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

CANDIDATE NAME			
CLASS		INDEX NUMBER	

CHEMISTRY 9746/03

Paper 3 Free Response **17 September 2009**

2 hours

Candidates answer on separate paper.

Additional Materials: Writing Papers
Data booklet

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 **4 out of 5** questions.

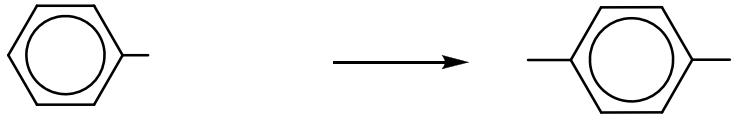
You are advised to show all working in calculations.
You are reminded of the need for good English and clear presentation in your answers.
You are reminded of the need for good handwriting.
Your final answers should be in 3 significant figures.

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 **11** printed pages and **1** blank page.

Answer 4 out of 5 questions

1 **(a)** Compound **A** reacts with bromine to form compound **B** as follows.



Describe the mechanism for this reaction, including curly arrows showing the movement of electrons, and all charges. [3]

(b) The following table gives the boiling points and relative molecular masses for four organic compounds.

Compound	Formula	Mr	b.p. / °C
C	$NH_2CH_2CH_2COOH$	89	235
D	$HOCH_2CH_2COOH$	90	75
E	$CH_3CH_2CH_2CH_2CH_3$	72	36
F	$(CH_3)_4C$	72	10

By comparing **C** with **D** and **E** with **F**, suggest explanations for the similarities or differences in the boiling points within each of these two pairs. [4]

(c) **(i)** When barium peroxide, BaO_2 is added to water, barium hydroxide and compound **G** are formed. When the solution is acidified, and added to potassium manganate solution, a colourless solution is formed. Identify compound **G**.

Write down the equation of barium peroxide with water and explain the observation.

(ii) Explain whether barium nitrate or calcium nitrate will be more thermally stable under strong heat.

[4]

(d) The standard reduction potential for the following reaction is +0.20 V.

$$2HCO_2^- (aq) + 2CO_2 (g) + 6H^+ (aq) + 6e \rightarrow C_4H_4O_6^{2-} (aq) + 2H_2O (l)$$

Using relevant information in the *Data Booklet*, calculate the E^{θ}_{cell} for the reaction when hydrogen peroxide solution is added to an acid solution containing CO_2, HCO_2^- and $C_4H_4O_6^{2-}$ ions.

Hence, predict whether the reaction is feasible and construct balanced equations for any reactions that occur. [2]

(e) When zinc metal is added to green solution of aqueous V^{3+} under acidic medium, the solution turns violet. The excess zinc is filtered off and the violet solution is allowed to stand for several hours. The solution slowly turns green.

Using relevant information in the *Data Booklet*, explain the above reactions and construct balanced equations for any reactions that occur. [3]

(f) An alkane **H** with the formula C_6H_{14} reacts with chlorine to yield three compounds with the formula $C_6H_{13}Cl$: **J**, **K** and **L**. Of these **only K** and **L** can react with ethanolic potassium hydroxide. Moreover, **K** and **L** yield the **same product**.

Deduce the structure of **H**, **J**, **K** and **L.** [4]

[Total:20]

2 **(a)** The table shows data, at 298K, for the following reaction.

$$H_2(g) + I_2\ (s) \rightleftharpoons 2HI\ (g)$$

	ΔS / J mol^{-1} K^{-1}
$H_2(g)$	130.6
I_2 (s)	116.8
HI (g)	206.5

(i) Calculate the entropy change of the reaction.

(ii) Given that enthalpy change of formation of HI is +26.5 kJ mol^{-1}, calculate ΔG of the reaction. [3]

(b) The enthalpy change of evaporation of I_2 at its boiling point of 183^{o}C is + 41.8 kJ mol^{-1}.

(i) Calculate the entropy change of evaporation of iodine.

(ii) Explain the significance of the sign of entropy change found in part **(i)**. [2]

(c) When boron trichloride (BCl_3) and iodine monochloride (ICl) react, a single product is formed. This product, compound **M**, contains an anion and one cation. The cation acts as an electrophile in the formation of iodobenzene from benzene.

(i) Suggest a formula for compound **M**.

(ii) Predict the shape and bond angle of the anion in compound **M**.

(iii) Compound **N** undergoes the following reaction:

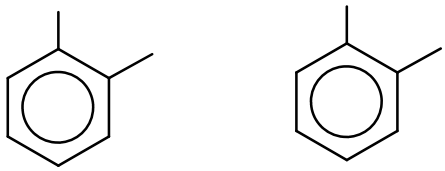
1. Suggest a structural formula of **N**.

2. Suggest reagents and conditions necessary for reaction **Q**.

3. Describe simple chemical test which could be used to distinguish compound **P** from 2,3-dichlorobutane. You should include the reagent, the reaction conditions, and the positive observation.

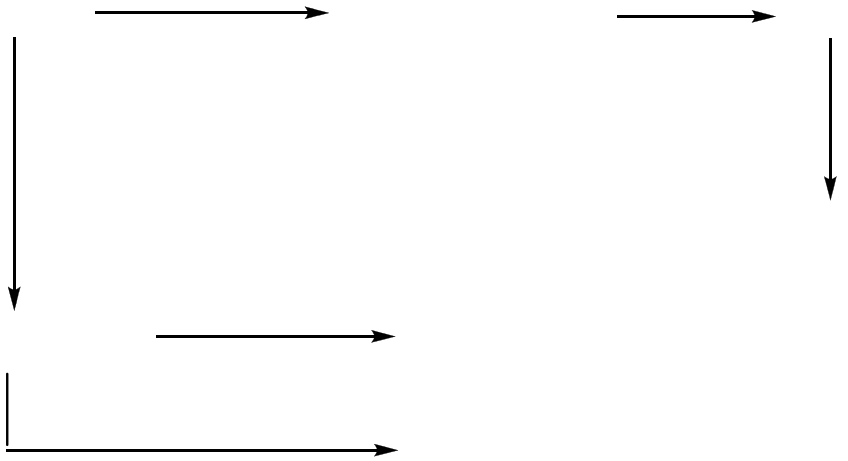
4. Suggest a structural formula of the product when phenol is shaken with ICl in trichloroethane.

(iv) Compare and explain the difference in the relative rates of hydrolysis of compound **R** and **S**. State the reagents and conditions for the relevant hydrolysis reactions.



[9]

(d) Consider the following reaction scheme undergone by sodium thiosulphate with halogens **T** and **U**.



(i) Suggest a suitable identity each for **T** and **U**.

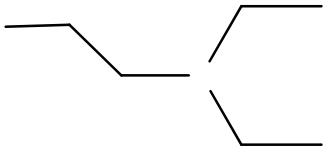
(ii) Write a balanced ionic equation for the reaction between $Na_2S_2O_3$ and **U**.

(iii) Use relevant data from the *Data Booklet* to explain the different reactions of halogen **T** and **U** with sodium thiosulphate.

(iv) Suggest a simple test which can be used to distinguish between **T** and **U**. You should state how each compound behaves in the test. [6]

[Total:20]

3 **(a)** When an organic compound Procaine, **V**, $C_{13}H_{20}N_2O_2$, is boiled with aqueous sodium hydroxide, it gives two compounds, one of which has the following structure **W** shown below and another compound **X**.

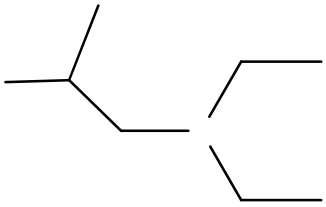


Compound **W**

When aqueous bromine is added to compound **X**, the orange brown solution decolourised, white precipitate, **Y**, $C_7H_4NO_2Br_2^-$, is formed and steamy fumes is liberated.

(i) Deduce the structures for **V**, **X** and **Y**. Give an account of the chemistry involved.

(ii) Describe one simple chemical test you could carry out to distinguish compound **W** from **Z**. State the reagents, conditions and observations expected.



Compound **Z**

[7]

(b) **(i)** Explain why transition metals form complexes readily.

(ii) When aqueous ammonia is gradually added to a solution containing copper (II) ions, a blue precipitate is formed.

To separate samples of the blue precipitate:

- The precipitate dissolves on addition of excess aqueous ammonia.
- The precipitate turns black upon heating.

Write equations, including state symbols, to explain the above observations.

[4]

(c) The following data indicates the effect of temperature and pressure on the equilibrium concentration of the product in a gaseous equilibrium.

Temperature/ K	% of product present in equilibrium mixture at		
	5 kPa	10 kPa	20 kPa
400	0.09	2.10	15.70
600	0.05	1.55	7.20
800	0.02	0.62	2.80

(i) Use the above information to explain whether the production of the product is due to increase or decrease in the total number of gaseous molecule.

(ii) Use the above information to explain whether the production of the product is an exothermic or endothermic process.

(iii) State the optimum conditions of temperature and pressure for the commercial production of this product.

[5]

(d) **(i)** A hydrogen oxygen fuel cell is a device that converts chemical energy of conventional fuel such as aqueous potassium hydroxide into electrical energy directly by oxidation with oxygen in the air.

Write the half equations for the reaction at the anode and cathode.

(ii) This fuel cell is able to supply 10 amperes a day. What volume of hydrogen at room temperature and pressure is consumed by the cell each day if 85% of the energy produced is converted to useable energy?

[4]

[Total:20]

4 **(a)** The purity of iodates (VII) can be estimated by adding an acidified solution of potassium iodide and titrating the iodine produced with aqueous sodium thiosulphate.
In one such analysis, a 0.100 g sample of impure sodium iodate (VII), Na_5IO_6, was dissolved in water and treated with an excess of acidified KI.

$$IO_6^{5-} + 7I^- + 12H^+ \rightarrow 4I_2 + 6H_2O$$

The iodine liberated required 22.0 cm^3 of 0.100 mol dm^{-3} sodium thiosulphate to reach its end point. Calculate the purity of the sodium iodate (VII). [3]

(b) In the questions below, each of the three elements **A**, **B** and **C** is one of the Period 3 elements.

(i) Both the chloride and the oxide of element **A** have high melting points. The oxide reacts readily with water. The chloride dissolves in water to form a neutral solution.

Identify element **A**.
Write an equation for the reaction between water and the oxide of element **A**.

(ii) Element **B** has a chloride and an oxide which react vigorously with water to form solutions containing strong acids.

Identify element **B**.
Identify an acid which is formed when both the oxide and the chloride of element **B** react separately with water.

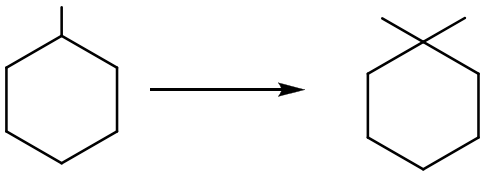
(iii) The oxide of element **C** is a crystalline solid with a very high melting point. This oxide is classified as an acidic oxide but it is not soluble in water.

Identify element **C**.
Write an equation for a reaction which illustrates the acidic nature of the oxide of element **C**.

[5]

(c) *α*-Hydroxy acids (AHAs) can be extracted from fruits of all sorts and were used by ancient Egyptians to improve their skin conditions. Today, they have become one of the main ingredients in anti-aging creams.

One type of AHA, compound **E** can be synthesised from compound **D** in 3 steps.



(i) Give the reagents, conditions and intermediates for this three-step synthesis.

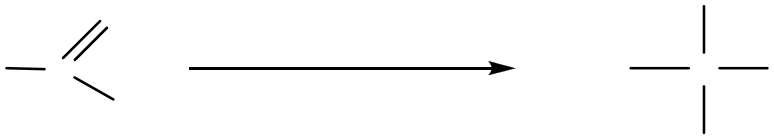
(ii) Draw the structure for the product formed when compound **E** is heated with HC*l* and anhydrous ZnCl_2.

[4]

(d) In 1901, the French chemist Victor Grignard observed that fine turnings of magnesium metal reacted with a warmed solution of bromoalkane in dry ether to form a grignard reagent, RMgBr.

The *nucleophile* R^-, from the grignard reagent react with molecules containing a C=O group to form ions with new C–C bonds. Reactions of these new ions with dilute acid give products which contain an OH group.

Alcohols can be formed from carbonyl compounds by reaction with grignard reagent, RMgBr followed by acidification.



An example of grignard reagent, ethylmagnesium bromide, CH_3CH_2MgBr can act as a source of *nucleophile*, $CH_3CH_2^-$.

(i) Explain the term *nucleophile*.

(ii) $CH_3CH_2^-$ reacts with ethanal followed by acidification. Propose a possible mechanism for this reaction.

(iii) Draw the structure of the organic product of the reaction of carbon dioxide with ethylmagnesium bromide, CH_3CH_2MgBr followed by acidification.

(iv) Suggest why ethylmagnesium bromide reacts with water and give the molecular formula of the organic product formed.

(v) Draw the organic product formed when ethanal reacts with alkaline Cu^{2+} complex.

[8]

[Total:20]

R' C

5 **(a)** A sample of nitrogen dioxide is prepared via the oxidation of nitrogen monoxide by oxygen in a reacting vessel.

$$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$$

The reaction is proposed to proceed via the following mechanism.

$$\text{Step 1: } NO\ (g) + O_2\ (g) \rightleftharpoons NO_3\ (g) \quad \text{(fast)}$$
$$\text{Step 2: } NO_3\ (g) + NO\ (g) \longrightarrow 2NO_2\ (g) \quad \text{(slow)}$$

(i) Deduce the rate equation.

(ii) Predict the effect on the rate when the volume of the reacting vessel is halved.

[2]

(b) The reaction between **F** and **G** is monitored by finding the time taken for **F**, a coloured reactant, to decolurise.

$$\mathbf{F} + \mathbf{G} \longrightarrow \mathbf{H}$$

The following results are obtained:

Experiment	Volume of **F** added / cm^3	Volume of **G** added / cm^3	Volume of H_2O added / cm^3	Relative rate or reaction
1	10	20	30	1
2	15	40	5	6
3	20	20	20	2
4	60	40	20	***X***

(i) Determine the order of reaction with respect to **F** and **G**.

(ii) Deduce the value of ***X.***

[3]

(c) **(i)** Iron(III) oxide, Fe_2O_3, also known as ferric oxide or simply rust is one of the several oxide compounds of iron, and has paramagnetic properties. Carbon monoxide can reduce iron (III) oxide to molten iron, becoming carbon dioxide in the process.

$$3CO\ (g) + Fe_2O_3\ (s) \rightarrow 2\ Fe\ (s) + 3\ CO_2\ (g)$$

Given the following data, find the enthalpy change of formation of carbon monoxide.

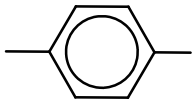
Hence or otherwise, by means of an energy cycle, calculate the standard enthalpy change of the above reaction.

Standard enthalpy change of formation of Fe_2O_3 (s) = – 824.2 kJ mol^{-1}
Standard enthalpy change of combustion of C (s) = – 393.5 kJ mol^{-1}
Standard enthalpy change of combustion of CO (g) = – 283.0 kJ mol^{-1}

(ii) Predict and explain how the magnitude of the lattice energy of Al_2O_3 might compare to that of Fe_2O_3.

[5]

(d) **(i)** Bromoanisole, also known as 1-bromo-4-methoxybenzene, is a clear liquid with a pleasant smell similar to that of anise seed.



Suggest a synthesis of bromoanisole from phenol.

(ii) Compound **J**, $C_9H_{10}Cl_2$ reacts with aqueous sodium hydroxide to form a compound which immediately loses a water molecule to give compound **K**, $C_9H_{10}O$.

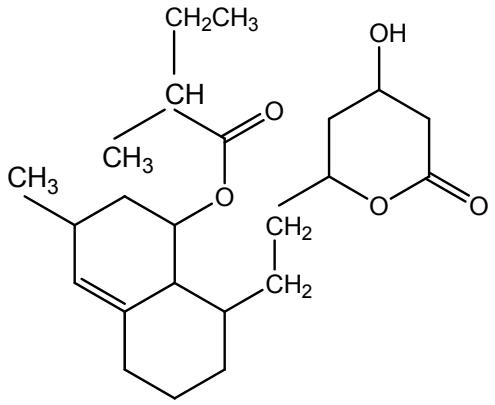
K gives an orange precipitate with 2,4–DNPH and a yellow precipitate with aqueous alkaline iodine. When treated with hot acidified $KMnO_4$, both **J** and **K** give a white precipitate, $C_7H_6O_2$.

Deduce the structures of **J** and **K**, explaining the chemical reactions involved.

[5]

(e) Lovastatin is a member of the drug class of statins, used for lowering cholesterol in those with hypercholesterolemia and so preventing cardiovascular disease.

A derivative of lovastatin is shown below.



Upon hydrolysis, all the hydrolysed products of the derivative of lovastatin react with aqueous sodium carbonate readily to give effervescence.

(i) Suggest suitable reagents and conditions to perform this hydrolysis.

(ii) Give the structural formulae of all the hydrolysed products.

(iii) One of the hydrolysed products of the derivative of lovastatin in part **(ii)** can subsequently react with acidified potassium manganate (VII) solution to give compound **L**.

Draw the structural formula of compound **L**.

[5]

[Total:20]

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