2-bromopropyl)benzene can form two structurally different alkenes upon elimination of HBr.



(1-bromopropyl)benzene can only form one alkene structure.

24 **(C)**



25 **(A)**

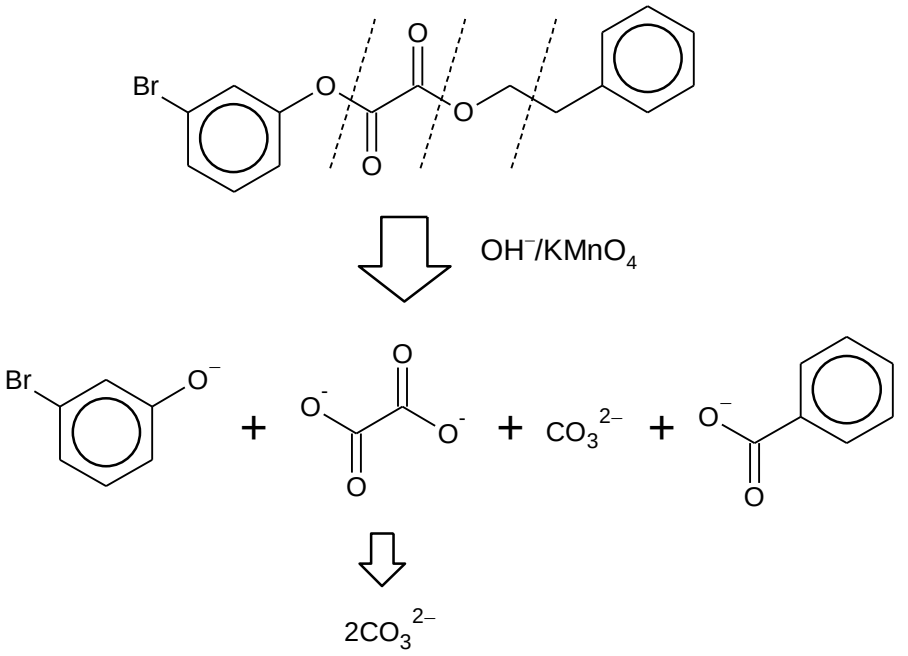
The best electrical conductor has the highest ionic concentration, which depends on extent of dissociation of weak acid, in turn due to strength of acid.

Pyruvic acid, with an electron-withdrawing $CH_3CO–$ acyl group that disperse the negative charge on $–COO^-$ of conjugate base, is the strongest weak acid.

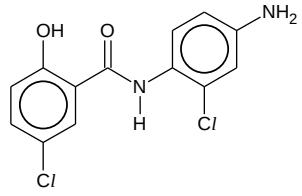
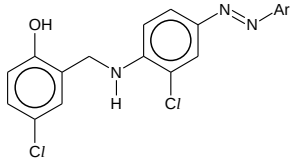
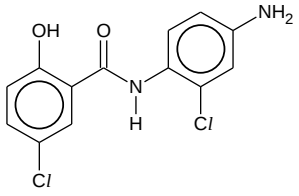
$CH_3–$ and $CH_3CH_2–$ groups of ethanoic acid and propanoic acid respectively are electron-donating groups that intensify the negative charge on $–COO^-$ of conjugate base, are weaker acids.

Pure ethanoic acid, like all simple covalent liquids, only undergo auto-ionisation, producing minuscule amounts of ions.

26 **(D)**



27 **(C)**

H_2 with Ni metal	$LiAlH_4$ in dry ether	$NaBH_4$ in ethanol	Sn in concentrated HC*l*
		no reduction	

28 **(C)**

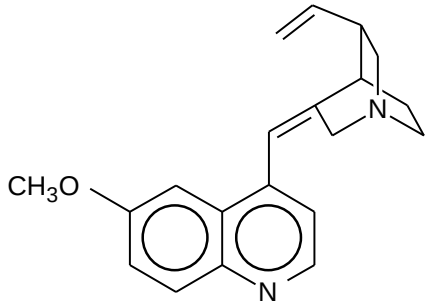
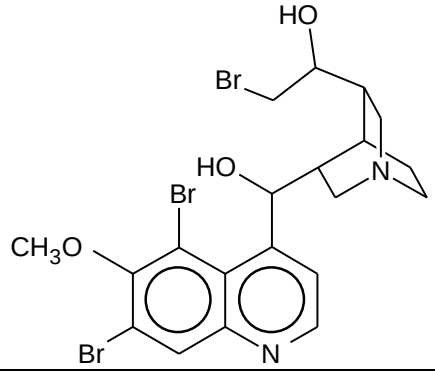
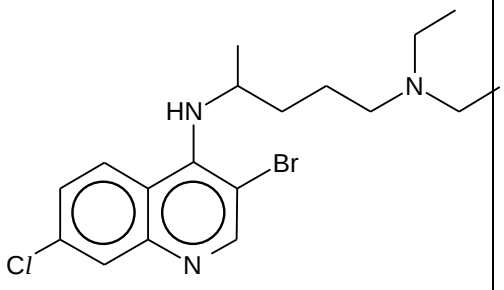
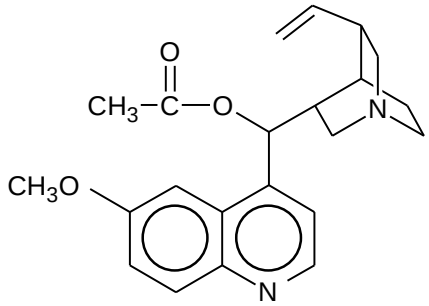
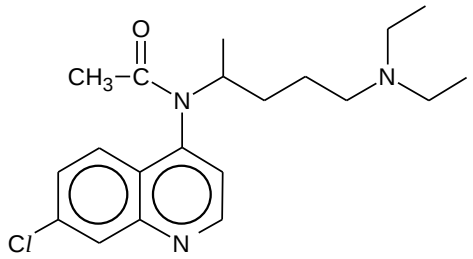
Ease of hydrolysis: P > Q > R

Statement 1 is only partially correct, more importantly, it cannot explain why acyl chlorides are hydrolysed so readily. C*l* is a net electron-withdrawing group as electron-withdrawing electronic effect of electronegative C*l* is stronger than the electron-donating resonance effect due to weak 3p–2p overlap.

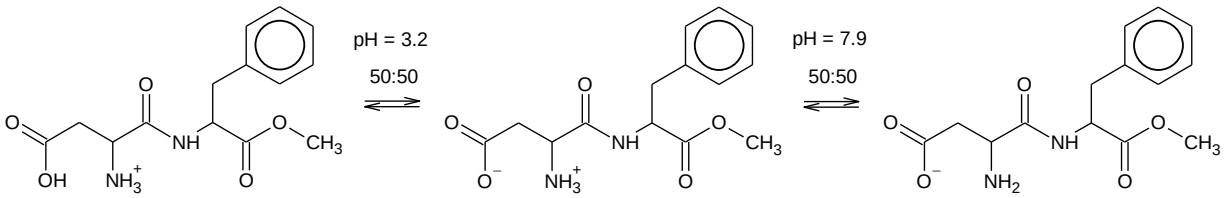
Statement 2 is correct. C*l* is an electronegative atom, causes a partial positive charge on the carbon of the C-C*l* bond.

Statement 3 is correct. One of 3 reasons why nucleophilic substitutions of chlorobenzene do not occur. The other two being stronger partial double bond and C-C*l* in chlorobenzene does not have a partial positive charge due to π electrons.

29 **(C)**

	quinine	chloroquine
aluminium oxide		no elimination reaction
aqueous bromine		
ethanoyl chloride		

30 **(B)**

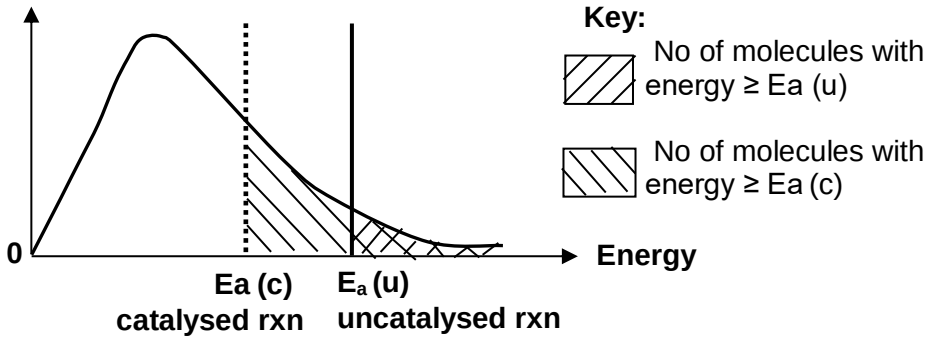


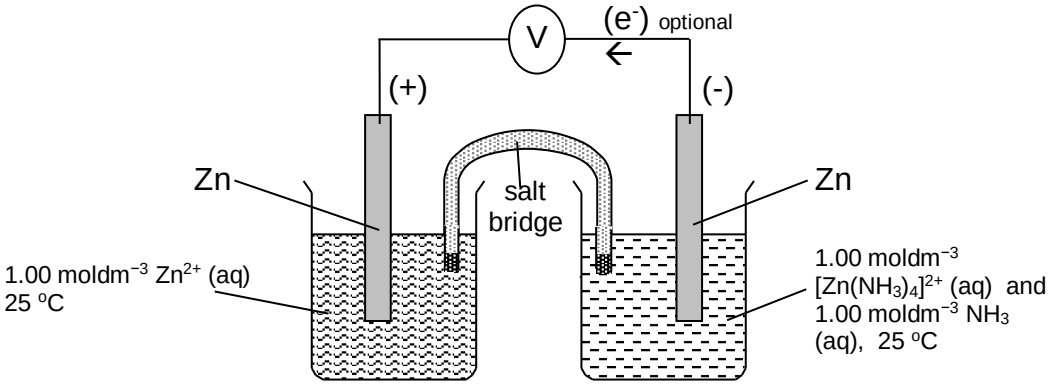
most dominant species below pH 3.2

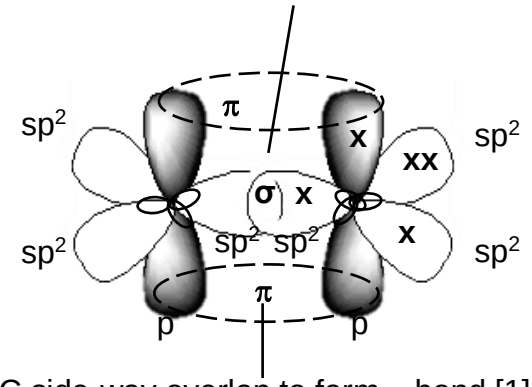
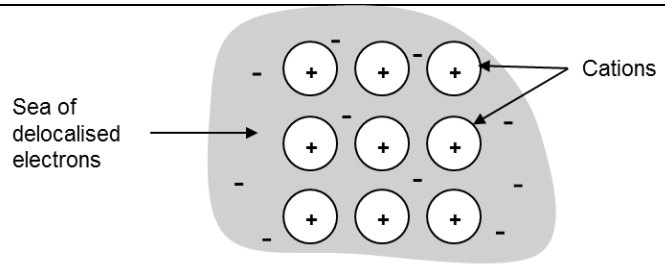
most dominant species between pH 3.2 and pH 7.9

most dominant species above pH 7.9

Paper 2 Answers

1	**(a)**	**(i)**	At a low temperature, by Le Chatelier's Principle, the forward exothermic reaction is favoured to produce more heat. Hence the position of equilibrium will shift to the right to increase yield of ammonia. [1] However the system will take a long time to reach equilibrium. Hence an optimal temperature of 500 ^{o}C is used to ensure rate of reaction is not too slow and makes the production process become uneconomical. [1]
		(ii)	The iron catalyst is in solid state while nitrogen and hydrogen are in gaseous state. It functions as a heterogeneous catalyst as it is in a different phase as compared to nitrogen and hydrogen. [1] Nitrogen and hydrogen (reactants) will be adsorbed to the surface of the catalyst. Bonds in the reactant molecules are weakened which lowers the activation energy. New bonds are then formed between adjacent reactant molecules to form the menthol. The product formed will be desorbed from the surface of the catalyst. [1]
		(iii)	• The catalyst provides an alternative reaction pathway with a lower activation energy, E_a (c) compared to the uncatalysed reaction, E_a. • More molecules will possess energy greater than this lowered activation energy. • The frequency of effective collisions increases. Hence, according to the Collision Theory, the rate of reaction increases. 3 pts: [2], 2 pts: [1] **No. of molecules**  [1] Diagram

		(iv)	Ammonia has a simple molecular structure with hydrogen bonding between molecules. Nitrogen and hydrogen have simple molecular structure with instantaneous dipole-induced dipole interactions between molecules. [1] Ammonia has a higher boiling point than nitrogen and hydrogen due to the stronger hydrogen bonds between molecules. The condenser helps to lower temperature so that ammonia is condensed into liquid while nitrogen and hydrogen remains as gases and is recycled back into the reactor. [1]
		(v)	Sketch of HN_3 shows more deviation from ideal gas than ammonia. [1] Both hydrazoic acid and ammonia have simple molecular structure. Hydrazoic acid has a large electron cloud which is more polarisable, resulting in stronger instantaneous dipole-induced dipole interaction between its molecules than the hydrogen bonds between ammonia molecules. The stronger id-id interactions causes hydrazoic acid to deviate more from ideal gas behavior. [1]
	(b)	**(i)**	 • label the electrode and ions in each half cell with concentration and temperature • salt bridge, voltmeter and label the polarity of the electrodes correctly [2]

		(ii)	[R]: $Zn^{2+} + 2e^- \rightarrow Zn$ [O]: $Zn + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+} + 2e^-$ Overall: $Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{2+}$ [1] $\Delta G^{\ominus} = -nFE^{\ominus} = -2 \times 96500 \times 0.28 = -54040\ Jmol^{-1} = -54.0\ kJ\ mol^{-1}$ [1] Or $\Delta G^{\ominus} = -nFE^{\ominus} = -2 \times 96500 \times 0.28 / 1000 = -54.04\ kJmol^{-1} = -54.0\ kJ\ mol^{-1}$
	(c)	**(i)**	<u>sp^2 orbital</u> of N and C <u>head-on</u> overlap to form σ bond  **x** : valence electrons of N. For reference in cii. <u>p orbital</u> of N and C <u>side-way</u> overlap to form π bond [1]
		(ii)	N_a is more basic than N_b. In N_a, lone pair of electrons are present in the sp^2 orbital that is pointing away from/perpendicular to the delocalised π electron cloud formed with neighboring carbon atom, hence it does not overlap with the delocalised π electron cloud and the lone pair are not delocalised, making the lone pair of electrons available for dative bonding with H^+. [1] N_b is part of amide. Lone pair of electron in N_b is present in the unhybridised p orbital of N, which overlaps with π electron cloud of C=O (and delocalised π electron cloud containing C=N_a), resulting in lone pair of electrons on N delocalising into the π electron cloud of C=O (and delocalised π electron cloud containing C=N_a) and are unavailable for forming a dative bond with H^+. Amides are hence considered to be neutral. [1]
2	**(a)**		 [1] Copper has a giant metallic lattice structure of Cu^{2+} cations surrounded by a sea of delocalised valence electrons, which can act as mobile charge carriers to conduct electricity. [1]

(b) (i) Magnesium.

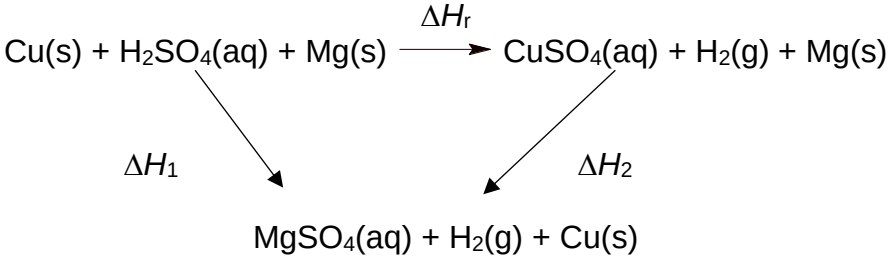
- Mg, Ca and Ba can undergo both reactions but Ag cannot.

  The $E^{\ominus}$ values for Mg, Ca and Ba are more negative than $E^{\ominus}(H^+/H_2)$ and $E^{\ominus}(Cu^{2+}/Cu)$, hence they can be oxidised in both reactions 1 and 2. Ag cannot be oxidised by Cu^{2+} and H^+ since $E^{\ominus}(Ag^+/Ag)$ is more positive. [1]
  (Accept $E^{\ominus}_{cell}$ calculation to prove that reactions are feasible / not feasible.)

- Ca and Ba are too reactive and will react violently with acid since reducing power increases down the group.

  The $E^{\ominus}(M^{2+}/M)$ values get <u>more</u> negative down the group, implying oxidation of metal becomes more favourable, and the reducing strength of metal increases and the reactivity of group 2 metals with acid increases down the group. Ca and Ba reacts vigorously, but reaction of Mg with cold water is very slow. [1]

(ii)



[1] energy cycle

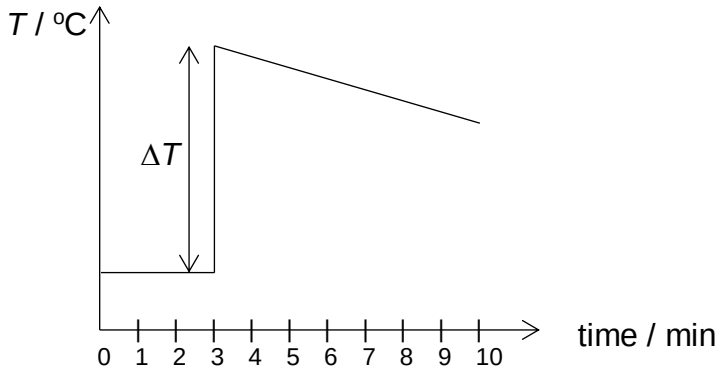
(iii)

1. Using the electronic balance, <u>measure accurately</u> the mass of the Ni bar.
2. Heat a water bath in a beaker on a hot plate until the water is boiling.
3. Tie the Ni bar using a string and lower it into the boiling water bath for 10 min (or any length of time sufficient for the temperature to equilibrate).
4. Measure the temperature of the water bath using a 1^{o}C thermometer. (accept 0.2 ^{o}C division thermometer)
5. Measure 100 cm^3 of water using a 100 cm^3 measuring cylinder and pour it into a polystyrene cup.
6. Measure the initial temperature of the water using a 1^{o}C thermometer. (accept 0.2 ^{o}C division thermometer)
7. Remove the Ni bar from the boiling water bath and place it in the polystyrene cup.
8. Measure the highest temperature reached.

Marking points:

- Measure mass of Ni bar,
- and volume of water using measuring cylinder.
- Use thermometer to measure initial temperature of water bath,
- and the highest temperature reached.
- Use of boiling water bath to heat Ni bar
- and allow time for Ni bar to be heated fully (mention heating for 10 min/time for temperature of Ni bar and water bath to equilibrate)

6 points. [1] for 1-2 point [2] 3-5 points [3] all 6 points

		(iv)	 [1] Label axes with correct units, correct shape of graph and labelling of ΔT
		(v)	Heat evolved = $mc\Delta T + C\Delta T$ = (50 x 4.18 x 34.8) + (9.7 x 34.8) = 7610 J [1] $n(CuSO_4)$ = 50/1000 x 0.3 = 0.015 mol $\Delta H_2 = -7610 / 0.015 \times 10^{-3} = -507$ kJ mol^{-1} [1]
	(c)		Cu has more protons, hence it has a higher nuclear charge. However, the additional electrons are added to the penultimate 3d orbitals. The d subshell shield less efficiently than s and p subshells. [1] Hence, Cu has a larger effective nuclear charge. The valence shell of Cu are more strongly attracted to the nucleus and hence Cu has a smaller atomic radius. [1]

3	**(a)**	**(i)**	$K_{sp} = [Fe^{3+}]\,[OH^-]^3$ units: $mol^4\ dm^{-12}$ [1]
		(ii)	$K_{sp} = 4.0 \times 10^{-38}$ $27x^4 = 4.0 \times 10^{-38}$ Solubility = 2.0×10^{-10} mol dm^{-3} [1]
		(iii)	$FeS_2(s) \rightleftharpoons Fe^{2+}(aq) + S_2^{2-}(aq)$ $K_{sp} = [Fe^{2+}]\,[S_2^{2-}]$ $1.3 \times 10^{-27} = [Fe^{2+}]_{min}(0.25)$ $[Fe^{2+}]_{min} = 5.2 \times 10^{-27}$ mol dm^{-3} $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$ $K_{sp} = [Fe^{2+}]\,[OH^-]^2$ $8.0 \times 10^{-16} = [Fe^{2+}]_{min}(0.40)^2$ $[Fe^{2+}]_{min} = 5.0 \times 10^{-15}$ mol dm^{-3} [1] for 2nd calculation – 1st working to prove that FeS_2 is a less soluble salt. When the first trace of $Fe(OH)_2$ appears, $[Fe^{2+}] = 5.0 \times 10^{-15}$ mol dm^{-3} To calculate the $[S_2^{2-}]$ present: $K_{sp} = [Fe^{2+}]\,[S_2^{2-}]$ $5.0 \times 10^{-15}\,[S_2^{2-}] = 1.3 \times 10^{-27}$ $[S_2^{2-}] = 2.6 \times 10^{-13}$ mol dm^{-3} [1] for final answer
	(b)	**(i)**	$\Delta G^\theta_{ppt} = 2.303RT \log K_{sp}$ $= 2.303\ (8.31)(298)\log\ (1.3 \times 10^{-27})$ $= -153\ 333$ J mol^{-1} $= -153.3$ kJ mol^{-1} [1] for value & correct dp (minus 1 overall if answers in (i) & (ii) are not 1 dp)
		(ii)	$\Delta G^\theta_{ppt} = \Delta H^\theta_{ppt} - T\Delta S^\theta_{ppt}$ $-153.3 = (-178.0) - 298\,\Delta S^\theta_{ppt}$ $\Delta S^\theta_{ppt} = -0.08277$ kJ mol^{-1} K^{-1} (or 8.28×10^{-2} kJ mol^{-1} K^{-1}) $\Delta S^\theta_{ppt} = -82.8$ J mol^{-1} K^{-1} [1] for value & sign [1] for correct units

(iii) ΔS^{θ}_{ppt} is negative which suggests that there is a decrease in entropy due to the formation of an ordered lattice as the solid precipitate forms (or there are less aqueous particles). There are less ways to arrange the particles. [1]

(c) **(i)**

Element	C	Fe	H	N	O
% composition by mass	19.3	14.9	3.2	11.2	51.4
A_r	12.0	55.8	1.0	14.0	16.0
Amount/mol	1.608	0.2670	3.21	0.800	3.213
Mole ratio	6	1	12	3	12

Empirical formula of Y: $C_6FeH_{12}N_3O_{12}$ [1]

(ii) Anion: $[Fe(C_2O_4)_3]^{3-}$ [1] Cation: NH_4^+ [1]

(iii) Coordination number: 6 Shape: octahedral [1]

(iv) In the presence of $C_2O_4^{2-}$ ligands, the partially filled 3d orbitals split into two energy levels, with an energy gap, ΔE.

The d electrons in the lower energy level absorbed energy in the visible spectrum corresponding to energy gap and become excited to a vacant d orbital at the higher energy level (d-d transition).

The complementary colour of violet corresponding to unabsorbed wavelengths of yellow is transmitted.

All 3 points – [2] 2 Points – [1]

4 (a) (i)

	$2SO_2$ +	O_2	$\rightleftharpoons$	$2SO_3$
Initial p/atm	2x	x		0
Change in p/atm	-2y	-y		+2y
Eqm p/atm	2x-2y	x-y		2y

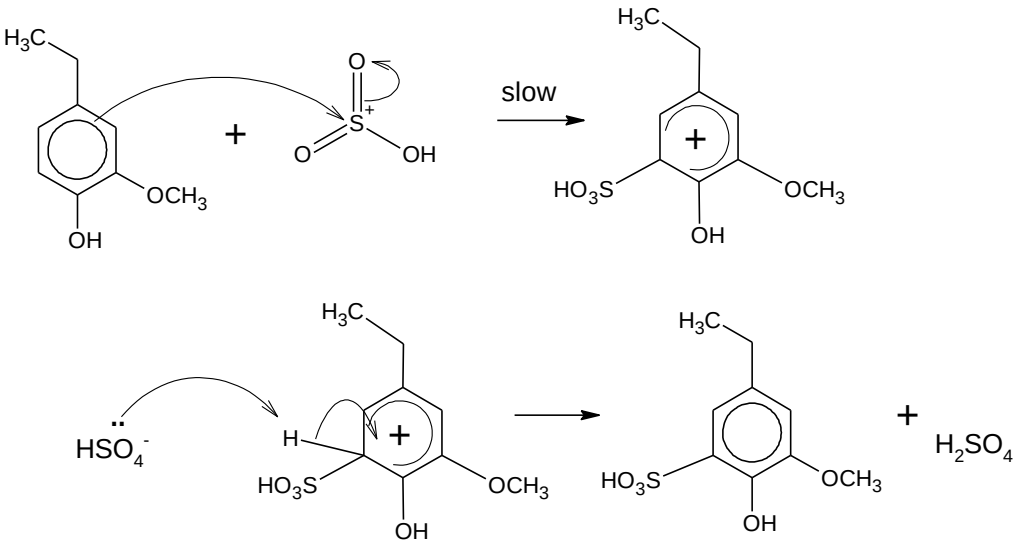
(to show ratio of SO_2 and O_2 is 2:1. Table not required)

At eqm, P_{SO2} is twice of P_{O2}
P_{O2} = 12 kPa

P_{SO3} 104 – 24 – 12 = 68 kPa [1]

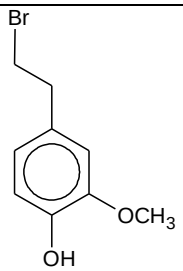
$K_p = 68^2 / [(24)^2(12)] = 0.669\ kPa^{-1}$ answer and units: [1]

(ii) Electrophilic substitution [1]



[2]

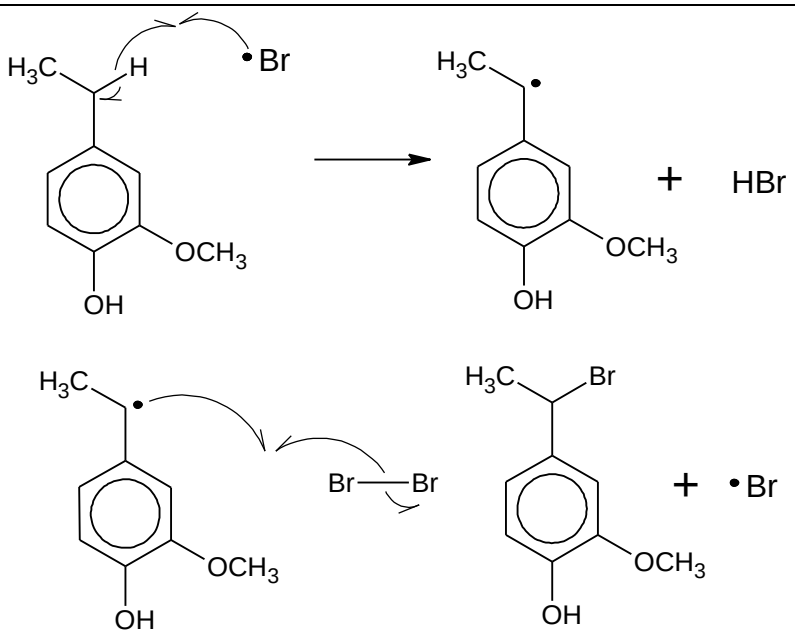
(b) (i)



B: A:B = 2:3

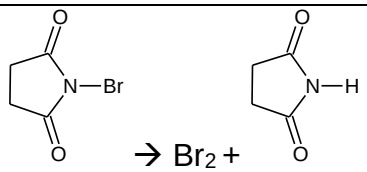
[1] structure
[1] ratio

(ii)

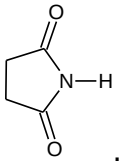


Equations: [1] each

(iii)



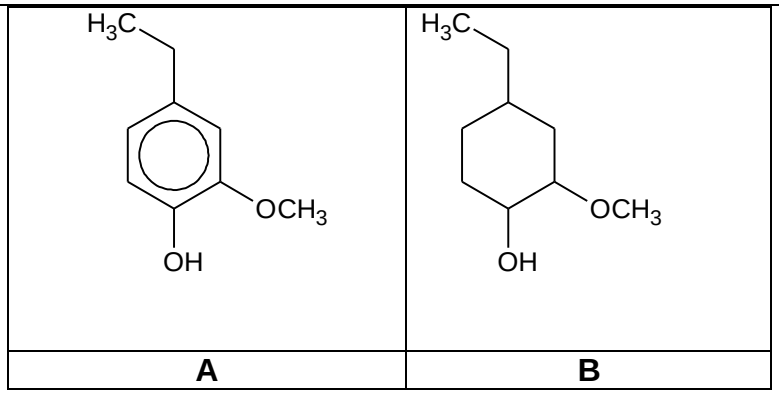
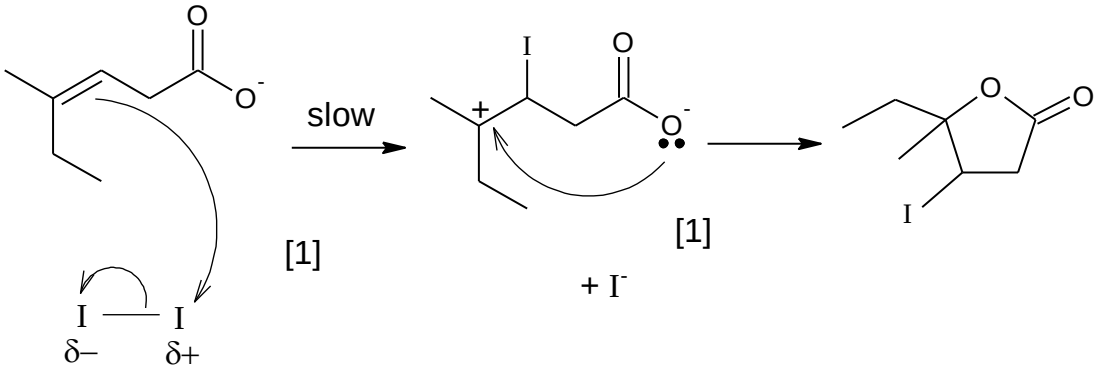
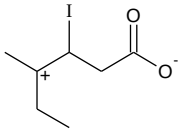
HBr + → Br_2 + [1]

Homolytic fission involves <u>breaking</u> covalent bond with <u>each bonded atom taking an electron</u> to form a radical. [1] H-Br and N-Br break homolytically before forming Br_2 and 

. (Alternatively, show arrows)

(iv)

The benzylic radical is <u>very stable</u>. The p orbital of radical C overlaps with the pi electron cloud system of the benzene ring. The <u>lone electron is delocalised into the benzene ring</u>. [1]

	(c)	**(i)**	 **A** **B** [1] each
		(ii)	The benzene is very stable due to the delocalised pi electron cloud. [1]
5	**(a)**	**(i)**	
		(ii)	$NaHCO_3$ reacts with the carboxylic acid to generate carboxylate ion which is a stronger nucleophile. [1]
		(iii)	4-membered ring lactone experience more significant ring strain, hence it is less stable. [1] There are more electron donating alkyl groups on the intermediate formed for 5-membered ring lactone,  that will disperse the positive charge on the carbon atom. The intermediate is more stable. [1]

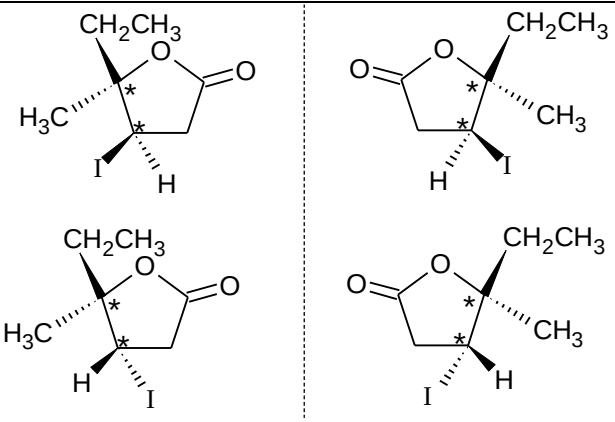
(iv) Add $K_2Cr_2O_7$, H_2SO_4(aq), heat. [1]

If orange $K_2Cr_2O_7$ turns green, 4-membered ring lactone is produced in step 2.
If orange $K_2Cr_2O_7$ remains, 4-membered ring lactone is not produced in step 2. [1]

$KMnO_4$ is not accepted. Alkene in the carboxylate ion (reactant) could be oxidised by $KMnO_4$.

(v) Bonds formed: BE (C-C*l*) = 340 kJ mol^{-1} > BE(C-I) = 240 kJ mol^{-1}
Bonds broken: BE (C*l*-C*l*) = 244 kJ mol^{-1} > BE(I-I) = 151 kJ mol^{-1}
The enthalpy change of reaction will be more exothermic. The product will be of a lower energy level, hence it is more stable. [1]

(b)



mirror plane

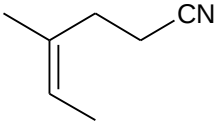
[2]

(c)

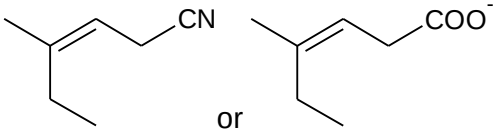
step 1: ethanolic KCN, heat under reflux [1]

step 2: HBr(g), room temperature [1]

step 3: ethanolic NaOH, heat under reflux [1]



[1]
D



or

[1]
E

Paper 3 Answers

1 (a) (i) Amount of $Ba(OH)_2$ = amount of H_2SO_4 = 0.98 / 98.1 = 0.00999 mol [1]

(ii) $2CH_3CO_2H + Ba(OH)_2 \rightarrow (CH_3CO_2)_2Ba + 2H_2O$ [1]

Amount of $Ba(OH)_2$ that reacts with ethanoic acid
= 23.30 / 1000 × 0.800 – 0.09989 = 0.00865 mol
Amount of ethanoic acid = 2 × n($Ba(OH)_2$)
= 2 × 0.00865 = 0.0173 mol [1] allow ecf if equation is not balanced

(iii) $K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$ [1]

	CH_3CO_2H	C_2H_5OH	$\rightleftharpoons$	$CH_3CO_2CH_2CH_3$	H_2O
Initial / mol	1.48 / 60.0 = 0.02466	0.92 / 46.0 = 0.02		0	1.8 / 18.0 = 0.10
Change / mol	-0.007366	-0.007366		+0.007366	+0.007366
Eqm / mol	0.0173 Allow ecf from (ii)	0.01263		0.007366	0.1073

[1] for working out the equilibrium amount of C_2H_5OH, $CH_3CO_2C_2H_5$ and H_2O

Let V be the volume.

$$K_c = \frac{[\frac{0.007366}{V}]\,[\frac{0.1073}{V}]}{[\frac{0.0173}{V}]\,[\frac{0.01263}{V}]} = 3.62$$, no units [1]

(iv) By Le Chatelier's Principle, as temperature is decreased, the forward exothermic reaction will be favoured to compensate for the heat lost, hence position of equilibrium shifts to the right. [1]

As forward reaction is favoured, more products are produced, hence value of K_c increases. [1]

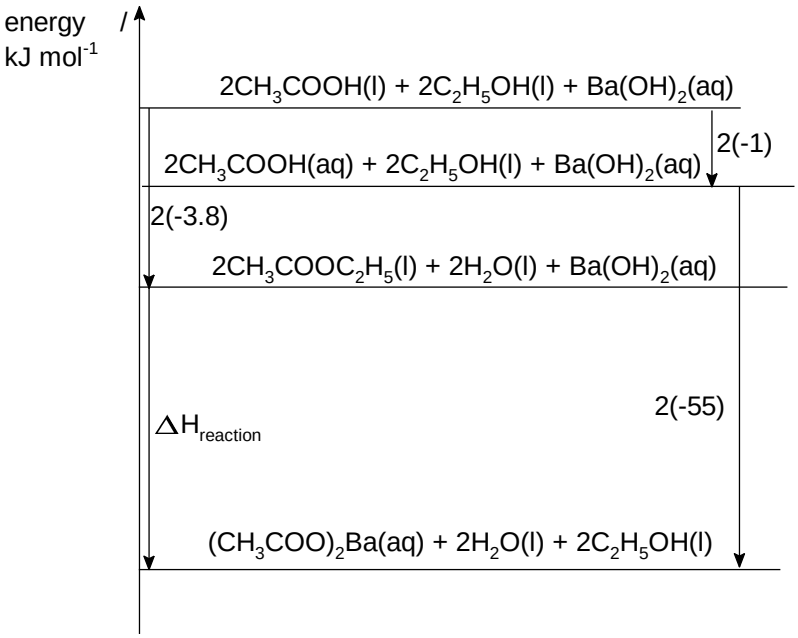
(b) (i)

$\Delta H = \Delta H_f (CH_3COO^-) + \Delta H_f (H^+) - \Delta H_f (CH_3COOH)$
$= -486 + 0 - (-485) = -1$ kJ mol^{-1} [1]

(ii)

Alkaline hydrolysis (nucleophilic acyl substitution) [1]

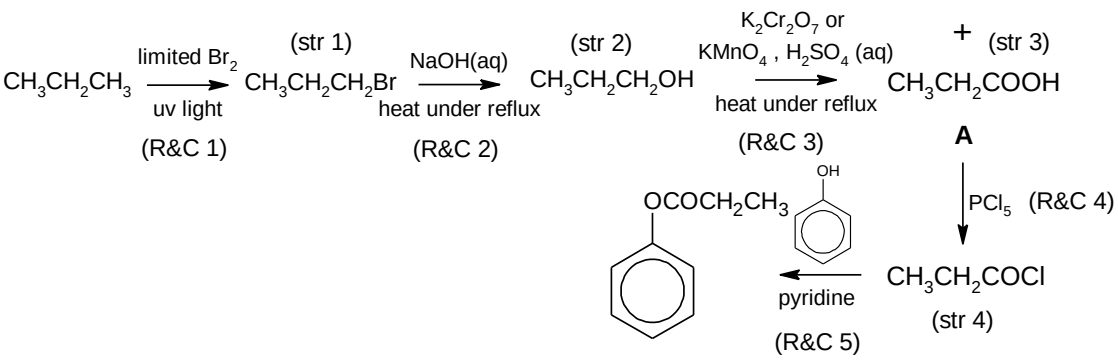
(iii)



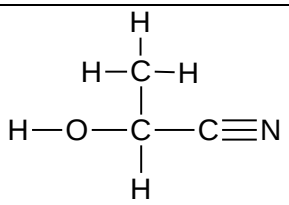
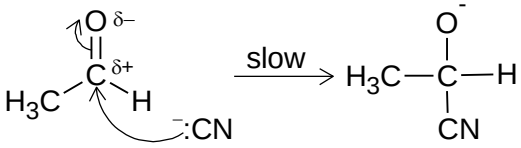
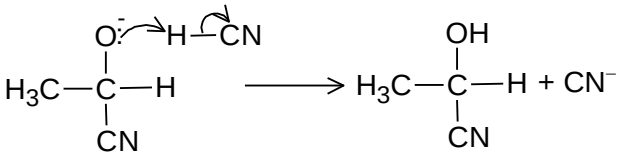
By Hess' Law,
$\Delta H(\text{reaction}) + 2(-3.8) = 2(-1) + 2(-55)$
$\Delta H(\text{reaction}) = -104.4$ kJ mol^{-1} [1]

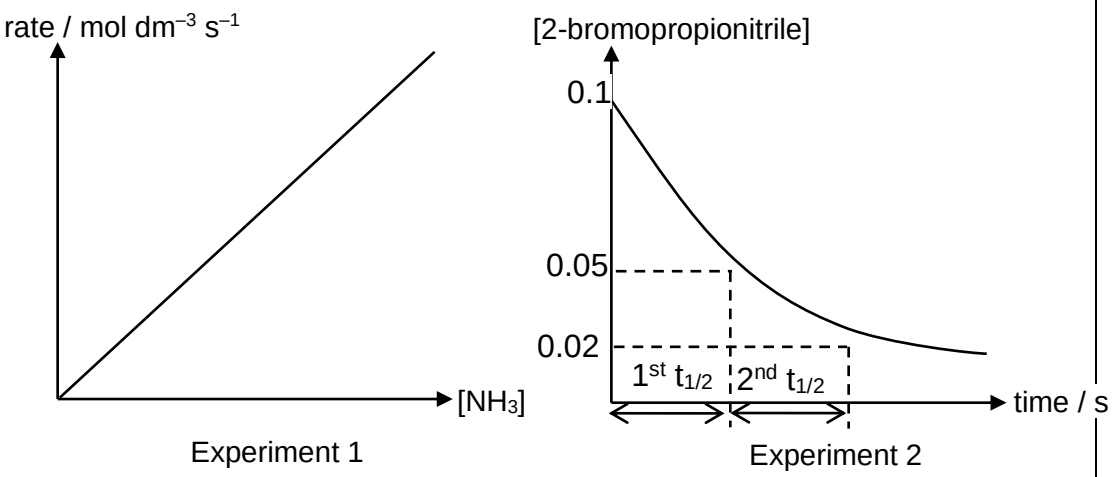
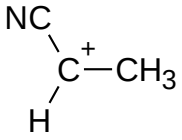
[2] correct energy level diagram
Deduct marks for incomplete cycle, state symbols, missing species in the non-balanced equations.

(c)



Each step (R&C and intermediate) is awarded 1 mark.

2	**(a)**	**(i)**	Aldehyde is unable to form intermolecular hydrogen bonding between molecules and has a low boiling point compared to an alcohol. Thus, the aldehyde will vaporise quickly (or extracted) once it is formed which subsequently condense and collect in the distillate. [1]
		(ii)	 Compound B [1] for correct structure and [1] for displayed formula
		(iii)	Nucleophilic Addition $NaOH + HCN \rightarrow NaCN + H_2O$ [1] for equation and name of mechansim  [1] for correct curly arrow, δ charges, lone pair and negative charge on CN^- and labelling slow step  [1] for correct curly arrow, lone pair and negative charge on intermediate and balanced equation
		(iv)	At step 1, methanol and ethanol are oxidised to methanal and ethanal respectively. There are zero and one electron-donating groups bonded to the C=O group of methanal and ethanal respectively. The carbonyl carbon of methanal is more electron-deficient than that of ethanal. [1] Therefore, the carbonyl carbon of methanal has a larger partial positive charge compared to that of ethanal, making it more susceptible towards nucleophilic attack. [1] or Methanal has two hydrogen atoms bonded to the C=O group compared to one sterically bulky methyl group in ethanal. Hence, CN^- nucleophile would face more steric hindrance when approaching the carbonyl carbon of the ethanal as compared to methanal. [1]

			Therefore, attacking nucleophiles are able to approach carbonyl carbon of methanal more readily than ethanal. [1]
		(v)	PBr_3, room temperature [1]
	(b)	**(i)**	 From experiment 1, the graph of rate against [ethanolic NH_3] is a straight line, with a positive gradient, passing through the origin (or rate is directly proportional to [ethanolic NH_3]). Hence, order of reaction with respect to ethanolic NH_3 is 1st order. [1] for experiment 1 graph and explanation From experiment 2, $\underline{1^{st}\ t_{1/2} = 2^{nd}\ t_{1/2}}$, order of reaction with respect to 2-bromopropionitrile is 1st order. [1] for experiment 2 graph and showing 1st $t_{1/2}$ = 2nd $t_{1/2}$ on graph to prove 1st order
		(ii)	1 mol dm^{-3} (must be at least 10 times greater than 0.1 mol dm^{-3}). This is ensure that [ethanolic NH_3] is in large excess compared to [2-bromopropionitrile]. Thus the reaction is overall first order reaction (or pseudo first order reaction). [1]
		(iii)	 The <u>carbocation formed</u> from 2-bromopropionitrile is <u>unstable</u> as there is an <u>electron withdrawing nitrile group</u> that intensifies the positive charge. [1]

	(c)	**(i)**	At 1st maximum buffering capacity (percentage composition of H_2A = HA^- = 50%), pH = pK_{a1} At 2nd maximum buffering capacity (percentage composition of HA^- = A^{2-} = 50%), pH = pK_{a2} pK_{a1} = 2.30 pK_{a2} = 9.70 [1] for both values
		(ii)	At pH 10.3, the mixture contain 20% HA^- and 80% A^{2-}. Amount of HA^- = 0.100 × 20% = 0.0200 mol Amount of A^{2-} = 0.100 × 80% = 0.0800 mol [1] for both values $H_2A + OH^- \rightarrow HA^- + H_2O$ … eqn 1 $HA^- + OH^- \rightarrow A^{2-} + H_2O$ … eqn 2 Amount of NaOH required for eqn 1 = 0.1000 mol Amount of NaOH required for eqn 2 = 0.08000 mol Total amount of NaOH required = 0.1800 mol Mass of NaOH required = 0.1800 × 40.0 = 7.20 g [1]
		(iii)	The change in ratio of $\frac{[HA^-]}{[A^{2-}]}$ is larger when 1 cm^3 HC*l*(aq) is added. [1] Thus, the new buffer will result in a larger change in pH. [1] or Addition of small amount/volume of acid will have a larger change in concentration of acid and salt. [1] Hence, pH change is larger. [1]
		(iv)	At isoelectric point, alanine exist as a zwitterion (HA^-). There will be strong ionic bonding formed between the zwitterions. [1] The amount of energy released when ion-dipole interaction formed between zwitterion and water molecules, may not be sufficient to overcome all the ionic bonding between zwitterions and hydrogen bonding between water molecules. [1] At low and high pH, alanine exist as cation and anion respectively. At low pH, the cations repel each other and at high pH, the anions repel each other. [1] The ions form ion-dipole interaction with the surrounding water molecules and dissolve. The amount of energy released when ion-dipole interaction formed between ions and water molecules, is sufficient to overcome all the ionic bonding between alanine salt and hydrogen bonding between water molecules. [1]

3 (a) (i)

	Cu	I
mass ratio	1	2
amt / mol	0.01574	0.01576
Simplest ratio	1	1

Hence, the empirical formula of D is CuI.

[1] Table not required. Working can be shown as calculation.

(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ [1]

(iii) There are 3 s orbitals, 6 p orbitals and 5 d orbitals.
p orbital is dumb-bell shaped.

[1] only diagram required

(iv) $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$ [1]

blue — white solid D — yellow/brown solution which dissolves in hexane to form purple layer.

Forms a yellow brown precipitate when mixed.

[1] for all colours

(v) $E_{cell} = E_R - E_O$
$= E(Cu^{2+}/Cu^+) - E(I_2/I^-)$
$= +0.15 - (+0.54)$
$= -0.39$ V <0 hence not feasible. [1]

(vi) As Cu^+ is precipitated by iodide, $[Cu^+(aq)]$ decreases, position of equilibrium of $Cu^{2+} + e^- \rightleftharpoons Cu^+$ shifts to the right and $E(Cu^{2+}/Cu^+)$ becomes more positive, making reduction more feasible/E_{cell} positive hence reaction is more feasible. [1]

	(b)	**(i)**	The complex ion $[NiF_6]^{x-}$ is a species that contains a central metal ion Ni^{n+} surrounded by F^- anions / ligands which forms coordinate bonds to the metal centre. [1]
		(ii)	Ni^{n+} is able to form a stable complex ion because it has energetically accessible vacant d-orbitals to accommodate the lone pairs of electrons donated by the ligands to form the dative bonds [1]
		(iii)	$n(O_2) = 48 / 24000 = 2.00 \times 10^{-3}$ mol [1]
		(iv)	Note: Solution H was divided into 2 equal portions for analysis. $n(H^+ \text{ in H}) = 2 \times n(OH^- \text{ required}) = 2 \times \frac{19.90}{1000} \times 0.20 = 7.96 \times 10^{-3}$ mol [1] $Q = I \times t = 0.40 \times 16 \times 60 = 384$ C $Q = nzF \Rightarrow n(Ni^{2+}) = (384 / (96500 \times 2)) \times 2 = 3.98 \times 10^{-3}$ mol [1]
		(v)	$n_{O_2} : n_{H^+} : n_{Ni^{2+}} = 2.00 : 7.96 : 3.98 = 1 : 4 : 2$ [1] $2K_xNiF_6 + 2H_2O \rightarrow 2xKF + 2NiF_2 + O_2 + 4HF$ Considering the number of F, $12 = 2x + 4 + 4 \Rightarrow x = \frac{12-8}{2} = 2$ [1] Hence, compound E is K_2NiF_6.
		(vi)	$2\ H_2O\ (l) \rightarrow O_2\ (g) + 4H^+\ (aq) + 4e^-$ [1] Oxygen gas is produced at the anode. H_2O and F^- are attracted to the anode. As the $E^\theta(O_2/H_2O) = +1.23$ is less positive than $E^\theta(F_2/F^-) = +2.87$, H_2O is preferentially oxidised to form O_2 at the anode. [1]

	(c)	**(i)**	Down the group, the halide ion <u>increases in size</u> hence the <u>bond length of X →Co/M increases</u>. This give rise to <u>less effective orbital overlap</u> and <u>strength of dative bond formed with the metal ion decreases</u>. [1] to adjust points required according to range of students answers
		(ii)	(A ligand is a species/molecule or anion with at least one lone pair of electrons that it can use to form a dative bond to the transition metal atom/ion.) CH_3CN contains an electron-donating alkyl group which makes the lone pair on N more available than that in NCS- to be used to form a dative bond to the transition metal centre, hence it is a stronger ligand. [1]
		(iii)	• ΔH for the reaction is approximately zero as the same (N→Co) bonds are broken and formed. • ΔS is positive as the number of particles increase, resulting in more ways to arrange the particles hence greater disorder. • Since $\Delta G = \Delta H - T\Delta S$ and $-T\Delta S$ is negative, ΔG is negative and hence ligand exchange of NH_3 with $H_2NCH_2CH_2NH_2$ is very feasible. 3 points [2]. 2 points [1]
4	**(a)**	**(i)**	Propanone, CH_3COCH_3 [1]
		(ii)	$Mg(CH_3COO)_2$ (s) → MgO(s) + CO_2(g) + CH_3COCH_3(g) [1] $Ba(CH_3COO)_2$ (s) → $BaCO_3$(s) + CH_3COCH_3(g) [1]
		(iii)	The Mg^{2+} ion is smaller than Ba^{2+} ion, hence its higher charge density [1] enables it to polarise the electron cloud of CH_3COO^- ion and distort the C-O bond to a greater extent resulting in complete decomposition. [1]
	(b)	**(i)**	Yes, since Al_2O_3 is an amphoteric oxide, it can react with an acidic oxide such as SO_2 to remove it. [1]
		(ii)	MgO in water: pH 8 – 9 Weakly alkaline solution formed as $Mg(OH)_2$ is only slightly soluble in water [1] (due to strong ionic bonds between Mg^{2+} and OH^- ions). Al_2O_3 in water: pH 7 Solution is neutral as Al_2O_3 is insoluble in water [1] (due to strong ionic bonds between Al^{3+} and O^{2-} ions). SO_3 in water: pH 1 - 2 Solution is acidic due to the formation of strong acid H_2SO_4(aq). [1] $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ $H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$
	(c)		The relative acidities of the compounds are in the order: $C_6H_5CH_2OH < C_6H_5OH < C_6H_5CO_2H$

The acidity of a compound depends on the relative stability of its conjugate base. The more stable the conjugate base, the more acidic the compound will be.

The $C_6H_5CO_2^-$ is the most stable as the p orbital of the oxygen atom overlaps with the electron cloud of the –C=O bond and the lone pair of electrons on the oxygen atom delocalise into the –C=O. The negative charge is dispersed over the carbon atom and the two electronegative oxygen atoms, stabilising the $C_6H_5CO_2^-$ ion. [1]

In $C_6H_5O^-$, the p orbital of the oxygen atom overlaps with the electron cloud of the benzene ring and the lone pair of electrons on oxygen atom delocalise into the benzene ring. This causes the dispersion of the negative charge into the benzene ring, stabilising the phenoxide ion.

However the charge dispersion in phenoxide ion is less effective than the dispersion in benzoate ion because the 2 electronegative oxygen atoms in benzoic acids can better accommodate the negative charge. [1]

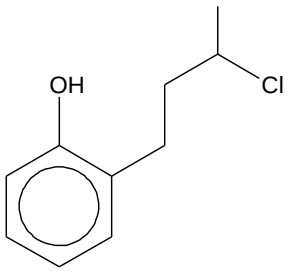
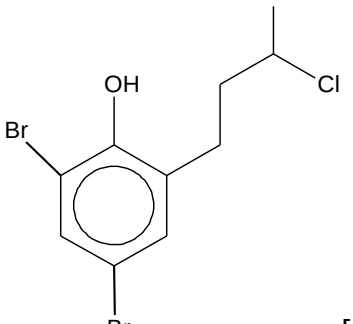
$C_6H_5CH_2O^-$ is destabilised as the electron-donating alkyl group intensifies the negative charge on oxygen. [1]

(d) (i)

Chemistry	Deduction
P reacts with 2,4-DNPH to form an orange ppt.	P contains either an aldehyde or a ketone functional group and undergoes condensation reaction.
P decolourises hot, acidified $KMnO_4$.	P may contain primary/secondary alcohol functional group or aldehyde functional group and undergoes oxidation reaction.
P is heated with excess NaOH(aq) to form Q. This involves the loss of a C*l* atom.	P contains an alky chloride and undergoes nucleophilic substitution to form an alcohol Q.
I_2(aq) is subsequently added to the hot mixture to form R.	Q contains both $–COCH_3$ and $–CH(OH)CH_3$ groups and gives a positive iodoform test. Note: The loss of 2 C atoms denotes the formation of 2 CHI_3 molecules per molecule of P.
P reacts with excess conc H_2SO_4 at 170 °C.	The alcohol group in P undergoes elimination to form alkenes.
P reacts with excess conc H_2SO_4 at 170 °C to give three possible isomeric products.	P contains a secondary alcohol functional group. OR The alcohol group in P is not a primary alcohol.

			OR The structure of P is not $CH_3CH(Cl)CH(OH)CH_2COCH_3$. This structure of P will give 4 possible isomeric products. [1] for each correct deduction. Maximum [3]. P: $CH_3CH(OH)CH(Cl)CH_2COCH_3$ [1] Q: $CH_3CH(OH)CH(OH)CH_2COCH_3$ [1] R: $NaOCOCH(OH)CH_2COO^-Na^+$ [1]
		(ii)	T and U are cis-trans isomers with a C*l* atom directly attached to the double bond, hence they are less susceptible to hydrolysis. [1] This is because the p orbital of the C*l* atom overlaps with the π electron cloud of the C=C bond, resulting in a lone pair of electrons in the p orbital delocalising into the C=C bond. This gives rise to partial double bond character in the C–C*l* bond, hence the bond is strengthened. [1]

5 (a)

A	P
 [1]	 [1]

- (Comparing the molecular formula of A and S, there is a loss of HCl when S is formed.)
  Hence A has <u>1 phenol group that undergoes reduction with 1 mol of Na to form a phenoxide ion</u>
- <u>which then undergoes (intramolecular) nucleophilic substitution with the alkyl halide group</u> to form S.

- A has a <u>1 phenol group that undergoes electrophilic substitution with only 2 mol of aq Br_2, as position 2 is already occupied by a side chain.</u>

- A has a <u>1 phenol group that undergoes neutralisation with 1 mol of NaOH, to form a phenoxide ion</u> which is soluble in water as it can form ion-dipole interactions.

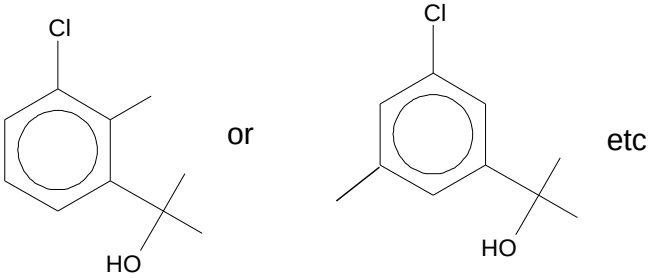
- <u>Methylamine</u> (a nucleophile) <u>undergoes nucleophilic substitution with the alkyl halide group in A.</u>

- 3 mol of A is reacted as the subsequent products also undergo nucleophilic substitution with A, and <u>forms R, a quaternary ammonium salt.</u>

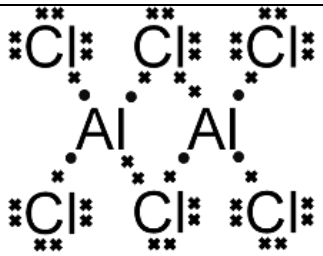
- R has a free Cl ion which reacts immediately with $AgNO_3$ to form AgCl, a white precipitate.

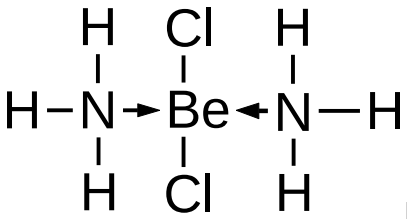
[1] for each bullet [can award max of 5mks]

(b) (i) Aryl halide, tertiary alcohol [1]

(ii)  etc

[1] for correct structure
[1] for correct skeletal formula

			(accept any of the positional isomers) • B does not react with aqueous Br_2, methylamine or sodium hydroxide. $\Rightarrow$ phenol, alkene, halogenoalkane, carboxylic acid absent. To account for the Cl atom in the molecular formula, an aryl halide must to be present. • B does not react with hot acidified potassium dichromate(VI) but with hot acidified potassium manganate(VII), B gives $C_8H_5O_4Cl$. $\Rightarrow$ 1^O and 2^O alcohols absent. 2 carbon containing side chains present • B does not react with alkaline aqueous iodine. $\Rightarrow$ methyl alcohol and ketone absent • 1 mol of B reacts with 1 mol of sodium. $\Rightarrow$ based on this point and above info, one 3^O alcohol present • B does not exhibit enantiomerism. B should not have any chiral carbon present
	(c)	**(i)**	 Bond angle about Al: 109^O [1] [1] for diagram: • each atom has 8 electrons around it • distinguish between the electrons of Cl and Al • show dative bonds
		(ii)	$pV = nRT = \frac{m}{M}RT$ average M $= \frac{mRT}{pV} = \frac{0.52 \times 8.31 \times (150+273)}{101325 \times 70 \times 10^{-6}}$ [1] correct conversion of units $= 257.7$ g mol^{-1} [1] correct numerical answer Assume that sample contain x mole fraction of Al_2Cl_6 and $(1 - x)$ of $AlCl_3$ $(1-x)(133.5) + (x)(267) = 257.7$ $133.5 + 267x - 133.5x = 257.7$ $x = 0.930$ Hence the percentage composition of the dimer is <u>93.0 %</u> [1]
		(iii)	As T increases, Al_2Cl_6 dimers will dissociate to form $AlCl_3$ molecules. Hence average M_r will decrease [1] OR As T increase, solid $AlCl_3$ forms liquid Al_2Cl_6. Hence average M_r will increase. [1]

		(iv)	(A Lewis acid is an electron pair acceptor.) $AlCl_3$ (s) + $6H_2O$ (l) → $[Al(H_2O)_6]^{3+}$ (aq) + $3Cl^-$ (aq) [1] The hydrated form of aluminium chloride exists $[Al(H_2O)_6]^{3+}$ and Cl^- ions. In $[Al(H_2O)_6]^{3+}$, Al is surrounded by six water ligand/molecules and does not have empty orbitals to accept electron pairs and act as a Lewis acid. [1]
	(d)		In $BeCl_2$, Be has only 2 bonding electron pairs around it and can accept 4 more electrons to achieve an octet. NH_3 has a lone pair of electrons. [1] for stating the no of electrons pairs for Be and N Hence $BeCl_2$ can form 2 dative bonds with NH_3, accepting 2 lone pairs of electrons from 2 mol of NH_3.  [1] accept dot & cross diagram too

Paper 4 Answers

1 (a) (i)

	1	2	
Final burette reading / cm^3	25.35	25.45	
Initial burette reading / cm^3	0.00	0.00	
Volume of **FA 2** used / cm^3	25.35	25.45	

Correct headers and units for table [1]
Record volume and burette readings to 2 d.p. [1]

(ii)

Ave $V_{FA\,2}$ used = $\frac{25.35 + 25.45}{2}$ = 25.40 cm^3

Consistent readings used, correct calculation, 2 d.p.[1]
titre value – reference value (δ) ≤ 0.20 Accuracy [1]
titre value – reference value (δ) ≤ 0.40 Accuracy [1]

(iii)

$n_{MnO_4^-}$ reacted = $\frac{0.0200 \times 25.40}{1000}$ = 5.08×10^{-4} mol

$n_{C_2O_4^{2-}}$ present in 25.0 cm^3 = $\frac{5}{2} \times 5.08 \times 10^{-4} = 1.27 \times 10^{-3}$ mol

(b)

n_{NaOH} reacted = $\frac{0.0400 \times 26.75}{1000}$ mol

$n_{H_2C_2O_4}$ present in 25.0 cm^3 = $\frac{\frac{0.0400 \times 26.75}{1000}}{2} = 5.35 \times 10^{-4}$ mol

(c) (i)

$n_{Na_2C_2O_4}$ in 25.0 cm^3 of **FA 1** = $1.27 \times 10^{-3} - 5.35 \times 10^{-4} = 7.35 \times 10^{-4}$ mol

$m_{Na_2C_2O_4}$ in 25.0 cm^3 of **FA 1** = $7.35 \times 10^{-4} \times 134.0 = 9.84 \times 10^{-2}$ g

(ii)

$m_{H_2C_2O_4}$ present in 25.0 cm^3 = $5.35 \times 10^{-4} \times 90.0 = 4.815 \times 10^{-2}$ g

Percentage by mass of $H_2C_2O_4$ in mixture = $\frac{4.815 \times 10^{-2}}{9.84 \times 10^{-2} + 4.815 \times 10^{-2}} \times 100$

= 32.85 ≈ 32.9 %

(d) Heating the solution will ensure the reactants have the required activation energy for effective collisions and reaction to take place.

OR

Reaction involves 2 negatively charge ions hence it has high activation energy.
Rate of reaction/ rate is slow because there is repulsion between MnO_4^- and $C_2O_4^{2-}$.

(e) Results would be more accurate. Lower concentration of **FA 2** would require larger titre volumes (with same uncertainty). Percentage error in volume measurement would be reduced.

(f) **(i)**

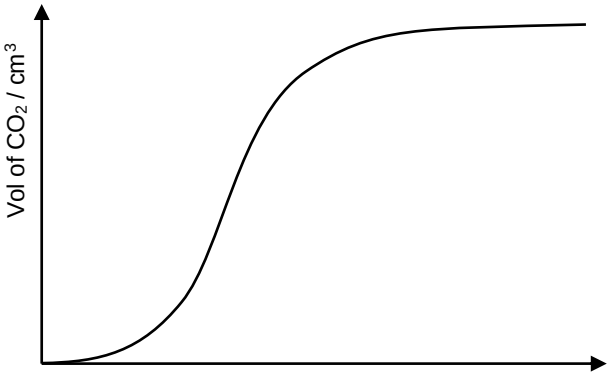


Fig 1.1 [1]

This is an autocatalytic reaction, where the product, Mn^{2+}, acts as a catalyst for the reaction.

- At the start, rate is slow as MnO_4^- and $C_2O_4^{2-}$ are negatively charged and repel each other hence frequency of effective collision is slower. (Or No Mn^{2+} forms at the start, hence reaction is slow)
- As the titration progresses, increasing amount of MnO_4^- is reduced to Mn^{2+} which acts as a catalyst and speeds up the rate of reaction.
- Towards the end of reaction, rate decreases as reactants are used up.

2 bullets – [1], All 3 bullets – [2]

(ii)

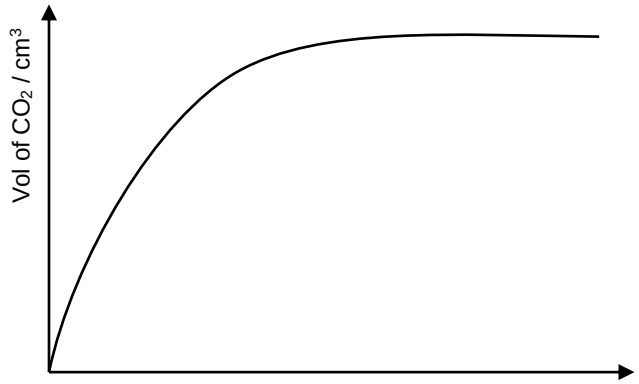


Fig 1.2

(g) **(i)**

1. Fill a burette with $Na_2S_2O_3$.
2. Using a 50 cm^3 measuring cylinder, measure 40.0 cm^3 of $K_2S_2O_8$.
3. Transfer 20.00 cm^3 of $Na_2S_2O_3$ from the burette into a 250 cm^3 conical flask.
4. Using a 25.0 cm^3 measuring cylinder, transfer 25.0 cm^3 of KI and 5.0 cm^3 of starch indicator into the conical flask.
5. Pour the $K_2S_2O_8$ from the measuring cylinder into the conical flask and <u>immediately start</u> the stop watch. Swirl the conical flask and leave it on the table.
6. Stop the stop watch when the colour of the mixture turns blue-black.
7. Record the timing and wash the conical flask and remove any excess water.
8. Repeat steps 2 to 7, using volume indicated in the table below. Add water using a 50 cm^3 measuring cylinder.

Expt	V_{K2S2O8} / cm^3	$V_{deionised\ water}$ / cm^3	V_{KI} / cm^3	$V_{Na2S2O3}$ / cm^3	V_{starch} / cm^3	Time taken / s
1	40.0	0.0	25.0	10.00	5.0	
2	30.0	10.0	25.0	10.00	5.0	
3	20.0	20.0	25.0	10.00	5.0	
4	10.0	30.0	25.0	10.00	5.0	

Mark scheme		
i	At least 2 more expts with lower concentration / vol of $S_2O_8^{2-}$ and equally spaced out.	[1]
ii	1 expt has to be at least half or less than half of original vol of $S_2O_8^{2-}$	[1]
iii	V_{total}, V_{KI}, V_{S2O32-}, V_{starch} all kept constant	[1]
iv	Burette used to measure $S_2O_3^{2-}$; measuring cylinder to measure $S_2O_8^{2-}$ and H_2O	[1]
v	$S_2O_8^{2-}$ must be separated from KI and $S_2O_3^{2-}$ before mixing	[1]
vi	Start timing immediately when mixing occurs; stop timing when blue-black appears	[1]
vii	Table with headers and units (penalised only once)	[1]
viii	Precision of burette to 2 d.p., measuring cylinder to 1 d.p.	[1]

(ii) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

(iii)

$$n_{I_2} \text{ produced} = \frac{V_{S_2O_3^{2-}} \times [S_2O_3^{2-}]}{2}$$

$$= \frac{0.020 \times 0.010}{2} = 1.00 \times 10^{-4} \text{ mol [1]}$$

$$[I_2] \text{ produced} = \frac{1.00 \times 10^{-4}}{0.080} = 1.25 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Rate of } I_2 \text{ formation} = \frac{1.25 \times 10^{-3}}{134} = 9.33 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} \text{ [1]}$$

(iv)

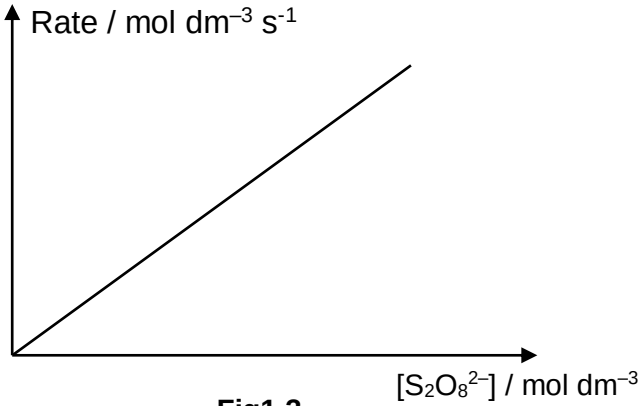


Fig1.3

2 (a)

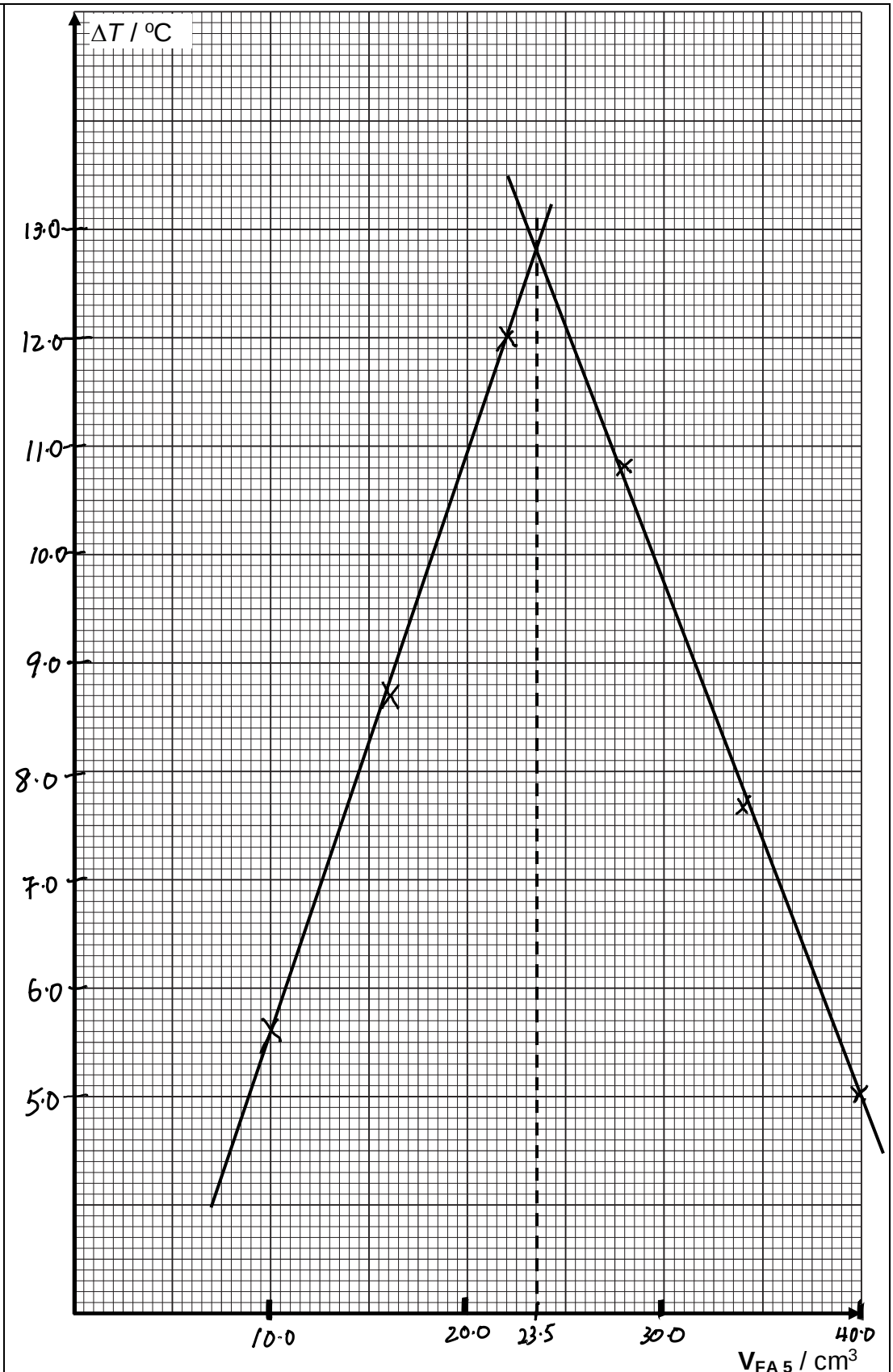
Expt	$V_{FA\,5}$ / cm^3	$V_{FA\,6}$ / cm^3	T_i / °C	T_{max} / °C	ΔT / °C
1	40.0	10.0	32.5	37.5	5.0
2	34.0	16.0	32.5	40.2	7.7
3	28.0	22.0	32.5	43.2	10.7
4	22.0	28.0	32.5	44.5	12.0
5	16.0	34.0	32.5	41.2	8.7
6	10.0	40.0	32.5	38.0	5.6

Correct headings and units, correct volumes of **FA 6** [1]

Recorded to correct precision: measuring cylinder (1 d.p.); temp (1 d.p.) [1]

Correctly calculates T_{max} and ΔT [1]

(b) **(i)**



Linear scale chosen to cover at least ½ of graph (no odd scale) + correct axes label (header/units) [1]

Plots all points within ½ small sq [1]

Draw two lines of best-fit to <u>intersect clearly</u> [1]

		(ii)	volume of **FA 5** = 23.5 cm^3 Reads correctly value of **FA 5** from intercept to nearest ½ sq [1]
	(c)	**(i)**	n_{HCl} in **FA 5** = $\frac{23.5 \times 2.00}{1000}$ = 0.0470 mol
		(ii)	[**FA 6**] = $\frac{0.0470}{\frac{50.0 - 23.5}{1000}}$ = 1.77 mol dm^{-3}
	(d)	1. Increase in total volume does not affect accuracy as there is no change in temperature rise, T, as volume increased proportionately with a corresponding increase in the amt of water / heat produced. 2. Accuracy increased with more experiments carried out as more data points helps to draw more accurate best fit lines / get a more accurate intercept.	

3

Table 3.1

		test	observations		
			FA 7	**FA 8**	**FA 9**
(a)	**(i)**	Add 2 or 3 drops of aqueous iodine.	blue-black / black / dark blue	no observable change / yellow / brown	no observable change / yellow / brown
	(ii)	Add 2 or 3 drops of acidified potassium manganate(VII) and **allow to stand for two minutes.**	no observable change / remains purple / pink	purple / pink / $KMnO_4$ / MnO_4^- decolourise	no observable change / remains purple / pink
	(iii)	Add a 3 cm depth of Sandell's solution and place the tube in the hot water bath for two minutes.	no observable change / solution remains blue	blue solution turns brick red / orange / red brown / orangebrown / yellowbrown / brown ppt	no observable change / solution remains blue

(iv) Starch in **FA 7** reacted with iodine to form a blue-black iodine-starch complex

Aldehyde in **FA 8** is oxidised by $KMnO_4$ / Sandell's solution to carboxylic acid.

(v) Add 1 cm^3 of Tollens' reagent to separate test tubes containing **FA 7**, **FA 8** and **FA 9** and warm in a water bath.

Silver mirror / grey / black ppt appears for solution containing aldehyde (**FA 8)**.

Table 3.2

		test	observations	
			FA 10	**FA 11**
(b)	**(i)**	Add a few drops of aqueous silver nitrate.	No observable change / no ppt / solution remains blue / solution turns more pale (blue)	brown ppt (dissolve in excess)
	(ii)	Add a few drops of aqueous barium nitrate or aqueous barium chloride, then	White ppt	No ppt / no observable change
		add dilute nitric acid.	Ppt insoluble in excess acid / no observable change / white ppt remains	No observable change
	(iii)	Add a few drops of aqueous iodine.	white / cream ppt in yellow / brown solution	Brown solution decolourised
	(iv)	Add a 1 cm depth of aqueous iron(II) sulfate.	No observable change / no ppt / solution remains blue / solution turns more pale (blue)	Green ppt formed (turns brown)
	(v)	Add a 1 cm depth of **FA 11**.	Light blue ppt formed	

		(vi)	Identify the ions in **FA 10** and **FA 11**.
			FA 10 cation Cu^{2+} anion SO_4^{2-} **FA 11** anion OH^-
		(vii)	Equation for **(b)(iii)** : $2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI\ (s) + I_2\ (aq)$ Note: $I_2 + I^- \Leftrightarrow I_3^-$ Equation for **(b)(v)** : $Cu^{2+}\ (aq) + 2OH^-\ (aq) \rightarrow Cu(OH)_2\ (s)$