INNOVA JUNIOR COLLEGE
JC 2 PRELIMINARY EXAMINATION
in preparation for General Certificate of Education Advanced Level
Higher 2

CHEMISTRY 9647/03

Paper 3 Free Response

26 August 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
  Data Booklet
  Cover Page

READ THESE INSTRUCTIONS FIRST

Write your name and class on all the work you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
Begin each question on a fresh sheet of paper.

You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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

This document consists of **18** printed pages.

Answer any **four** questions.

1   Data concerning the elements of group II of the Periodic Table, at 298K, are given in the table. Further data may be found in the Data Booklet. M refers to elements of group II.

|	1st and 2nd IE of M / kJ mol^{-1}	ΔH_{atom} of M / kJ mol^{-1}	$\Delta H_{hydration}$ of M^{2+} / kJ mol^{-1}	$E^{\ominus}$/ V
Ca	1740	178	−1650	−2.87
Sr	1608	164	−1480	−2.89

(a)   The electrode reduction potential $E^{\ominus}$ of Group II elements gives an indication of the ease with which the following reaction occurs:

$$M(s) \longrightarrow M^{2+}(aq) + 2e \qquad \text{— reaction 1}$$
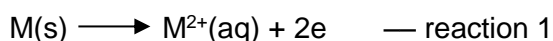
The *enthalpy change of reaction 1* can be related to the following factors:
*   *first and second ionisation energy* of the element
*   *enthalpy change of atomisation* and
*   *enthalpy change of hydration* of its gaseous ion.

(i)   Construct an energy cycle relating the factors above, and use the values given above to calculate the enthalpy change of reaction 1 for calcium.   [3]
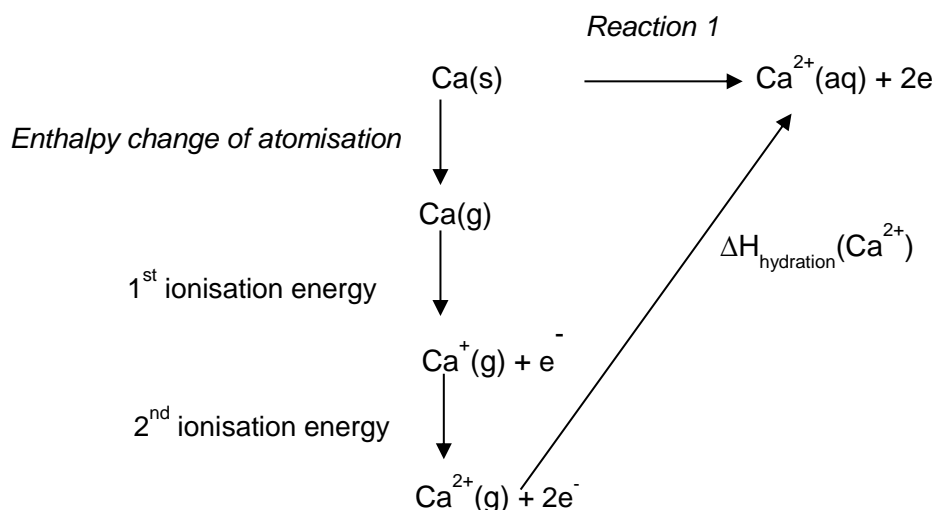
Reaction 1

Cycle: all correct compounds with state symbols [2]
(deduct 1m for omission of state symbols,
Enthalpy change of reaction 1 = 178 + 1740 + (-1650) = +268 kJ mol^{-1} [1]

(ii)   By quoting appropriate data from Data Booklet, explain the difference in enthalpy change of hydration of calcium and strontium ions.   [2]
Ca^{2+} (0.099nm) has smaller ionic radius than Sr^{2+}(0.113nm) -[1]
Since they have the same charge, the charge density of Ca^{2+} is larger,
Thus Ca^{2+} forms stronger ion-dipole interactions with water molecules [1]
$\Delta H_{hydration}$ of Ca^{2+} is more exothermic than that of Sr^{2+}.

(c) Calcium oxide is the key ingredient for the process of making cement.

When calcium is burned in oxygen, calcium oxide is produced.
When 1.50g calcium is burned in air, a mixture of ionic solids calcium oxide and red brown solid is formed.

The red brown solid has the following composition by mass: Ca, 81.1%; N,18.9%.

Adding water to the red brown solid produces calcium hydroxide and 19.2 cm^3 of ammonia gas at room temperature and pressure.

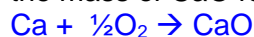**(i)** Calculate the formula of the red brown solid. [1]

	Ca	N
Mass in 100g	81.1	18.9
Amt in 100g	2.0224	1.35
Simplest ratio	1.50	1
ratio	3	2

Empirical formula of solid: Ca_3N_2

(ii) Write an equation for the reaction between red brown solid with water. [1]
$Ca_3N_2 + 6H_2O \rightarrow 2NH_3 + 3Ca(OH)_2$

(iii) Write equations for the reactions of calcium with air and use them to calculate the mass of CaO formed when 1.5g of calcium is burnt in air. [3]
$Ca + \frac{1}{2}O_2 \rightarrow CaO$
$3Ca + N_2 \rightarrow Ca_3N_2$
2 equations correct : [1]
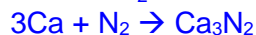
No. of moles of ammonia produced = 19.2/24000 = 0.0008
No. of moles of Ca_3N_2 produced = 0.0008/2 = 0.0004
No. of moles of calcium used to react with nitrogen= 0.0004 x 3 = 0.0012
mass of CaO formed = (1.5/40.1 – 0.0012)(40.1+16) = 2.03g

(d) Calcium oxide is normally made by heating calcium carbonate to a temperature above 825°C. A gas which turns lime water chalky is produced in the process.

(i) Write an equation for the decomposition of $CaCO_3$. [1]
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

**(ii)** Explain why barium carbonate decomposes at a higher temperature than calcium carbonate. [2]
- Ba^{2+} has larger cation size than Ca^{2+}, thus has lower charge density. [1]
- The polarising power of Ba^{2+} is lower, thus less able to polarize electron cloud of carbonate anion, weakening covalent bonds (C—O) in the anion to a smaller extent [1]
- More energy is needed to break down the anion and hence decomposition temperature for $BaCO_3$ is higher.

(e) Methylcyclohexene reacts with hydrogen bromide to form alkyl bromides.

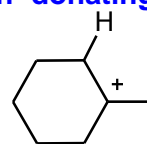methylcyclohexene

+ HBr ⟶ $C_7H_{13}Br$
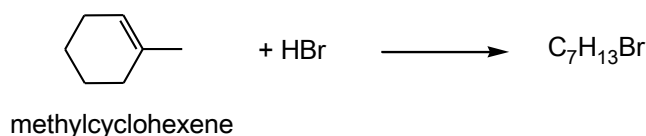
(i) The above reaction could produce two isomers with molecular formula $C_7H_{13}Br$. However, when the reaction is carried out, mainly one product is formed. Give the structural formula of the major product, explaining your answer. [2]
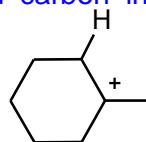

[1]
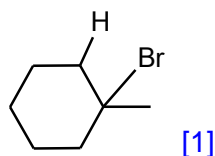
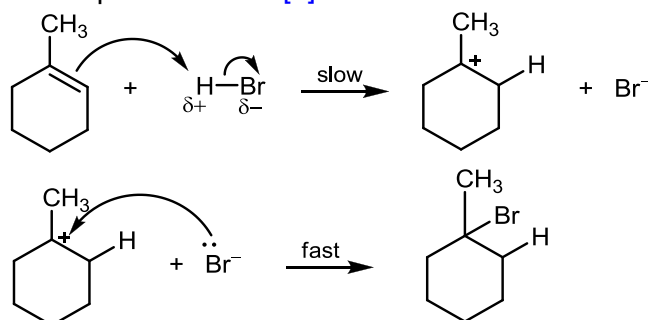Presence of an **additional (more) electron donating alkyl group** directly bonded to the positively charged carbon in disperse the positive charge to a greater extent thus **is more stable**, leading to the formation of the major product. [1]

(ii) Describe the mechanism of the reaction between hydrogen bromide and methylcyclohexene, $C_6H_9CH_3$. [3]

Electrophilic addition [1]

2 marks for mechanism
(penalise 1 mark for 1-2 errors, penalise 2 marks for 3 errors or more)
- slow step and balanced equation
- arrows and lone pair
- polarity
- correct intermediate

Unsymmetrical dihalides reacts with alkene in a similar way as hydrogen halides.

(iii) Predict the structure of the product when IBr reacts with methylcyclohexene, and explain your answer by considering the polarity within the molecule IBr. [2]
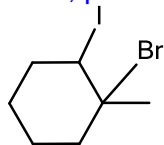
Understanding that iodine is less EN than bromine:
Iodine is less electronegative (or electron-deficient or electrophile) than bromine

[√]

Thus, iodine will be added across the C=C first. [√]
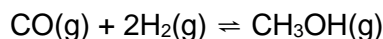(or Br⁻ will attack the carbocation formed)

Thus, product is

product [1]

[Total: 20]

2 Alcohols and carboxylic acids have many scientific, medical and industrial uses worldwide.

(a) Methanol is made from the following gaseous reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

A 1:2 mixture of CO and H_2 was pumped into a sealed reactor at 6 atm and then heated to 227 °C and maintained at this temperature for some time. When equilibrium was reached, the partial pressure of CH_3OH was found to be 1.6 atm.

(i) Write an expression for K_p for the reaction. Hence, determine the value of K_p stating its units.

[3]

$$K_p = \frac{P_{CH_3OH}}{P_{CO}P_{H_2}^2} \text{ [1]}$$

	CO(g) +	2H$_2$(g)	$\rightleftharpoons$	CH$_3$OH(g)
Initial / atm	2	4		0
Change / atm	−1.6	−3.2		+1.6
Equilibrium / atm	**0.4**	**0.8**		**1.6**

Correct equilibrium pressure for each reactant and product **[1]**

$$K_p = \frac{1.6}{0.4 \times 0.8^2} = \textbf{6.25 atm}^{-2} \text{ [1] (correct units and values)}$$

(ii) Suggest the effect on the position of equilibrium and value of K_p when methanol is removed from the reaction vessel. Explain your answer. [2]

When methanol is removed from the equilibrium, **the partial pressure of methanol decreases** [√]. By Le Chatelier's Principle, **the equilibrium position would shift to the right to increase the partial pressure of methanol** [√].

The value of K_p would remain the same **[1]** as there is no change in temperature. (K_p is temperature dependent)

(b) Grignard reagent, RMgX, is an important reagent in organic synthesis. Grignard reagents are prepared by the addition of activated magnesium on an alkyl halide or aryl halide in non-polar solvents such as ether in anhydrous conditions.

$$R-CH_2-X + Mg \longrightarrow R-\overset{\delta-}{C}H_2-\overset{\delta+}{M}gX \qquad X = Cl \text{ or } Br$$
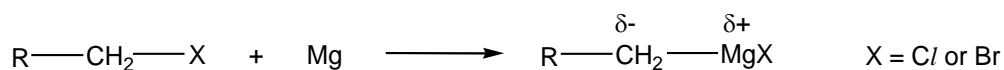
An example of a Grignard reagent reacting with a ketone to form an alcohol via a two stage process is given below:

Stage 1 : $R\!-\!CH_2\!-\!MgCl$ + $\longrightarrow$
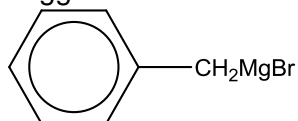
Stage 2 : $\xrightarrow{H_2O}$ $+$ $Mg(OH)Cl$
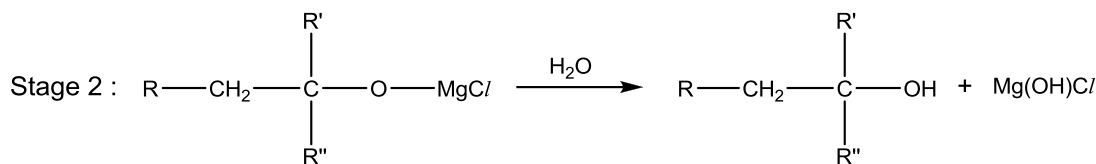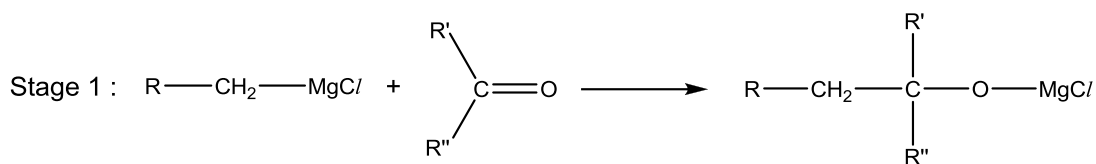
R' and R" could be alkyl / aryl group / H atoms

(i)   Suggest the type of reaction occurring in Stages 1 and 2. [2]
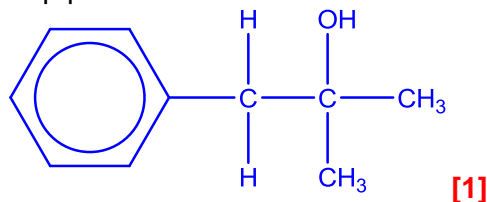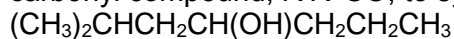Stage 1: Nucleophilic Addition [1]
Stage 2: Hydrolysis [1]

(ii)   Suggest the structural formula of the final organic product formed when

is reacted with propanone, CH_3COCH_3, in a similar two-step process. [1]

(iii)   Deduce the structures of a suitable Grignard reagent, RMgBr, and a suitable carbonyl compound, R'R"CO, to synthesize the following alcohol.
$(CH_3)_2CHCH_2CH(OH)CH_2CH_2CH_3$
[2]
$(CH_3)_2CHCH_2CHO$ [1] and $CH_3CH_2CH_2MgBr$ [1]

OR

$CH_3CH_2CH_2CHO$ [1] and $(CH_3)_2CHCH_2MgBr$ [1]

(iv)   The Grignard reagent $CH_3CH_2CH_2MgBr$ can be readily converted into a carboxylic acid by using carbon dioxide.

Suggest the structural formula for the organic product formed. [1]
$CH_3CH_2CH_2COOH$ [1]

(v)   The product formed by using Grignard reagent in **(b) (iii)** does not rotate the plane polarised light. Explain your reasoning. [2]

As the Grignard reagents can attack the **sp^2 hybridised carbonyl carbon (trigonal planar shape)** [√] either from the **top or the bottom of the plane with equal chance** [√], it results in a **racemic mixture** [√] of products being formed. **The optical activity of the two isomers cancel out each other** [√] and the resulting mixture does not the rotate plane polarised light.

(c) Describe and explain the relative acidities of phenol, benzoic acid and phenylmethanol.

[3]

Acid strength: **benzoic acid > phenol > phenylmethanol [1]**

In benzoate ion, **$C_6H_5COO^-$** , the **negative charge on oxygen is delocalised over the two highly electronegative oxygen atoms. [√]** The **$C_6H_5COO^-$ anion is most stable among the 3 anions** and hence **benzoic acid is the most acidic**.

In the phenoxide ion of phenol, **$C_6H_5O^-$**, **the p-orbital of O overlaps with the π-electron cloud of the benzene ring so that the negative charge on O delocalises into the benzene ring**. **[√]** This stabilization is not as great as that in the $C_6H_5COO^-$ ion in which the negative charge is delocalized over 2 highly electronegative O atoms. **The phenoxide ion is less stable than benzoate ion** and hence **phenol is less acidic than benzoic acid**.

In the phenylmethoxide, **$C_6H_5CH_2O^-$**, **the electron-donating alkyl/benzyl group intensifies the negative charge on O atom**. **[√]** The **$C_6H_5CH_2O^-$ ion is**, therefore, **the least stable** and **phenylmethanol is least acidic**.
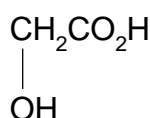
[√] – comparing the stability of the 3 anions
Marking along the line of giving credit for the EDG/EWG/delocalisation + stability of anions
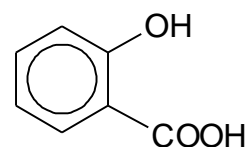
(d) Lactic acid, glycolic acid and salicylic acid are three organic acids commonly used in chemical peel.
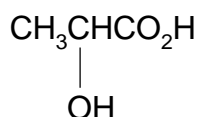
lactic acid   glycolic acid   salicylic acid

Suggest a simple chemical test that can be used to distinguish each of the following pairs. State what you would observe for each chemical test.

1) lactic acid from glycolic acid, and
2) glycolic acid from salicylic acid.

[4]

1) reagents and conditions: **I_2, NaOH (aq), warm [1]**
    Yellow ppt of CHI_3 formed for lactic acid but not glycolic acid [1]

OR
    reagents and conditions: **$KMnO_4$(aq), H_2SO_4(aq), heat [1]**
    Purple $KMnO_4$ decolourises for lactic acid and glycolic acid. For glycolic acid, effervescence of colourless gas which formed white ppt with calcium hydroxide was observed but not for lactic acid. [1]

2) reagents and conditions: **neutral FeCl_3(aq)** [1]
Violet complex formed for salicylic acid but not for glycolic acid. [1]
OR

reagents and conditions: **Br$_2$(aq)** [1]
Observation with: Reddish brown Br$_2$(aq) decolourised for salicylic acid but not for glycolic acid. [1]

*NaOH cannot be used to distinguish these 2 compounds as there is no observable change in both compounds although phenol reacts with NaOH.

[Total: 20]

3 Aluminium, is the third most abundant element (after oxygen and silicon) found in the Earth's crust. Aluminium reacts readily with carbon to form aluminium carbide, Al_4C_3.

(a) Aluminium carbide can react with protic reagents such as hydrochloric acid to produce methane gas and aluminium(III) chloride.

(i) Write a balanced equation for the reaction between aluminium carbide and hydrochloric acid. [1]

$Al_4C_3(s) + 12HCl\ (aq) \longrightarrow 4AlCl_3(aq) + 3CH_4(g)$ **[1] ss not required**
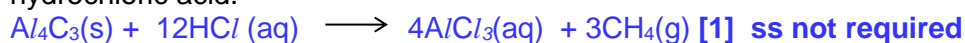
(ii) Using the equation in **(a)(i)**, calculate the maximum volume of methane gas that can be produced when 12.0 g of aluminium carbide reacts with 250 cm³ of 2.0 mol dm⁻³ hydrochloric acid at standard temperature and pressure. [3]

Amt of $Al_4C_3 = \dfrac{12.0}{4(27.0) + 3(12.0)} = 0.08333$ mol

Amt of $HCl = 0.250 \times 2.0 = 0.5$ mol **[1]**
If Al_4C_3 is limiting, amt of HCl required = 12 x 0.08333= 1.000 mol
So Al_4C_3 is in excess. HCl is limiting reagent **[1]**
Amt of CH_4 produced = $\dfrac{0.5}{12} \times 3 = 0.125$ mol
Volume of CH_4 obtained = 0.125 x 22.4= 2.80 dm³ **[1]**

(b) Aluminium chloride is used as a catalyst in electrophilic substitution reactions. The chlorination of benzene is represented by the following overall equation.
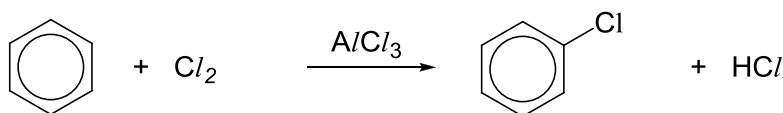

The reaction occurs in several steps.

- The first step is the reaction between Cl_2 and $AlCl_3$.

$$Cl_2 + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$$

- The benzene ring is then attacked by the Cl^+ cation in the second step.

$AlCl_3$ reacts in a similar way with halogenoalkanes and acyl chlorides, producing a carbocation that can then attack a benzene ring.

Using the reactions described above as parts of a synthesis route, a student suggested the following route to form phenyl 4-phenylbutanoate, from benzene.
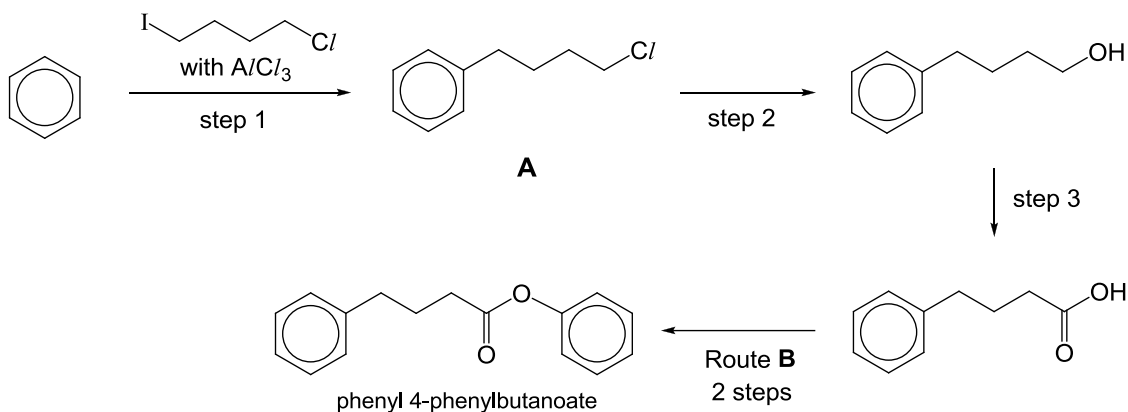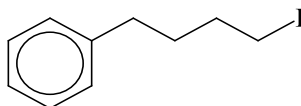
(i) Explain why step 1 has to be carried out in an anhydrous condition. [1]

$AlCl_3$ undergoes **hydrolysis** when reacted with water. **[1]**
(Accept hydration)

(ii) Draw the carbocation formed in step 1. [1]
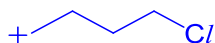
(iii) A student suggested that **A** could have the following structure:

By quoting appropriate data in the *Data Booklet*, explain why the structure suggested by the student is less likely to be formed. [2]

$E(C–I) = + 240$ kJ mol^{-1} $E(C–Cl) = + 340$ kJ mol^{-1} **[1] for quoting data**
Since E(C-I) is smaller than $E(C–Cl)$ and thus **C–I bond is weaker than the C–Cl bond**, **[1]** it is easier to break C–I bond. Hence, **F** should contain the C*l* atom, rather than I atom.

**(iv)** Give appropriate reagents and conditions necessary for steps 2 and 3. [2]

Step 2: KOH(aq) or NaOH(aq), heat **[1]**

Step 3: $K_2Cr_2O_7$, dilute H_2SO_4, heat **[1]**

(v) Suggest the reagents and conditions for each of the two steps in route **B**. [2]
Route B step 1: PCl_5(s), room temp *OR* PCl_3, room temp *OR* $SOCl_2$, room temp
Route B step 2: NaOH(aq), phenol or phenoxide ion

(vi)

Predict the structure of the product of each of the following reactions. Both compounds **E** and **F** react with 2,4-dinitrophenylhydrazine. [2]
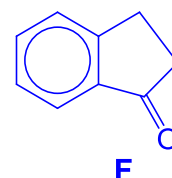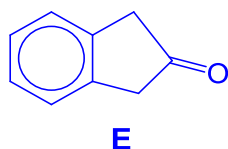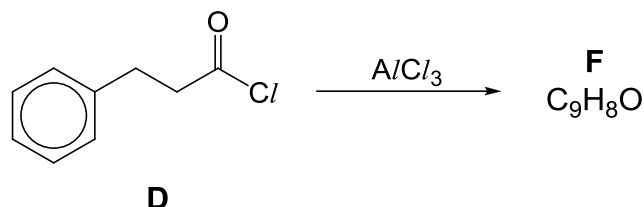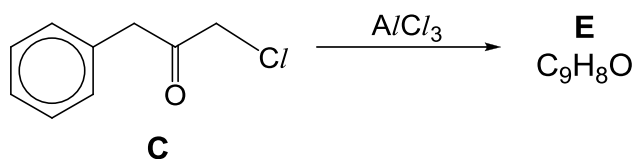
[1] for each structure

(vii) Describe and explain the relative ease of hydrolysis of the two chloro-compounds **C** and **D**. [2]

Compound D undergoes hydrolysis more readily than compound C. **[1]**

The **C atom of the acyl group** in compound D is attached to **two electronegative atoms**, C*l* and O. Hence this carbon atom is **more electron deficient** [√] and thus more **susceptible to nucleophilic attack** [√] compared to the carbon atom of C-Cl in compound C.

(c) By considering the structure and bonding, explain why

(i) the boiling point of aluminium fluoride is higher than that of aluminium chloride. [2]

AlCl$_3$ has **simple molecular structure** while AlF$_3$ has **giant ionic structure.** [√]

More energy [√] is required to overcome the **stronger electrostatic forces of attraction between oppositely charged ions in AlF$_3$** [√] than the **weak van der waal's forces of attraction between AlCl$_3$ molecules** [√]. This results in the higher boiling point in AlF$_3$.

salicylic acid, , is less soluble in water than benzoic acid, . [2]
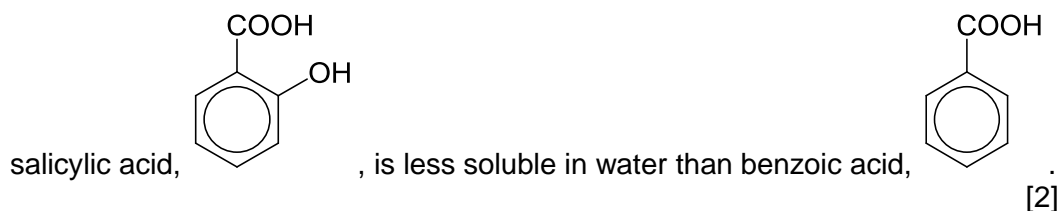
Both compounds are simple covalent molecules and can form hydrogen

9647/03/2016   **[Turn over**

bonding with water molecules.

However, **<u>intramolecular hydrogen bonding present in salicylic acid</u>** due to the <u>close proximity</u> of the carboxyl group and hydroxyl group. **[1]**

Thus, the **<u>intermolecular hydrogen bonding between salicylic acid and water is less extensive</u>** than the hydrogen bonding between benzoic acid and water. **[1]**

This results in the lower solubility of salicylic acid in water.

[Total: 20]

4   The Strecker synthesis is a term used for a series of chemical reactions that synthesize an amino acid from an aldehyde or ketone. This reaction requires acid and HCN is supplied from cyanide salts.
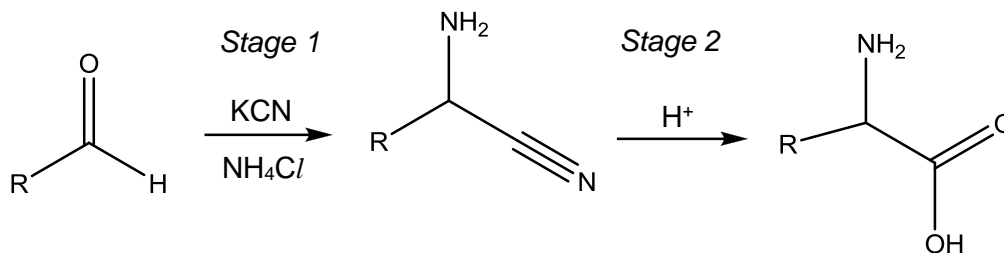
One example of the Strecker synthesis is a multikilogram scale synthesis of amino acids.

(a)   Name the type of reaction occurring in **Stage 2** and state the reagent and conditions used in this reaction. [2]
Acidic hydrolysis [1]
Reagents and conditions: dilute sulfuric acid , heat [1]

(b)   In *Stage 1*, ammonia formed from the reaction between KCN and NH_4Cl reacts with the aldehyde.
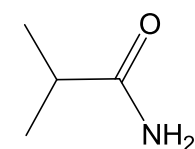
Suggest an equation for the formation of ammonia from the reaction between KCN and NH_4Cl and describe the role of KCN in stage 1.   [2]
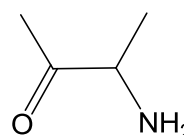
$NH_4Cl + KCN \rightleftharpoons NH_3 + HCN + KCl$ [1]
Accept if above reaction is irreversible.
KCN supplies CN- which acts as **a proton acceptor or base**.[1] **OR** CN- acts a nucleophile [1]

(c)   Explain why isobutyramide is less basic than 3-aminobutan-2-one.


isobutyramide   3-aminobutan-2-one   [2]

.

Isobutyramide is an amide and is neutral as **lone pair of electrons on N atom is delocalised into the pi electron cloud**[1] of the adjacent C=O group **making the lone pair on N atom unable to accept a proton**[√] In 3-aminobutan-2-one, **the lone pair on N atom is available to accept a proton** [√].

(d) Predict the outcomes of the following reactions starting from isobutyramide, drawing the structures of the intermediate **J** and the products **K** and **L**.

isobutyramide

NaOH(aq), reflux
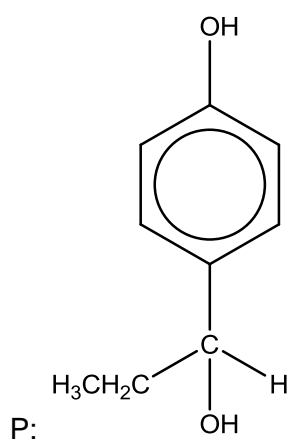
L + gas

[3]

Ans:

J

K

L
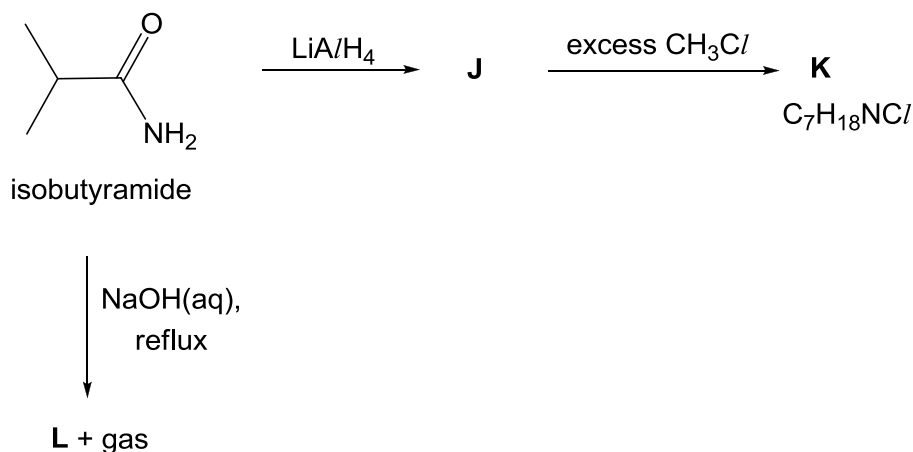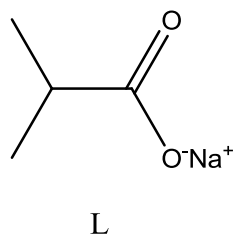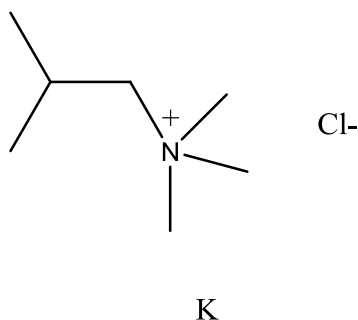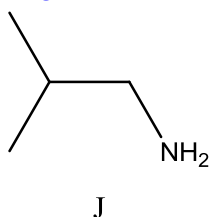
1m each

(e) Compound **P**, $C_9H_{12}O_2$, shows optical activity and does not react with aqueous potassium carbonate. However, it is soluble in aqueous potassium hydroxide.
When **P** reacts with hot acidified potassium dichromate(VI), the solution turns from orange to green. **P** also decolourises aqueous bromine to form a white precipitate, **Q**, $C_9H_{10}O_2Br_2$.
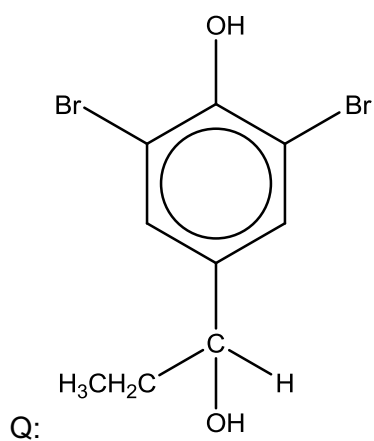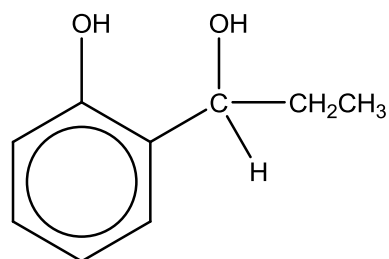
Upon heating with concentrated sulfuric acid, **P** gives only compound **R**, $C_9H_{10}O$, which displays geometric isomerism. **R** gives compound **S** and ethanoic acid on reacting with hot acidified potassium manganate(VII) solution.
Suggest the structures of **P**, **Q**, **R** and **S**, explaining the reactions involved.
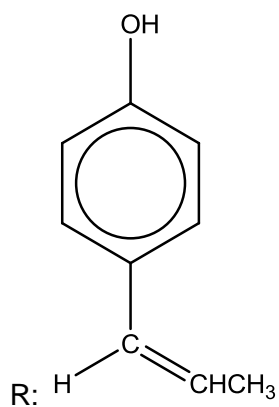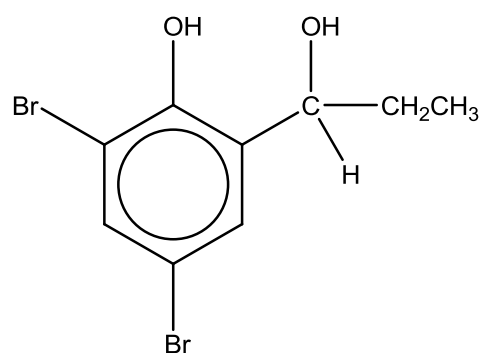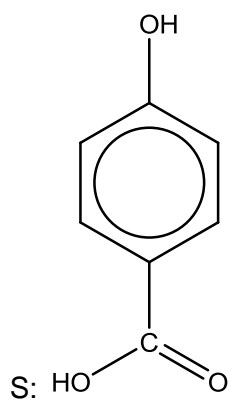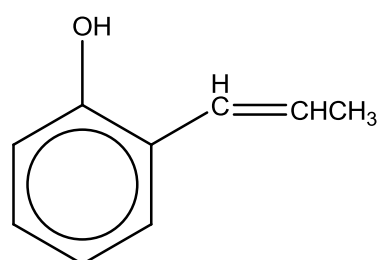
[7]

P: OR

Q: OR

R: OR

S: OR
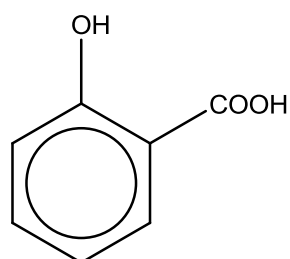
1m for each structure

|	
P shows optical activity	**P** has **chiral carbon**[√]
P does not react with aqueous potassium carbonate. However, it is soluble in aqueous potassium hydroxide.	No -COOH Undergoes **acid-base reaction. Contains phenol** [√]
P reacts with hot acidified potassium dichromate(VI), the solution turns from orange to green	**P** undergoes **oxidation.** [√] Contains **primary or secondary alcohol** [√]
P also decolourises aqueous bromine to form a white precipitate, **Q**, $C_9H_{10}O_2Br_2$.	**P** undergoes **electrophilic substitution**[√] **P** contain **phenol** group[√] Br atoms added to 2 or 4 positions on ring
Upon heating with concentrated sulfuric acid, **P** gives only compound **R**, $C_9H_{10}O$, which displays geometric isomerism.	P undergoes **elimination of H_2O**[√] R is an **alkene**/ contains C=C[√]
R gives compound **S** and ethanoic acid on reacting with hot acidified potassium manganate(VII) solution.	R undergoes **oxidative cleavage**[√]

9 [√] – 3m
6-8 [√] – 2m
3-5 [√] – 1m
0-2 [√] – 0m

(f) The structure of squaric acid is shown below.
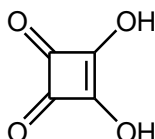
(i) State the functional groups in squaric acid.[2]

Ketone, alkene and alcohol
2m for all 3 functional groups ; 1m for 2 functional groups

(ii) Squaric acid is a stable molecule although it has high angle strain associated with a four-membered ring. It is a strong diprotic acid with a pKa values 1.5 and 3.4 respectively. Explain the high acidity of squaric acid. [2]
The high acidity of the squaric acid is due to the formation of a **very stable anion[1] due to negative charges being delocalised across the sp^2 hybridised carbon [1]**.

[Total: 20]

5 Iron is, by mass, the most common element on Earth, forming much of Earth's outer and inner core. Iron and its compounds have been used as catalysts in many reactions. For example, aqueous iron(II) chloride can be used to catalyse the reaction between between I^- and $S_2O_8^{2-}$, to form I_2 and SO_4^{2-} ions.

(a) (i) Write an equation to represent the **third** ionisation energy of Fe. [1]

$Fe^{2+}(g) \rightarrow Fe^{3+}(g) + e$ **[1, state symbols must be included]**

(ii) Write the electronic configuration for Fe^{2+}. Hence, suggest why the third ionisation energy of $_{26}Fe$ is lower than that of $_{25}Mn$. [2]

Fe^{2+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6$ **[1]**

The lower 3rd IE of Fe is due to **inter-electronic repulsion [√]** by the **paired electrons in the d orbital [√]**.

(iii) State the type of catalysis for the reaction between I^- and $S_2O_8^{2-}$ that is catalysed by aqueous iron(II) chloride. [1]

Homogenous catalysis **[1]**

(iv) The reaction between I^- and $S_2O_8^{2-}$ can also be catalysed by aqueous cobalt(II) chloride. Using relevant $E^{\ominus}$ values from the *Data Booklet*, explain why cobalt(II) chloride can be a catalyst for this reaction. [2]

$S_2O_8^{2-} + 2Co^{2+} \rightarrow 2Co^{3+} + SO_4^{2-}$
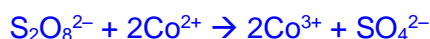
Ecell $= +2.01 - (+1.82)$
$= +0.19$ V (reaction is energetically feasible) **[1]**

$2I^- + 2Co^{3+} \rightarrow 2Co^{2+} + I_2$
Ecell $= +1.82 - (+0.54)$
$= +1.28$ V (reaction is energetically feasible) **[1]**
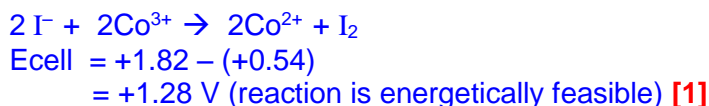
(b) A green solution of aqueous iron(II) chloride is reacted with acidified potassium manganate(VII). The resultant solution **D** is treated with aqueous sodium carbonate to form a reddish brown precipitate **E**, together with a colourless gas which forms white precipitate in aqueous calcium hydroxide. When aqueous NH_4SCN is added to **D**, a blood red solution is formed.

(i) Explain why aqueous iron(II) chloride is coloured. [2]

$FeCl_2(aq)$ is coloured due to:

- presence of **incompletely filled 3d orbitals [√]** in the **Fe^{2+} ions**.

- In the **presence of ligands**, **3d orbitals split into two groups with small energy gap [√]**

- Some of the **light energy is used to promote an electron from a 3d orbital of lower energy into the partially filled 3d orbital of higher energy. [1]**

- Colour seen is the **complement of the colour absorbed in the visible region** of the spectrum

**(ii)** Identify precipitate **E**. [1]

***iron(III) hydroxide* [1]**

(iii) Suggest the type of reaction that has occurred for the formation of the blood red solution. [1]

Ligand exchange **[1]**

(c) Iron is also used in making iron-air battery which is a low-cost and environmental friendly rechargeable energy source. An iron-air battery comprises of iron electrode, porous carbon-containing air electrode. The electrolyte used is aqueous potassium hydroxide.
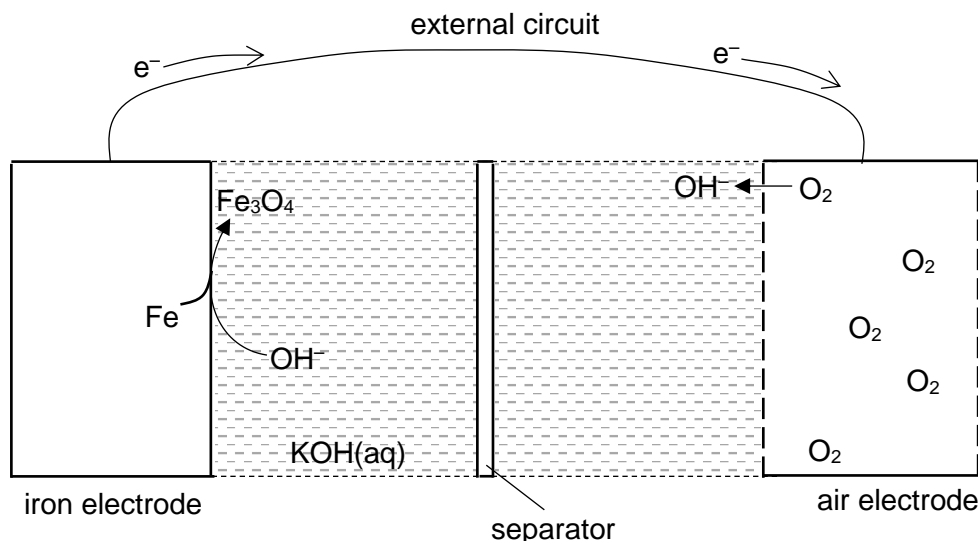

At the iron electrode, iron is oxidised to magnetite, Fe_3O_4, during discharging, according to the following reaction:

$$3Fe + 8OH^- \longrightarrow Fe_3O_4 + 4H_2O + 8e$$
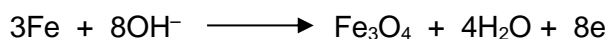
At the air electrode, oxygen is reduced to form hydroxide ions.

(i) Write the half-equation for the reaction that occurred at the air electrode during discharging. [1]

$O_2 + 2H_2O + 4e \rightarrow 4OH^-$ **[1]**

**(ii)** During discharging, the cell acts as a power source and the overall reaction occurred is as follows:

$$3Fe + 2O_2 \longrightarrow Fe_3O_4$$
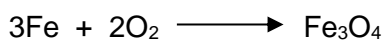
Suggest, with explanation, for the sign of the $\Delta G^\ominus$ for this reaction. [1]

Negative **[√]**. The reaction that occurred during discharging should be a **spontaneous reaction [√]**.

(iii) The battery is capable of producing an e.m.f. of 1.28V. By using suitable data from the *Data Booklet*, suggest a value for the $E^\ominus$ of the $Fe_3O_4|Fe$ electrode reaction. [1]

Ecell = Ered – Eox
+1.28 = +0.40 – E($Fe_3O_4|Fe$)
E($Fe_3O_4|Fe$) = –0.88 V **[1]**

During charging, at the iron electrode, magnetite and water undergo the following reaction:

$$Fe_3O_4 + 4H_2O + 8e \longrightarrow 3Fe + 8OH^-$$
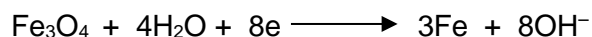
At the same electrode, a competing side-reaction occurs where water reacts to form hydrogen gas according to the following reaction:

$$2H_2O + 2e \longrightarrow H_2 + 2OH^-$$
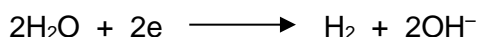
After a 1-hour charging, the volume of H_2 gas evolved, measured at r.t.p., is 0.652 dm^3.

(iv) Calculate the amount of electrons that was required to produce H_2 gas.

[1]

Amount of H_2 evolved = 0.652/24 = 2.717 x 10^{-2} mol
Amount of electrons required = 5.434 x 10^{-2} mol **[1]**

(v) A current of 9.5 A is supplied to the battery during the 1-hour charging.

Use this information and your answer in **(c)(iv)** to calculate the amount of iron produced during the charging. [2]
It = n_eF
Ne = (9.5)(3600)/96500 = 0.3544 mol **[1]**

Amount of electrons reacted with Fe_3O_4 = 0.3544 - 5.434 x 10^{-2} = 0.3001 mol

Amount of Fe produced = 0.3001 x 3/8 = 0.113 mol **[1]**

Ignore if student went on to calculate mass of Fe.

(d) The separator used in the iron-air battery is an organic polymeric membrane, made from compound **X**.

Compound **X** has a molecular formula C_3H_3N. On heating with dilute sulfuric acid, **X** forms compound **Y**, $C_3H_4O_2$. Both **X** and **Y** decolourise aqueous bromine, however, only **Y** reacts with sodium carbonate to form gas which forms white precipitate in $Ca(OH)_2$(aq).

Suggest structures for compounds **X** and **Y**, giving reasons for your answers. [4]

Evidence	Deduction	
Both **X** and **Y** decolourise aqueous bromine	Both **X** and **Y** undergoes **electrophilic addition**. **X** and **Y** contains **alkene group**.	**[1]**
Y reacts with sodium carbonate to form gas which forms white precipitate in $Ca(OH)_2$(aq).	**Y** undergoes **acid-carbonate reaction** with sodium carbonate. **Y** contains **carboxylic acid group.**	**[1]**
On heating with dilute sulfuric acid, **X** forms compound **Y**, $C_3H_4O_2$.	**X** undergoes **acidic hydrolysis** to form **Y**. **X** contains **nitrile group**	**[1]**

[max 2m]

X: CH_2=CHCN **[1]**   **Y**: CH_2=CHCOOH **[1]**

[Total: 20]