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

CANDIDATE NAME

CLASS | INDEX NUMBER

CHEMISTRY 9647/02

Paper 2 Structured Questions **18 August 2016**

2 hours

Candidates answer on the Question Paper

Additional Materials: *Data Booklet*

READ THESE INSTRUCTIONS FIRST

Write your index number, name and civics group.
Write in dark blue or black pen.
You may use pencil for any diagrams, graphs or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the space provided.
A Data Booklet is provided.

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.

You may use a calculator.

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

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

For Examiner's Use	
Section A	
1	**/ 12**
2	**/ 17**
3	**/ 10**
4	**/ 18**
5	**/ 15**
Significant figures	
Handwriting	
Total	**/ 72**

This document consists of **17** printed pages and **1** blank page.

Answer ALL questions on the spaces provided.

1 Planning

Using the information below, you are to write a plan for determining number of molecules of water of crystalisation, n, in barium chloride crystals, $BaCl_2.nH_2O$ where n = 1,2 or 3. The basis of this investigation is a technique known as *precipitation titration* with the use of silver nitrate solution, $AgNO_3(aq)$.

$AgCl$, Ag_2CrO_4 and $BaCrO_4$ are sparing soluble salts and relevant information about these salts are given in the table below.

compound	colour	numerical value of K_{sp} at 25 ^{O}C
$AgCl$	white	2.0×10^{-10}
Ag_2CrO_4	red	2.0×10^{-12}
$BaCrO_4$	yellow	1.0×10^{-10}

Some barium chloride crystals, $BaCl_2.nH_2O$, is dissolved to make up 250.0 cm^3 of standard solution. Approximately 10 cm^3 of 0.2 mol dm^{-3} of reagent ***X*** solution is added to a portion of this standard solution to precipitate the barium ions *before* a few drops of K_2CrO_4 indicator solution is added. A titration is then carried out on this portion of solution against silver nitrate solution, $AgNO_3(aq)$. Ag_2CrO_4 would just precipitate only when almost all of the Cl^- ions have been precipitated as $AgCl$. The titration is repeated until a more reliable average value, ***V*** cm^3, can be determined.

(a) (i) Identify reagent ***X***.

……..…… [1]

(ii) A student suggested that $BaCrO_4$ is more soluble than Ag_2CrO_4 as $BaCrO_4$ has larger numerical value of K_{sp} than Ag_2CrO_4.

Suggest whether this student's claim is valid.

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(iii) Suggest why reagent ***X*** is added *before* a few drops of K_2CrO_4 indicator solution is added.

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(b) You may assume that you are provided with

- 0.10 mol dm^{-3} silver nitrate
- 0.2 mol dm^{-3} of reagent ***X*** solution
- 10 g of barium chloride crystals, $BaCl_2.nH_2O$
- Potassium chromate solution, $K_2CrO_4(aq)$
- The equipment and materials normally found in a school or college laboratory.

Your plan should include the following

- brief, but specific details of the apparatus you would use, bearing in mind the levels of precision they offer
- details, including quantities, for preparation of 250.0 cm^3 of $BaCl_2$ solution from barium chloride crystals, $BaCl_2.nH_2O$
- essential details of the titration procedure
- an outline of how the results obtained, including ***V*** cm^3, would be used to determine n, in barium chloride crystals ($BaCl_2.nH_2O$)

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(c) Explain why this titration cannot be conducted under acidic *or* alkaline medium.

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[Total: 12]

2 This question is about the oxides of nitrogen and its reactions. Oxides of nitrogen constitute air pollutants originating from emission of car exhaust that cause acid rain and photochemical smog.

The two gases of NO and N_2O_4 slowly react to form the blue compound, N_2O_3 according to the following equation.

$$2NO(g) + N_2O_4(g) \rightleftharpoons 2N_2O_3(g)$$

(a) **(i)** Draw the dot and cross diagrams of the two molecules, NO and N_2O_3.
The N_2O_3 molecule contains a N−N bond.

[2]

(ii) From your answer in **(a)(i)**, suggest why the forward reaction is likely to occur.

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…… [1]

(b) In an experiment, a mixture containing NO and N_2O_4 was introduced into a 1.48 dm^3 evacuated vessel was allowed to reach equilibrium at 280 K. The equilibrium pressure is 98.9 kPa.

Calculate the total number of moles of gases at equilibrium, assuming the gases behave ideally.

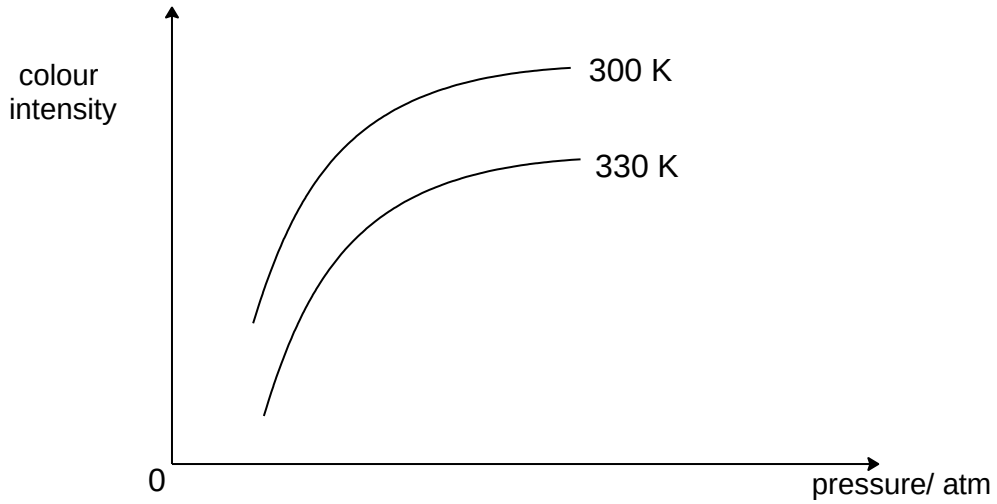
[2]

(c) Two colourless gases NO and N_2O_4 slowly react to form the blue compound, N_2O_3 according to the following equation.

$$2NO(g) + N_2O_4(g) \rightleftharpoons 2N_2O_3(g)$$

Equimolar mixtures of NO and N_2O_4 are mixed at varying pressure P but at two different temperatures of 300 K and 330 K, and the variation in colour intensity was monitored over a period of time.

The graphs below show the variation of the colour intensity with pressure at temperatures of 300 K and 330 K.



(i) What is the significance of the colour intensity in this reaction?

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……..…….. [1]

(ii) Explain why colour intensity of the reaction mixture increases with increasing pressure.

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(iii) Using information from the graphs, state and explain whether the formation of N_2O_3 from NO and N_2O_4 is an exothermic reaction.

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(d) Nitrogen monoxide reacts with chlorine to form nitrosyl chloride, according to the equation:

$$2NO(g) + Cl_2(g) \longrightarrow 2NOCl(g).$$

In an experiment, the amount of $Cl_2(g)$ was kept in *large excess* while the initial partial pressure of NO(g) was varied at constant temperature of 500K.
The table below shows the experimental results obtained.

time / s	P_{NO} / atm	(Rate / P_{NO}) / s^{-1}	(Rate / $(P_{NO})^2$) / (atm^{-1} s^{-1})
0	0.917	1.033×10^{-4}	1.126×10^{-4}
1000	0.827	9.312×10^{-5}	1.126×10^{-4}
2000	0.753	8.486×10^{-5}	1.127×10^{-4}
3000	0.691	7.788×10^{-5}	1.127×10^{-4}
4000	0.638	7.190×10^{-5}	1.127×10^{-4}

(i) Suggest why the amount of $Cl_2(g)$ was kept in *large excess.*

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(ii) Using the data from the table above, deduce the order of reaction with respect to NO(g).

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(iii) In another experiment, the initial partial pressure of NO(g) was 4.2 atm and it was reacted with $Cl_2(g)$ at a constant temperature of 500 K. The partial pressure of $Cl_2(g)$ was recorded at time intervals of 30 s. The data obtained are tabulated below.

time / s	partial pressure of $Cl_2(g)$ / atm
0	0.78
30	0.76
60	0.72
90	0.70
120	0.66
150	0.63
180	0.59
210	0.57
240	0.54
270	0.52

time / s	partial pressure of $Cl_2(g)$ / atm
300	0.49
330	0.46
360	0.44
390	0.42
420	0.39
450	0.38
480	0.36
510	0.34
540	0.33
570	0.32

Using the data but without the plotting of any graph, deduce the order of reaction with respect to $Cl_2(g)$.

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(iv) Write the rate equation for this reaction.
Hence, calculate the rate constant, including its units

[3]

(v) One possible mechanism of the reaction is given below.

Step I $NO(g) + Cl_2(g) \rightleftharpoons NOCl_2(g)$ fast

Step II $NOCl_2(g) + NO(g) \longrightarrow 2NOCl(g)$ slow

Explain whether it is consistent with the observed kinetics data in **(d)(iv)**.

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[Total: 17]

3 Organic compounds can undergo combustion. Chemical companies produce containers filled with butane for use by campers.

The enthalpy change of combustion of butane is – 3000 kJ mol^{-1}.

(a) **(i)** Define the term *standard enthalpy of combustion of butane*.

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……..…….. [1]

(ii) Calculate the mass of water at 25 ºC that could be brought to the boiling point by the combustion of 1.2 dm^3 of butane gas. Assume 75 % of the heat from the butane is absorbed by the water.

[2]

(b) Explain in terms of structure and bonding, why butanone has a higher boiling point than pentane.

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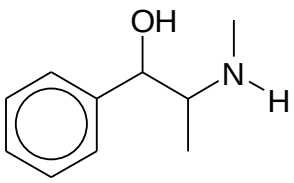
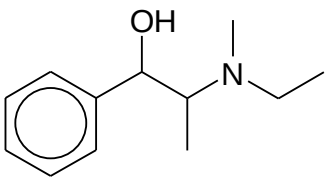
(c) Organic compounds are also widely used for pharmaceutical purposes such as ephedrine which is an anti-asthmatic and stimulant. Ephedrine can be converted into ethylephedrine via a S_N2 reaction.



Ephedrine



Ethylephedrine

(i) Suggest the reagent that can be used to perform this conversion.

……..…….[1]

(ii) Explain why an S_N2 mechanism is favoured for this reaction.

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……[1]

(d) Complete hydrolysis of proteins produces individual units of amino acids, but partial hydrolysis can break the protein down into dipeptide or tripeptide fragments.

Partial hydrolysis of a tetrapeptide (containing four amino acid residues) produces the following three dipeptides, as well as the individual amino acids.

$NH_2CH_2CONHCH(CH_3)CO_2H$

$NH_2CH_2CONHCH_2CO_2H$

$NH_2CH(CH_3)CONHCH(CH_3)CO_2H$

(i) Define the *primary structure* of a protein.

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……..…….. [1]

(ii) Deduce the order in which the amino acids are bonded together in the tetrapeptide.

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(iii) Suggest suitable reagents and conditions to hydrolyse the tetrapeptide into its individual amino acids.

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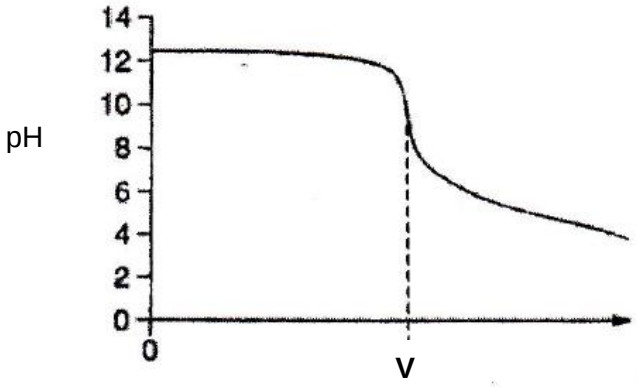
[Total: 10]

4 **(a)** A 0.031 mol dm^{-3} solution of a base, MOH, has a pH of 12.5. (M is a metal.)

25 cm^3 of the solution of MOH was titrated with 0.025 mol dm^{-3} propanoic acid, CH_3CH_2COOH, at 25 °C. The pH of the solution was followed using a pH meter and the following titration curve was obtained.

pK_a of propanoic acid = 1.29 x 10^{-5} mol dm^{-3}



(i) Calculate the concentration of hydroxide ions present in the sample of MOH and use it to explain whether it is a strong or weak base.

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(ii) Calculate the value of **V**.

[1]

(iii) Explain, with the aid of an equation, why the pH when **V** cm^3 of propanoic acid was added, is greater than 7.

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…… [2]

(b) The colour of blackberries is due to a compound known as cyanidin. Cyanidin is a weak organic acid which may be represented by CyH. In aqueous solution, CyH dissociates slightly:

$$\underset{\text{red}}{CyH\ (aq)} \rightleftharpoons \underset{\text{purple}}{Cy^-\ (aq)} + H^+\ (aq)$$

The colours of CyH and Cy^- are indicated in the above equation.
Acid dissociation constant, K_a, of CyH is 5.0×10^{-5} mol dm^{-3} at 25 °C.

A glass of blackberry juice has a pH of 3.00 at 25 °C. Calculate the ratio of the red to purple form in the juice, and hence predict its colour.

[3]

(c) When chlorine is bubbled through cold sodium hydroxide solution and acidified silver nitrate solution, only half of the chlorine that has dissolved is precipitated as silver chloride. When the sodium hydroxide is hot, up to five–sixth of the chlorine can be precipitated. Explain the observations, giving balanced equations where appropriate.

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……..…….. [3]

(d) The table below gives data about some physical properties of the elements calcium, nickel and copper.

	calcium	nickel	copper
atomic radius / nm	0.197	0.124	0.128
electronic configuration	$[Ar]4s^2$	$[Ar]3d^8 4s^2$	$[Ar]3d^{10}4s^1$

(i) What do you understand by the term *transition element*?

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……..…….. [1]

(ii) Although the nickel and copper atoms have more electrons than the calcium atom, the atomic radii of nickel and copper are smaller than that of calcium.

Suggest an explanation for this.

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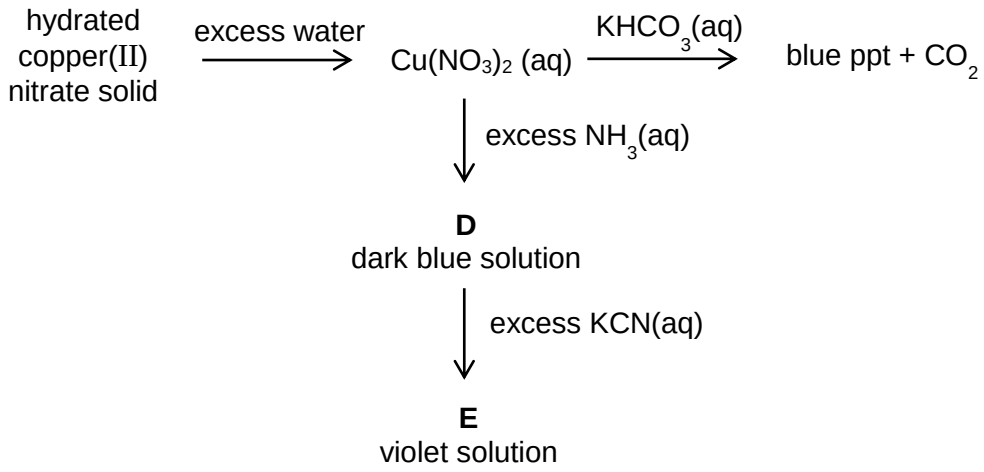
……..……[3]

(e) The following are some reactions involving copper(II) nitrate.



(i) Explain why carbon dioxide is evolved when $KHCO_3(aq)$ is added to aqueous copper(II) nitrate. Include any relevant equations with state symbols in your answer.

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……[2]

(ii) Suggest a formula for the complex ion present in **D**.

…….. [1]

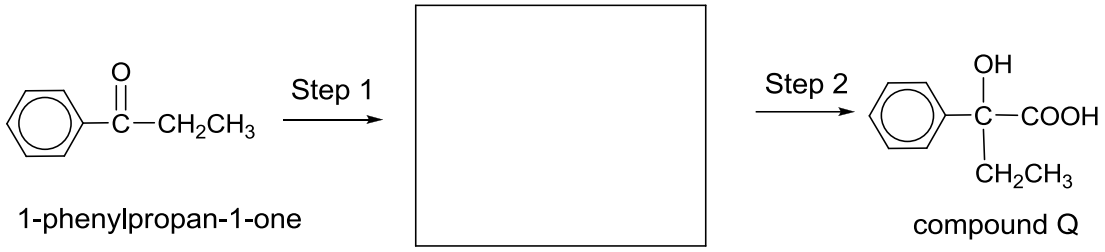
(iii) The metal ion in complex **E** is known to have a coordination number of four. Suggest a formula for complex ion **E**.

…….. [1]

[Total: 18]

5 Benzene reacts with propanoyl chloride and 1-phenylpropan-1-one is formed in the reaction.

(a) State the reagents and conditions needed to convert 1-phenylpropan-1-one into compound **Q**. Show the structure of the intermediate in the box provided.



1-phenylpropan-1-one

compound Q

Reagents and conditions

Step 1 ……

Step 2 ……

[3]

(b) Describe the mechanism in Step 1 in part **(a)**. In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows.

[3]

(c) The 2,4-D weed killer, $C_8H_6Cl_2O_2$, is widely used on cereal crops, pastures and orchards. Compound **R** is an isomer of the weed killer under development to improve its properties. It is an aromatic compound which contains **three** functional groups.

The following tests are carried out in the order given. In **each** case, state **all** deductions about the compound **R** you can make at **that** stage. When identifying the functional groups, your answers should be unambiguous.

(i) When Compound **R** is treated with Na, $C_8H_5Cl_2O_2Na$ is formed.

deduction(s).....

.....[1]

(ii) When Fehling's solution is added to Compound **R**, red brick precipitate is obtained.

deduction(s).....

.....[1]

(iii) When 1 mole of Compound **R** is boiled with ethanolic silver nitrate, 287 g of white precipitate is formed.

deduction(s).....

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.....[2]

(iv) When Compound **R** is treated with concentrated nitric acid, $C_8H_3Cl_2N_3O_8$ is formed.

1. What type of reaction takes place?

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2. Name the functional group present in Compound **R** that is confirmed by this reaction.

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[2]

(v) You now have enough information to determine the structural formula of **R**.

1. Draw the fully displayed structure of **R**.

2. Explain clearly why you have placed each of the aromatic substituent groups in their particular positions.

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