

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 **12** printed pages.

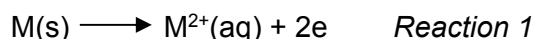


Answer any **four** questions.

- 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.

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

- (a) The electrode reduction potential E° of Group II elements gives an indication of the ease with which the following reaction occurs:



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]
- (ii) By quoting appropriate data from *Data Booklet*, explain the difference in enthalpy change of hydration of calcium and strontium ions. [2]

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

When calcium is burned in oxygen, calcium oxide is produced.

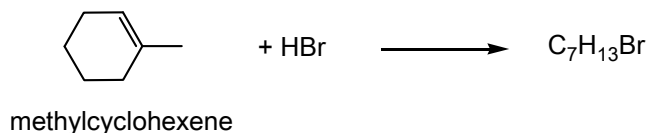
When 1.50 g calcium is burned in air, a mixture of ionic solids calcium oxide and red brown solid is formed.

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 cm³ of ammonia gas at room temperature and pressure.

- (i) Calculate the formula of the red brown solid. [1]
- (ii) Write an equation for the reaction between red brown solid with water. [1]
- (iii) Write equations for the reactions of calcium with air and use them to calculate the mass of CaO formed when 1.5 g of calcium is burnt in air. [3]
- (c) 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 CaCO₃. [1]
- (ii) Explain why barium carbonate decomposes at a higher temperature than calcium carbonate. [2]

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

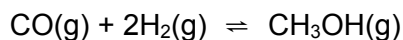


- (i) The above reaction could produce two isomers with molecular formula $C_7H_{13}Br$. However, when the reaction is carried out, mainly one product is formed. Give the structural formula of the major product, explaining your answer. [2]
- (ii) Describe the mechanism of the reaction between hydrogen bromide and methylcyclohexene, $C_6H_9CH_3$, showing curly arrows, charges, dipoles and any relevant lone pairs. [3]
- (iii) Unsymmetrical dihalides reacts with alkene in a similar way as hydrogen halides. Predict the structure of the product when IBr reacts with methylcyclohexene, and explain your answer by considering the polarity within the molecule IBr . [2]

[Total: 20]

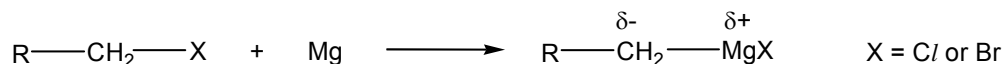
- 2 Alcohols and carboxylic acids have many scientific, medical and industrial uses worldwide.

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

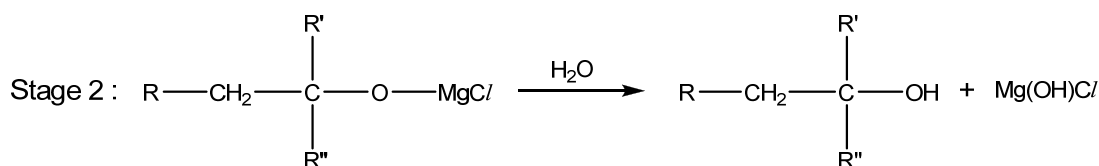
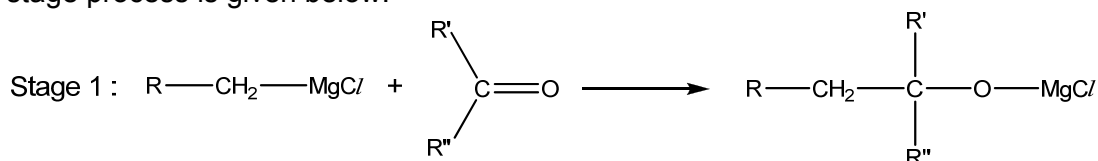


A 1:2 mixture of CO and H₂ was pumped into a sealed reactor at 6 atm and then heated to 227 °C and maintained at this temperature for some time. When equilibrium was reached, the partial pressure of CH₃OH was found to be 1.6 atm.

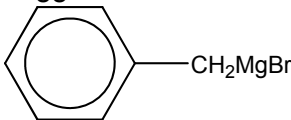
- (i) Write an expression for K_p for the reaction. Hence, determine the value of K_p stating its units. [3]
- (ii) Suggest the effect on the position of equilibrium and value of K_p when methanol is removed from the reaction vessel. Explain your answer. [2]
- (b) Grignard reagent, RMgX, is an important 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.



An example of a Grignard reagent reacting with a ketone to form an alcohol via a two stage process is given below:



R' and R'' could be alkyl / aryl group / H atoms

- (i) Suggest the type of reaction occurred between the Grignard reagent and the carbonyl compound in Stage 1 and 2. [2]
- (ii) Suggest the structural formula of the final organic product formed when  is reacted with propanone, CH₃COCH₃, 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, (CH₃)₂CHCH₂CH(OH)CH₂CH₂CH₃. [2]

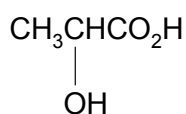
- (iv) The Grignard reagent $\text{CH}_3\text{CH}_2\text{CH}_2\text{MgBr}$ can be readily converted into a carboxylic acid by using carbon dioxide.

Suggest the structural formula of the organic product formed. [1]

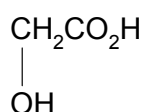
- (v) The product formed by using Grignard reagent in (b) (iii) does not rotate the plane polarised light. Explain your reasoning. [2]

- (c) Describe and explain the relative acidities of phenol, benzoic acid and phenylmethanol. [3]

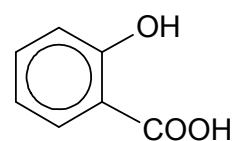
- (d) Lactic acid, glycolic acid and salicylic acid are three organic acids commonly used in chemical peel.



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]

[Total: 20]

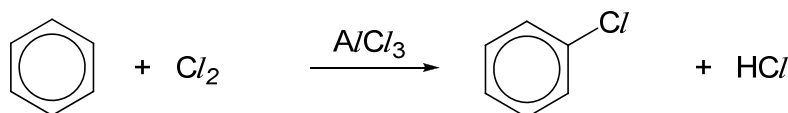
- 3 Aluminium, is the third most abundant element (after oxygen and silicon) found in the Earth's crust. Aluminium reacts readily with carbon to form aluminium carbide, Al_4C_3 .

(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]

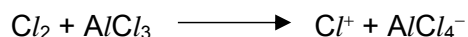
(ii) Using the equation in (a)(i), calculate the maximum volume of methane gas that can be produced when 12.0 g of aluminium carbide reacts with 250 cm^3 of 2.0 mol dm^{-3} hydrochloric acid at standard temperature and pressure. [3]

(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.

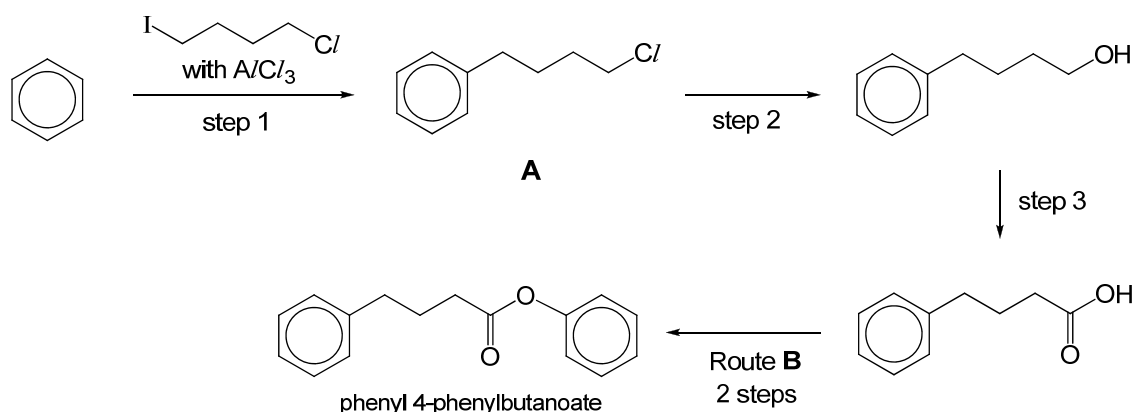
- The first step is the reaction between Cl_2 and AlCl_3 .



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

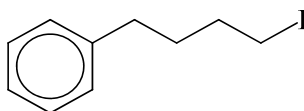
AlCl_3 reacts in a similar way with halogenoalkanes and acyl chlorides, producing a carbocation that can then attack a benzene ring.

Using the reactions described above as parts of a synthesis route, a student suggested the following route to form phenyl 4-phenylbutanoate, from benzene.



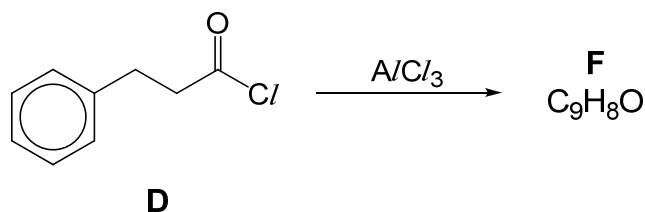
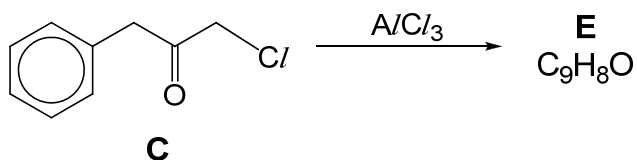
- (i) Explain why step 1 has to be carried out in an anhydrous condition. [1]
- (ii) Draw the carbocation formed in step 1. [1]

- (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]

- (iv) Give appropriate reagents and conditions necessary for steps 2 and 3. [2]
- (v) Suggest the reagents and conditions for each of the two steps in route **B**. [2]
- (vi) Predict the structure of the product of each of the following reactions. Both compounds **E** and **F** react with 2,4-dinitrophenylhydrazine. [2]

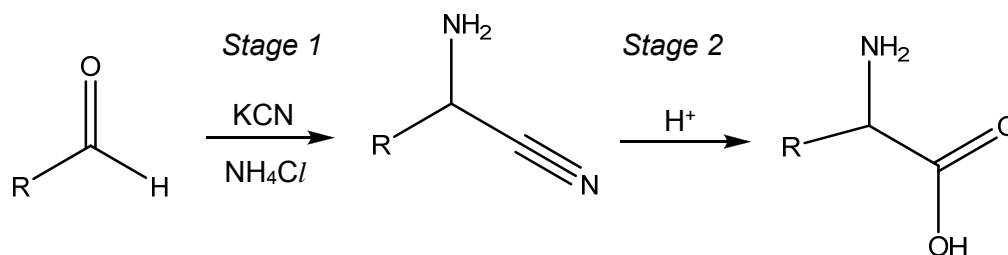


- (vii) Describe and explain the relative ease of hydrolysis of the two compounds **C** and **D**. chloro- [2]
- (c) By considering the structure and bonding, explain why
- (i) the boiling point of aluminium fluoride is higher than that of aluminium chloride. [2]

- (ii) salicylic acid, is less soluble in water than benzoic acid, . [2]

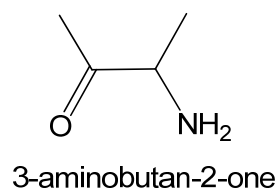
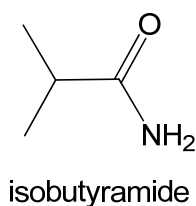
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- 4 The *Strecker synthesis* is a term used for a series of chemical reactions that synthesize an amino acid from an aldehyde or ketone. This reaction requires acid and HCN is supplied from cyanide salts.

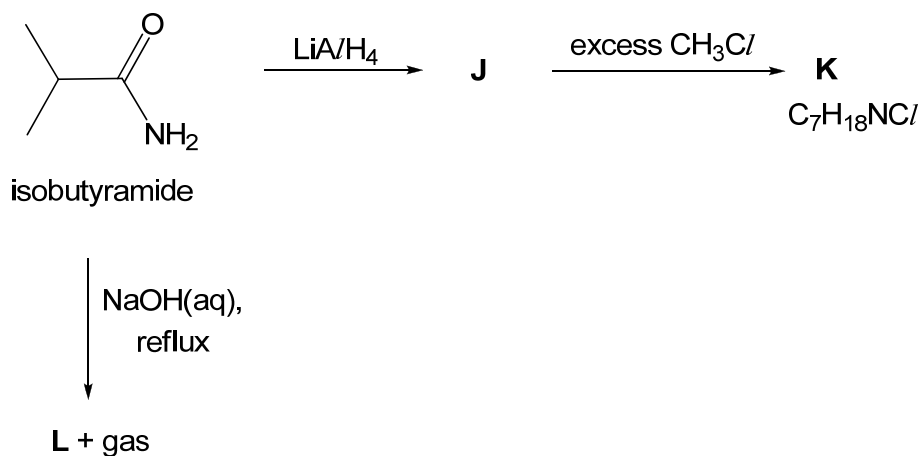


One example of the Strecker synthesis is a multikilogram scale synthesis of amino acids.

- (a) Name the type of reaction occurring in *Stage 2* and state the reagent and conditions used in this reaction. [2]
- (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]
- (c) Explain why isobutyramide is less basic than 3-aminobutan-2-one. [2]



- (d) Predict the outcomes of the following reactions starting from isobutyramide, drawing the structures of the intermediate **J** and the products **K** and **L**. [3]

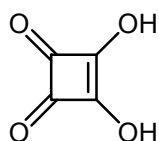


- (e) Compound **P**, $C_9H_{12}O_2$, shows optical activity and does not react with aqueous potassium carbonate. However, it is soluble in aqueous potassium hydroxide. When **P** reacts with hot acidified potassium dichromate(VI), the solution turns from orange to green. **P** also decolourises aqueous 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]

- (f) The structure of squaric acid is shown below.



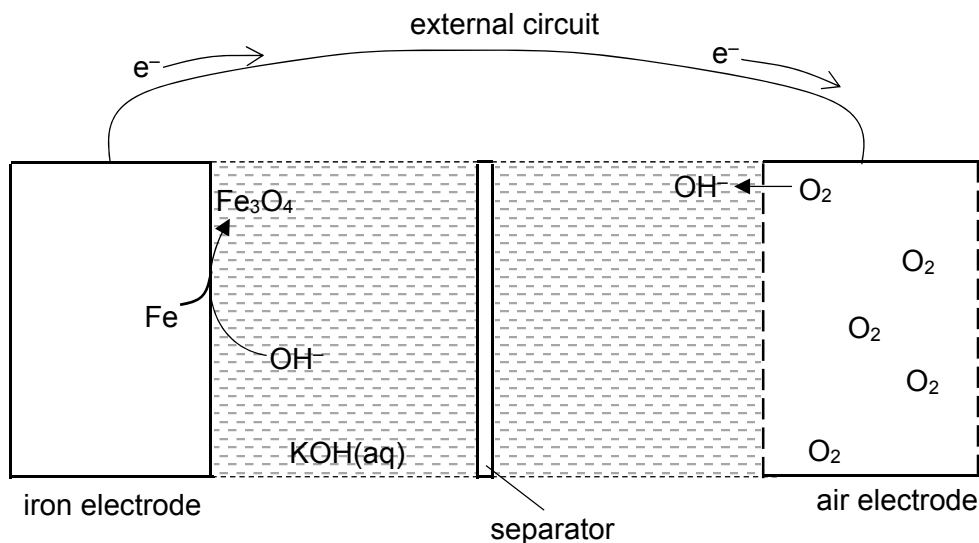
- (i) State the functional groups in squaric acid. [2]
- (ii) Squaric acid is a stable molecule although it has high angle strain associated with a four-membered ring. It is a strong diprotic acid with pK_a values 1.5 and 3.4 respectively. Explain the high acidity of squaric acid. [2]

[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 I^- and $\text{S}_2\text{O}_8^{2-}$, to form I_2 and SO_4^{2-} ions.

- (a) (i) Write an equation to represent the **third ionisation energy** of Fe. [1]
- (ii) Write the electronic configuration for Fe^{2+} . Hence, suggest why the third ionisation energy of $_{26}\text{Fe}$ is lower than that of $_{25}\text{Mn}$. [2]
- (iii) State the type of catalysis for the reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ that is catalysed by aqueous iron(II) chloride. [1]
- (iv) The reaction between I^- and $\text{S}_2\text{O}_8^{2-}$ 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]
- (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]
- (ii) Identify precipitate **E**. [1]
- (iii) Suggest the type of reaction that has occurred for the formation of the blood red solution. [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.

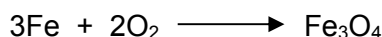


At the iron electrode, iron is oxidised to magnetite, Fe_3O_4 , during discharging, according to the following reaction:



At the air electrode, oxygen is reduced to form hydroxide ions.

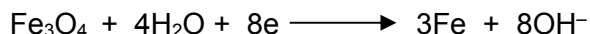
- (i) Write the half-equation for the reaction that occurred at the air electrode during discharging. [1]
- (ii) During discharging, the cell acts as a power source and the overall reaction occurred is as follows:



Suggest, with explanation, for the sign of the ΔG^\ominus for this reaction. [1]

- (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 $\text{Fe}_3\text{O}_4|\text{Fe}$ electrode reaction. [1]

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



At the same electrode, a competing side-reaction occurs where water reacts to form hydrogen gas according to the following reaction:



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]

(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]

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

Compound **X** has a molecular formula $\text{C}_3\text{H}_3\text{N}$. On heating with dilute sulfuric acid, **X** forms compound **Y**, $\text{C}_3\text{H}_4\text{O}_2$. Both **X** and **Y** decolourise aqueous bromine, however, only **Y** reacts with sodium carbonate to form gas which forms white precipitate in $\text{Ca}(\text{OH})_2(\text{aq})$.

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

[Total: 20]