ANDERSON JUNIOR COLLEGE

2016 JC2 PRELIMINARY EXAMINATIONS

NAME:_____ **PDG:**____ /15 **Register No:** ____

CHEMISTRY **9647/02**

Higher 2 **16 September 2016**

Paper 2 Structured Questions **2 hours**

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, PDG and register number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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.

For Examiner's Use				
Paper 2	1		Total	/ 72
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	3			
	4			
	5			
	6			

This document consists of **20** printed pages.

1 Planning (P)

Group II nitrates decompose on heating to form metal oxide, nitrogen(IV) oxide and oxygen.

Group II nitrates and their oxides are solids that can be easily weighed to determine the amount present. Nitrogen(IV) oxide is an acidic gas and can be absorbed by a known amount of excess strong alkali such as sodium hydroxide.

$$2NaOH + 2NO_2 \longrightarrow NaNO_2 + NaNO_3 + H_2O$$

The amount of strong alkali remaining can then be determined by titrating against a standard solution of strong acid.

The oxygen produced from the decomposition can be trapped by a simple gas collection set–up to measure the volume collected.

You are to plan an experiment to confirm that the molar quantities of magnesium oxide, nitrogen(IV) oxide and oxygen produced agree with the equation for the thermal decomposition of magnesium nitrate.

(a) Write an equation for the thermal decomposition of magnesium nitrate. You should include state symbols in your equation.

…….. [1]

(b) Suggest the capacity of the apparatus to be used to collect the oxygen gas.

Hence calculate the mass of magnesium nitrate to be heated to produce a stated volume of oxygen gas appropriate for the apparatus.

You should assume that one mole of any gas occupies 24.0 dm^3 under room conditions.

capacity of apparatus: ……

mass of magnesium nitrate to be heated: …… [2]

(c) Use your answer to **(b)** to calculate the minimum volume of 1.00 mol dm^{-3} aqueous sodium hydroxide needed to absorb the nitrogen(IV) oxide produced from the thermal decomposition of magnesium nitrate.

volume of sodium hydroxide needed: …….... [1]

(d) You may assume that you are provided with:

- solid magnesium nitrate
- 1.00 mol dm^{-3} sodium hydroxide
- 0.20 mol dm^{-3} hydrochloric acid
- the apparatus and chemicals normally found in a school or college laboratory

Your plan should include:

- a diagram of the assembled apparatus capable of absorbing the nitrogen(IV) oxide and collecting the oxygen separately and in sequence;
- an outline of how the results would be obtained, including the essential details of the titration procedure;
- measures to ensure reliability of results;
- brief, but specific, details of how the results will be used to
  - determine the amounts in moles of reactant and all products at the end of complete thermal decomposition
  - confirm that the decomposition had occurred according to the molar ratios in the equation.

[8]

[Total: 12]

2 (a) Ethoxyethane, $CH_3CH_2OCH_2CH_3$, may be regarded as a water molecule in which each of the hydrogen atoms has been replaced by an ethyl group.

At room temperature, boron trifluoride is a gas and ethoxyethane is a liquid. When boron trifluoride is mixed in a 1 : 1 molar ratio with ethoxyethane, a liquid with a boiling point of 127 ^oC is formed.

(i) Suggest what type of bond is formed between boron trifluoride and ethoxyethane, explaining your answer.

……..

……..

…… [2]

(ii) Draw a diagram to illustrate the shape of and bonding in the product.

(You may represent the $–CH_2CH_3$ group with –R)

[1]

Often in the preparation of an organic compound the product is obtained as an aqueous solution. The chemist needs to separate the organic compound from water by using solvent extraction method. Organic compounds are more soluble in organic solvents than in water.

Ethoxyethane is a good solvent for many organic compounds. It is immiscible with water and has a low boiling point (35 ^oC). When an aqueous solution containing an organic compound is shaken with ethoxyethane in a separating funnel, the compound distributes itself between the two layers, in accordance with its partition coefficient between ethoxyethane and water, until equilibrium is reached.

The partition coefficient, $K_{partition}$, of an organic compound, **J**, between ethoxyethane and water is given by the following expression.

$$K_{partition} = \frac{\text{concentration of } \mathbf{J} \text{ in ethoxyethane (organic layer)}}{\text{concentration of } \mathbf{J} \text{ in water (aqueous layer)}}$$

where the concentration of **J** can be expressed in g cm^{-3}.

The partition coefficient is a constant at a constant temperature.

(b) When 20 cm^3 of ethoxyethane were shaken with 75 cm^3 of an aqueous solution containing 5.00 g of **J**, it was found that 2.14 g of **J** were extracted into the ethoxyethane.

(i) Calculate the partition coefficient, $K_{partition}$, of **J** between ethoxyethane and water.

[1]

(ii) In another experiment

- 10 cm^3 of ethoxyethane were shaken with 75 cm^3 of an aqueous solution containing 5.00 g of **J** and the layers were separated.
- The aqueous layer was shaken with a second 10 cm^3 portion of ethoxyethane and the layers were separated.
- The two organic layers were combined.

Use the value of $K_{partition}$ you calculated in **(b)(i)** to calculate the total mass of **J** extracted by this procedure.

[2]

(iii) Hence comment whether it is more efficient to use one 20 cm^3 portion of ethoxyethane or two successive portions of 10 cm^3 ethoxyethane for extraction.

……..... [1]

(c) Anhydrous calcium chloride was then added to the combined organic layers obtained in **(b)(ii)**.

Suggest the reason for the addition of anhydrous calcium chloride.

……..... [1]

[Total: 8]

3 Nitrogen and phosphorus are both Group V elements. Nitrogen exists in its elemental form as simple molecules, N_2, while phosphorus occurs in one of the many forms, including 'white' phosphorus and 'red' phosphorus. Some data about these two forms of phosphorus are shown in **Table 1.1**.

Table 1.1

	'white' phosphorus	'red' phosphorus
appearance at room temperature	creamy white solid	red solid
melting point / ^oC	44	590
solubility in methylbenzene	soluble	insoluble

(a) Suggest the type of structure and bonding in 'red' phosphorus. Explain your reasoning.

……

……

……

…… [2]

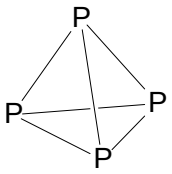
(b) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.

Suggest the type of hybridisation in N_2 and draw the arrangement of the hybrid orbital(s) around each nitrogen atom.

type of hybridisation ……

[2]

(c) The corresponding form of phosphorus, P_2, is not stable under standard conditions. Instead, 'white' phosphorus consists of molecules with a tetrahedral structure as shown.



'white' phosphorus

(i) Unlike N_2, P_2 is not stable under standard conditions. Suggest a reason for this.

……..

…….. [1]

(ii) Using the data in **Table 1.2**, construct an appropriate energy cycle and use it to determine the enthalpy change for the conversion of 'white' phosphorus to the gaseous diatomic molecule, P_2.

$$P_4(s) \longrightarrow 2P_2(g)$$

Table 1.2

P–P bond energy	200 kJ mol^{-1}
P≡P bond energy	485 kJ mol^{-1}
enthalpy change of vaporisation of $P_4(s)$	+12 kJ mol^{-1}

[3]

(iii) The formation of $P_2(g)$ from 'white' phosphorus is not spontaneous under standard conditions.

Suggest how the conditions would need to be changed to make it spontaneous. Explain your reasoning.

……..

……..

……..

…….. [2]

(d) Although nitrogen gas makes up about 79% of the atmosphere, it does not easily form compounds.

(i) Explain why the conditions in a car engine lead to the production of oxides of nitrogen.

……..

…….. [1]

(ii) Give an equation for a reaction involved in the removal of nitrogen monoxide, NO, from a car's exhaust gases, in the catalytic converter.

…….. [1]

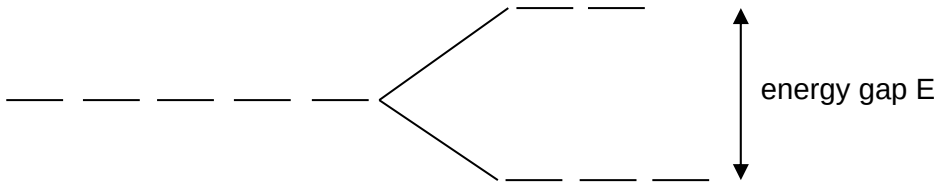
[Total: 12]

4 (a) (i) What is meant by the term *ligand* in the context of transition element chemistry?

……..

……... [1]

(ii) Although the five d–orbitals are at the same energy in an isolated atom, when a transition element ion is in an octahedral complex the orbitals are split into two groups, as shown in the following diagram.



d–orbitals of an isolated transition element ion

d–orbitals of the transition element ion in an octahedral complex

Use this diagram as an aid in explaining the following.

- Transition element complexes are often coloured.

……..

……..

……..

……..

……..

……..

- The colour of a complex of a given transition element often changes when the ligands around it are changed.

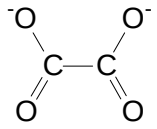
……..

……..

…… [5]

(b) Heating a solution containing potassium ethanedioate, iron(II) ethanedioate and hydrogen peroxide produces the light green complex $K_3Fe(C_2O_4)_3$, which contains the ion $[Fe(C_2O_4)_3]^{3-}$.

The structure of the ethanedioate ion is as follows.



(i) Determine the oxidation number of carbon in this ion.

…….... [1]

(ii) Determine the oxidation number of iron in $[Fe(C_2O_4)_3]^{3-}$.

…….... [1]

(iii) The iron atom in the $[Fe(C_2O_4)_3]^{3-}$ ion is surrounded octahedrally by six oxygen atoms. Draw a three–dimensional diagram to show the shape of this ion.

[2]

(c) Kidney stones are usually made up of an inorganic salt of calcium with ethanedioate. Thus, people who are prone to kidney stones have to limit or avoid eating foods with high ethanedioate content such as spinach, peanuts and sweet potatoes.

(i) Write the expression for the solubility product of calcium ethanedioate.

…….... [1]

(ii) The value of K_{sp} for calcium ethanedioate is 2.3×10^{-9}. Calculate $[C_2O_4^{2-}]$ in a saturated solution of calcium ethanedioate.

[1]

(iii) A solution **W** is saturated with both calcium ethanedioate and calcium chloride.

The concentration of ethanedioate ions in solution **W** is less than that calculated in **(c)(ii)**. Explain why this is so.

……

…… [1]

(d) By quoting relevant data from the *Data Booklet*, explain the following observations:

compound	pH of a 1.0 mol dm^{-3} solution in water
NaC*l*	7.0
$MgCl_2$	6.5
$AlCl_3$	3.0

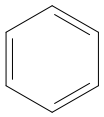
……

……

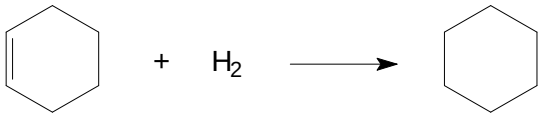
…… [2]

[Total: 15]

5 **(a)** Kekulé proposed the following structure for benzene.



The enthalpy change of hydrogenation of cyclohexene, as shown, is –121 kJ mol^{-1}.



Based on this value for cyclohexene it is possible to calculate the enthalpy change of hydrogenation of benzene, based on Kekulé's structure, to be –363 kJ mol^{-1}.

Explain the difference between this calculated value and the actual value for the enthalpy change of hydrogenation of benzene of –209 kJ mol^{-1}.

……..……..

……..... [1]

(b) Benzene undergoes electrophilic substitution reactions.

Nitrobenzene, $C_6H_5NO_2$, can be formed from benzene. Give the reagents and conditions necessary for this process and identify the electrophile.

reagents ……..

conditions ……..

electrophile ……..…… [2]

(c) **Fig. 5.1** shows a reaction scheme starting from nitrobenzene.

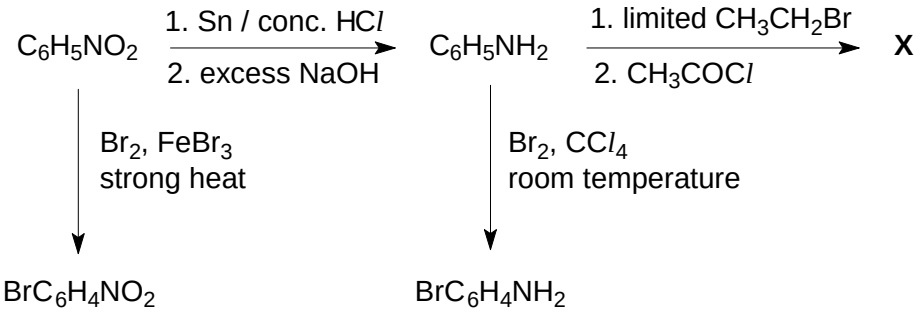


Fig. 5.1

(i) Explain why the bromination of phenylamine, $C_6H_5NH_2$, is possible with the milder conditions shown in **Fig. 5.1**.

……...

……...

……...

……..…….. [2]

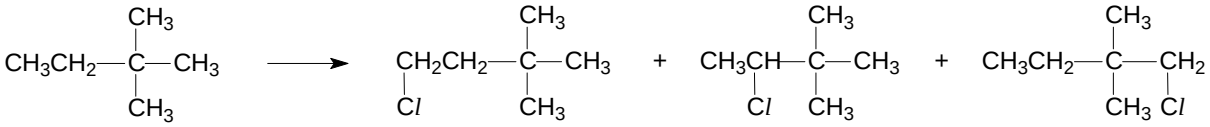
(ii) Write an equation for the reaction between nitrobenzene and the reducing mixture, Sn / conc. HC*l*. Use [H] to represent the formula of the reducing agent in your equation.

…… [1]

(iii) Draw the structural formula of **X**.

[1]

(d) When heated with chlorine, the hydrocarbon 2,2–dimethylbutane produces compounds **L**, **M** and **N**.



2,2-dimethylbutane **L** **M** **N**

It is observed that the rate of substitution of a hydrogen atom in 2,2–dimethylbutane by a chlorine atom is dependent on the type of hydrogen substituted – *primary*, *secondary* or *tertiary*.

The table below shows the relative rate of substitution by chlorine.

Reaction	Type of hydrogen substituted	Relative rate
$RCH_3 \longrightarrow RCH_2Cl$	*primary*	1
$R_2CH_2 \longrightarrow R_2CHCl$	*secondary*	7
$R_3CH \longrightarrow R_3CCl$	*tertiary*	21

Using the information from the table and by considering the number of hydrogen atoms of each type (*primary*, *secondary* or *tertiary*) within 2,2–dimethylbutane, predict the ratio of the three products **L**, **M** and **N**.

Explain how you arrived at your answer.

ratio of **L** to **M** to **N**: ……..

explanation:

…….....

…….. [2]

[Total: 9]

6 **(a)** The interhalogen compound IC*l* reacts with alkenes in an addition reaction. IC*l* reacts faster with alkenes than the pure halogens.

(i) Describe the mechanism of the reaction between IC*l* and propene.

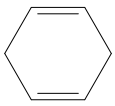
[3]

(ii) Suggest why IC*l* reacts with alkenes faster than the pure halogens, Cl_2, Br_2 and I_2.

……

…… [1]

Cyclohexa–1,4–diene behaves as a typical alkene.



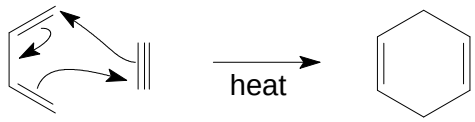
cyclohexa–1,4–diene

(b) State the total numbers of σ bonds and π bonds in a molecule of cyclohexa–1,4–diene.

number of σ bonds ……

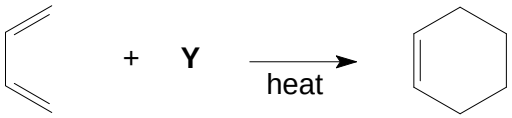
number of π bonds …… [1]

(c) Cyclohexa–1,4–diene can be made by heating buta–1,3–diene with ethyne in the Diels–Alder reaction. The diagram below shows the movement of electron pairs, represented by curly arrows, needed to generate the cyclohexa–1,4–diene in a single step.



buta–1,3–diene ethyne cyclohexa–1,4–diene

(i) In a similar type of reaction, cyclohexene can be formed from buta–1,3–diene and another alkene, **Y**.



buta–1,3–diene cyclohexene

Suggest the **name** of the alkene, **Y**, that would react with buta–1,3–diene to form cyclohexene in this type of reaction.

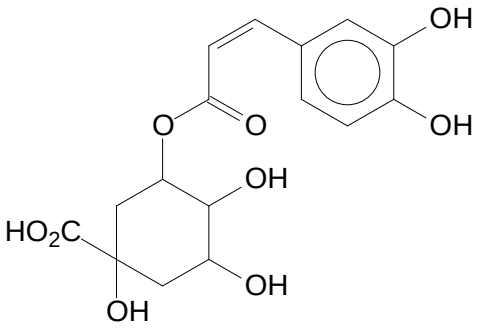
…….. [1]

(ii) In another similar reaction, penta–1,3–diene reacts with propene to form two products that are structural isomers.

Deduce the structures of these two isomers.

[2]

(d) Chlorogenic acid occurs naturally in coffee and an edible species of bamboo.

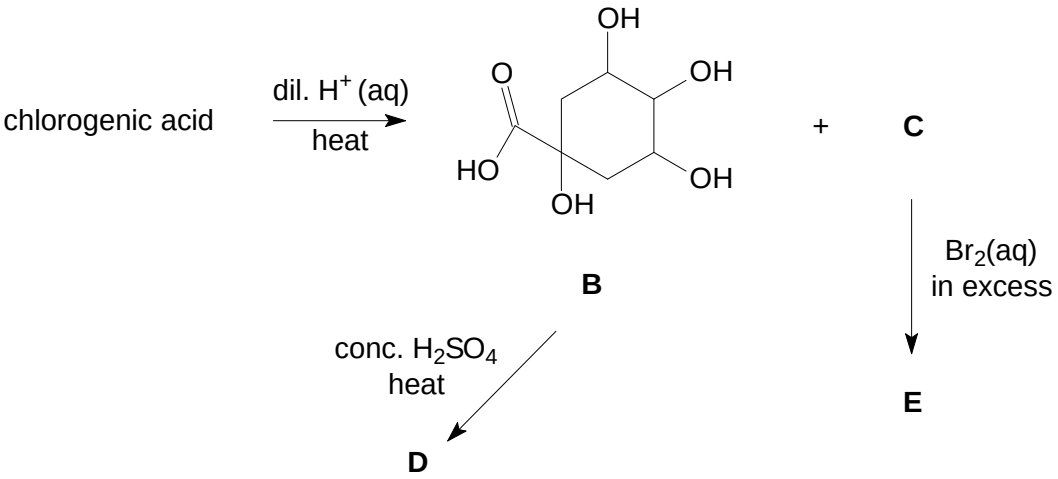


chlorogenic acid

(i) Draw the structural formula of the compound formed when chlorogenic acid is treated with an excess of sodium metal.

[1]

On heating with dilute acid, chlorogenic acid produces two compounds, **B** and **C**.



(ii) State the *type of reaction* undergone by chlorogenic acid when **B** and **C** are formed. Draw the displayed formula of compound **C**.

type of reaction ……

compound **C**

[2]

When compound **B** is heated with concentrated H_2SO_4, compound **D**, $C_7H_6O_3$, is formed.

CO_2 is evolved when compound **D** is treated with Na_2CO_3(aq). Compound **D** decolourises Br_2(aq) giving a white precipitate, but does not react with cold, alkaline $KMnO_4$.

When compound **C** is treated with an excess of Br_2(aq), compound **E** is produced.

(iii) Identify the functional group that would have been shown to be present in **D** if the test with cold, alkaline $KMnO_4$ had been positive.

…… [1]

(iv) Name the functional groups in compound **D** that react with the following.

Na_2CO_3(aq) …….. Br_2(aq) …….. [2]

(v) Suggest structures for compounds **D** and **E**.

D	**E**

[2]

[Total: 16]