Section A

Answer **all** the questions in this section.

1 The Group 17 elements and its halides can react with many transition metals.

(a) **(i)** Use the *Data Booklet* to describe the relative reactivity of the Group 17 elements as oxidising agents and relate this reactivity to relevant $E^\ominus$ values. [2]

(ii) The following reagents are contained in three bottles labelled A, B and C.

NaBr(aq) **B** Cl_2(aq) **C** I_2(aq) **A**

Table 1.1 shows the results of tests that were carried out using the reagents in the bottles. In each test, equal volumes of the reagents were mixed and the resultant colour of the solution was recorded.

Table 1.1

test	reagents mixed	colour of resultant solution
1	A and B	brown
2	C and B	orange
3	A and C	brown

State the identity of the reagent in bottle A and write equations for any reactions that occur. [2]

(i) Down the group, $E^\ominus$ becomes **less positive**[1] . Hence, the **oxidising power of the halogens decreases down the group.** (or **lower tendency for the halogen (X_2)** **to** **gain electrons/be reduced.**) **[1] for both trend and explanation**

(ii) The reagent in bottle A is **I_2(aq).** **[1]**

$Cl_2(aq) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$ **[1]**

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Marker Comments for (a):

- For (a)(i), some candidates included unnecessary details such as the trend of electronegativity, bond strengths or effective nuclear charge. This question merely required candidates to use the relevant $E^\ominus$ values and relate them to the oxidising power.
- For (a)(ii), it should be noted that only test 2 has a reaction taking place. Some candidates wrote equations such as $I_2 + Br^- \longrightarrow 2I^- + Br_2$ which is incorrect as I_2 is a weaker oxidising agent than Br_2 and hence will not be able to oxidise Br^- to Br_2.

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(b) Cobalt forms many complexes with ligands such as H_2O, NH_3 and Cl^-. The most common oxidation states of cobalt are +2 and +3.

Table 1.2 gives information about two octahedral cobalt(III) complexes **D** and **E**.

Table 1.2

	complex	colour of aqueous ion
D	$[CoCl_2(NH_3)_4]^+$	violet
E	$[Co(NH_3)_6]^{3+}$	yellow

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

(ii) The five d orbitals in a gas-phase transition metal ion are degenerate, but are split into two levels when the ion is in an octahedral complex.

Explain why the d orbitals are split into two levels in an octahedral complex, including which of the d orbitals are in each level. [2]

(iii) Draw the shapes of the d orbitals that occupy the higher energy level. [2]

(iv) The colour of the complexes is due to the absorption of light at specific wavelengths. The colour observed is the complement of the colour absorbed.

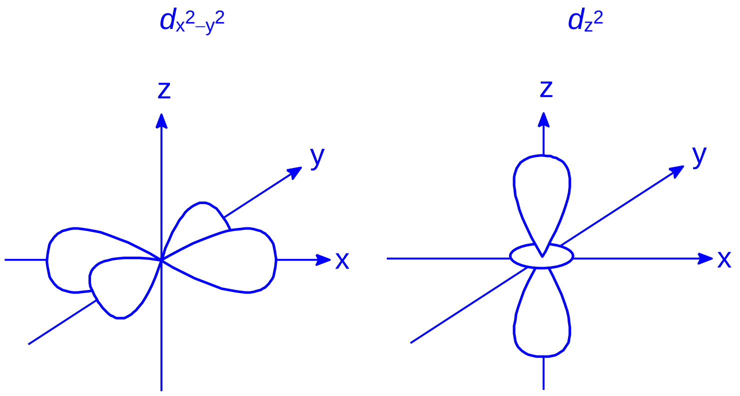
Suggest why the two complexes **D** and **E** have different colours. [1]

(i) A complex **contains a central metal atom/ion attached to ligands through dative / coordinate bonds.** **[1]**

(ii) The $d_{x^2-y^2}$ and d_{z^2} **orbitals have their lobes pointing at the ligands along the axes.** Hence, they experience **greater repulsion** from the ligands**.** On the other hand, the d_{xy}, d_{xz} and d_{yz} orbitals experience less repulsion as their lobes are in between the coordinate axes. **[1]**

As a result, the five *d* orbitals are split into 2 energy levels, with the **$d_{x^2-y^2}$ and d_{z^2} orbitals having the higher energy level** and **the d_{xy}, d_{xz} and d_{yz} orbitals having the lower energy level.** **[1]**

(iii)



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(iv) Cl^- and NH_3 **have different ligand (field strength)**, resulting in **different size of energy gap**. **[1]**

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Marker Comments for (b):

- For (b)(i), it was disappointing that candidates were unable to give the definition of a complex when this is the basic bookwork that should have been done. Candidates are reminded to avoid giving unnecessary details for definition questions as this may result in the imposition of conditions which is not necessarily the case e.g. complex does not necessarily need to include transition metal atoms/ions. Non-transition metal atoms/ions can be part of a complex too.
- For (b)(ii), it was encouraging to see that candidates generally knew how to describe the process of d orbital splitting, although some incorrectly identified the d orbitals present at each energy level. Candidates are reminded to revise the naming of d orbitals e.g. there are no such orbitals as d_x, d_y, d_x or $d_{x^2y^2}$
- For (b)(iii), a sizeable number of candidates were careless and labelled the axes incorrectly, especially when drawing the d_{z^2} orbital for (b)(iii)· Hence, no credit was given despite the correct shape drawn.
- For (b)(iv), candidates were generally able to attribute the difference in colour of the complexes to the difference in energy gap.

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(c) An electrochemical cell is set up using a $Co^{3+}(aq)/Co^{2+}(aq)$ half-cell and a $[Ag(NH_3)_2]^+(aq)/Ag(s)$ half-cell under standard conditions.

The electrode potential of the $[Ag(NH_3)_2]^+(aq)/Ag(s)$ half-cell is –0.37 V.

When the cell discharges, the following reaction occurs.

$$Co^{3+}(aq) + Ag(s) + 2NH_3(aq) \longrightarrow Co^{2+}(aq) + [Ag(NH_3)_2]^+(aq)$$

(i) Write a half-equation for the oxidation of Ag to $[Ag(NH_3)_2]^+$. [1]

(ii) With the aid of the *Data Booklet*, calculate the $E^\ominus_{cell}$ and $\Delta G^\ominus$ for the above electrochemical reaction. [2]

(iii) Explain the effect on $E^\ominus_{cell}$ when H^+ is added to the $[Ag(NH_3)_2]^+(aq)/Ag(s)$ half-cell. [2]

[Turn over

(iv) The Nernst equation can be used to determine the cell potential under non-standard conditions and is given as follows:

$$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n} \log_{10} Q$$

where the value of Q is calculated using this expression $\frac{[Co^{2+}][Ag(NH_3)_2{}^{+}]}{[Co^{3+}][NH_3]^2}$

and n is the number of moles of electrons transferred per mole reaction.

When the electrochemical cell described in **(c)** discharges, the concentration of Co^{3+} in the $Co^{3+}(aq)/Co^{2+}(aq)$ half-cell decreases from 1.00 mol dm^{-3} to 0.75 mol dm^{-3}.

Show that the value of Q is 8.33 when $[Co^{3+}]$ is 0.75 mol dm^{-3}.

Hence, calculate the cell potential at this Co^{3+} concentration. [3]

(i) Overall (given): $Co^{3+} + Ag(s) + 2NH_3 \longrightarrow Co^{2+} + [Ag(NH_3)_2]^{+}$

Oxidation: $\mathbf{Ag(s) + 2NH_3 \longrightarrow [Ag(NH_3)_2]^{+} + e^{-}}$ **[1]**

(ii) $E^{\ominus}_{cell} = +1.89 - (-0.37) = \underline{\mathbf{+2.26\ V}}$ **[1]**

$\Delta G^{\ominus} = -nFE^{\ominus}_{cell} = 1 \times 96500 \times 2.26$ **=** $\underline{\mathbf{-2.18 \times 10^{5}\ J\ mol^{-1}}}$**[1]**

(iii) $[Ag(NH_3)_2]^{+} + e^{-} \rightleftharpoons Ag(s) + 2NH_3 \quad E^{\ominus}_{ox} = -0.37\ V$

H^{+} will react with NH_3 in the half cell causing •**$[NH_3]$ to decrease**. By Le Chatelier's Principle, the •**equilibrium position will shift right** to increase $[NH_3]$ and •**$E^{\ominus}_{ox}$ becomes more positive**. As a result, •**$E^{\ominus}_{cell}$ will become less positive**.

4 points = [2]; 2 – 3 points = [1]

(iv) $Co^{3+}(aq) + Ag(s) + 2NH_3(aq) \longrightarrow Co^{2+}(aq) + [Ag(NH_3)_2]^+(aq)$

Initial	1.00		1.00	1.00	1.00
Change	–0.25		–2(0.25)	+0.25	+0.25
Final	0.75		0.50	1.25	1.25

When $[Co^{3+}] = 0.75$ mol dm^{-3},
$[NH_3] = 0.50$, $[Co^{2+}] = [Ag(NH_3)_2]^+ = 1.25$ mol dm^{-3} [1]

$Q = \frac{[Co^{2+}][Ag(NH_3)_2{}^+]}{[Co^{3+}][NH_3]^2} = \frac{1.25 \times 1.25}{0.75 \times (0.5)^2}$ = **<u>8.33 (shown)</u> [1]**.

$E_{cell} = E^{\ominus}_{cell} - \frac{0.0592}{n} \log_{10} Q$

$= 2.26 - \frac{0.0592}{1} \log_{10} 8.33$ [allow ECF for E_{cell}]

= +**<u>2.21 V</u> [1]**

<u>Marker Comments for (c):</u>

- For (c)(i), candidates were generally able to write the half-equation for oxidation. However, some incorrectly used the reversible arrow instead of the single arrow.
- For (c)(ii), most candidates were able to calculate the $E^{\ominus}_{cell}$, though some used the incorrect value of +0.80V for the $E^{\ominus}_{ox}$, when the value was already given in the question. However, more candidates struggled with the $\Delta G^{\ominus}$ as they have either forgotten the formula linking $\Delta G^{\ominus}$ and $E^{\ominus}_{cell}$ or to include the negative sign to the numerical answer.
- For (c)(iii), many candidates did not write the equilibrium equation which they were referencing to in their explanation regarding the shifting of the equilibrium position, resulting in only partial credit given. Candidates are once again reminded to write the equilibrium equation whenever the answer is linked to LCP. There were some candidates who managed to identify the correct direction of the shift in the equilibrium position, but were unable to give the correct change in $E^{\ominus}_{ox}$ as they did not realise that the equation they have written in (i) was the oxidation equation (reminder: $E^{\ominus}$ value is defined for the direction of the reduction reaction).
- (c)(iv) was the most challenging part for this question. Majority of the candidates failed to consider the fact that the electrochemical cell described in (c) was at standard conditions i.e. concentration of all the aqueous species started out at 1 mol dm^{-3}. Hence, many ended up with the final $[Co^{2+}]$ and $[Ag(NH_3)_2]^+$ as 0.25 mol dm^{-3} and hence could not prove that Q = 8.33. Even so, some candidates should have realised that they could still use the value of Q = 8.33 to calculate the cell potential, which would have warranted 1 mark.

[Turn over

2 Inorganic compounds have various uses in the food and medical industry. For example, sodium hydroxide is used in the chemical peeling of fruits and vegetables, whereas magnesium compounds are used as food additives.

(a) Sodium hydroxide is formed in an explosive reaction between sodium metal and water, as shown in *reaction 1* in Table 2.1. The table also shows some other equations and their related standard enthalpy changes.

Table 2.1

		standard enthalpy change / kJ mol^{-1}
reaction 1	$Na(s) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + ½H_2(g)$	$\Delta H_1^\ominus$
reaction 2	$Na(s) \longrightarrow Na(g)$	+107
reaction 3	$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$	–58
reaction 4	$Na^+(g) + e^- + H^+(aq) \longrightarrow Na^+(aq) + ½H_2(g)$	–850

(i) Deduce the sign of $\Delta S^\ominus$ for *reaction 1*. [1]

(ii) Hence, predict how an increase in temperature affects the spontaneity of *reaction 1*. Explain your answer. [1]

(iii) Write an equation to represent the first ionisation energy of sodium. [1]

(iv) Use the data in Table 2.1 and relevant data from the *Data Booklet* to draw an energy cycle to calculate the standard enthalpy change of *reaction 1*, $\Delta H_1^\ominus$. [3]

(i) $\Delta S^\ominus$ is **positive** because there is **increase in the moles of gaseous particles (or there are mobile ions in aqueous solution),** leading to **greater degree of disorder/increase in entropy**.

[1] for both prediction and explanation

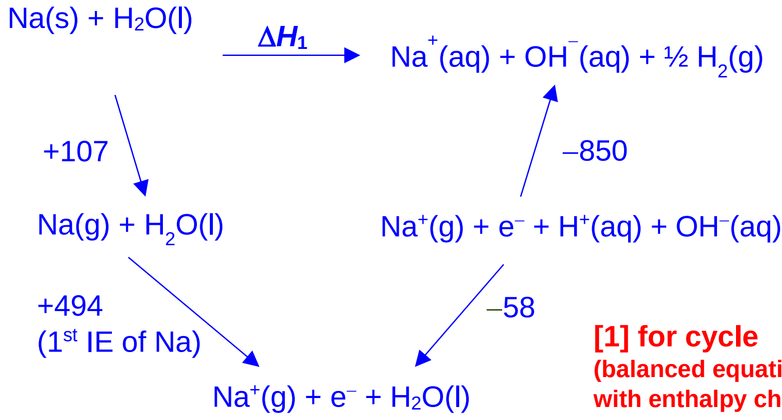
(ii) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

Since $\Delta H < 0$ and $\Delta S > 0$, **ΔG becomes more negative as temperature increases**. Therefore *reaction 1* becomes **more spontaneous as temperature increases**.

[1] for both prediction and explanation

(iii) **$Na(g) \rightarrow Na^+(g) + e^-$** **[1] with state symbols**

(iv)



[1] for cycle
(balanced equations with enthalpy changes)

By Hess' Law,

+107 + 494+ (–850) = ΔH_1 +(–58) **[1] application of Hess Law**

ΔH_1 = **<u>–191 kJ mol^{-1}</u>** **[1]**

Marker Comments for (a):

(i) Students are reminded that when the question is to 'deduce', they are expected not only to state the answer but also to include the **reason** for the answer.

(ii) This reaction already has a negative ΔG due to the negative ΔH and negative (-TΔS). It is not sufficient to just mention that reaction is always spontaneous. It is important to state that when the temperature factor (T) increases, ΔG will become an even more negative value, thus increasing spontaneity. Many students also did not refer to the fact that ΔS is positive, even though the question stated "hence".

(iii) Students are reminded that thermochemical equations must always include the state symbols of reactants and products. Students are also firmly reminded to write **legibly at all times**, especially when some letters of the alphabet are essential as part of written answers, such as state symbols 's' and 'g' in thermochemical equations where each letter represent different physical states of materials.

(iv) Many energy cycles were actually poorly drawn but still credited. Students should take reference from the suggested answer. Common poor practices included separating the Na reactions as a stand-alone path that somehow merges back again; or drawing many additional arrows thinking that every compound needs an arrow.

[Turn over

(b) Magnesium sulfate is used as an additive to enhance the firmness of canned vegetables. It decomposes into magnesium oxide and sulfur trioxide according to the following equation.

$$MgSO_4 \xrightarrow{\Delta} MgO + SO_3 \qquad \Delta H^\ominus = +287.6\ \text{kJ mol}^{-1}$$
$$\Delta S^\ominus = +193\ \text{J mol}^{-1}\,\text{K}^{-1}$$

(i) Calculate $\Delta G^\ominus$ for the above reaction. [1]

(ii) Calculate the theoretical minimum temperature at which decomposition of $MgSO_4$ starts to occur. [2]

(iii) It has been found experimentally that magnesium sulfate starts to decompose at 1124 °C. Suggest a possible reason for the discrepancy between your calculated value in **(ii)** and the experimental value provided. [1]

(iv) The product of the above decomposition, magnesium oxide, is a white hygroscopic solid with a melting point 2850 °C.

Draw a labelled diagram to illustrate the arrangement of the lattice particles in solid magnesium oxide. Your diagram should show clearly the relative size of the different types of particles. [1]

(v) Magnesium oxide and silicon dioxide are both used as lining for furnaces. Using structure and bonding, explain why the melting point of magnesium oxide is higher than that of silicon dioxide. [3]

(i) $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$

$= +287.6 - (298)(+193/1000) =$ **+230 kJ mol^{-1}** **[1] with (+) sign**

(ii) For reaction to be spontaneous, $\Delta G < 0$

$\Delta G = \Delta H - T\Delta S < 0$

$\Delta H < T\Delta S$

$+287.6 < T\left(\frac{193}{1000}\right)$ **[1]**

T > **1490 K** **[1]** **(or 1220 °C (3sf))**

(iii) Value obtained in **(ii)** was based on the **assumption that entropy and enthalpy changes were independent of temperature or decomposition reaction does not occur under standard conditions** **[1]**

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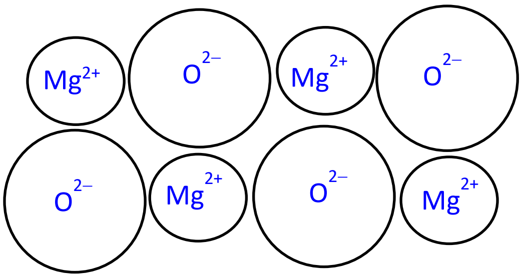
(iv)



[1] cations and anions alternately arranged in regular lattice & size of O^{2-} larger than Mg^{2+}

(v) Magnesium oxide has a •**giant ionic lattice structure**
Silicon oxide has a •**giant molecular structure**.
•**More energy** required to overcome the **stronger •ionic bonds/electrostatic forces of attraction between ions** in MgO than the •**covalent bonds between Si and O atoms** in SiO_2.

[1] 2 points **[2]** 3-4 points **[3]** 5 points

Marker Comments for (b):

(i) Students are reminded that change variables such as ΔG, ΔH, ΔS, ΔT etc should always include a sign to represent the change in the variable being discussed.
Students are also reminded to not be confused between the various temperature and pressure conditions. Standard conditions are not the same as standard temperature and pressure (All these can be derived from the Data Booklet).

Standard conditions:	298 K, 10^5 Pa (1 bar), 1 mol dm^{-3} (solutions)
Standard temperature and pressure:	273 K, 10^5 Pa (1 bar)
Room temperature and pressure:	293 K, 101325 Pa (1 atm)

(iii) This question was to illicit responses which suggested to how ΔH, ΔS values are dependent when temperature changes but the theoretical decomposition temperature which was calculated using the equation $\Delta G = \Delta H - T\Delta S$ would have assumed that these variables were independent of temperature, hence the different values observed, or that the conditions were not of standard conditions. Reasons such as heat loss or heat gained are irrelevant as they are effectively assuming the experiment execution was flawed. Some students suggested that is due to $MgSO_4$ having partial covalent character, but that can only explain deviation from theoretical calculation, whereas ΔH and ΔS values in a typical context must be experimentally derived.

(iv) Students are reminded to clearly label the species in any diagrams drawn clearly (atoms, ions etc). Mg^{2+} and O^{2-} ions are isoelectronic, thus with a higher nuclear charge for Mg^{2+}, the cation should be smaller in size as compared to O^{2-} ion.

(v) In this question, the mention of SiO_2 being used as 'lining for furnaces' suggested that it should have a very high melting point to withstand the high temperatures of furnaces, thus implying that it has a giant molecular structure rather than simple molecular structure. Students are reminded to state clearly the forces broken during melting or boiling for the various bonding structures, whether the forces are being oppositely charged ions for ionic bonds, or covalent bonds **between atoms** in a giant molecular structure.

(c) Magnesium carbonate is sparingly soluble in water. It is therefore commonly used as an additive in table salt to prevent it from clumping. Magnesium carbonate has a solubility of 1.26×10^{-4} mol dm^{-3} at 25 °C.

(i) Write the solubility product, K_{sp}, expression for magnesium carbonate, stating its units. [2]

(ii) Calculate a value for the solubility product, K_{sp}, for magnesium carbonate. [1]

(iii) When 0.0500 mol of solid Na_2CO_3 is added to a 1.0 dm^3 saturated solution of $MgCO_3$ at 25 °C, a precipitate forms in the solution.

Calculate the concentration of $[Mg^{2+}]$ in the resultant solution. [2]

(i) $K_{sp} = \mathbf{[Mg^{2+}][CO_3^{2-}]}$ **[1]** **mol^2 dm^{-6}** **[1]**

(ii) $K_{sp} = [Mg^{2+}][CO_3^{2-}]$

$= (1.26 \times 10^{-4})^2$

$= \underline{\mathbf{1.59 \times 10^{-8}}}$ **[1]** mol^2 dm^{-6}

(iii) Let the $[Mg^{2+}]$ in this resultant solution be s mol dm^{-3}.

$$\mathbf{MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)}$$

Eqm conc. $\quad s \quad (s + 0.0500)$

$K_{sp} = s(s + 0.0500)$ **[1]** $\approx s(0.0500)$ [assume $s << 0.0500$]

$\underline{\mathbf{1.59 \times 10^{-8}}} = s(0.0500)$

$[Mg^{2+}] = s = \underline{\mathbf{3.18 \times 10^{-7}}}$ mol dm^{-3}

[1] ecf K_{sp} value from **(ii)**

Marker Comments for (c):

(iii) In this question, though the initial solution contained a saturated solution of $MgCO_3$, the addition of a common ion CO_3^{2-} from Na_2CO_3 (initial total concentration 0.050126 mol dm^{-3}) would result in a shift in equilibrium position to reduce the solubility of the $MgCO_3$ and it is this new solubility that is required to be calculated. Many students were unaware of how to make mathematical approximations, where $(A+B) \approx A$ if $A \gg B$.

[Total: 19]

3 **(a)** Remifentanil ($C_{20}H_{28}N_2O_5$) is a synthetic opioid drug. It is given to patients during surgery to relieve pain and as an adjunct to an anesthetic.

A possible synthesis route of Remifentanil is shown in Fig. 3.1.

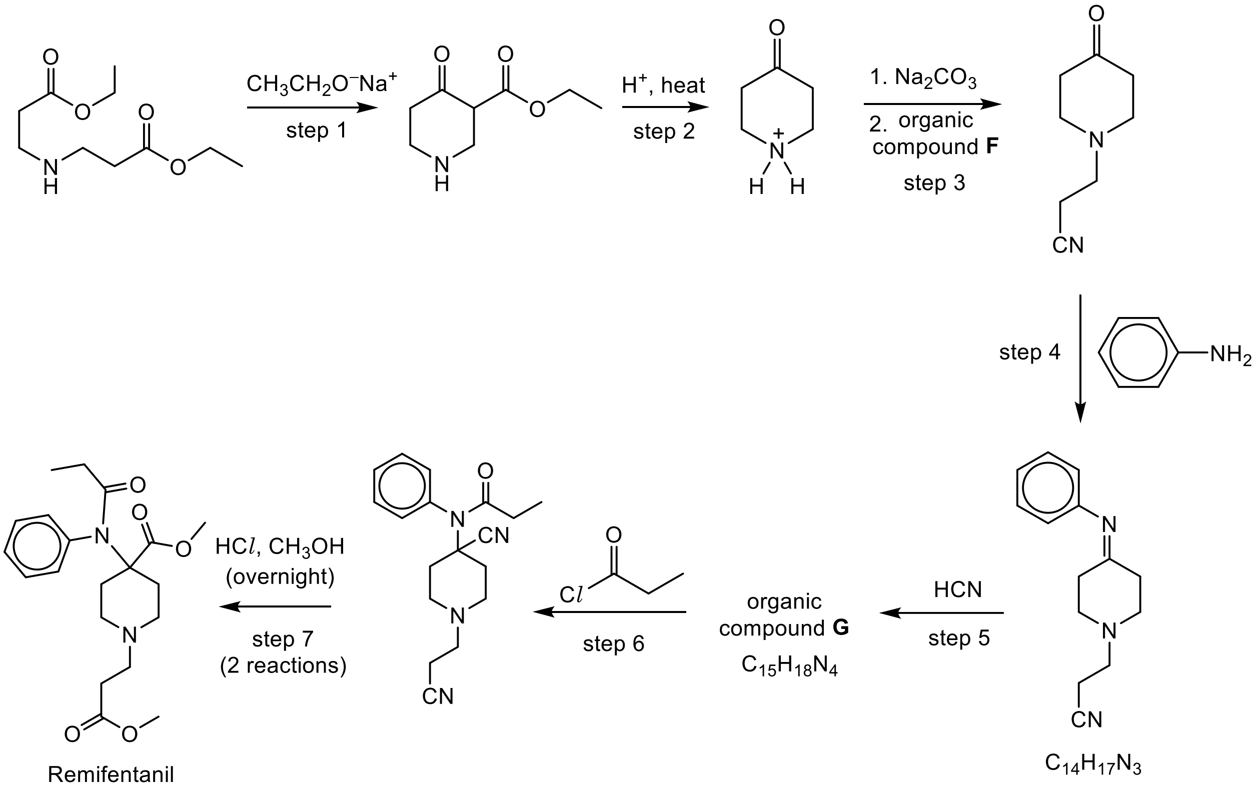
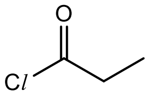
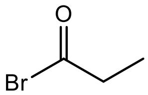


Fig. 3.1

(i) Name the types of reactions occurring in step 4 and step 7 (2 reactions occur in step 7). [3]

(ii) Draw the structure for the organic compound **G.** [1]

(iii) Suggest why step 5 is carried out at a temperature of about 10 °C. [1]

(iv) When the reagent  in step 6 is replaced by , it was found that the reaction was five times faster. Suggest an explanation for this observation. [1]

(v) Given that step 3 is a nucleophilic substitution reaction, suggest:

- why sodium carbonate was used and
- the structure of the organic compound **F**. [2]

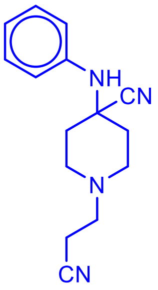
(i) Step 4: **condensation** **[1]**

Step 7: **acidic hydrolysis** **[1]**
condensation or nucleophilic (acyl) substitution **[1]**

Marker Comments:

Drawing from their knowledge of the 2,4-DNPH reaction with carbonyl compounds, most students can readily identify reaction 4 as a condensation reaction. However, reaction 7 presents a slightly more challenging scenario for students. Despite their familiarity with the reactants and products involved, some students find it perplexing. Ideally, they should have been able to deduce two possible reactions: the transformation of a nitrile into a carboxylic acid through acidic hydrolysis (inferred from the overnight reaction with HCl) and a condensation reaction with methanol resulting in an ester. Curiously, a group of students erroneously categorizes it as a basic hydrolysis reaction.

(ii) **G** is



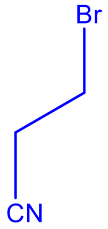
[1]

(iii) **HCN is a toxic gas with a low boiling point.** **[1] for both**

(iv) **C−Br is weaker than C−Cl**, thus **less energy is required to break the bond**. **[1]**

(iv) Na_2CO_3 was added to **neutralise the acidic salt/cation to form the amine/nucleophile.** **[1]**

F is



[1] (accept Cl or I in place of Br)

Marker Comments:

(ii) Most students are capable of drawing the structure of compound **G** based on the given reagent/condition and the product from step 6. However, a significant number of them lose points due to a recurring error that mirrors their performance in paper 2 - they neglect to include the hydrogen bonded to the nitrogen atom. In skeletal formulas, it's commonly understood that only hydrogen atoms attached to carbon atoms are typically omitted.

(iii) Upon reviewing the students' responses, it becomes evident that many failed to recognize this as a straightforward nucleophilic addition of HCN to the C=N bond. They could have applied their knowledge of carbonyl compound reactions with HCN to arrive at the correct answer. It's noteworthy that some students missed the point that HCN has a low boiling point, making it a potentially toxic gas if the temperature exceeds 10°C.

Marker Comments:

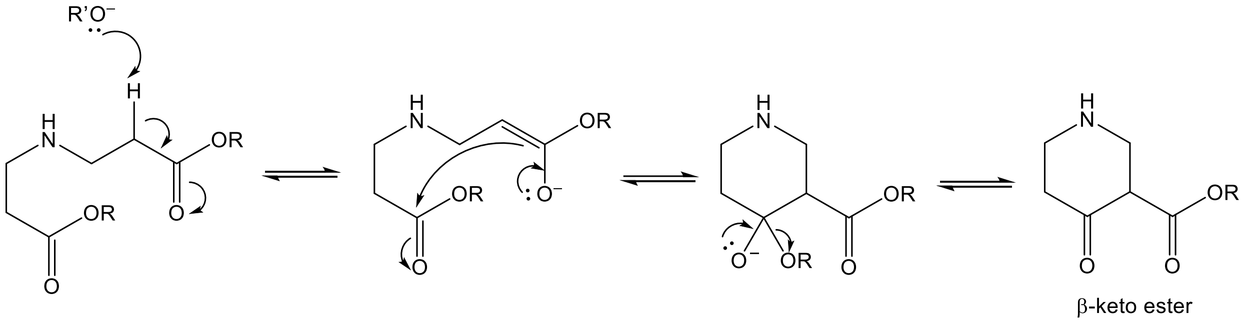
(iv) While the question was generally well-attempted, there is a notable tendency among some students to rely on the electronegativity factor in their explanations.

(v) Although most realized that sodium carbonate acted as a base, they failed to provide an explanation for its necessity. The reasoning behind its role lies in the fact that the reactant is acidic, and the nitrogen atom lacks a lone pair, making it incapable of functioning as a nucleophile to attack organic compound **F**. By engaging in a neutralization reaction, the lone pair of electrons from the nitrogen atom becomes available to attack organic compound **F**. Regrettably, many students also provided an incorrect structure for organic compound **F**, with a surprising number incorrectly suggesting CH_3CH_2CN. Students should understand that this is a nucleophilic substitution reaction, and organic compound **F** must indeed be an RX compound to facilitate an attack on an electron-deficient carbon atom.

(b) Step 1 of the reaction scheme in Fig. 3.1 involves the Dieckmann condensation.

This intramolecular condensation reaction occurs between 2 ester groups to give a cyclic β-keto ester.

Fig. 3.2 shows the mechanism for the Dieckmann condensation.

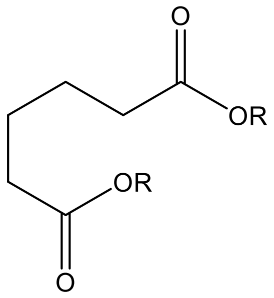


R and R' are alkyl groups

Fig. 3.2

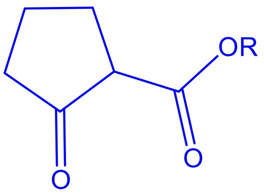
(i) Suggest the role of $R'O^-$ in the first step of the reaction. [1]

(ii) Suggest the structure of the organic product formed when the following compound undergoes the Dieckmann condensation. [1]



(i) **base / proton acceptor/electron pair donor/nucleophile [1]**

(ii)



[1]

Marker Comments:

(ii) Numerous students overlooked the essential count of carbon atoms, which amounts to five in this context. Instead, a significant portion of them mistakenly depicted a cyclohexane structure rather than the correct cyclopentane structure.

(c) Under acidic conditions, ketones react with halogens to give substitution at the alpha(α)-carbon. Fig. 3.3 shows the mechanistic steps that occur with propanone as the organic reagent.

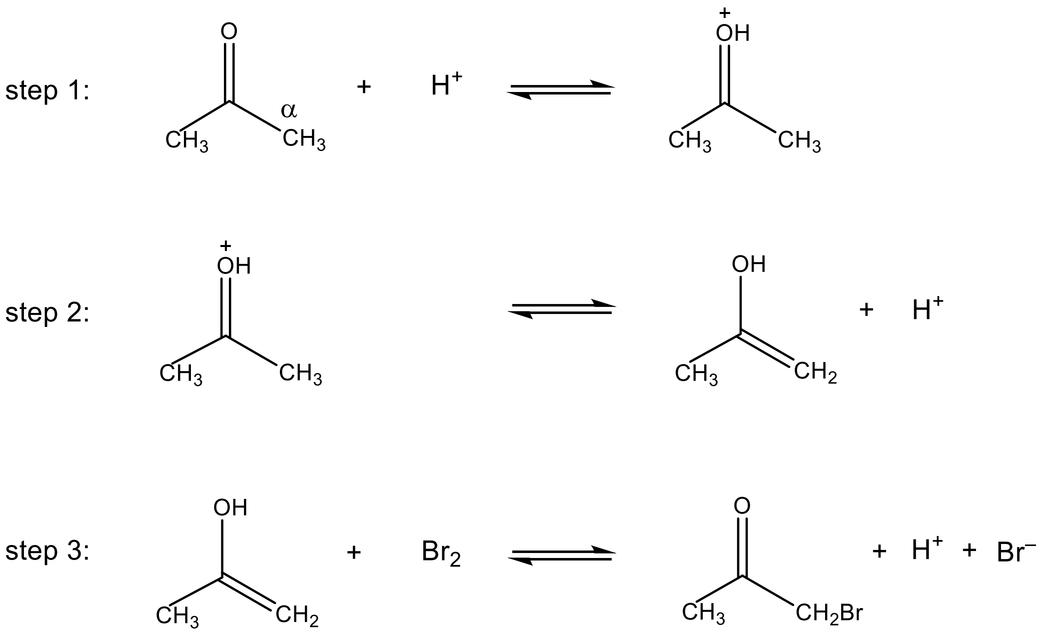


Fig. 3.3

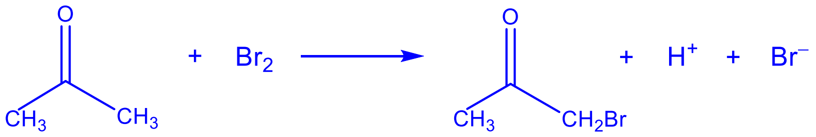
(i) Write a balanced equation for the overall reaction that occurs when propanone is mixed with acidified Br_2. [1]

(ii) Briefly outline how the initial rate of the reaction in **(c)** could be measured. [2]

(iii) A student conducted an experiment and determined that the rate equation for the reaction in **(c)** is rate = k[propanone][H^+], but was unable to conclude whether step 1 or step 2 is the slow step. Suggest why. [1]

....

(i)



[1]

(ii) **Measure** the **change in colour intensity of Br_2/electrical conductivity/pH with time**. [1]

Then **plot the graph of colour intensity of Br_2 gas used against time.** Determine the **gradient at t = 0** which is the initial rate. [1]

(iii) Regardless of whether step 1 or step 2 is the slow step, the **same rate equation is obtained**. [1]

Marker Comments:

(i) A considerable number of students struggled with balancing the composite equation or eliminating common terms on both sides of the reaction or equilibrium.

(ii) Many students did not grasp the question's essence. The question specifically calls for students to devise an experiment for tracking the reaction over time, constituting a continuous experiment where they must monitor either the colour intensity of the bromine or the pH of the solution.

(d) Groundwater contaminated with arsenite, AsO_3^{3-}, presents a grave concern in many developing countries. To protect public health, the World Health Organisation sets a permissible limit for **arsenic**(As) in drinking water; typically at 10 micrograms per dm^3 ($\mu g\ dm^{-3}$ or 10^{-6} g dm^{-3}). The level of arsenic toxicity is tested based on the amount of arsenite that is presented in the water source.

A 100 cm^3 sample of water is drawn from a polluted source. 50.00 cm^3 of 0.00110 mol dm^{-3} acidified $Cr_2O_7^{2-}$ (aq) ions, which is in excess, is added to the solution. The two half-equations for the reaction that occurs are as shown:

$$AsO_3^{3-} + H_2O \longrightarrow AsO_4^{3-} + 2H^+ + 2e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

An excess of iodide ions is then added to react with the remaining $Cr_2O_7^{2-}$, liberating iodine.

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$$

The liberated iodine is then titrated against 0.0150 mol dm^{-3} $Na_2S_2O_3$.

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

The end-point is reached when 21.20 cm^3 of $Na_2S_2O_3$ has been added.

(i) Construct the ionic equation for the reaction between arsenite ions, AsO_3^{3-}, and acidified dichromate(VI) ions, $Cr_2O_7^{2-}$. [1]

(ii) Determine the amount of arsenite, AsO_3^{3-}, in the 100 cm^3 sample of water. [3]

(iii) Hence calculate how many times the **arsenic** level in the water sample exceeds the permissible limit for drinking water. [2]

(i) $Cr_2O_7^{2-} + 8H^+ + 3AsO_3^{3-} \longrightarrow 3AsO_4^{3-} + 2Cr^{3+} + 4H_2O$ **[1]**

(ii) Moles of $S_2O_3^{2-} = \frac{21.20}{1000} \times 0.0150 = 3.18 \times 10^{-4}$ mol

$2S_2O_3^{2-} \equiv I_2 \equiv \frac{1}{3}Cr_2O_7^{2-}$

Moles of $Cr_2O_7^{2-}$ (unreacted excess) $= \frac{1}{6} \times (3.18 \times 10^{-4})$

$= \underline{\mathbf{5.30 \times 10^{-5}\ mol}}$ **[1]**

Initial moles of $Cr_2O_7^{2-}$ added $= \frac{50}{1000} \times 0.00110 = 5.50 \times 10^{-5}$ mol

Moles of $Cr_2O_7^{2-}$ reacted with AsO_3^{3-}

$= (5.50 \times 10^{-5}) - (5.30 \times 10^{-5}) = \underline{\mathbf{2.00 \times 10^{-6}\ mol}}$ **[1]**

Moles of AsO_3^{3-} in 100 cm^3 sample = $3(2.00 \times 10^{-6})$

$= \underline{\mathbf{6.00 \times 10^{-6}}}$ mol **[1]**

Marker Comments:

(ii) Students who approached the question correctly demonstrated a strong attempt. It's important for students to recognize that surplus $Cr_2O_7^{2-}$ is employed, and any remaining $Cr_2O_7^{2-}$ is introduced to facilitate the formation of iodine in excess with added iodide.

(iii) Mass of As in 100 cm^3 sample = $74.9 \times 6.00 \times 10^{-6}$

$= \underline{\mathbf{4.494 \times 10^{-4}\ g}}$ **[1]**

Mass of As in 1 dm^3 = $4.494 \times 10^{-4} \times 10$
$= 4.494 \times 10^{-3}$ g
$= 4494 \times 10^{-6}$ g

It exceeds the permissible limit by = $\frac{4494}{10}$ = **449.4 times** **[1]**

Marker Comments:

(iii) The question received poor attempts from students, primarily due to several instances of not thoroughly reading the question:

1. The inquiry pertained to the arsenic level, not the arsenite level.
2. The acceptable level specified was 10 x 10-6 g per dm^3, not 10^{-6} g per dm^3.

(e) Aromatic compound **J** ($C_{10}H_{12}O_3$) gives a positive result with both Tollens' reagent and Fehling's solution. It forms a yellow precipitate when heated with alkaline aqueous iodine and produces white fumes when exposed to $SOCl_2$.

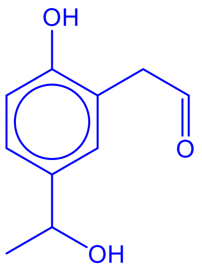
When **J** reacts with concentrated H_2SO_4 under hot conditions, it forms **K** ($C_{10}H_{10}O_2$), which does not exhibit stereoisomerism. Both **J** and **K** decolourise aqueous Br_2 but in different mole ratios, as shown in Table 3.1.

Table 3.1

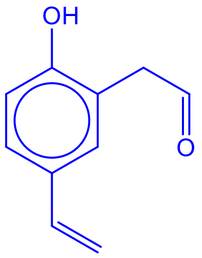
compound	moles of Br_2(aq)
J	1
K	2

K, when heated with acidified potassium dichromate and subsequently treated with PCl_5, forms **L**($C_{10}H_8O_2$), which emits a sweet smell. Both **J** and **K** form a violet complex with neutral $FeCl_3$ but **L** does not.

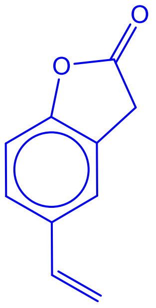
Give the structure of compounds **J**, **K** and **L**. [3]



J



K



L

[1] each

Marker Comments:

(e) No deductive statement is necessary. The majority of students correctly identified the presence of functional groups such as benzene, aliphatic aldehyde, methyl alcohol, and phenol. It would have been beneficial for students to calculate the degree of unsaturation (5 in total) in compound **J** - the contributions of the benzene ring (4) and the aliphatic aldehyde (1). One crucial piece of information that eluded many students was the mole ratio of Br_2 with compounds **J** and **K**, which could have aided in determining the positions of these groups in relation to the phenol group.

[Total: 23]

[Turn over

Section B

Answer **one** question from this section.

4 Aromatic compounds serve as important building blocks in organic synthesis. They are widely used as starting materials to produce pharmaceuticals, dyes, fragrances, and many other chemicals.

(a) Both methylbenzene and phenol form nitro compounds with nitric acid under different conditions as shown in Fig. 4.1.

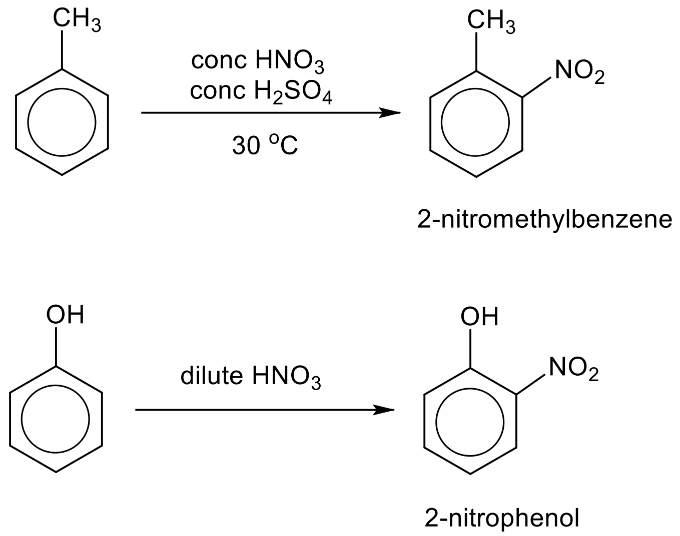


Fig. 4.1

(i) Explain why different conditions are needed for the formation of 2-nitrophenol and 2-nitromethylbenzene as shown in Fig. 4.1. [2]

(ii) Hence suggest the reagents and conditions required for a similar reaction of benzoic acid to form the corresponding nitro compound. [1]

(i)

- The **lone pair of electrons on O atom** in phenol **delocalised into the benzene ring,**
- **increasing the electron density** and
- hence **increasing reactivity towards electrophile**.
- Hence, the **–OH group** in phenol is **more activating than –CH_3** in methylbenzene.
- Since phenol is more susceptible to electrophilic substitution, **conc. H_2SO_4** is **not required** to **generate the electrophile.**

5 points [2], 2-4 points [1]

(ii) **conc HNO_3, conc H_2SO_4, heat (or 55~100°C)** **[1]**

Marker Comments for (a)(i):

- Several students have shown **misconception** that -OH is an ***electron withdrawing*** group or stating that -OH is better ***electron donating*** group than -CH_3. Students are reminded that the substituent groups on benzene ring have either the **activating or deactivating effect**. Both -CH_3 and -OH are ***activating groups*** but -OH is more activating that -CH_3.
- Most students did not explain the different condition, conc. H_2SO_4 is not required for the electrophilic substitution of phenol.

(b) Phenol is usually used for the synthesis of *paracetamol* which is a medication for treatment of pain and fever. *Paracetamol* can be prepared from phenol via a three-step synthesis as shown in Fig. 4.2.

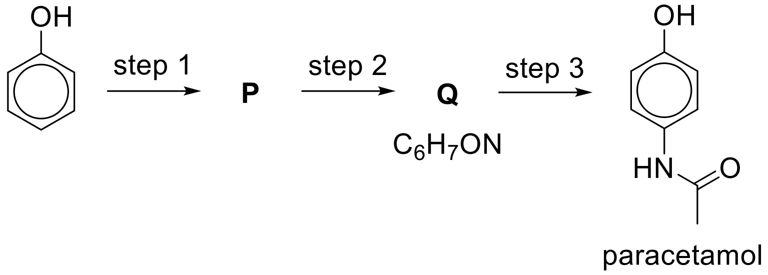


Fig. 4.2

(i) Suggest the structures of compounds **P** and **Q**, and the reagents and conditions for steps 1 and 2. [3]

(ii) A student suggested that ethanoyl chloride, CH_3COCl, could be used as a reagent for step 3. However, this reagent may form another compound **R** instead of paracetamol.

Suggest the structure of compound **R**. [1]

Aspirin can also be used for treatment of pain and fever. The industrial production of aspirin involves the conversion of phenol to salicylic acid by the Kolbe-Schmitt reaction. In the reaction, phenol is strongly heated with CO_2 and NaOH as shown in Fig. 4.3.

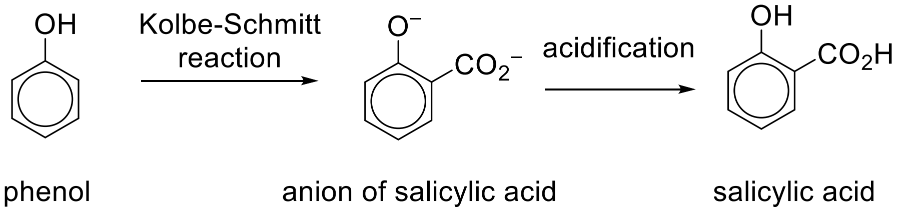
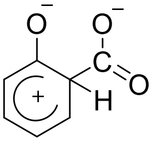


Fig. 4.3

One suggested mechanism for the Kolbe-Schmitt reaction is similar to an electrophilic substitution reaction. The three steps of the mechanism are described below.

Step 1: Phenol undergoes acid-base reaction with hydroxide ion to form a phenoxide ion.

Step 2: CO_2 acts as an electrophile to react with phenoxide ion to form the following intermediate.

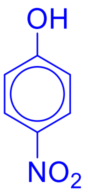


Step 3: The hydroxide ion reacts with the intermediate to form the anion of salicylic acid.

(iii) Suggest the mechanism for the reaction described above, showing all charges, dipoles and using curly arrows to show the movement of electron pairs in each step. [3]

[Turn over

(i) step 1: **dilute nitric acid** **(from Fig 4.1)**



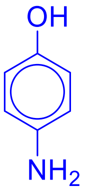
P

Marker Comments for (b)(i):

- This part was well attempted. A few students mistaken that the NO_2 should be -Cl. Students are reminded that chlorobenzene cannot undergo nucleophilic substitution.

[reagent and correct structure of P – 1 mark]

step 2: **Sn and concentrated HC*l*, heat followed by NaOH(aq)** **[1]**

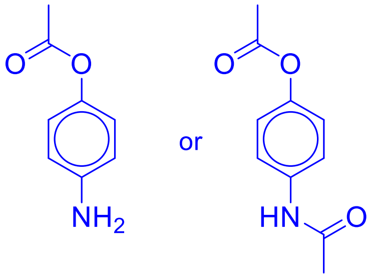


Q **[1]**

Marker Comments for (b)(i):

- The common error for the reagents and conditions for step 2 was **not** adding **heat** right after **Sn** and **conc. HC*l***. NaOH(aq) is added to neutralise the $-NH_3^+$ group to form $– NH_2$.

(ii)



R

Marker Comments for (b)(ii):

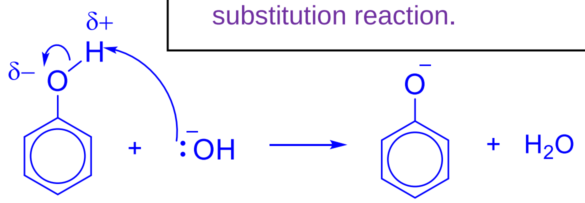
- This part was well attempted. Students are reminded to bond the ester group on the benzene ring.

(iii)

Marker Comments for (b)(iii):

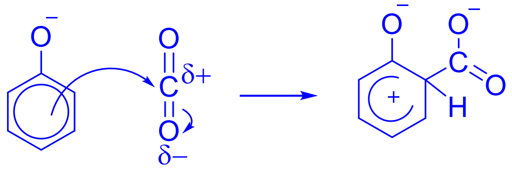
- Many students were not able to write the 3 steps for the mechanism. Students are reminded to put in the **dipoles δ+ or δ-** for the relevant atoms and follow the instructions to direct the **electron arrow pushing** given in the question for the electrophilic substitution reaction.

Step 1



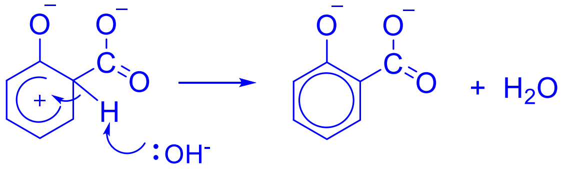
[1]

Step 2



[1]

Step 3



[1]

(c) The reactions of the Period 3 chlorides with water vary across the Period.

(i) Describe the reactions of $MgCl_2$ and PCl_5 with water, suggesting the pH of the resulting solutions. Explain the reaction of these chlorides in water based on their structure and bonding. Write equations for all reactions that occur. [3]

(ii) Both CCl_4 and $SiCl_4$ are Group 14 chlorides. $SiCl_4$ fumes in moist air due to a vigorous reaction with water. However, CCl_4 does not react with water. Suggest a reason for the unreactivity of CCl_4 towards water. [1]

(i) **$MgCl_2$**

- $MgCl_2$ has a **giant ionic lattice structure** and **strong electrostatic attraction/ionic bonds between Mg^{2+} and Cl^- ions**.
- $MgCl_2$ **dissolves in water** readily
- to form an acidic solution of **pH 6.5**.
- $MgCl_2$ undergoes **hydration and partial hydrolysis of $Mg^{2+}(aq)$** due to the polarisation of water molecules by the Mg^{2+} ion.
- **$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$** **[hydration]**
- **$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5OH]^{+}(aq) + H_3O^{+}(aq)$** **[partial hydrolysis]**

PCl_5

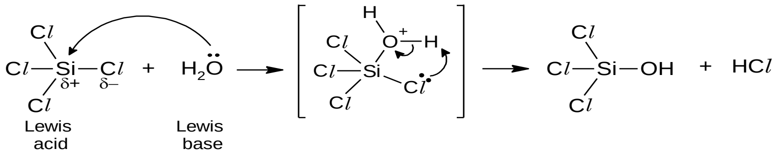
- PCl_5 has a **simple molecular structure** and
- undergoes complete **hydrolysis** in water.
- It forms **white fumes** of HCl and
- an acidic solution of **pH 2**.
- **$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(aq)$**

8-11 points [3], 5-7 points [2], 3-4 points [1]

Marker Comments for (c)(i):

- Students are reminded to have ***thorough revision*** and not to confuse with the chemistry of **Period 3 chlorides with Period 3 oxides.**
- Most students did not mention that **Mg^{2+} undergoes hydration with water to form $[Mg(H_2O)_6]^{2+}$.** The equation for **hydration should be "single arrow" as $MgCl_2$ dissolves completely in water.** However, the equation for **partial hydrolysis of $[Mg(H_2O)_6]^{2+}$** should be **double arrow**.

(ii)



The hydrolysis of $SiCl_4$ is as shown above. CCl_4 is unreactive towards water as carbon **does not have energetically accessible empty 3d orbitals to accept the lone pair of electrons/expand its octet structure** from water molecules. **[1]**

Marker Comments for (c)(ii):

This question was not well attempted. There were misconceptions that the C-Cl bond is too strong to be broken or stating that CCl_4 is non-polar and hence insoluble in water.

(d) Upon heating, PCl_5 undergoes decomposition to form PCl_3 and Cl_2 as shown.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H > 0$$

A mixture of 0.0625 mol of PCl_5 and 0.0705 mol of Cl_2 were placed into a 2.0 dm^3 sealed vessel at 250 °C. After dynamic equilibrium was established, the total pressure in the vessel was 3.25 atm. You may assume that the gases behave ideally under the stated conditions.

(i) By calculating the total amount of gases in the vessel at equilibrium or otherwise, calculate the amount of PCl_3 formed at equilibrium at 250 °C. [2]

(ii) Calculate the equilibrium constant, K_p at 250 °C, stating the units of K_p clearly. [2]

(iii) State and explain how the K_p value would change when the temperature of the vessel is increased. [2]

(i)

$$pV = nRT$$

$$(3.25 \times 101325) \times (2 \times 10^{-3}) = (n) \times 8.31 \times (273 + 250) \text{ [M1]}$$

$\underline{\mathbf{n = 0.1515\ mol}}$ (total amt of gases)

Let the amount of PCl_3 formed at equilibrium be y.

	PCl_5	$\rightleftharpoons$	PCl_3	+	Cl_2
Initial amount /mol	0.0625		0		0.0705
Change in amount /mol	$-y$		$+y$		$+y$
Equilibrium amount /mol	$0.0625 - y$		y		$0.0705 + y$

Total amount of gas = $0.0625 - y + y + 0.0705 + y$

$0.1515 = 0.133 + y$

$y = 0.0185$

Amount of PCl_3 formed at equilibrium = **<u>0.0185 mol</u>** **[A1]**

<u>Marker Comments for (d)(i):</u>

- Some students found calculating the total number of moles of gases challenging. As such, they could not calculate the amount of PCl_3.
- Students are reminded to give the **correct headers** and **not using short form** for the **ICE** table.

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

……………………………………………………………………………………

[Total: 20]

(ii) Eqm partial pressure of PCl_5 = $\frac{0.0625-0.0185}{0.1515}\times 3.25 =$ **0.944 atm**

Eqm partial pressure of Cl_2 = $\frac{0.0705+0.0185}{0.1515}\times 3.25 =$ **1.91 atm**

Eqm partial pressure of PCl_3 = $\frac{0.0185}{0.1515}\times 3.25 =$ **0.397 atm**

$K_p = \frac{P_{PCl_3}P_{Cl_2}}{P_{PCl_5}} = \frac{0.397 \times 1.91}{0.944}$ **[M1]** = **0.803 atm** **[A1, include units]**

Marker Comments for (d)(ii):
This part could be solved easily if students know how to find the partial pressure of each of the gases. $P_A = \frac{n_A}{n_T}\times P_T$

(iii) By LCP, when temperature is increased, •**position of equilibrium will shift right** •**towards the endothermic reaction** •**in order to absorb some heat.** Hence the • **value of K_p increases.**

4 points [2]; 2-3 points [1]

Marker Comments for (d)(iii):
This part is well attempted by students. However, some students were confused and shift the ***position of equilibrium*** to the left instead of to the right.

5 **(a)** The Group 2 carbonates are widely used in the construction and agriculture industry.

On heating, the Group 2 carbonates decompose as shown:

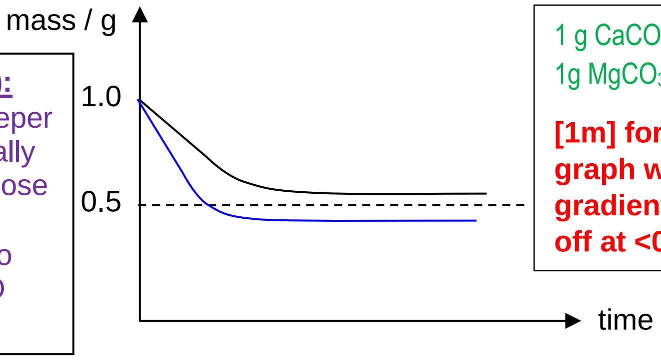
$MCO_3(s) \rightarrow MO(s) + CO_2(g)$ where M is the Group 2 element

(i) Describe and explain the trend in the thermal stabilities of the Group 2 carbonates. [2]

(ii) The graph in Fig. 5.1 represents the change in mass that occurs when 1.0 g of powdered calcium carbonate, $CaCO_3$, is heated at a certain temperature.

Marker Comments for (a)(ii):

- Gradient (rate) must be steeper (faster) as $MgCO_3$ is thermally less stable and will decompose at a faster rate.
- Calculations was required to determine the mass of MgO residue.



1 g $CaCO_3 \rightarrow$ 0.56 g CaO
1g $MgCO_3 \rightarrow$ 0.48 g MgO

[1m] for similar shape graph with steeper gradient and levelling off at <0.5 g mass

Fig. 5.1

Sketch, on the same axis, a graph that would be obtained by heating 1.00 g of magnesium carbonate, $MgCO_3$, at the same temperature.
Your answer should illustrate clearly the relative ease of thermal decomposition of the two carbonates and the relative mass of residue formed.

Include any relevant calculations.
[M_r: $MgCO_3$, 84.3 ; $CaCO_3$, 100.1] [2]

(i)
- Down Group 2, **charge density of cations decreases**.
- **Polarising power** of the cation decreases / ability of cations to distort the anion **decreases**.
- **C−O bond** in the anion is **weakened to a lesser extent** / less energy required to break C−O bond in anion.
- **Thermal stability** of Group 2 carbonates **increases down the Group**.

[every 2 points 1m]

(ii) $MCO_3 \rightarrow MO + CO_2$

1 g $CaCO_3$ gives $\frac{1}{100.1} \times 56.1 = 0.560$ g of CaO residue.

1 g $MgCO_3$ gives $\frac{1}{84.3} \times 40.3 = 0.478$ g of MgO residue

[1] for relevant calculations to determine mass of residue.

Marker Comments for (a)(i): [BOOKWORK]
Question well-attempted by most students. Students are expected to score for question on **thermal stability of Group 2 carbonates or Group 17 hydrides as specified in the syllabus!**

(b) The biological process of forming proteins from amino acids is enzyme catalysed.

Graph 1 in Fig. 5.2 shows how the rate of an enzyme catalysed reaction varies with substrate(reactant) concentration for a given enzyme concentration.

Graph 2 in Fig. 5.2 shows how the rate of an enzyme catalysed reaction varies with enzyme concentration when the enzyme concentration is significantly lower than the substrate concentration.

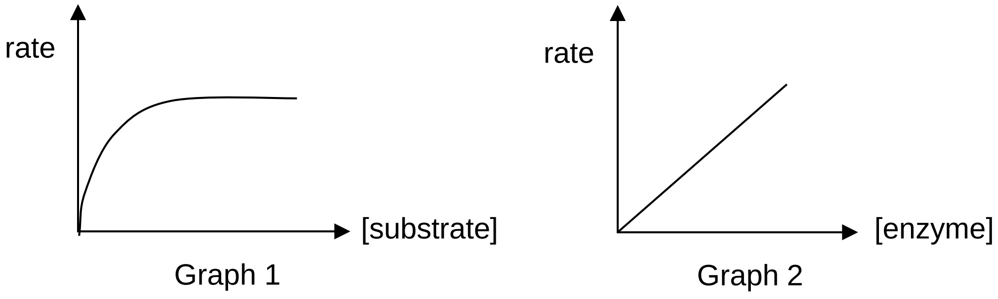


Fig. 5.2

(i) Explain why Graph 1 in Fig. 5.2 levels off at high [substrate]. [1]

(ii) State the relationship between reaction rate and enzyme concentration as shown in Graph 2. Suggest a reason for this. [1]

(i) Graph 1 levels off at high [substrate] as the **active sites on the enzyme are saturated/completely occupied**. **[1]**

(ii) Graph 2 shows that **reaction rate is directly proportional to [enzyme]** as **increasing [enzyme] provides more active sites for more substrate to be reacted**. **[1] for BOTH relationship and reason**

Marker Comments for (b)

- The concept of **enzymes functioning as catalyst through the use of active sites** MUST be used to answer this question.
- (b)(i) is BOOKWORK and reference to the concept of all active sites on the enzyme being occupied is necessary for credit.
- (b)(ii) required clarity in stating the relationship shown.
  A straight line graph passing through origin shows: **rate is directly proportional to [enzyme]**.
  Answers simply describing that rate increases when [enzyme] concentration increases gain NO credit as this is VAGUE and can also apply to straight line graph not passing origin and also to curves.
- (b)(ii) ALSO required a discussion involving the concept of active sites for credit to be awarded.

(c) The Strecker Synthesis is a laboratory method of forming amino acids from aldehydes.

Fig. 5.3 shows an overview of this multi-step synthesis that involves forming an α-aminonitrile, which is then subsequently carefully hydrolysed to form the amino acid.

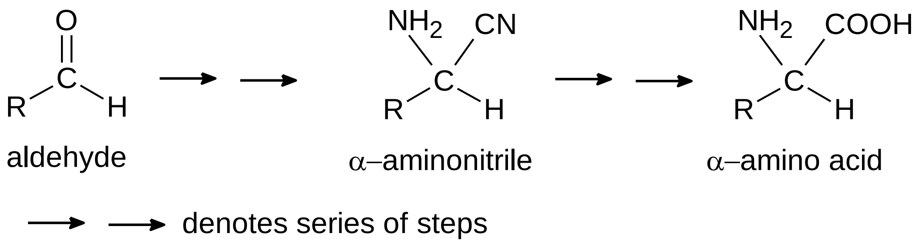
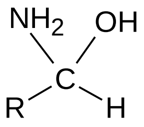


Fig. 5.3

(i) In the conversion of the aldehyde to an α-aminonitrile shown in Fig. 5.3, the first 2 steps involve a nucleophilic addition which occurs as described:

- nucleophilic attack of ammonia on the carbonyl carbon to yield a dipolar ion consisting of both a positive and a negative charge;
- internal proton transfer to form a neutral molecule with the structure below.

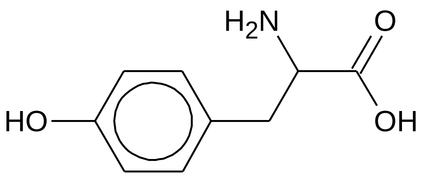


Draw the mechanism described in the 2 steps above, showing clearly the structure of the dipolar ion. Include curly arrows and relevant dipoles in your answer. [3]

(ii) By considering the information given in **(c)(i)**, explain why the product formed is likely a racemic mixture. [1]

(iii) Suggest why the α-aminonitrile had to be "carefully hydrolysed" to form the amino acid. [1]

(iv) Draw the **skeletal** formula of the aldehyde that can be used to form the amino acid *tyrosine* via the Strecker Synthesis. [1]

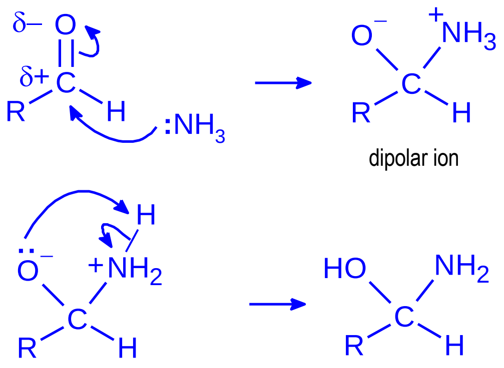


tyrosine

(v) *Tyrosine* has three pK_a values associated with it: 2.2, 9.1 and 10.0.

Given that pK_a = 10.0 is for the phenolic R group, draw the structure of the predominant species of tyrosine at pH 7. [1]

(i) **[1] nucleophilic attack (both curly arrows and dipole)**
[1] structure of dipolar ion
[1] balanced equation showing proton transfer to obtain the neutral product



Marker Comments for (c)(i)

- Nucleophile is given as NH_3 (not NH_2).
- Bond breaking of N-H bond has to be shown.

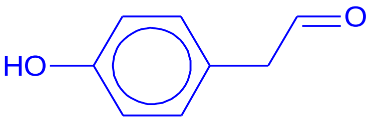
(ii) **Ammonia/nucleophile attacks the trigonal planar sp^2 hybridised electron-deficient(δ+) carbon from above and below the plane with equal probability**, resulting in equal amounts of (+) and (−) enantiomers. **[1]**

Marker Comments for (c)(ii)
The nucleophile attacks the NEUTRAL carbonyl carbon. Any reference to "carbocation" is awarded ZERO.

(iii) The hydrolysis had to be controlled **so that the $-NH_2$ would not be protonated/neutralised to form $-NH_3^+$**. **[1]**

Marker Comments for (c)(iii)
Too many students discussed $-NH_2$ group undergoing 'hydrolysis'. The $-NH_2$ group does NOT undergo hydrolysis on reaction with acid!!! **$-NH_2$ group is basic and undergoes NEUTRALISATION with the acid**.

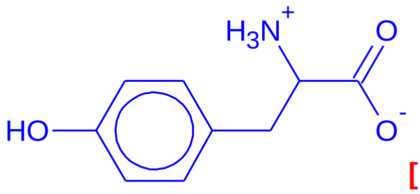
(iv)



[1]

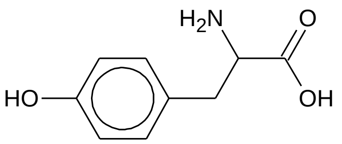
Marker Comments for (c)(iv)
Too many students did not get any credit despite having the correct structure as they forgot that the question required **skeletal** formula!

(v)



[1]

pKa 9.1 > 7 ⇒ protonated

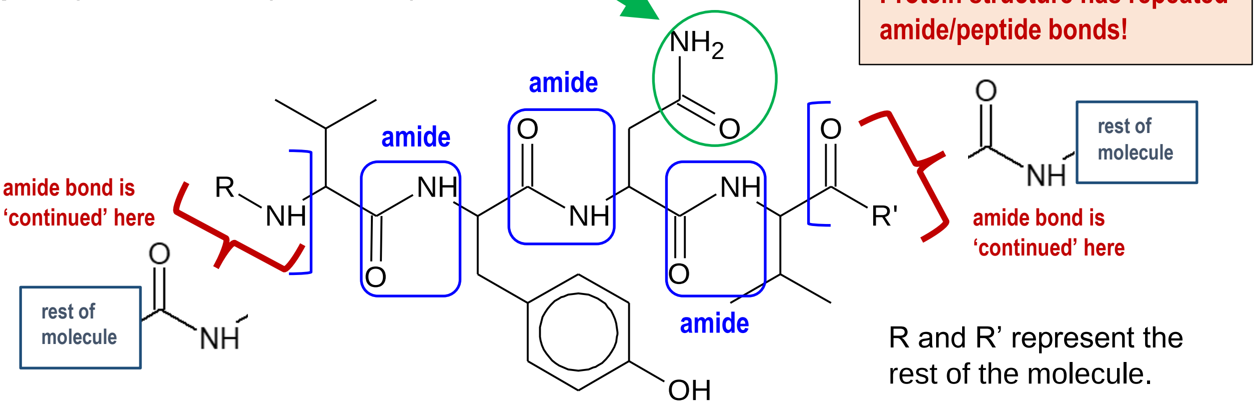


pKa 10.0 > 7 ⇒ protonated

pKa 2.2 < 7 ⇒ deprotonated

Marker Comments for (c)(v)
Too many students did not pay attention to the given pK_a of the groups and made assumptions leading to incorrect answers.

(d) Fig. 5.4 shows a part of the protein structure of human insulin.



This amide group belongs to the 'side-chain' of one of the amino acids that make up the protein. It will also get hydrolysed.

Protein structure has repeated amide/peptide bonds!

R and R' represent the rest of the molecule.

Fig. 5.4

(i) State the reagents and conditions required to completely hydrolyse a protein molecule into its constituent amino acids. [1]

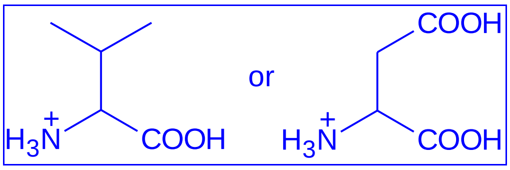
(ii) The insulin molecule is hydrolysed using the reagent and conditions given in **(i)**. Draw the structure of a species in the resulting reaction mixture that is formed from one of the amino acids other than tyrosine. [1]

(i) **HC*l*(aq) or H_2SO_4(aq) OR NaOH(aq);**

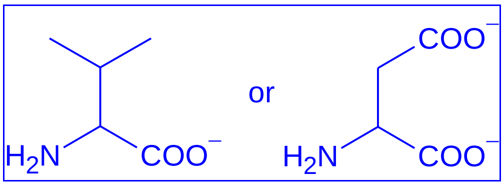
prolonged heating (or heat under reflux) **[1] for both**

(ii)

acidic hydrolysis



basic hydrolysis



Marker Comments for (d)

- Students are reminded that for the specific context of "complete hydrolysis of proteins", the concept of prolonged heating MUST be present.
- Students are reminded to take note of the structure of protein, which can be seen as repeated amide bonds separated by 1 C in between. [Refer to working shown on diagram above.]
- Students are reminded to take into account the medium of hydrolysis (acidic or basic) when drawing the products of hydrolysis.

(e) Compound **X** has molecular formula $C_7H_{13}NO_2$. On boiling **X** with aqueous sodium hydroxide, ethylamine is formed.

⇒ basic; reacts to form ionic salt which is soluble

(i) Ethylamine dissolves readily in dilute acid at room conditions whereas compound **X** does not.

⇒ NOT basic; does NOT form ionic salt

Suggest the nitrogen-containing functional group that could be present in **X.** Explain the observed difference in acid-base nature of the nitrogen-containing functional groups. [2]

(ii) Compound **X** is optically active. Compound **Y**, $C_7H_{17}NO$, which is also optically active, is formed when **X** reacts with $LiA\mathit{l}H_4$. On heating with $A\mathit{l}_2O_3$, **Y** forms two different compounds which readily decolourise aqueous bromine.

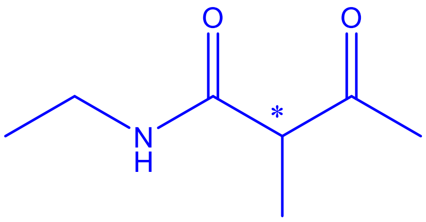
⇒ undergoes elimination to form C=C in '2 ways' ⇒ likely alcohol group and NOT 1°

Suggest possible structures for **X** and **Y**, stating the type of reaction that has occurred for each. [3]

(i) **Ethylamine has a lone pair of electrons on N which is available for dative bonding with H^+.** Hence it **is basic/undergoes neutralisation with dilute acid.** **[1]**

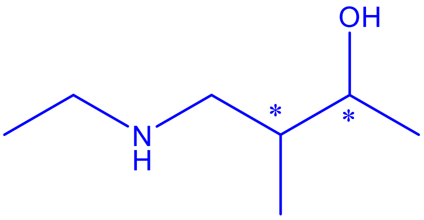
X contains an **amide functional group** in which the **lone pair on nitrogen in delocalised into the adjacent C=O**. Hence it is **neutral/not basic (or lone pair unavailable to accept H^+).** **[1]**

(ii) **X** is



[1] for X

Y is



[1] for Y

X : **reduction** with $LiA\mathit{l}H_4$,

Y : **elimination** with $A\mathit{l}_2O_3$ **[1] for both**

Marker Comments for (e)

It was apparent that many students did not have time to reach this part of the question and it was mostly unattempted.

[Total: 20]