

RAFFLES INSTITUTION
2016 YEAR 6 PRELIMINARY EXAMINATION

Higher 2



CHEMISTRY

Paper 3 Free Response

9647/03

16 September 2016

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Do not open this question booklet until you are told to do so.

Write your name, class and index number 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.

A Data Booklet is provided. Do not write anything in it.

You are reminded of the need for good English and clear presentation in your answers.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [] at the end of each question or part question.

This document consists of **12** printed pages.

Answer any **four** questions.

Begin **each** question on a **fresh sheet** of paper.

- 1 (a) Gallium trichloride, GaCl_3 , can be formed by direct combination of the elements. It has a melting point of 78°C .

Suggest the type of chemical bonding present in GaCl_3 and explain why gallium has a high tendency to form chlorides of this nature. [2]

- (b) Gallium hydride, with empirical formula GaH_3 , can be prepared from GaCl_3 . A 0.55 g sample of gaseous gallium hydride occupies a volume of 68 cm^3 at a temperature of 243 K and a pressure of $1.12 \times 10^5\text{ Pa}$.

Determine the M_r of gallium hydride and hence its molecular formula. [3]

- (c) GaH_3 reacts with $(\text{CH}_3)_3\text{N}$ at 178 K to give compound **A**, which has the following composition by mass:

H, 11.0%; C, 37.8%; N, 14.7%; Ga, 36.5%.

A molecule of compound **A** has only one Ga atom.

- (i) Determine the molecular formula of **A**. [1]

- (ii) Draw a structure to show clearly

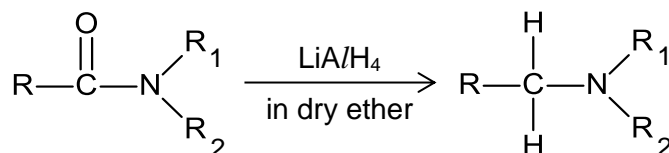
- the shape of **A** around the gallium atom **and**
- the types of bonds around the gallium atom.

[2]

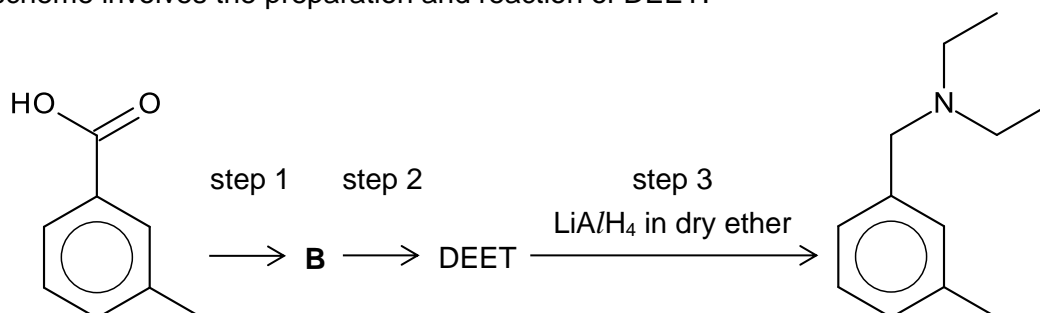
- (d) Lithium aluminium hydride, LiAlH_4 , and lithium gallium hydride, LiGaH_4 , are both donors of hydride, H^- . Thus, they are capable of reducing a large number of organic molecules.

Suggest a possible reason why LiAlH_4 is a stronger reducing agent than LiGaH_4 . [1]

- (e) LiAlH_4 can be used to reduce amides to amines as shown below:



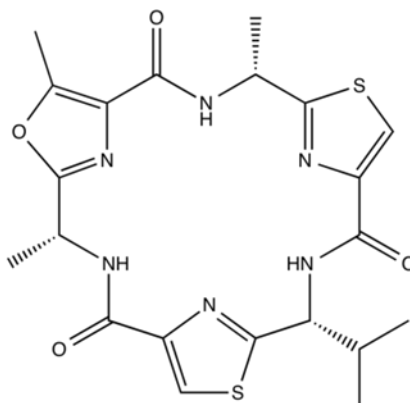
DEET is the active ingredient in many insect repellents. The following reaction scheme involves the preparation and reaction of DEET.





(i) Suggest the structures of compound **B** and DEET. [2]

(ii) Suggest the organic reactant used in step 2. [1]

(f) Venturamide A is a cyclic peptide with anti-malarial activity. It has the following structure.



Suggest reagents and conditions for the basic hydrolysis of Venturamide A and draw the structures of the organic products.

Assume that the 2 rings,  and , are inert in the reaction. [3]

(g) The identity of the side-chain and pK_a values associated with aspartic acid, asp, and alanine, ala, are as follows :

amino acid	aspartic acid, asp	alanine, ala
R	$-\text{CH}_2\text{COOH}$	$-\text{CH}_3$

amino acid	aspartic acid, asp	alanine, ala
pK_{a1}	2.10	2.35
pK_{a2}	3.86	9.87
pK_{a3}	9.82	

(i) Draw the structures of the major species present in a solution of the asp-ala dipeptide at **each** of the following pH values at room temperature.

pH = 1

pH = 3.86

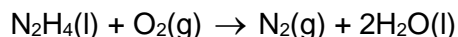
pH = 12

[3]

(ii) Draw the zwitterionic form of asp-ala and write an equation to show how it can remove small amounts of H^+ . [2]

[Total: 20]

- 2 (a) Hydrazine, N_2H_4 , is used as a rocket fuel.
It combusts in oxygen according to the equation:



Using the following data, calculate the enthalpy change of combustion of hydrazine.

compound	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{N}_2\text{H}_4(\text{l})$	+51
$\text{H}_2\text{O}(\text{l})$	-286

[2]

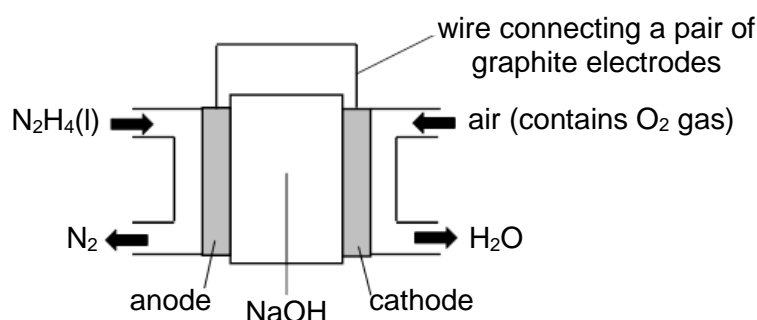
- (b) The standard electrode potential for the $\text{O}_2/\text{H}_2\text{O}$ half-cell was measured.



Draw a labelled diagram to show how the standard electrode potential of the $\text{O}_2/\text{H}_2\text{O}$ half-cell was measured. Include in your diagram the direction of electron flow.

[3]

- (c) (i) Hydrazine is increasingly used in fuel cells, and these direct hydrazine fuel cells are a more practical and viable source of energy as compared to hydrogen fuel cells.



Write balanced half-equations, with state symbols, for the reactions taking place at the anode and the cathode when the fuel cell, using aqueous sodium hydroxide as electrolyte, is in operation.

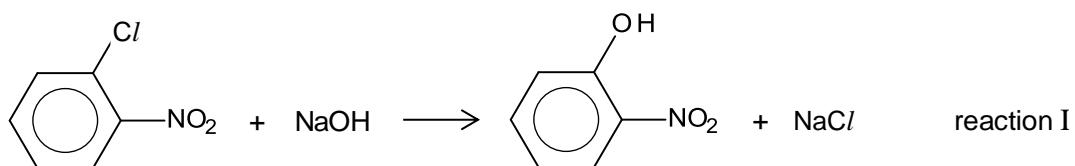
[2]

- (ii) Given that E^\ominus_{cell} for the reaction that takes place in the fuel cell is +1.56 V, use values from the *Data Booklet* to calculate the standard electrode potential for the $\text{N}_2/\text{N}_2\text{H}_4$ half-cell.
- (iii) Suggest an advantage of using hydrazine as a fuel over hydrogen gas in a fuel cell.

[1]

[1]

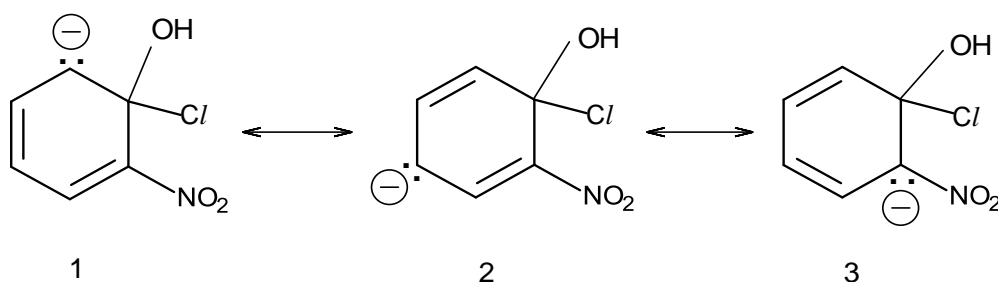
- (d) 2-chloronitrobenzene undergoes nucleophilic aromatic substitution when heated with aqueous NaOH at 100 °C.



2-chloronitrobenzene

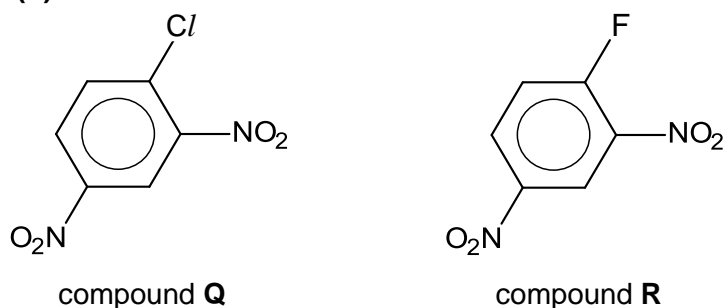
- (i) Suggest what is unusual about reaction I. [1]

The mechanism for reaction I involves a negatively charged anion intermediate. Three resonance structures of the anion intermediate are shown below:

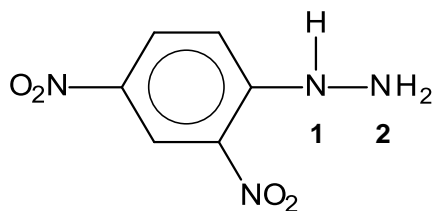


- (ii) Explain why structure 3 is the most stable resonance structure. [1]

Compounds **Q** and **R** can undergo nucleophilic aromatic substitution that is similar to reaction I in (d).

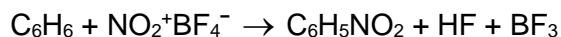


- (e) Despite the stronger C–F bond in **R** as compared to the C–Cl bond in **Q**, **R** is more reactive than **Q**. Suggest why this is so. [2]
- (f) The structure of 2,4-dinitrophenylhydrazine is given below.

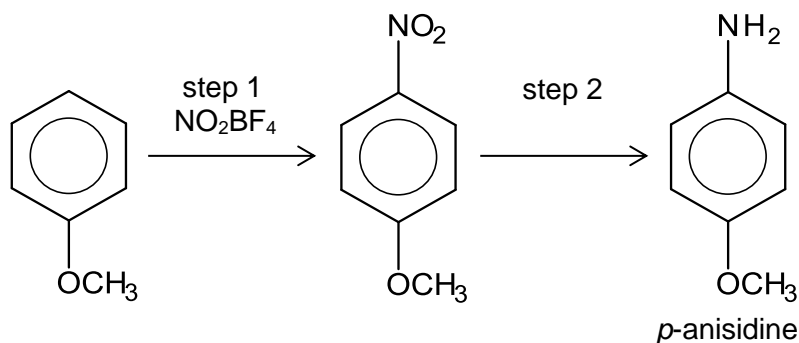


Suggest, with reasons, how the basicity of the N atoms labelled N-1 and N-2 on 2,4-dinitrophenylhydrazine compare with each other. [1]

- (g) Nitronium tetrafluoroborate, $\text{NO}_2^+\text{BF}_4^-$, is a nitronium salt which can be used as a nitrating agent for aromatic compounds.



p-anisidine may be prepared using the following route.
(Assume that the $-\text{OCH}_3$ group is unreactive.)



- (i) Name the type of reaction and describe the mechanism for the reaction in step 1. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [3]
- (ii) Suggest reagents and conditions for step 2. [1]

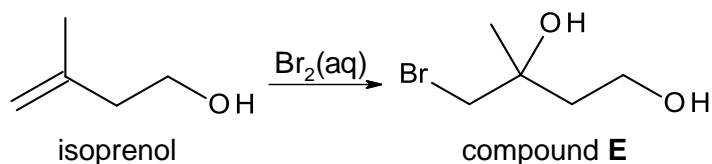
Fats and oils are sometimes oxidised to form aldehydes and ketones that cause a rancid smell in food. *p*-anisidine is widely used for detecting the presence of such aldehydes and ketones.

The reaction between an aldehyde and *p*-anisidine is similar to the reaction between an aldehyde and 2,4-dinitrophenylhydrazine.

- (iii) Name the type of reaction which RCHO , an aldehyde found in palm oil, undergoes with *p*-anisidine. [1]
- (iv) Draw the displayed formula of the product formed by the reaction between RCHO and *p*-anisidine. [1]

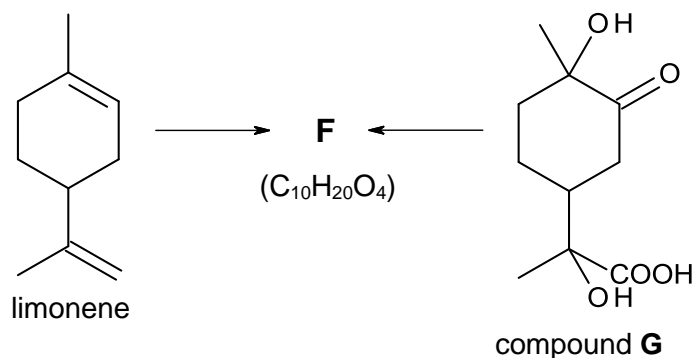
[Total: 20]

- 3 (a) Isoprenol is a terpenoid that can be used to prepare other useful compounds.



Name and draw a mechanism for the conversion of isoprenol to compound **E**. Show relevant lone pairs and charges, and use curly arrows to indicate the movement of electrons. [4]

- (b) Limonene is a compound used in perfumery because of its strong orange scent.



Compound **F** can be prepared from either limonene or compound **G**. One mole of **F** reacts with excess PCl_5 to produce 4 moles of gas.

- (i) Suggest a structure for compound **F**. [1]

- (ii) Suggest reagents and conditions for the preparation of compound **F** from
- limonene
 - compound **G**
- [2]

- (c) Compound **W**, $\text{C}_{10}\text{H}_{16}$, is a structural isomer of limonene. It is used in perfumery for its sweet herbal scent.

W exhibits geometric isomerism. When **W** is reacted with hydrogen in the presence of platinum catalyst, $(\text{CH}_3)_2\text{CH}(\text{CH}_2)_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ is formed.

When **W** is treated with hot acidified $\text{KMnO}_4(\text{aq})$, it produces three organic compounds **X**, **Y** and **Z**, each having the same number of carbon atoms.

Both compounds **X** and **Z** react with 2,4-dinitrophenylhydrazine to give an orange precipitate.

Both compounds **Y** and **Z** react with excess magnesium to give an explosive gas.

Suggest structures for compounds **X**, **Y** and **Z**, and draw the geometric isomers of compound **W**. [5]

- (d) Platinum(IV) chloride reacts with ammonia to form a platinum(IV) salt with the formula, $\text{Pt}(\text{NH}_3)_x\text{Cl}_y$. The cation in the salt is an octahedral complex.

When 0.100 mol of $\text{Pt}(\text{NH}_3)_x\text{Cl}_y$ is dissolved in excess aqueous AgNO_3 , 28.7 g of white precipitate is formed.

Determine the formula of the cation present in $\text{Pt}(\text{NH}_3)_x\text{Cl}_y$. [2]

- (e) $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is a square planar complex which displays geometric isomerism.

Cisplatin, the cis-isomer of $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, kills cancer cells by altering the configuration of their DNA. The trans-isomer, transplatin, does not exhibit such anti-cancer activity.

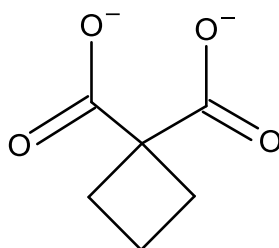
- (i) Draw the structures for both cisplatin and transplatin. [1]

- (ii) When cisplatin enters cancer cells, one of the chloride ligands in the complex is first replaced by a water molecule.

Write a balanced equation for this reaction. [1]

- (f) Carboplatin also exhibits anti-cancer activity, but it does not result in the severe side-effects which cisplatin causes.

Carboplatin has a square planar structure around Pt and it can be made by replacing the two chloride ligands in cisplatin with a bidentate cyclobutanedicarboxylate ion.



cyclobutanedicarboxylate ion

- (i) Explain what is meant by a *bidentate* ligand. [1]

- (ii) Draw the structure of carboplatin. [1]

- (g) Another method of killing cancer cells involves injecting concentrated ethanol directly into the tumour.

Explain, in terms of bonding, how ethanol may cause the denaturation of proteins in cancer cells. [2]

[Total: 20]

Use of the Data Booklet is relevant to this question.

- 4 (a) Phosphorus pentachloride, PCl_5 , is a solid which melts at 162°C .

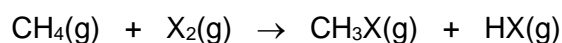
Describe how a **pure** solid sample of PCl_5 can be made from its elements. [2]

- (b) Phosphazenes are a group of P(V)/N(III) compounds with cyclic structures.

PCl_5 reacts with NH_4Cl to give phosphazene **S**, $\text{N}_3\text{P}_3\text{Cl}_6$, and steamy white fumes are evolved.

Write an equation for this reaction and suggest a structure for phosphazene **S**. [2]

- (c) Some halogens also react readily with methane.



- (i) Use bond energy data from the *Data Booklet* to calculate the ΔH^\ominus of this reaction where X is iodine, I. [2]

- (ii) Hence, suggest why it is not possible to make iodomethane, CH_3I , by this reaction. [1]

- (d) Halogenoalkanes can undergo *homolytic fission* in the upper atmosphere.

- (i) Explain the term *homolytic fission*. [1]

- (ii) Suggest the most likely organic radical that would be formed by the homolytic fission of bromochloromethane, CH_2BrCl . Explain your answer. [1]

- (e) Methylene, $:\text{CH}_2$, is a neutral carbon electrophile containing **two unpaired** electrons.

Methylene has a few possible structures. In one of them, the centre carbon atom is sp^3 hybridised, with each unpaired electron occupying a hybrid orbital. The $\text{H}-\text{C}-\text{H}$ bond angle is 136° .

Explain why

- (i) methylene can act as an electrophile, [1]

- (ii) the $\text{H}-\text{C}-\text{H}$ bond angle is larger than a regular tetrahedral angle of 109.5° . [1]

- (f) Two moles of methylene combine to form one mole of ethene.

A **saturated** hydrocarbon **T**, C_4H_8 , can be formed by combining four moles of methylene.

Draw the structure of **T**. [1]

- (g) Methylene undergoes further homolytic fission to form a CH fragment with **three unpaired** electrons. In 1978, a symmetrical and saturated molecule, *tetrahedrane* (CH)₄, was made by a German chemist, by combining 4 CH fragments.

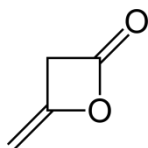
Draw the structure of *tetrahedrane*. [1]

- (h) Ketenes are very reactive organic compounds. A ketene **J** can be prepared by reacting methylene with carbon monoxide. **J** can also be prepared from ethanoyl chloride by an elimination reaction in which HCl is lost.

(i) Use the information to deduce the structure of **J**, and hence, draw its displayed formula. [1]

(ii) Identify the type of hybridisation of **each** carbon atom in **J**. [2]

- (i) Diketene **K** is formed by dimerisation of ketene **J**.



diketene **K**

Ethyl acetoacetate is used in perfume to achieve a sweet smell similar to that of green apples.

1 mole of diketene **K** reacts with 1 mole of ethanol to form 1 mole of ethyl acetoacetate as the only product.

Heating 1 mole of ethyl acetoacetate with alkaline aqueous iodine produces 1 mole of propanedioate ions and 2 moles of yellow precipitate.

(i) Determine the molecular formula of ethyl acetoacetate. [1]

(ii) Explain why one mole of ethyl acetoacetate forms two moles of yellow precipitate after heating with alkaline iodine solution, and hence suggest the structure of ethyl acetoacetate. [2]

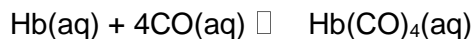
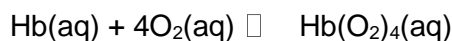
(iii) Ethylamine reacts with diketene **K** in the same way as ethanol.

Deduce the structure of the product formed when diketene **K** reacts with ethylamine. [1]

[Total: 20]

- 5 An oxocarbon is a chemical compound consisting of only carbon and oxygen, with the most common being carbon monoxide (CO) and carbon dioxide (CO₂).

- (a) Carbon monoxide is one of the most widespread and dangerous industrial hazards. The formation of carboxyhaemoglobin, Hb(CO)₄, takes place much more readily than the formation of oxyhaemoglobin, Hb(O₂)₄.



- (i) Draw a dot-and-cross diagram for CO. [1]
- (ii) With reference to haemoglobin, describe and explain what is meant by the *quaternary structure* of proteins. You should state the type of bonding or interaction involved. [2]
- (iii) A treatment method for carbon monoxide poisoning is to provide the patient with pure oxygen gas over a period of time.

With reference to the equations given above, explain why this is a suitable treatment method. [2]

- (b) The water-gas shift reaction is used to produce hydrogen gas industrially by reacting carbon monoxide with water vapour.



- (i) Write an expression for the equilibrium constant, K_p . [1]

An evacuated tank was initially filled with 0.0197 atm of CO and 0.0394 atm of H₂O at 600 K. It was sealed and left to stand. At equilibrium, the partial pressure of CO₂ was found to be 0.0191 atm.

- (ii) Calculate the value of K_p at 600 K. [2]

The table below shows how the value of K_p varies with temperature.

T / K	300	900	1500
value of K_p	1.170×10^5	1.978	0.2195

- (iii) Suggest whether the forward reaction of the water-gas shift reaction is an exothermic or an endothermic reaction. Explain your answer. [1]

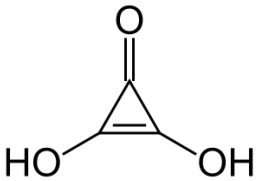
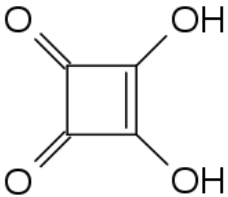
The Gibbs free energy, ΔG^\ominus (in J mol^{-1}), and the equilibrium constant, K_p , of a reaction are related by the following equation:

$$\Delta G^\ominus = -RT \ln K_p,$$

where R is the molar gas constant and T is the temperature in kelvins.

- (iv) Using the given values of K_p , calculate the values of ΔG^\ominus at 300 K and 900 K. Hence, determine the value of ΔS^\ominus for the water-gas shift reaction. (Assume that both ΔH^\ominus and ΔS^\ominus are independent of temperature.) [3]
- (v) Comment on the magnitude of the calculated value of ΔS^\ominus . [1]

(c) Two organic acids which dissociate to form oxocarbon anions are shown below.

Name	Deltic acid	Squaric acid
Structure		
pK_{a1}	2.6	1.5
pK_{a2}	6.0	3.4

- (i) Sketch a clearly labelled titration curve to show how pH changes when a 10 cm^3 solution of $0.100 \text{ mol dm}^{-3}$ deltic acid is titrated against 30 cm^3 of $0.100 \text{ mol dm}^{-3}$ aqueous sodium hydroxide. [3]
- (ii) Suggest a reason why squaric acid has a lower pK_{a1} value than deltic acid. [1]
- (d) An aromatic compound **X**, $\text{C}_{12}\text{H}_6\text{O}_{12}$, produces carbon dioxide when reacted with aqueous sodium carbonate.
- Heating **X** with concentrated sulfuric acid for several hours produces a neutral oxocarbon **Y**, C_{12}O_9 .
- When **Y** is heated strongly with ammonia, a compound **Z**, $\text{C}_{12}\text{H}_3\text{O}_6\text{N}_3$, is formed.
- When **Z** is heated strongly with dilute sulfuric acid, compound **X** is formed.
- Suggest structures for compounds **X**, **Y** and **Z**. [3]

[Total: 20]

– END OF PAPER –