Anderson Serangoon Junior College Preliminary Examinations H2 Chemistry (9729) Paper 3 Mark Scheme

Section A

Answer all questions.

- 1 Many naturally occurring organic compounds contain either acidic groups or basic groups or both. The strength of the acid or the base depends on the structure of the molecule.
 - (a) The pK_a values of ethanoic acid and two amino acids are given in Table 1.1 below.

name	structure	р <i>К</i> а1	р <i>К</i> _{а2}	р <i>К</i> _{а3}
ethanoic acid	CH₃COOH	4.7	-	-
serine (ser)	H ₂ N—CH—CO ₂ H CH ₂ OH	2.2	9.2	Ι
aspartic acid (asp)	H ₂ N—CH—CO ₂ H CH ₂ CO ₂ H	1.9	3.7	9.6

Table 1.1

(i) Suggest two reasons why the pK_{a1} value of serine is so much less than the pK_{a1} of ethanoic acid. [2]

<u>Electron withdrawing $-NH_3^+$ (or $-NH_2$) group</u> is in close proximity to the negative charge of the carboxylate anion of deprotonated serine, hence <u>dispersing the negative charge</u> and stabilizing the anion, and

-OH of the R group of serine is able to form intramolecular hydrogen bond with the O atom of $-COO^{-}$. This stabilizes the carboxylate anion.

Hence, carboxylate anion of serine is more stabilised than ethanoate ion

(ii) Draw a skeletal structure for the dipeptide, asp-ser.



Electrophoresis is a technique used to separate charged particles placed in an electric field. The system consists of two oppositely–charged electrodes connected by a conducting medium, typically a gel. The separation of the charged particles is based on their electrical charge and M_r .

A sample consisting of serine and aspartic acid was analysed by electrophoresis using a gel buffered at pH 5.7. The small quantity of the mixture was placed at the centre of the gel, at equal distance from the two electrodes.

(iii) Using the information given in Table 1.1, suggest the structures of the major species present in the buffer solution. Label the structures clearly. [2]



(iv) Hence, describe the relative positions of the two species in the gel after the separation by the electrophoresis process. Explain your answer.
 You may find it helpful to draw a diagram to illustrate your descriptions. [2]

Ser has no net charge / electrically neutral / exists as a zwitterion. Hence it will not move and remain at the centre of the strip.

Asp has an overall negative charge, and so it will migrate towards the anode.



- (b) A student prepared a buffer solution of pH 5.7 by adding solid sodium hydroxide to 200 cm³ of 0.200 mol dm⁻³ ethanoic acid.
 - (i) With reference to the information in Table 1.1, calculate the mass of sodium hydroxide the student would have used. [2]

pK_a (CH ₃ COOH) = 4.7 $K_a = 10^{-4.7}$ mol dm ⁻³	<u>Alternative:</u> <i>K</i> a = [H⁺]([A⁻]/[HA]) [A⁻]/[HA] = 10
Initial n(CH₃COOH) = 200 x 10 ⁻³ x 0.200	
= 0.04 mol	Let x be amt of HA left
	11x = 0.04
Let the no.of mol of NaOH needed be a mol.	x = 3.636 x 10 ⁻³
$CH_3COOH + NaOH \rightarrow CH_3COO^-Na^+ + H_2O$	mass of NaOH added
a mol a mol	$= (0.04 - 3.636 \times 10^{-3}) \times 40.0$

= <u>1.45 g</u>

$$\begin{array}{l}
\left[\begin{array}{c} [H^{+}][A^{-}] \\
[HA] \end{array}\right] \\
10^{-4.7} = \quad \frac{(10^{-5.7}) \quad (a \ge \frac{10^{3}}{200})}{(0.04 - a) \ge \frac{10^{3}}{200}} \\
10^{-4.7} \quad (0.04 - a) = 10^{-5.7} \ge a \\
a = \underline{0.03636 \text{ mol}} \\
mass of \text{ NaOH} = 0.036359 \ge 40.0 = \underline{1.45 \text{ g}}
\end{array}$$

A buffer solution generally loses its effectiveness when one component of the buffer pair is less than about 10% of the other.

(ii) Calculate the percentage of ethanoic acid component present in the buffer solution in
 (b)(i) above and hence comment on the effectiveness of the buffer. [2]

To determine the percentage of ethanoic acid component present in the buffer solution

$$K_{a} = \frac{[H^{+}][A]}{[HA]}$$

$$\frac{[HA]}{[A^{-}]} = \frac{[H^{+}]}{K_{a}} = \frac{10^{-5}}{10^{-4}} = 0.1$$

$$\% [HA] = \frac{0.1}{1 + 0.1} \times 100\% = 9.09\% \quad [1]$$

Alternative: from previous part [HA]/[A⁻] = 0.1 %HA in buffer = $(0.1)/1.1 \times 100\%$ = 9.09%

Alternative method in terms of amount of acid:

<u>To comment on the effectiveness of the buffer</u>, need to find <u>ratio of one component</u> to the <u>other component</u> of the buffer. That is, ratio $\frac{[acid]}{[salt]}$.

From the above calculation, $\frac{[acid]}{[salt]} = 0.1$

% [HA] with respect to the <u>salt</u> = $0.1 \times 100\% = 10\%$

Comment and mention of how the above percentage is determined:

 Buffer is useful/within limits of effectiveness as the % of one component is equal to 10% of the other component. (c) Nicotinic acid and its amide, nicotinamide, are present in Vitamin B3 and are used to increase good cholesterol levels.



The structure of nicotinamide consists of a single delocalised system of electrons which includes:

- an electron in the unhybridised p-orbital of the nitrogen atom in the six-membered ring
- electrons from the carbon atoms of the six-membered ring
- two electrons in the π bond of the >C=O group
- two electrons in lone pair on the nitrogen atom of the amide group
- (i) State the number of delocalised electrons in one molecule of nicotinamide. [1]
 10
- (ii) Using the information provided, suggest the H–N–H bond angle in the NH₂ group in nicotinamide. [1]

120°

High tendency for the lone pair of electrons on N atom to delocalised and reduces it availability. Lone pair-bond pair repulsion is not as significant and thus greater chance of it forming a trigonal planar structure about the N atom resulting in bond angle to go close to 120°.

(iii) Predict and explain the relative basicity of the two N atoms, labeled N1 and N2, in the nicotinamide molecule. [2]

N2 is <u>neutral</u> because the <u>lone pair on nitrogen atom is delocalised into the π bond of the adjacent C=O by resonance, hence not available for donation to a proton.</u>

<u>N1 is more basic</u> as the lone pair of electrons on the nitrogen are not in the same plane as the unhybridised 2p orbitals, thus making it <u>more available for dative bond to a proton</u>.

- 2 (a) A lithium–iodine electrochemical cell can be used to generate electricity for a heart pacemaker. The cell is non–rechargeable and it consists of a lithium electrode and an inert electrode immersed in bodily fluids. When current flows, lithium is oxidised and iodine is reduced.
 - (i) Write two half-equations for the reactions taking place at the two electrodes. Hence, write the overall equation. [2]

 $\begin{array}{l} \text{Oxidation: Li} \rightarrow \text{Li}^{+} + e^{-} \\ \text{Reduction: I}_{2} + 2e^{-} \rightarrow 2I^{-} \\ \text{Overall equation 2Li} + I_{2} \rightarrow 2\text{Li}^{+} + 2I^{-} \end{array}$

(ii) Use the *Data Booklet* to calculate the E°_{cell} for this cell.

 $E^{\circ}_{cell} = +0.54 - (-3.04) \\ = +3.58 \text{ V}$

(iii) A current of 2.5×10^{-5} A is drawn from this cell.

Calculate how long a pacemaker will last when 0.1 g of lithium electrode is remaining in the cell.

Assume the current remains constant throughout this period. Give your answer to the nearest day. [3]

Amount of Li = $0.10/6.9 = 1.45 \times 10^{-2}$ mol Q = $96500 \times 1.45 \times 10^{-2} = 1399$ C t = $1399/(2.5 \times 10^{-5}) = 5.60 \times 10^{7}$ s = 648 days

(iv) Hence, suggest a reason why lithium-iodine battery can be used to power a heart pacemaker. [1]

A small mass of lithium anode is sufficient to power the pacemaker for very long (0.10 g can last for almost 2 years (648 days)

- This ensures that the battery is very lightweight (and can be used in the body without too much additional load)
- can last for very long without replacement needed
- (b) Unlike the lithium–iodine cell, Lithium–ion (Li–ion) batteries are designed to be recharged hundreds of times.

One type of lithium–ion battery consists of a cobalt oxide, CoO_2 , electrode and a graphite electrode with lithium atoms inserted between the layers. An electrolyte of LiPF₆ dissolved in ethylene carbonate is used between the two electrodes.

During discharge, the Li atoms in the graphite electrode form Li⁺ ions. Electrons are released and move through external circuit to the cobalt oxide electrode. The Li⁺ ions migrate through the electrolyte and are incorporated into the cobalt oxide electrode. This is illustrated in Fig. 2.1 in which C–C–C–C–C is a simplified representation of a layer of carbon atoms in graphite.

[1]



Fig 2.1

The overall redox equation can be represented as:

 $LiC_6 + CoO_2 \implies C_6 + LiCoO_2$

where C₆ represents the graphite layers.

(i) Suggest the type of bonding between the lithium atoms and the layers of graphite. Explain your answer. [1]

Metallic bonding between the lithium ions and the delocalised electrons on the graphite layers.

(ii) State the change in oxidation number of cobalt in the cobalt oxide electrode during discharging process.
 Hence, or otherwise, suggest if this electrode is the anode or cathode during discharge.

[2]

From +4 to +3 It is the cathode as shown by the decrease in oxidation state of Co. OR It is the cathode as it gains electrons for reduction during discharge process. (iii) The cell potential, E_{cell} is said to be related to the standard cell potential, E_{cell}^{Θ} by the Nernst equation:

$$E_{\text{cell}} = E_{\text{cell}}^{\Theta} - \frac{\text{RT}}{\text{F}} \ln \frac{[\text{LiCoO}_2][\text{C}_6]}{[\text{LiC}_6][\text{CoO}_2]}$$

where concentration of the species are measured in the solid phase electrodes.

With reference to the Nernst equation, discuss how the cell potential changes as discharging takes place. [2]

During discharging, the concentration of the products C_6 and $LiCoO_2$ increase while concentration of the reactants LiC_6 and CoO_2 falls.

Since E_{cell}^{θ} is a constant, E_{cell} becomes <u>less positive</u>.

(iv) During charging, the reverse of the discharging process takes place and eventually, all the lithium atoms will be stored between the graphite layers.

Suggest a property of graphite, other than its electrical conductivity, that allows the storage of lithium atoms upon charging. [1]

It has <u>weak intermolecular forces of attraction between layers</u> that makes it easier to overcome and expand the gap between layers to accommodate all the lithium atoms.

(c) Zinc and silver are often present as impurities in crude copper obtained from minerals.

Explain, in terms of electrode reactions, how zinc and silver are removed in the industrial process of the purification of copper, using relevant data from the *Data Booklet*. Illustrate your answer with a labelled diagram.

[4]



 $E^{\circ}_{Zn2+/Zn} = -0.76 \text{ V}$ $E^{\circ}_{Cu2+/Cu} = +0.34 \text{ V}$ $E^{\circ}_{Ag+/Ag} = +0.80 \text{ V}$

At the <u>anode</u>, Zn is oxidised to Zn^{2+} (can be described in equation form) as <u> $E^{\circ}_{Zn2+/Zn}$ is more</u> <u>negative than $E^{\circ}_{Cu2+/Cu}$ and dissolves into the electrolyte with Cu</u>.

Ag will not be oxidised as $\underline{E^{\circ}_{Ag+/Ag}}$ is more positive than $\underline{E^{\circ}_{Cu2+/Cu}}$, hence Ag drops off as anode sludge.

At the <u>cathode</u>, only Cu^{2+} is reduced as <u> $E^{\circ}_{Cu2+/Cu}$ is more positive than $E^{\circ}_{Zn2+/Zn}$. Hence Cu is collected, whereas <u> Zn^{2+} is not reduced/remains in solution</u>.</u>

(d) A set-up similar to what you have described in (c) can be used in copper electroplating.

Explain the effect, if any, each of the following changes have on the mass of copper plated if the duration of the electroplating process is kept constant.

- Doubling the concentration of copper ions in the electrolyte.
- Doubling the current of the electroplating process.
- Doubling the concentration of copper ions in the electrolyte <u>will not increase the mass</u> as it <u>does not change the quantity of charge supplied for deposition</u> of copper atoms.
- Doubling the current of the electroplating process. <u>Yes.</u> Since <u>Q = It</u>, increasing the current will lead to <u>twice the amount/quantity of charge/amount</u> of electrons and <u>twice the mass of copper</u> plated.
- (e) A fixed current was passed through two electrolytic cells connected in series for a known duration. The first cell contains aqueous copper(II) sulfate while the second cell contains aqueous silver nitrate. Inert electrodes were used in both cells.

Calculate the ratio of $\frac{\text{mass of silver deposited}}{\text{mass of copper deposited}}$ under these conditions. [2]

Reaction at the first cathode:	$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu (s)$
Reaction at the second cathode:	$Ag^{+}(aq) + e^{-} \rightarrow Ag (s)$

Since the same amount of charge was passed thru the 2 cells (connected in series), $\frac{n_{Ag}}{n_{Cu}} = \frac{2}{1}$

mass of Ag deposited = $2 \times 107.9 \text{ g}$ mass of Cu deposited = $1 \times 63.5 \text{ g}$

 $\frac{\text{mass of Ag deposited}}{\text{mass of Cu deposited}} = \frac{2 \times 107.9}{1 \times 63.5}$ $= \frac{3.40}{1}$

- **3** Organic compounds are molecules that contain carbon atoms covalently bonded to hydrogen atoms.
 - (a) The boiling points of some organic compounds are shown in Table 3.1.

compound	formula	Mr	boiling point / °C
ethylbenzene	CH ₂ CH ₃	106.0	136
benzylamine	CH ₂ NH ₂	107.0	185
phenylmethanol	CH ₂ OH	108.0	205
benzylchloride	CH ₂ Cl	126.5	179

Table 3.1

Suggest explanations for these differences.

[3]

All four compounds have simple molecular structures.

Benzylchloride has higher boiling point than ethylbenzene as <u>more energy</u> is required to overcome the <u>stronger permanent dipole</u>—permanent dipole attractions between the benzylchloride molecules as compared to the <u>weaker instantaneous dipole</u>—induced dipole between ethylbenzene molecules.

Benzylchloride has higher boiling point than ethylbenzene as it has <u>greater number of</u> <u>electrons</u> / <u>larger electron cloud size</u> so <u>more energy</u> is needed to overcome the <u>stronger</u> <u>instantaneous dipole–induced dipole</u> in benzylchloride compared to the <u>weaker instantaneous</u> <u>dipole–induced dipole</u> between ethylbenzene molecules.

Less energy required to overcome the <u>weaker permanent dipole</u>_permanent dipole attractions / <u>weaker instantaneous dipole_induced dipole</u> between the benzylchloride molecules compared to the <u>stronger hydrogen bonding</u> between the respective molecules of phenylmethanol and benzylamine,

The <u>O-H bond</u> in phenylmethanol is <u>more polar than</u> the <u>N-H bond</u> in benzylamine. Hence <u>more energy</u> is needed to overcome the <u>stronger hydrogen bonding</u> between molecules of phenylmethanol than between molecules of benzylamine. Hence, phenylmethanol has a higher melting point than benzylamine.

OR

(b) (i) 2-methyl-1,3-butadiene, also called isoprene, is a colourless, volatile liquid hydrocarbon obtained in processing petroleum.

Draw the structures of the products A and B formed and suggest reagents and conditions for reaction I shown in Fig. 3.1.





Isoprene can be synthesised from the product obtained via a substitution reaction between compound \bf{C} and a suitable halogen.



(ii) Suggest a suitable halogen and the condition for the substitution reaction. [1]

(Limited) Cl₂ / Br₂, uv light

(iii) Draw the structure of the two possible products formed via the substitution reaction of C with the halogen and hence, determine the expected ratio in which they will be formed assuming equal rate of substitution of H atom.



(c) Hydration of alkenes can be carried out by reacting alkenes with borane, BH₃ followed by treatment with alkaline hydrogen peroxide, H₂O₂.

An example of such a reaction is shown in Fig. 3.2.



Fig. 3.2

Reaction II occurs via a mechanism similar to electrophilic addition and it involves the BH₃ acting as an *electrophile*.

(i) Explain what do you understand by the term *electrophile*. [1]

An electrophile is a cation or electrically neutral molecule which <u>has an electron deficient</u> <u>atom / is an electron–pair acceptor</u> which is attracted to an electron–rich site.

(ii) It is suggested that the mechanism for reaction II goes through the formation of a transition state as shown in Fig. 3.3.



Fig. 3.3

Using information given in Table 3.2, complete Fig. 3.3. In your answer, indicate clearly the polarity of the B–H bond in borane by drawing δ + and δ – on the appropriate atoms and draw curly arrows for the movement of electrons.

Table	3.2
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element	electronegativity
boron	2.0
hydrogen	2.2



(iii) By determining the change in the oxidation number of the reactive carbon, suggest the role of hydrogen peroxide in reaction III. [2]

O.N. of C bonded to $-BH_2$ <u>changes from -2 to 0</u>. H₂O₂ acts as an <u>oxidising agent</u>.

(iv) Two possible molecular arrangements of H_2O_2 exhibiting cis–trans isomerism despite the absence of double bond to restrict rotation is shown in Fig 3.4.



Fig 3.4

Using the principles of the Valence Shell Electron Pair Repulsion theory, explain the shape of the H_2O_2 molecule and suggest which molecular arrangement, 1 or 2, would result in a more stable molecule. [2]

The <u>4 electron pairs around each oxygen atom</u> are arranged in a <u>as far apart as possible</u> / <u>tetrahedral manner</u> in order <u>to minimise inter–electronic repulsion</u>. Hence the shape is <u>bent about each O atom</u>.

<u>Molecular arrangement 2 is more stable</u> than 1 as <u>lone – pair repulsion > lone pair –</u> <u>bond pair repulsion > bond pair – bond – pair repulsion / the lone pairs of electrons are</u> <u>arranged away from one another</u> which minimises repulsion.

(d) (i) Benzene rings are commonly found in many naturally occurring organic compounds.

Explain why benzene tends to undergo substitution reactions instead of addition reactions like alkenes. [2]

Benzene does not undergo addition reactions as an <u>addition reaction</u> will require a <u>pi</u> <u>bond</u> to be <u>broken</u>.

This leads to the loss of resonance stability in the product formed as the continuous π electron cloud is disrupted

(ii) The position of substitution in the electrophilic substitution of arenes can be explained based on the stability of the intermediate carbocation formed.

Fig. 3.5 shows the possible carbocation intermediates that can be formed from the bromination of methylbenzene.



Fig. 3.5

Use the information and your knowledge about the stability of carbocations to suggest why the CH_3 group directs incoming electrophiles to the 2– and 4–positions in preference to the 3–position. [2]

Substitution at 2– and 4– position forms <u>tertiary carbocations</u> which <u>are more stable</u> compared to the <u>secondary carbocation</u> formed at the 3–position.

The <u>greater number of electron–donating alkyl groups</u> attached to the positively charged carbon in the tertiary carbocation <u>help to disperse the positive charge</u> <u>more</u>, making the tertiary carbocation more stable than a secondary carbocation.

(iii) Suggest a synthesis of 2–bromobenzoic acid starting from methylbenzene according to the scheme in Fig. 3.6.



Fig. 3.6

[3]



Section B

Answer **one** question from this section.

4 (a) Describe the reactions, if any, when separate samples of the oxides Na₂O, Al₂O₃ and P₄O₁₀ are added to water. Write equations where appropriate and suggest the pH of any aqueous solution formed. [4]

Na₂O <u>dissolves / is soluble</u> in water to give a colourless solution of NaOH with <u>pH 13</u>. NaO(s) + H₂O(I) \rightarrow 2NaOH(aq)

 Al_2O_3 is <u>insoluble</u> in water and hence <u>pH</u> remains at <u>7</u>.

 P_4O_{10} <u>hydrolyses / dissolves / is soluble in water / reacts with water</u> to give a colourless solution of H_3PO_4 with <u>pH 2</u> (accept 1) $P_4O_{10}(s) + 6H_2O(I) \rightarrow 4H_3PO_4(aq)$

(b) Lithium metal reacts with bromoalkanes to give organolithium compounds.

$$R-Br + 2Li \rightarrow R-Li + LiBr$$

The carbon–lithium covalent bond in organolithium compounds is polarised C–Li. These compounds are useful carbon–nucleophiles. They react with carbonyl compounds to give lithium alkoxides, which form alcohols on treatment with dilute acid as shown in Fig 4.1.



(R is alkyl; R' and R" are either alkyl or H)

Fig 4.1

(i) Butan–2–ol, CH₃CH₂CH(OH)CH₃ is formed when CH₃CH₂CHO reacts with CH₃Li in a similar two–step process.

Draw the mechanism for this reaction, assuming that CH_3Li produces the methyl anion, $:CH_3^-$, as the reacting species. In your answer, show any relevant charges, lone pairs of electrons and movement of electrons. [2]

(nucleophilic addition)



(ii) With reference to the mechanism you have described in (b)(i), explain why the butan-2-ol formed does not rotate plane-polarised light.

 $:CH_3^-$ nucleophile attacks the (trigonal) <u>planar carbonyl carbon</u> of CH₃CH₂CHO from both sides of the plane with <u>equal probability</u>, producing an <u>equimolar mixture</u> of <u>two</u> <u>enantiomers</u> (racemic mixture)

(iii) Deduce the structures of a suitable bromoalkane, RBr and a suitable carbonyl compound, R'R"CO, to synthesise each of the following isomeric alcohols.

•	CH ₃ CH ₂ CH ₂ CH(OH)CH ₃
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product	RBr	R'R''CO	
	CH₃Br	CH ₃ CH ₂ CH ₂ CHO	
	CH ₃ CH ₂ CH ₂ Br	CH₃CHO	
(CH ₃ CH ₂) ₂ CH(OH)	CH ₃ CH ₂ Br	CH ₃ CH ₂ CHO	

• (CH₃CH₂)₂CH(OH)

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(c) p-coumaric acid, C₉H₈O₃ (M_r = 164.0), occurs in tomatoes, carrots and strawberries and is thought to help prevent the development of stomach cancer. It is an aromatic compound with two substituents occupying positions 1 and 4 of the benzene ring.

8.2 g of *p*-coumaric acid reacts with excess sodium metal to give 1.2 dm³ of hydrogen gas at room temperature and pressure conditions.

When solid NaHCO₃ is added to *p*-coumaric acid, compound **G** is formed, together with liberation of CO_2 .

p-coumaric acid reacts with aqueous bromine to give compound H, C₉H₇O₄Br₃.

(i) Deduce the structures of compounds **G**, **H** and *p*-Coumaric acid, explaining the reactions described. [6]

n(*p*-coumaric acid) reacted with Na = $\frac{8.2}{164.0}$ = 0.0500 mol n(H₂) evolved = $\frac{1.2}{24}$ = 0.0500 mol

- <u>Redox reaction</u> occurs between *p*-coumaric acid and Na(s).
 Since <u>n(H₂) : n(*p*-coumaric acid) is 1:1</u>, there are two hydroxy groups in *p*-coumaric acid. (each mole of –OH group liberates ½ mol of H₂)
- One of the hydroxy groups is a <u>carboxylic acid</u> (only 3 O atoms) as CO₂(g) is liberated upon addition of NaHCO₃(s). <u>Acid-base reaction</u> occurs and **G** is the <u>carboxylate salt of p-coumaric acid</u>.
- Presence of phenol and alkene because p-coumaric acid is 1,4-disubstituted so only 2 Br atoms can substitute the H atoms on benzene ring via electrophilic substitution. Hence the 3rd Br atom must have been added to a >C=C< together with -OH group (aqueous Br₂) via electrophilic addition.



(ii) *p*-coumaric acid consists of two stereoisomers. State the type of isomerism shown here, and draw structures to illustrate your answer.
 [2]



Compounds J and K are two isomers of *p*-coumaric and their structures are given below.



(iii) When these two compounds are heated separately under reflux with alkaline KMnO₄ followed by acidification, the same compound is formed in each case.

Suggest the structure of this compound.

[1]



(iv) Describe how compounds J and K could be distinguished using a simple chemical test.

[2]

Add to separate test-tubes containing **J** and **K**, <u>Tollens' reagent</u> and <u>warm</u> **K** will give a <u>silver mirror</u> but **J** will not.

<u>Fehling's solution, warm</u> **K** will give a <u>brick red precipitate</u> but **J** will not.

<u>K₂Cr₂O₇, dilute H₂SO₄, heat (KMnO₄ is not accepted) **K** will <u>turn orange K₂Cr₂O₇ green</u> but **J** will not.</u>

<u>I₂(aq), NaOH(aq), warm</u> J will give yellow ppt but **K** will not

- **5** (a) The halogens react with hydrogen to form hydrogen halides which are colourless gases at room temperature.
 - (i) With reference to the HCl molecule, explain the meaning of the term bond energy. [1]

Bond energy of H-Cl bond is the <u>(average) amount of heat absorbed</u> to break <u>one mole</u> of <u>H-Cl (covalent) bond</u> in the <u>gaseous state</u> to form the gaseous H and Cl atoms.

Some bond energy values are given in the Table 5.1.

Bond	Bond Energy / kJ mol ⁻¹	
H—H	436	
P—P	200	
C <i>l</i> —C <i>l</i>	244	
P—H	320	
H—Cl	431	

Table 5.1	

(ii) The P—H bond energy is approximately the average of the H—H and P—P values. However, the H—C*l* bond energy is higher than the average of the H—H and C*l*—C*l* values.

Explain why this is so.

<u>Cl is more electronegative than H</u>. Hence the <u>H–Cl bond is polar</u> and the bond has ionic character which results in <u>extra bond strength</u> due to the <u>additional</u> electrostatic forces of <u>attraction</u> between the partial charges of the polar bond.

The <u>electronegativity of P and H are similar</u>, hence the bond energy of the P–H bond is just the average of the H–H and P–H bond energies.

(iii) Explain how the thermal stabilities of the hydrogen halides vary down the group. [2]

Down the group, <u>H–X bond strength decreases</u> (as shown by bond energy data) \Rightarrow <u>Less energy</u> required to <u>break</u> the weaker H–X bond.

 \Rightarrow Thermal stabilities of HX decreases.

[1]

(b) Chlorine finds various uses as organochlorine compounds.

Chloroethanoyl chloride, C*l*CH₂COC*l*, is used in the synthesis of the local anaesthetic, lidocaine, from 2,6–dimethylphenylamine as shown below.



Fig. 5.1

(i) State the type of reaction that occur during step I.

[1]

nucleophilic (acyl) substitution / condensation

(ii) A student suggested that compound **B**, an isomer of compound **A**, was produced in Step I instead.



compound B

Explain clearly whether you agree with this suggestion.

[2]

Disagree with the student suggestion. Reason: As both the <u>chlorine and oxygen are highly electronegative</u>, they attract the electrons from the acyl carbon atom, making the <u>acyl carbon atom more electron deficient</u>.

Hence the acyl carbon is <u>more susceptible to nuclephilic attack by lone pair of electron</u> <u>on nitrogen</u> on 2,6–dimethylphenylamine nucleophile.

Step II proceeds by an $S_N 2$ mechanism.

(iii) Draw the structure of the transition state formed in the mechanism.



(iv) Suggest a reason which explains why step II did not proceed via S_N1 mechanism.

If step II proceeds via $S_N 1$ mechanism, the carbocation formed would be



This carbocation is unstable due to <u>presence of electron-withdrawing O</u> (or C=O) (which would intensify the positive charge)/or, unstable because of <u>absence of electron-</u><u>donating alkyl groups</u>

(v) Suggest the **skeletal** formula of the product formed when lidocaine is reacted with lithium aluminium hydride.



[1]

(c) Fig. 5.2 shows the reaction scheme involving chloroethanoyl chloride as a starting material.



Compound L, C₅H₇O₂N is neutral and has a pleasant fruity smell.

Compound **M**, $C_3H_4O_4$ and **N**, C_2H_6O are two of the products formed in step II.

Effervescence is observed when solid sodium carbonate is added to compound M. One mole of compound M is neutralised by two moles of potassium hydroxide.

Upon adding alkaline aqueous iodine to compound **N**, a yellow precipitate is obtained.

(i) Deduce the structures of compounds L, M and N and suggest the reagents and conditions for step III. [4]

	Observations	Type of reaction	Deductions		
1	Compound L, C ₅ H ₇ O ₂ N , is neutral and has a pleasant fruity smell		 L is likely an ester, amide or nitrile L is not an amine 		
		Hydrolysis	M and N are carboxylic acid and alcohol		
2	Effervescence observed with \mathbf{M} C ₃ H ₄ O ₄ on adding solid sodium carbonate	Acid-base reaction	M is a carboxylic acid		
3	One mol M reacts with 2 mol KOH	Acid-base reaction	M is a dibasic acid		
4	N C ₂ H ₆ O reacts with alkaline $I_2(aq)$ to give yellow ppt	Oxidation	Yellow ppt = CHI_3 H CH_3 -C H Presence of OH		
	$M = HO_2CCH_2CO_2H$ $N = CH_3CH_2OH$ O_{\parallel} $L = NC - CH_2 - C - O - CH_2CH_3$				
	Step III: Dilute H ₂ SO ₄ , heat under reflux				

(ii) Hence, suggest the reagents and conditions for the 2–step synthetic route to form L from chloroethanoyl chloride.
 [2]



(d) Chloroethanoyl chloride, C*l*CH₂COC*l*, has four non–cyclic isomers. None of the isomers contains O–C*l* bond.

One of these isomers, compound **P**, exhibits different chemical properties from the other three.

(i) Draw the structures of **all** the four non-cyclic isomers of chloroethanoyl chloride and identify which isomer is compound **P**.



(ii) Describe a chemical test you would conduct to distinguish compound **P** from the other three isomers. Include the observations expected for each isomer in your answers.

P is an aldehyde

- (1) Add Tollen's reagent to all 4 isomers and warm. Silver (mirror) obtained for P, no silver (mirror) for the other 3 isomers
- (2) Add 2,4–dinitrophenylhydrazine to all 4 isomers and warm. Yellow/orange obtained for P, no ppt for the other 3 isomers

[2]